

EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)

Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries

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EXECUTIVE SUMMARY

The BREF (Best Available Techniques reference document) on Mineral Oil and Gas Refineries reflects an information exchange carried out according to Article 16(2) of Council Directive 96/61/EC. This Executive Summary – which is intended to be read in conjunction with the BREF preface's explanations of objectives, usage and legal terms – describes the main findings, the principal BAT conclusions and the associated emission levels. It can be read and understood as a stand-alone document but, as a summary, it does not present all the complexities of the full BREF text. It is therefore not intended as a substitute for the full BREF text as a tool in BAT decision making. In this information exchange more than 40 people have participated directly. Oil companies are typically international companies, so people from outside the EU have also been involved in the process.

Scope

The scope of this BREF for the Mineral Oil and Gas Refinery Industry is based on Section 2.1 of Annex I of the IPPC Directive 96/61/EC, from which it also takes its title. This document addresses the mineral oil refining industry as well as the natural gas plants. Other related activities such as exploration, production, transportation or marketing of products are not included here. All types of mineral oil refineries regardless of capacity and all types of process activities typically found there are covered in this document. Some activities that are or may be found in refineries are not covered here because they are covered in other BREFs (e.g. low olefins and solvent production, generation of power with natural gas). Other activities have not been fully covered in this document because they are partially covered in other BREFs (e.g. cooling, storage, waste water and waste gas). Thus, when implementing IPPC permits for a specific site, other BREFs should also be considered. Soil remediation is not included in this BREF because it is not a contamination prevention or control technique.

The European Refinery industry

The mineral oil and gas refinery industry is an important and strategic industry. Mineral oil refineries alone provide 42% of EU energy requirements and 95% of the fuels required for transport. About 100 mineral oil refineries have been identified in EU, Switzerland and Norway and together they process around 700 million tonnes per year. Installations are well spread around the European geography, generally located near the coast. Estimations show that the mineral oil refinery sector has 55000 direct employees and some 35000 indirect employees. 4 on-shore natural gas plants have been identified.

Refinery processes and the most important environmental issues

The document provides an updated picture of the technical and environmental situation of the two industrial sectors. It contains a brief technical description of the major activities and processes found in the sectors complemented by the actual emissions and consumptions found in European installations.

Refinery installations are typically big and fully integrated. Refineries are industrial sites that manage huge amounts of raw materials and products and they are also intensive consumers of energy and water. In their storage and refining processes, refineries generate emissions to the atmosphere, to the water and to the soil, to the extent that environmental management has become a major factor for refineries. The type and quantity of refinery emissions to the environment are typically well known. Oxides of carbon, nitrogen and sulphur, particulates (mainly generated from combustion processes), and volatile organic carbons are the main air pollutants generated by both sectors. Water is used intensively in a refinery as process water and for cooling purposes. Its use contaminates the water with oil products. The main water contaminants are hydrocarbons, sulphides, ammonia and some metals. In the context of the huge amount of raw material that they process, refineries do not generate substantial quantities of waste. Currently, waste generated by refineries are dominated by sludges, non-specific refinery waste (domestic, demolition, etc.), and spent chemicals (e.g. acids, amines, catalysts).

Emissions to air are the main pollutants generated by mineral oil refineries and, to a much lesser extent, natural gas plants (i.e. number of emission points, tonnes emitted, number of BAT developed). For every million tonnes of crude oil processed (European refineries range from 0.5 to more than 20 million tonnes), refineries emit from 20000 – 820000 t of carbon dioxide, 60 - 700 t of nitrogen oxides, 10 – 3000 t of particulate matter, 30 – 6000 t of sulphur oxides and 50 – 6000 t of volatile organic chemicals. They generate, per million tonnes of crude oil refined, from 0.1 – 5 million tonnes of waste water and from 10 – 2000 tonnes of solid waste. Those big differences in emissions from European refineries can be partially explained by the differences in integration and type of refineries (e.g. simple vs. complex). However, the main differences are related to different environmental legislation schemes in Europe. Main air emissions from natural gas plants are CO_2, NO_x, SO_x, and VOC. Water and waste are typically less important than for mineral oil refineries.

Given the progress that refineries have made in the abatement of sulphur emissions to air, the focus has started to shift towards VOC (including odour), particulates (size and composition) and NO_x, as it has in the environmental debate generally. When the carbon dioxide emissions debate gathers momentum, it will also strongly affect refineries. Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted to prevention and reduction. Reduction of water use and/or the concentration of pollutants in the water can have effects in reducing the final emission of pollutants.

Techniques to consider in the determination of BAT

Close to 600 techniques have been considered in the determination of BAT. Those techniques have been analysed following a consistent scheme. That analysis is reported for each technique with a brief description, the environmental benefits, the cross-media effects, the operational data, the applicability and economics. In some cases the driving force for implementation has been explored and references to the number of installations containing the technique have been included. The description of the techniques ends with the reference literature supporting the data in Chapter 4. Those techniques have been put into in 25 sections as shown in the following table.

		Techniques applied to				
Chapter section	Activity/Process	production and prevention	gases and waste gas	waste water	solid waste	TOTAL
1	General					
2	Alkylation	3	0	0	0	3
3	Base oil production	14	4	2	1	21
4	Bitumen production	2	5	1	2	10
5	Catalytic cracking	17	13	2	5	37
6	Catalytic reforming	3	3	0	0	6
7	Coking processes	9	19	8	3	39
8	Cooling	3	-	-	-	3
9	Desalting	13	0	4	1	18
10	Energy system	56	22	2	0	80
11	Etherification	1	0	1	1	3
12	Gas separation processes	3	2	0	0	5
13	Hydrogen-consuming processes	8	0	0	2	10
14	Hydrogen production	6	0	0	0	6
15	Integrated refinery management	33	0	24	6	63
16	Isomerisation	3	0	0	0	3
17	Natural gas plants	0	12	5	3	20
18	Polymerisation	1	0	0	2	3
19	Primary distillation units	3	2	3	3	11
20	Product treatments	5	2	4	0	11
21	Storage and handling of refinery materials	21	19	2	12	54
22	Visbreaking	3	1	1	1	6
23	Waste gas treatments	-	76	-	1	77
24	Waste water treatments	-	-	41	-	41
25	Waste management	-	-	-	58	58
	TOTAL	207	180	100	101	588

As can be calculated from the above table, 35 % of the techniques included in Chapter 4 are techniques dedicated to production and to the prevention of contamination, 31 % are air abatement techniques and 17 % are for techniques to reduce water pollution and to reduce waste or to prevent soil contamination. Those figures again reflect the fact that air emissions are the most important environmental issue in the refinery sector.

Best Available Techniques for Mineral Oil and Gas Refineries

The conclusions on Best Available Techniques for both sectors as a whole are considered the most important part of this document and are included in Chapter 5. Where possible, the associated emission, consumption and efficiency levels have been included. Once again, this BAT chapter reflects that emissions to air are the most important environmental concern of refineries. More than 200 BAT have been reported in Chapter 5 that relate to all environmental issues found in refineries. Because of the complexity of the sector, the different raw materials used, the great number of cross-media issues and the different environmental perceptions, it has not been easy to define a structure for Chapter 5. For example, this chapter does not prioritise the environmental goals or the steps towards achieving them, because of the differences of opinion within the TWG and the different site-specific possibilities to reach the same environmental goal.

This section of the executive summary highlights the most relevant environmental issues and the key findings that are given in Chapter 5. During the discussion of the information exchanged by the TWG, many issues were raised and discussed. Only some of them are highlighted in this summary.

Unit- based BAT approach vs. generic BAT approach
A most controversial issue during the preparation of the BREF, given its bearing on most of the conclusions on BAT in Chapter 5, has been the issue of process integration within the refinery as a whole, notably on the basis of the bubble approach, versus an integrated multi-media approach per individual process unit, i.e. the unit-by-unit approach. An important conclusion has been that both approaches should be respected as having their own merits in the permitting procedure and can complement each other rather than opposing each other. Chapter 5 has therefore been divided into two sections (generic and process BAT). So, BAT for any specific refinery is the combination of the non-unit-specific elements, i.e. those applicable to refineries as a whole (generic BAT), and the unit-specific-BAT applicable to that particular case.

Implementation of IPPC permits based on BAT
As totally new refineries are unlikely to be built in Europe, the application of the BAT concept is most relevant to the permitting of new process units in existing refineries or the update and renewal of permits for existing facilities. Implementation of some concepts or techniques related to BAT in those existing refineries may be very difficult. This difficulty is related to the complex nature of the refinery sector, its diversity, the high degree of process integration or its technical complexity.

Emission or consumption levels "associated with best available techniques" are presented where relevant within BAT chapter. BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. Those levels are neither emission nor consumption limit values and should not be understood as such. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

It was acknowledged that the implementation of BAT in each refinery needs to be addressed in each case and that multiple technical solutions exist. That is why prevention or control techniques are given in the BAT as a group of possibilities.

Amongst the many environmental issues addressed in the BREF, the five that are dealt with below are probably the most important:
- increase the energy efficiency
- reduce the nitrogen oxide emissions
- reduce the sulphur oxide emissions
- reduce the volatile organic compounds emissions
- reduce the contamination of water

BAT is to increase refinery energy efficiency
It was recognised during the exchange of information that one of the most important BAT for the sector is to increase energy efficiency, the principal benefit of which would be a reduction in the emissions of all air pollutants. Techniques to increase energy efficiency within refineries were identified (~32) and data were provided, but it was not possible, with any of the several methods available, to quantify what constitutes an energy efficient refinery. Only some reported figures on the Solomon index for ten European refineries were included. It is recognised in the BAT chapter that an increase in energy efficiency should be tackled on two fronts: increasing the energy efficiency of the various processes/activities and enhancing energy integration throughout the refinery.

BAT is to reduce nitrogen oxides emissions
NO_x emissions from refineries were also identified as an issue that should be analysed from two perspectives: that of the refinery as a whole and that of specific processes/activities, notably the energy system (furnaces, boilers, gas turbines) and catalytic cracker regenerators, because that is where they are mainly generated. The TWG has therefore tried to reach consensus using both the bubble concept and scrutiny of the individual processes that generate NO_x emissions. The TWG has not been able to identify a single range of emissions associated with the application of

BAT under the bubble concept. Five different ranges or values were provided by the TWG for the concentration bubble approach (three based on different scenarios when implementing BAT) and two for the load bubble approach (one based on the scenario of implementation of BAT). BAT related to NO_x emissions (~17) typically contain associated emission values.

BAT is to reduce sulphur oxides emissions

The third area identified as an issue that should be examined from those two perspectives is SO_x emissions, which are typically generated in the energy system (from fuels containing sulphur compounds), catalytic cracker regenerators, bitumen production, coking processes, amine treating, sulphur recovery units and flares. An additional difficulty here is that sulphur appears in the products manufactured by the refinery. A sulphur balance has therefore been included as a technique to consider as part of the Environmental Management System. As a consequence of all that, the TWG tried to reach consensus using the bubble concept and by examining the individual processes that generate SO_x emissions. The TWG was not able to identify a single range of emissions associated with the application of BAT under the bubble concept. Five different ranges or values were provided by the TWG for the concentration bubble approach (two based on different scenarios when implementing BAT) and two for the load bubble approach (one based on the scenario of implementation of BAT). BAT related to SO_x emissions (~38) typically contain associated emission values.

The Commission has noted the divergent views of the TWG concerning the average sulphur dioxide emission levels when burning liquid fuels, associated with the use of BAT. The Commission further notes that Council Directive 1999/32/EC on the sulphur content of certain liquid fuels prescribes a maximum emission limit value of 1700 mg/Nm^3, which equates to 1 % sulphur in heavy fuel oil, as a monthly mean value averaged over all plants in the refinery from 1 January 2003. In addition, the more recently adopted Directive 2001/80/EC on large combustion plants provides for emission limit values in the range of 200 to 1700 mg/Nm^3 depending on the characteristics of plants covered by that directive.

In this perspective, the Commission believes the range of 50 to 850 mg/Nm^3, as average sulphur dioxide emission levels when burning liquid fuels to be consistent with BAT. In many cases, achieving the lower end of this range would incur costs and cause other environmental effects which outweigh the environmental benefit of the lower sulphur dioxide emission (reference in Section 4.10.2.3). A driver towards the lower end could be the national emission ceiling for sulphur dioxide as fixed in Directive 2001/81/EC on national emission ceilings for centain atmospheric pollutants or if the installation is located in a sulphur sensitive area.

BAT is to reduce VOC emissions

VOC emissions from refineries were identified more as a global issue than a process/activity issue, because VOC emissions in the sector come from fugitives, for which the point of emission is not identified. However, those processes/activities with a high potential for VOC emissions are identified in the Specific BAT for processes/activities. Because of this difficulty in identifying points of emission, the TWG concluded that one important BAT is to quantify the VOC emissions. One method is mentioned in Chapter 5 as an example. In this case the implementation of a LDAR programme or equivalent is also recognised as very important. The TWG was not able to identify any range of emissions associated with the application of BAT, mainly because of a lack of information. Many (~19) BAT related to VOC emissions have been identified.

BAT is to reduce contamination to water

As mentioned repeatedly in the document, air emissions are the most important environmental issues that appear within a refinery. However, because refineries are extensive consumers of water, they also generate great quantities of contaminated waste water. The (~37) BAT related to water are on two levels. One deals with water management and waste water management in the refinery as a whole and the other deals with specific actions to reduce contamination or reduce water consumption. In this case, benchmarks for fresh water usage and process effluent volume are included in Chapter 5 as well as water parameters for the effluent of the waste water treatment. Chapter 5 contains many (~21) BAT related to the possibility of recycling of waste water from one process to another.

Emerging techniques
This brief chapter includes the techniques that have not yet been commercially applied and are still in the research or development phase. However, because of the implications they may have in the refinery sector, they have been included here to raise awareness during any future revision of the document.

Concluding remarks
The environmental situation of European refineries varies greatly across the European Community, so the starting point for each case is very different. Different environmental perceptions and priorities are also evident.

Level of consensus
The refineries sector is a large and complex one, spread across all Member States except Luxembourg. This size and complexity are reflected in the number of processes / activities addressed in the BREF and the number (200+) of BAT it contains. The fact that agreement has been reached on all but 27 of those 200+ BAT is a measure of the broad commitment of TWG members to the conclusions reached. Those 27 split views can be summarised and classified in the following three ways:

- One relates to the general introduction to Chapter 5
- eleven relate to the Generic BAT
- fifteen relate to Specific BAT.

- Nineteen relate to the figures in the ranges given in Chapter 5. They represent two points of view; the first is that control techniques are almost always applicable in all cases and the second is that control techniques are hardly applicable
- four relate to the structure of the parts of Chapter 5 that relate to SO_x and NO_x emissions and are driven by the bubble concept approach
- two relate to the water emissions table; one to the average time period given in the concentration column and the other to how the metal content should be expressed within the table
- one is addressed to the introduction to Chapter 5 and relates to the way in which the upper value of the ranges in Chapter 5 is selected
- only one split view relates fundamentally to a technique; base oil production.

- Nine relate to the water emissions table
- eight relate to SO_x emissions
- eight relate to NO_x emissions
- two relate to particulates emissions.

Recommendations for future work
In preparation for future BREF reviews, all TWG members and interested parties should continue to collect data on the current emission and consumption levels and on the performance of techniques to be considered in the determination of BAT. For the review, it is also important to collect more data on the achievable emission and consumption levels and the economics of all production processes under analysis. It is also important to continue collecting information on energy efficiency. Apart from these general areas, some techniques in Chapter 4 need more information in order to be complete. Other complementary data missing in the document is about characteristics of particulates, noise and odour. It is also recognised that other organisations such as technology providers, may enhance the appearance and validation of data within the document.

Recommendations for future R&D work

The previous paragraph highlights many areas for attention in future work. Much of the future work concerns the collecting of information to be used in reviewing this BREF. Proposals for future R&D work focus on the techniques that are identified in this BREF, but are too expensive or cannot be used yet in the sector.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

PREFACE

1. Status of this document

Unless otherwise stated, references to "the Directive" in this document means the Council Directive 96/61/EC on integrated pollution prevention and control. As the Directive applies without prejudice to Community provisions on health and safety at the workplace, so does this document.

This document forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available technique (BAT), associated monitoring, and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term "best available techniques", are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community's industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term "best available techniques" is defined in Article 2(11) of the Directive as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." Article 2(11) goes on to clarify further this definition as follows:

"techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

"available" techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

"best" means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of "considerations to be taken into account generally or in specific cases when determining best available techniques.. bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention". These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3. Objective of this Document

Article 16(2) of the Directive requires the Commission to organise "an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them", and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that "the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the world-wide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive."

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4. Information sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

This document provides information for two industrial sectors: Mineral Oil refineries and Natural Gas plants. The rest of this section describes the type of information that is provided in each section of the document.

The document has been divided into seven chapters plus annexes. **Chapters 1** and **2** provide general information on the mineral oil refinery and natural gas sector and on the production processes and activities that can be found within the sector. **Chapter 3** provides data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing. **Chapter 4** describes the prevention (including production techniques) and control techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. Each technique within Chapter 4 includes information on consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. **Chapter 5** presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense for the mineral oil refineries and natural gas plants as a whole. **Chapter 6** describes briefly techniques that may be applied in both sectors in the future. **Chapter 7** summarises the conclusions and recommendations of the document. In order to help the reader, a Glossary is also included. Complementing the document, the **Annexes** contain a summary of the legislation applicable to the sector as well as summaries of the type of refinery configurations and descriptions of the refinery products/intermediates generated within refineries.

The purpose of Chapter 5 is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In the case of existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, and these judgements will often be influenced by local considerations. Although an attempt is made to address some of above-mentioned issues, it is not possible for some of them to be considered fully in this document. The techniques and levels presented in Chapter 5 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

6. How chapters have been structured

Chapters 2, 3, 4 and 6 as well as Section 5.2 have a common internal structure, so as to facilitate the reading and understanding of the document. Each of those chapters has been structured per type of process or activity found in the refinery sector and classified in alphabetical order to make it easier to find them in the document. Those sections do not pretend to be of equal importance from the environmental impact point of view. Some have more relevance than others, but this structure is considered a good and clear way to tackle the BAT assessment for these industrial sectors. Moreover, it is unlikely that a completely new mineral oil refinery installation will be built in Europe, but it is very likely that new processes will be installed in existing European refineries.

The first section in each of those chapters is dedicated to a general description of the chapter issue under consideration in refineries as a whole. Then follow 20 sections covering all the mineral oil refinery processes and activities and one covering natural gas plants.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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SCOPE

This document, together with other BREFs in the series, are intended to cover the activity described in point 1.2 described in Annex 1 of Council Directive 96/61/EC, namely Mineral Oil and Gas refineries.

The mineral oil and gas industry is organised into four broad sectors: exploration and production of crude oil and natural gas; transportation; refining; and marketing and distribution. This document addresses only the refining industry from both sectors (Mineral Oil refineries and Natural Gas plants); specifically the activities and processes set out in the table below. The table indicates other reference documents dealing with related issues as shown.

Section no. within this document	Activity name used within this document	Subactivities or processes included in each category of processes	Reference to additional information
2	Alkylation	HF, H_2SO_4 alkylation processes	
3	Base oil production	Deasphalting, aromatic extraction, high pressure hydrogenation unit, dewaxing, wax processing and lubricant oil hydrofinishing	
4	Bitumen production		
5	Catalytic cracking	All types of catalytic cracking units. Types according to feedstock and process conditions	
6	Catalytic reforming	Continuous, cyclic and semiregenerative	
7	Coking processes	Delayed and fluid coking and coke calcination	
8	Cooling		Industrial cooling systems BREF
9	Desalting		
10	Energy system	Refinery power plants including all types of technologies applied and all types of fuels used within EU refineries	Large Combustion Plants BREF
11	Etherification	MTBE, ETBE and TAME production	
12	Gas separation processes	Separation of light fractions of the crude oil (e.g. refinery fuel gas, LPG)	
13	Hydrogen consuming processes	Hydrocracking, hydrorefining, hydrotreatments, hydroconversion, hydroprocessing and hydrogenation processes	
14	Hydrogen production	Gasification (coke and heavy oils), steam reforming and hydrogen purification	
15	Integrated refinery management	Environmental management activities, utility management and overall refinery management (noise, odour, safety, maintenance)	
16	Isomerisation	C_4, C_5 and C_6 isomerisation	
17	Natural gas plants	Processes related with the processing of natural gas	
18	Polymerisation	Polymerisation, dimerisation and condensation	
19	Primary distillation units	Atmospheric and vacuum distillation units	
20	Product treatments	Sweetening and final product treatments	
21	Storage and handling of refinery materials	Storage, blending, loading and unloading of refinery materials	Storage BREF
22	Visbreaking		
23	Techniques for the abatement of emissions (only in Chapters 2)	It merges the contents related to waste gas, waste water and solid wastes in Chapters 2	
23	Waste gas treatments		Waste gas and waste water BREF
24	Waste water treatments		Waste gas and waste water BREF
25	Waste management	Waste treatment, waste disposal and incineration	
26	Monitoring (only in Chapter 3)		Monitoring BREF

As can be seen in the above table, most of the processes and activities under analysis are specifically dedicated to mineral oil refineries. The only exception is Section 17, which deals with the processes that can be found in inland natural gas plants (name used in this document to

identify this industrial sector). Those plants also use some of the end-of-pipe techniques (in Sections 23 to 25) used in mineral oil refineries and, for this reason, no distinction is made between the two types of industry.

Some processes or activities that may be present in refineries are not included or are only partially included in this document, because they are covered in other BREFs. Some examples are:

- the steam cracker for the production of lower olefins, the production of aromatics (i.e. BTX), cyclohexane and cumene or alkylation of aromatics in Large Volume Organic Chemicals BREF
- the energy production techniques when commercial fuel oil, natural gas or gasoil are used are included in the Large Combustion Plant BREF
- horizontal BREFs as industrial cooling, monitoring, storage and waste water and waste gas treatments are also applicable to refineries.

TWG has considered that soil remediation techniques are not a part of study within this BREF. The reason given is that those techniques are not techniques to prevent nor to control emissions. They are techniques used to clean up the soil when it has been already contaminated.

1 GENERAL INFORMATION

1.1 The purpose of refineries

The purpose of refining is to convert natural raw materials such as crude oil and natural gas into useful saleable products. Crude oil and natural gas are naturally occurring hydrocarbons found in many areas of the world in varying quantities and compositions. In refineries, they are transformed into different products as:

- fuels for cars, trucks, aeroplanes, ships and other forms of transport
- combustion fuels for the generation of heat and power for industry and households
- raw materials for the petrochemical and chemical industries
- speciality products such as lubricating oils, paraffins/waxes and bitumen
- energy as a by-product in the form of heat (steam) and power (electricity).

In order to manufacture these products, these raw materials are processed in a number of different refining facilities. The combination of these processing units to convert crude oil and natural gas into products, including its supporting units and facilities, is called a refinery. The market demand for the type of products, the available crude quality and certain requirements set by authorities influence the size, configuration and complexity of a refinery. As these factors vary from location to location no two refineries are identical.

1.2 Refinery sector in the EU

The economic and political worldwide refining industry has undergone considerable changes. The increased effort in oil and gas exploration and production as well as cost reductions achieved in those activities has resulted in a worldwide maintenance of the total world reserves.

Oil provides 42 % of the European Union's (EU) energy requirement, and 94 % of the fuels required for transport. The health and viability of the refining industry is of critical strategic importance to the Union for maintaining a successful and internationally competitive position for industry as a whole, and for providing competitively priced products to consumers.

The refining industry has suffered from a structural distillation overcapacity most of the time since the oil crisis in 1973/1974. Only in the early 1980s, early 1990s and last years were attractive margins achieved due to high oil prices at those times. Moreover, severe competition costs, environmental compliance of the refining industry and regulatory uncertainty have added to the decrease in profitability in certain periods. This long-lasting recession led oil and gas companies to make significant adjustments in upstream and downstream operations such as cuts in production costs, innovations in technology and organisational restructuring.

However co-operation in the form of partnerships, alliances, joint ventures or mergers between companies, governments and local communities, contractors and suppliers has led to significant cost reductions. This trend is also fuelled by increased environmental awareness in society at large and is supported by the current process of harmonisation of legislation, particularly within Europe. Examples of new forms of co-operation are the recent (mid-1998) downstream merger between BP and Mobil which started as a partnership in refining and marketing in 1996 and secured reportedly significant pre-tax cost savings. Recently a Total-Fina-Elf merger and an Esso-Mobil merger were concluded. A further recent example is the refining capacity exchange between Statoil (Mongstad-Norway) and Shell (Sola/Pernis-Netherlands).

Some European refineries have been closed in the last 20 years, but crude oil processing capacity has increased in recent years, mainly by ‘capacity creep’ (debottlenecking, improvement in equipment reliability and longer cycles between turnarounds) to cope with the low but steady increase in product demand of 1 - 2 % per year in Europe. Worldwide ‘capacity

creep' is estimated to be 'equivalent to six to ten additional world scale refineries going on stream every year'.

The crude oil refining industry is complex, with the following issues at stake in Europe:

Feed stock: steady production and a shift towards lighter (North Sea) crudes specifically in the North of Europe. World reserves of crude oil seems to guarantee the availability of raw materials for a reasonably long period (~40 years). Table 1.1 shows a summary of the world reserves and the consumption of crude oil per geographical area during the last decade.

RESERVES (Mt)	1990	1993	1996	1999
Europe	2400	2200	2500	2800
North America	5300	5000	11500	8700
South and Central America	17600	17350	11300	12200
USSR (former)	8200	8100	9100	8900
China	3200	3200	3300	3400
Middle East	89300	89600	91600	92000
Africa	7800	8430	9000	10200
Other Regions	3000	2790	2400	2600
Total	**136800**	**136670**	**140700**	**140800**
CONSUMPTION (Mt)				
Europe	217.5	256.6	328.1	755.2
North America	656.5	653.8	660.7	1047.1
South and Central America	229.8	257.0	313.9	218.8
USSR (former)	570.7	402.3	352.6	182.0
China	138.3	144.0	158.5	200.0
Middle East	861.9	945.8	983.3	215.0
Africa	320.7	332.2	359.6	115.6
Other Regions	184.7	190.8	204.9	728.7
Total	**3180.1**	**3182.5**	**3361.6**	**3462.4**

Table 1.1: Crude oil reserves and consumption per geographical region
Source: [247, UBA Austria, 1998], [246, BP-AMOCO, 2001]

The advent of North Sea crude oils and the continuous increase in the production of these light, low-sulphur crudes is mainly responsible for the lowering of the average sulphur content of the crude oils processed in European refineries. Since 1985 the average sulphur content has fluctuated around 1.0 and 1.1 %. However, the difference between type of crude processed in each European region should be noted, i.e. an average of 1.17 % S in the crude oils processed in the refineries of North West Europe, an average of 0.91 % S in the Atlantic region, of 1.2 % S in the Mediterranean and of 0.64 %S in the 'Others'. The availability of the type of crude oil to refineries is not the same. In Figure 1.1, the differences in average sulphur content of the crude feedstock of refineries in different regions/countries are stated.

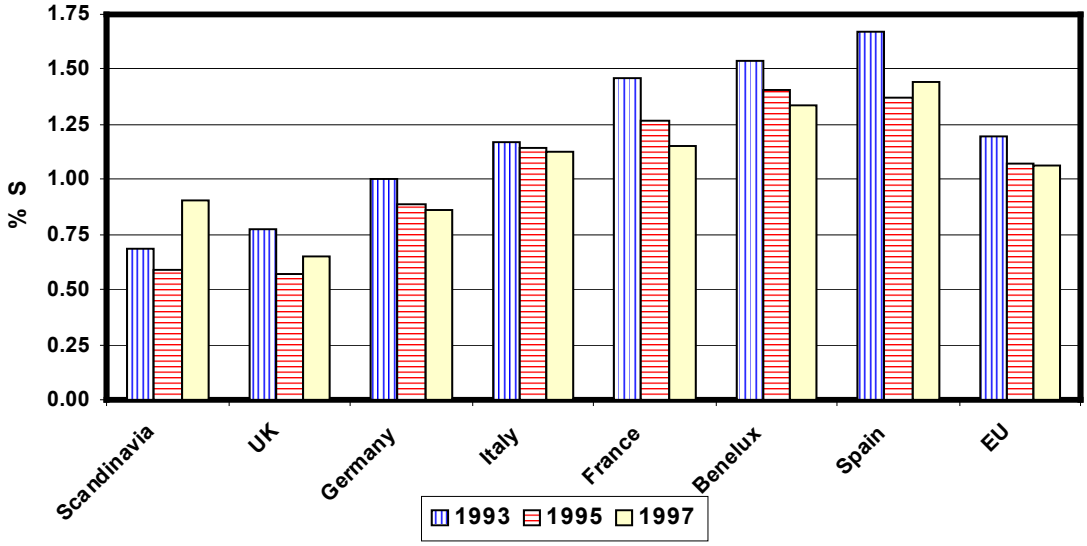


Figure 1.1: Percentage of sulphur in the crude used in each European Country
Source: [261, Canales, 2000]

Some local factors for those differences are the following:

- location close to oil fields where low-sulphur crudes are produced (freight for crude from the North Sea to Mediterranean costs up to 1 $/bbl, so low-sulphur crudes from the North Sea are rarely processed in the Mediterranean area.)
- refinery equipped with insufficient desulphurization / upgrading capacity to process (heavy) high-sulphur crudes
- exclusion from markets where high-sulphur products can be sold (e.g. bitumen, bunker fuel)
- some other form of specialisation in the use of low-sulphur crudes (e.g. luboil production).

Any refinery that is not influenced by local factors such as those mentioned above will try to process high-sulphur crudes to the maximum extent, as their prices are considerably lower. (e.g. in September 1999 Platt's quoted Arab heavy with sulphur content 2.8 % was 1.1 $/bbl cheaper than Arab Light with sulphur content 1.8 %). If the flexibility of refineries would be theorically high, the product slate would be altered to suit market requirements irrespective of the crude type by the inclusion of conversion units. As consequence of that all refineries would continuously be running on the cheapest crude available, which probably would be very heavy and high-sulphur [253, MWV, 2000] [310, Swain, 2000].

Refinery capacity: excess in primary processing capacity, some 'misfits' (incompatibility between production and market demand) and excess in conversion capacity. European downstream sectors show too many refineries producing too much gasoline. Table 1.2 shows the charge and production capacity of European oil refineries for European Union countries and Switzerland and Norway (hereafter called EU+ or European). The table also reflects capacities per type of process. The EU+ crude oil capacity in 1999 was around 700 million tonnes per year with Italy and Germany having the greatest capacity.

Charge capacity, Mm^3/yr

Country	Number of refineries	Crude	Vacuum distillation	Coking	Thermal operations	Catalytic cracking	Catalytic reforming	Catalytic hydrocracking	Catalytic hydrorefining	Catalytic hydrotreating
Austria	1	12.2	3.8		1.0	1.6	1.3	3.0	2.9	2.3
Belgium	5	41.7	15.8		3.7	6.5	6.0		13.4	16.2
Denmark	2	7.8	1.3		3.1		1.2		0.6	2.5
Finland	2	11.6	5.5		2.0	2.6	2.5	1.2	6.0	3.4
France	15	113.0	44.6		9.0	21.4	15.4	0.9	11.2	46.9
Germany	17	130.3	50.3	7.0	12.1	19.5	22.9	7.0	43.3	54.0
Greece	4	22.9	7.9		2.8	4.2	3.3	1.6	5.0	10.1
Ireland	1	3.9					0.6		0.8	0.6
Italy	17	141.9	44.6	2.6	24.2	17.4	16.4	11.4	20.3	42.6
Netherlands	6	69.0	25.0	2.1	7.0	6.1	10.0	6.2	5.0	32.5
Norway	2	15.0		1.5	1.8	3.1	2.2		2.0	6.2
Portugal	2	17.7	4.5		1.4	1.8	2.9	0.5	1.8	8.4
Spain	10	77.3	25.0	1.7	8.6	11.1	12.0	0.9	4.9	26.3
Sweden	5	24.8	7.8		3.6	1.7	4.1	2.8	4.1	11.0
Switzerland	2	7.7	1.4		1.2		1.6	0.4	1.6	4.3
UK	13	107.6	46.9	3.9	5.5	26.1	21.4	3.2	15.0	50.2
EU+	104	804.3	284.4	18.9	86.7	123.2	123.8	39.1	137.9	317.5

Vacuum distillation has been included in primary distillation sections in this document.
Thermal operations include visbreaking (within this document) and thermal cracking (within LVOC BREF).
Catalytic hydrocracking, hydrorefining and hydrotreatment are included in hydrogen-consuming processes.
Catalytic hydrorefining: Includes processes where 10 % of the feed or less is reduced in molecular size. It includes desulphurisation of atmospheric residues and heavy fuel gas oil, catalytic cracker treatments and mid-distillates.
Catalytic hydrotreating: No reduction in molecular size of feed occurs. It includes pretreatment of catalytic reformer feed, naphtha desulphurisation, naphtha olefin/aromatic saturation, straight-run distillate, pretreating catalytic cracker feed, pretreatments of other distillates and polish of base oils.

Production capacity, Mm^3/yr

Country	Alkylation	Polymerisation Dimerisation	Aromatics	Isomerization	Base Oil production	Etherification	Hydrogen (MNm^3/d)	Coke (t/d)	Sulphur (t/d)	Bitumen
Austria				0.6		0.1			180	0.1
Belgium	0.8			0.1		0.3	4.4		1184	1.5
Denmark				0.3						0.5
Finland	0.2	0.02				0.2	0.6		156	0.7
France	1.1	0.35	0.3	4.0	2.3	0.2	1.3	701	850	2.6
Germany	1.4	0.14	3.8	3.4	1.5	0.9	35.5	3570	1982	5.2
Greece	0.1	0.51		1.2	0.2	0.1	0.5		186	0.3
Ireland									2	
Italy	2.1	0.18	1.3	5.2	1.6	0.3	6.5	2000	1410	1.3
Netherlands	0.7		1.5	0.8	0.7	0.2	4.1		823	0.8
Norway		0.67		0.2				610	24	
Portugal	0.3		1.0						180	
Spain	0.9		1.9	0.8	0.5	0.6	3.0	1250	703	2.8
Sweden		0.20		1.6	0.1		1.3		312	1.7
Switzerland				0.6						0.3
UK	5.4	0.97	0.9	5.6	1.4	0.2	2.7	2300	612	3.5
EU+	13.1	3.04	10.7	24.6	8.3	3.2	59.9	10431	8604	21.0

Aromatic production is included in the LVOC BREF, although some refineries have it.

Table 1.2: EU+ capacity for mineral oil refining
Source: Data from [73, Radler, 1998] reviewed by the TWG

Refining distillation capacity decreased substantially in the early 1980s following the oil price shocks of the 1970s. At the same time, the industry had to invest heavily in conversion capacity to convert fuel oil and the rebalance demand for lighter transport fuels. Official figures for nameplate capacity show small further capacity reductions to the end of 1995. Combined with a slow rise in demand since 1986 this has increased apparent distillation capacity utilisation from a low point of 60 % in 1981 to an average above 90 % in 1997, higher in northern Europe and lower in southern Europe.

There are differences in supply and demand balances between different countries, with Germany in particular having a large supply deficit. Growth of oil products demand in Iberia has been well above the average for the EU, particularly in transport fuels. However, oil demand growth in the 1990s shows the Mediterranean region to be in line with the rest of Europe. Even in the most favourable scenario, European refining capacity will almost certainly exceed demand for at least the next decade. International trading opportunities will only have a limited impact on Europe's over-capacity. There is a refining capacity surplus of 70 - 100 million tonnes per year (equivalent to 9 to 13 refineries) in the EU.

Economics: low refinery margins and low return on investment stimulate refiners either to look at other products such as electricity, hydrogen and petrochemicals with higher margins or to shut down (e. g. Sola in Norway).

Political: the political pressures and the economic recession in some regions of the world will have a significant bearing on European economies and the pace at which upgrading of refineries or even new refinery projects will be undertaken world-wide.

Product market: growing demand for kerosene and diesel; a stable demand for gasoline; a declining demand for light heating oil and heavy fuel oil; and an increasing demand for petrochemicals. Competition is expected from refineries in the Russian Federation and the Middle East. A picture for the demand in Western Europe is presented in Table 1.3.

	Demand 1995		Average annual growth in %
Refinery products	**Mt**	**% of total**	**1995 - 2010**
Naphtha chemical feed stock	40	7	1.5
Gasoline	125	20	0.7
Jet fuel (kerosene)	40	7	2.7
Diesel	115	19	2.3
Fuel oil (Light inland)	110	18	-1.4
Heavy fuel oil for electricity	75	13	-2.6
Heavy fuel oils for bunker	30	5	0.7
Other products *	65	11	-
TOTAL	600	100	-

Notes:
- Values in the table corresponding to Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, United Kingdom together.
- * Other products (in 1995 at 65 Mt) include lubes and bitumen products and refinery fuel (estimated at 38.7 Mt/yr).

Table 1.3: Product demand development Western Europe
Source: [118, VROM, 1999]

Product quality: cleaner fuels. New specifications require reductions of the sulphur content for all types of automotive fuels, lower aromatics, particularly benzene in gasoline and reduced polyaromatic hydrocarbons and a higher cetane number in diesel; the phasing out of lead from gasoline will be further pursued. The trend is that environmental quality requirements will become more stringent for all refinery products. These requirements will be especially true for automotive fuels (Auto-Oil I and II) (see Table 1.4).

Refinery product	Unit	Product specification Before 2000	Auto-Oil I 2000	Auto-Oil II 2005
Gasoline				
Sulphur	ppm	500 max.	150 max.	50 max.
Aromatics	% v/v	no spec	42 max.	35 max.
Olefins	% v/v	no spec	18 max.	? max.
Benzene	% v/v	5 max.	1.0 max.	? max.
Evaporation at 100°C (summer)	%	65/70 max.	46 min.	? min.
Evaporation at 150°C (winter)	%	--	75 min.	? min.
RVP, summer	kPa	80	60 max.	?
Oxygen	%	2.5 max.	2.3 max.	? max.
Diesel				
Sulphur	ppm	500 max.	350 max.	50 max.
Cetane number		49 min.	51 min.	? min.
Density @ 15°C	kg/m^3	860 max.	845 max.	? max.
T95 %	°C	370 max.	360 max.	? max.
Polycyclic Aromatics	% w/w	none	11 max.	? max.
Heating gas oil				2008
Sulphur	(% w/w)			0.1 max
Inland heavy fuel oil				2003
Sulphur	(% w/w)			1
Bunker fuel oil in SO_x emission control zones				IMO-2003
Sulphur	(% w/w)			1.5

Table 1.4: Mineral oil product specifications
Sources: [118, VROM, 1999], [61, Decroocq, 1997] and EP decision of 29/6/98

Moreover, EU acidification will put additional pressure on the sulphur content of liquid fuels, and therefore also on the sulphur content of the fuels used in refineries. Meeting these new specifications will require additional investments, particularly in desulphurisation capacity, adding more pressure to the restructuring process of the sector mentioned above.

Environmental: emission reduction from refineries is a major issue. As regards the future, refinery fuel consumption will be higher because of increased conversion (consumption at 49 Mt/yr at current energy efficiency). The composition of the refinery fuel will be adapted and cannot excluded that the use of the liquid refinery fuel component (estimated at 11 Mt/yr in 1995) may be phased out. Such a reduction of use of liquid refinery fuels, some of them residual components, leads further to more distillation residue upgrading investments (like coking, thermocracking or gasification) (on top of the reduced demand for HFO by some 25 Mt/yr by 2010) [118, VROM, 1999].

Automation: application of information techniques features such as enhanced process control and management's systems. These investments have enabled considerable cost/manpower savings and efficiency improvements.

1.3 European refineries

There are currently around hundred crude oil refineries spread around the EU+ countries. Of these refineries, 10 are specialist refineries producing mainly lubricating oil basestocks or bitumen. It is difficult to be precise about the actual numbers as there are several situations where, as a result of amalgamations, what were separate refineries are now managed as one, sharing some facilities, even though the component parts may be some kilometres apart. Germany and Italy are the countries with the most refineries in Europe. Luxembourg has none. Four on-shore natural gas plants have been identified in Europe. Table 1.2 above also shows the distribution of European refineries by country. As can be seen in the map at Figure 1.2, refineries are mainly placed close to the sea or to a big river, to satisfy their need for large

amounts of cooling water as well as to facilitate the sea transport of raw materials and products. There are some places in Europe with a high concentration of refineries (e.g. Rotterdam Netherlands (5); Antwerp Belgium (5) and Sicily Italy (4).

As a result of over-capacity in the European refinery sector, very few new oil refineries have been built in the last twenty-five years. In fact, only nine percent of the existing refineries have been built in this period and only two percent in the last ten years, 95 % built before 1981 and 44 % before 1961 (see Table 1.5). Although most refineries will have had upgrades and new units built since they were first commissioned, their overall structure, and in particular items like the pattern of sewer systems, will have remained essentially unchanged.

Time period	Number of refineries built in the time period	Percentage of refineries built during the time period (%)	Cumulative percentage
Before 1900	1	1	1
1900 - 1910	2	2	3
1911 - 1920	1	1	4
1921 - 1930	9	9	13
1931 - 1940	7	7	19
1941 - 1950	8	8	27
1951 - 1960	17	17	44
1961 - 1970	41	40	83
1971 - 1980	12	12	95
1981 - 1990	3	3	98
1991 - 2000	2	2	100
Total	**103 ***		
* Refinery in Martinique not included within the table. Some refineries have been demolished recently.			

Table 1.5: Percentage of refineries built during different time periods
Source: CONCAWE

Four on-shore natural gas plants have been identified in Europe. Three have been identified in the Netherlands and one in Norway.

N	Country	Refinery location
1	Austria	Schwechat
2-6	Belgium	Antwerp
7	Denmark	Fredericia
8		Kalundborg
9	Finland	Naantali
10		Porvoo
11,12	France	Dunkirk
X		Martinique
13		Petit Couronne
14		Reichstett-Vendenheim
15		Donges
16		Feyzin
17		Grandpuits
18		Gonfrevill l'Orcher
19		Port Jerome
20		Notre Dame Gravenchon
21		La Mede
22		Berre l'Etang
23		Fos sur Mer
24		Lavera
25	Germany	*Hamburg Grasbrook*
26		*Hamburg-Neuhof*
27		Hamburg-Harburg
28		Hamburg-Wilhelmsburg
29		Godorf
30		Wesseling
31		Ingolstadt
32		Ingolstadt/Vohburg/Neustadt
33		Karlsruhe
34		Spergau/Leuna
35		Heide
36		Burghausen
37		Schwedt
38		*Salzbergen*
39		Gelsenkirchen
40		Wilhelmshaven
41		Lingen
42	Greece	Thessaloniki
43		Asprogyrgos
44		Elefsis
45		Aghii Theodori
46	Ireland	Whitegate
47	Italy	Livorno
48		Porto Marghera
49		Pavia
50		Taranto
51		Falconara Marittima
52		La Spezia
53		Augusta, Siracusa
54		Busalla
55		Priolo Gargallo

N	Country	Refinery location
56	Italy	Frassino, Mantova
57		Gela, Ragusa
58		Siracusa
59		Milazzo, Messina
60		Roma
61		Sarroch
62		S. Martino Di Trecate
63		Cremona
64	Netherlands	Rotterdam
65		Rotterdam
66		Europoort
67		Pernis
68		Vlissingen
69		*Amsterdam*
69.a		Den Helder/Emmen
69.b		Uithuizermeeden
70	Norway	Slagen
71		Kårstø
72		Mongstad
73	Portugal	Leca da Palmeira-Porto
74		Sines
75	Spain	Tarragona
76		Castellón de la Plana
77		Huelva
78		Algeciras-Cádiz
79		Tenerife
80		Somorrostro-Vizcaya
81		Cartagena-Murcia
82		La Coruña
83		Puertollano-Ciudad Real
84		*Tarragona*
85	Sweden	Gothenburg
86		Gothenburg
87		*Gothenburg*
88		*Nynashamn*
89		Brofjorden-Lysekil
90	Switzerland	Cressier
91		Collombey
92	U. Kingdom	South Killingholme
93		Killingholme S. Humberside
94		Fawley
95		Milford Haven
96		Coryton Essex
97		Port Clarence
98		*Ellesmere Port*
99		Stanlow
100		Grangemouth
101		*Dundee*
102		Pembroke, Dyfed
103		*Llandarcy, Neath*
104		*Shell Haven*

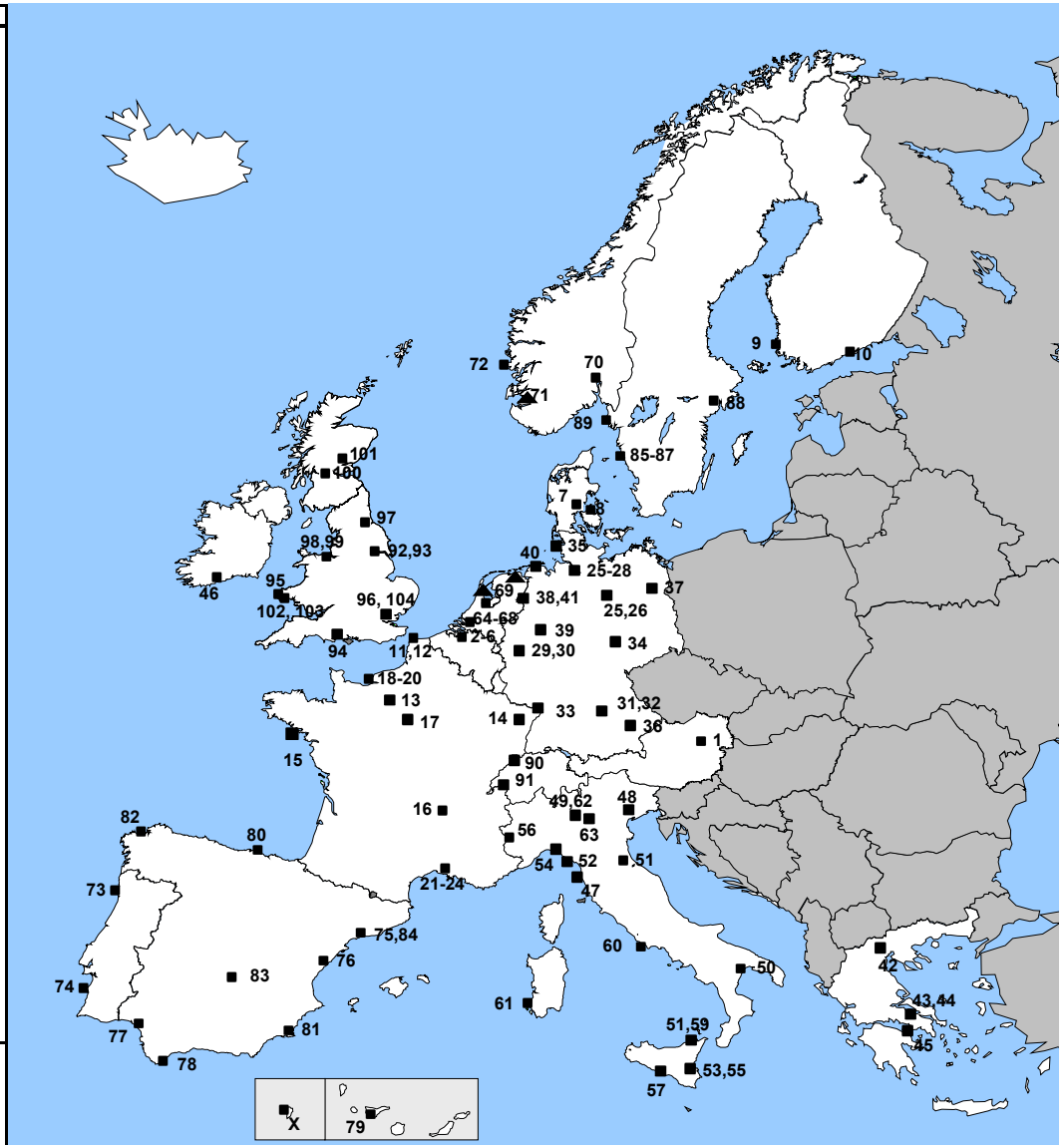


Figure 1.2: Geographical distribution of the European refineries
(■ Oil refineries (Italics: lubricant and bitumen refineries) ▲ Natural gas plants (underlined))

1.3.1 Technical characteristics of European refineries

Table 1.6 shows the number of processes currently operated in the mineral oil refineries in each country. As can be seen, crude and vacuum distillations, catalytic hydrotreatment and catalytic reforming are the most common processes, as they are found in the simplest of refineries. It may be surprising that the number of catalytic hydrotreatment processes is higher than the number of refineries, but the reason is simply that there is on average more than one catalytic hydrotreatment in each European refinery. The least common processes in European refineries are coking and polymerisation/dimerisation.

Country	Number of refineries	Crude	Vacum distillation	Coking	Thermal operations	Catalytic cracking	Catalytic reforming	Catalytic hydrocraking	Catalytic hydrorefining	Catalytic hydrotreating
Austria	1	2	2		1	1	2	2	3	2
Belgium	5	5	4		2	2	4		3	5
Denmark	2	2	1		2		2		1	3
Finland	2	3	5		2	2	2	1	6	8
France	15	14	14		8	12	14	1	7	29
Germany	17	14	15	5	10	9	18	5	14	28
Greece	4	6	4		2	2	4	1	5	11
Ireland	1	1					1		1	1
Italy	17	17	15	1	15	7	18	6	13	26
Netherlands	6	6	6	1	4	2	5	3	1	15
Norway	2	2		1	1	1	3		2	5
Portugal	2	2	2		1	1	3	1	1	6
Spain	10	10	10	2	5	6	9	1	25	17
Sweden	5	5	4		2	1	3	1	3	7
Switzerland	2	2	1		2		2	1	1	4
UK	13	10	11	1	3	7	9	1	7	13
EU+	**104**	**101**	**94**	**11**	**60**	**53**	**99**	**24**	**93**	**180**

Country	Number of refineries	Alkylation	Polymerisation Dimerisation	Aromatics	Isomerization	Base Oil production	Etherification	Hydrogen	Coke	Sulphur	Bitumen
Austria	1				1		2			1	1
Belgium	5	2	1		1		1	2		4	3
Denmark	2				1						1
Finland	2	1	1	1		1	2	1		3	4
France	15	4	2	2	7	5	4	4	3	6	6
Germany	17	3	2	13	6	5	5		4	10	9
Greece	4	1	2		3	1	2	5		3	2
Ireland	1									1	
Italy	17	6	1	4	12	2	5	11	1	7	5
Netherlands	6	2		1	2	2	2	4		3	3
Norway	2		1		1				1	1	
Portugal	2	1		1						1	
Spain	10	3		5	2	4	5	7	2	18	7
Sweden	5		1		3	1		3		4	2
Switzerland	2				2						1
UK	13	6	3	3	4	4	2	2	1	4	7
EU+	**104**	**29**	**14**	**30**	**45**	**25**	**30**	**39**	**12**	**66**	**51**

For definitions of processes see bottom of Table 1.2 in pg. 4

Table 1.6: Number of type of processes per country
Source: Data from [73, Radler, 1998] reviewed by the TWG.

Some of these refining processes have been analysed in order to discover the type of technique or techniques used to perform a certain process. For instance, there are currently two technologies to carry out alkylation, namely sulphuric and hydrofluoric. In this case these two technologies are competitors but in other cases, such as hydrotreating, one technique does not exclude another (those cases are marked with an asterisk in Table 1.7). The percentage of techniques for each process is shown in Table 1.7, based on data in [73, Radler, 1998] reviewed by TWG members. As can be seen in that table, some techniques are really predominant in particular processes in European refineries. This category includes delayed coking, visbreaking, fluid catalytic cracking, hydrofluoric alkylation, C_5 and C_6 isomerisation, MTBE production and steam reforming for the production of hydrogen. Other processes where one technique is less predominant are catalytic reforming, catalytic hydrorefining, catalytic hydrotreating and hydrogen recovery process.

Process		Technique used	%
Coking		Delayed coking	82%
		Other	18%
		Fluid coking	0%
Thermal operations		Visbreaking	82%
		Thermal cracking	18%
Catalytic cracking		Fluid	94%
		Other	6%
Catalytic reforming		Semiregenerative	55%
		Continous regenerative	27%
		Cyclic	14%
		Other	4%
Catalytic hydrocracking	Used for	Distillate upgrading	68%
		Other	27%
		Residual upgrading	5%
		Lube oil manufacturing	0%
	Severity	*conventional*	64%
		mild to moderate hydrocracking	36%
Catalytic hydrorefining (*)		mid distillate	46%
		Heavy gas oil desulfurisation	32%
		catalytic cracker and cycle stock treatment	13%
		Residual desulfurization	6%
		Other	3%
Catalytic hydrotreating (*)		Naphtha desulfurizing	28%
		Straight-run distillate	24%
		Pretreatment cat reformer feeds	24%
		Lube oil "polishing"	7%
		Naphtha olefin or aromatic saturation	5%
		Other distillates	5%
		Other	5%
		Pretreating cat cracker feeds	3%
Alkylation		hydrofluoric acid	77%
		sulphuric acid	20%
		Other	3%
Polymerisation Dimerisation		Polymerisation	79%
		Dimerisation	21%
Aromatics (*)		BTX	59%
		Hydrodealkylation	28%
		Cyclohexane	10%
		Cumene	3%
Isomerization		C5 and C6 feed	80%
		C5 feed	11%
		C4 feed	9%
Etherification		MTBE	79%
		TAME	11%
		ETBE	7%
		Other	4%
Hydrogen	Production	Steam methane reforming	57%
		Steam naphtha reforming	32%
		Partial oxidation	11%
	Recovery	*Pressure swing adsorption*	52%
		Membrane	29%
		Cryogenic	19%

For definitions of processes see bottom of Table 1.2

Table 1.7: Percentage of EU+ refineries that have a certain process (per type of process)
Source: Data from [73, Radler, 1998] reviewed by the TWG.
Note: Total number of EU+ refineries that have a certain process are shown in previous table

Following the analysis of the type of processes, Table 1.8 shows the capacity ranges for the different processes found in EU+ refineries. As can be seen, the ranges are quite large, explaining again the diversity of type of refineries found in the EU+. For instance, there exist huge differences in the capacity of crude units or catalytic hydrotreating. Smaller differences exist in the coking processes and alkylation processes.

Process	Maximum	Average	Minimum
	Charge capacity, Mm^3/yr		
Crude	23.21	7.96	0.46
Vacuum distillation	10.73	3.03	0.26
Coking	3.95	1.72	0.78
Thermal operations	3.50	1.45	0.39
Catalytic cracking	5.22	2.33	0.52
Catalytic reforming	3.08	1.26	0.08
Cat hydrocracking	3.77	1.63	0.05
Cat hydrorefining	6.96	1.48	0.23
Cat hydrotreating	8.01	1.78	0.02
	Production capacity, Mm^3/yr		
Alkylation	1.89	0.45	0.14
Pol./Dim.	0.67	0.22	0.02
Aromatics	1.49	0.36	0.04
Isomerization	1.18	0.55	0.11
Base Oil production	1.03	0.33	0.03
Etherification	0.50	0.11	0.01
Hydrogen (MNm^3/day)	3.23	1.54	0.003
Coke (t/d)	2300	869	173
Sulphur (t/d)	650	130	2
Bitumen	1.16	0.41	0.07
For definitions of processes see bottom of Table 1.2 in pg. 4			

Table 1.8: Capacity of the various processes in EU+ refineries
Source: [73, Radler, 1998] reviewed by the TWG members.

There are various approaches to defining refinery complexity [287, Johnston, 1996]. The Nelson refinery complexity index was used for the construction of Figure 1.3. In Dutch notes [118, VROM, 1999] EU refineries are grouped by configuration, as shown in Table 1.9. CONCAWE [115, CONCAWE, 1999] has grouped refineries by types (that differ in definition from the configurations of Table 1.9) in Figure 1.4 as they existed in the period 1969 - 1997. Other definitions are used in the industry, such as FCC equivalent (used by CEC DG Transport reports on the refining industry) or the Equivalent Distillation Capacity as used by Solomon Associates.

Figure 1.3 tries to illustrate the variety of complexity of refineries within Europe. The Y axis represents refinery complexity calculated according to the Nelson refinery complexity index [287, Johnston, 1996][1]. The X axis represents the different EU+ countries. If we divide the Y gap of the EU+ refineries into four categories (less than 3.9, between 3.9 and less than 6.1, between 6.1 and 8.4 and more than 8.4[2]), we see that 18 % of the refineries belong to the lowest category, 30 % belong to the second category, 41 % to the third and 11 % to the group of more complex refineries. Consequently, 7 out of 10 refineries of the EU+ can be considered as refineries with medium complexity.

[1] Nelson developed a system to quantify the relative cost of components that make up a refinery. It is a pure cost index that provides a relative measure of the construction costs of a particular refinery based on its crude and upgrading capacity. Nelson assigned a factor of 1 to the distillation unit. All other units are rated in terms of their cost relative to this unit.

[2] Limits of the categories calculated as average ± standard deviation

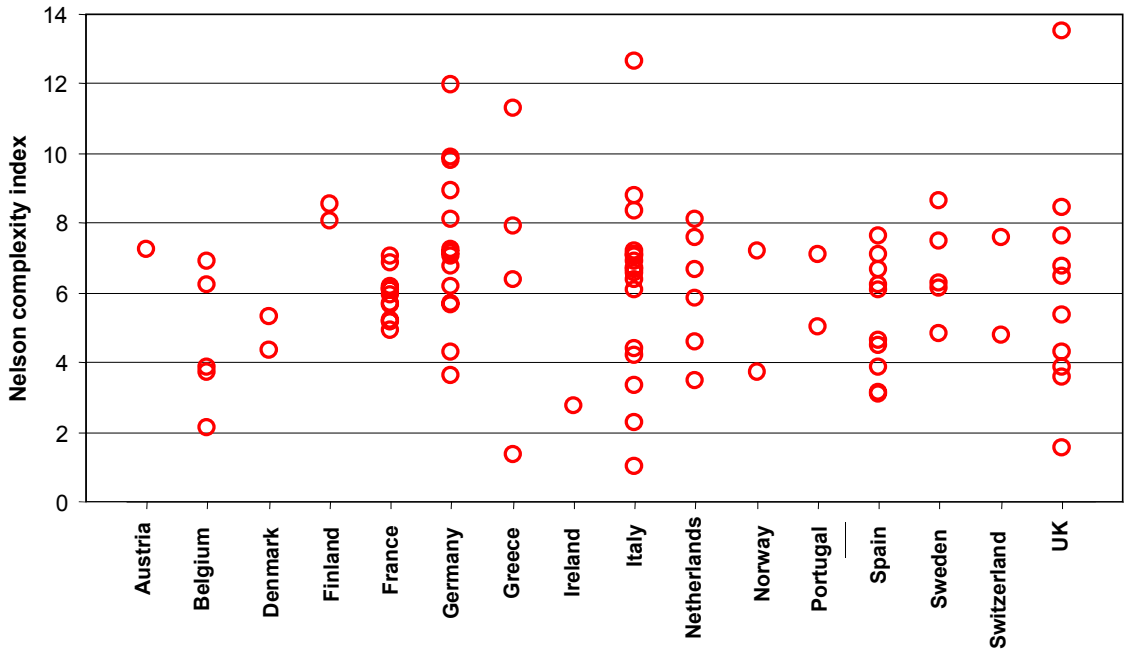


Figure 1.3: Nelson complexity index of European refineries per country (average 6.1)

In some studies it is common to distinguish between several types of refinery configuration according to complexity (For further information see Annex 10.2). One classification of refineries is to define five different types of configuration, as shown in Table 1.9. According to this classification, some 26 hydroskimmers (with or without thermal crackers) are still in operation in Europe. The most common configuration in EU+ refineries is the catalytic cracker configuration.

COUNTRY	No. refineries	Base oil and bitumen refineries	Configuration 1 hydroskimming + isomerisation Unit	Configuration 2 catcracker configuration	Configuration 3 hydrocracker configuration	Configuration 4 very complex refinery with catcracking
Austria	1			1		
Belgium	5		1	2	1	1
Denmark	2		2			
Finland	2			1		1
France	15		4	10		1
Germany	17	3	2	8	3	1
Greece	4		2	1		1
Ireland	1		1			
Italy	17		6	4	4	3
Netherlands	6	1	1	1	2	1
Norway	2		1	1		
Portugal	2		1		1	
Spain	10	1	2	6	1	
Sweden	5	2	2			1
Switzerland	2		1		1	
UK	13	3		7	1	2
TOTAL	104	10	26	42	14	12

Table 1.9: European refineries by configuration
Source: [118, VROM, 1999] reviewed by the TWG

Figure 1.4 shows the evolution of the complexity of EU+ refineries. It can be seen that the number of type I refineries has decreased over the years. To make more efficient use of the crude, increasingly deeper conversion units have been installed in European refineries.

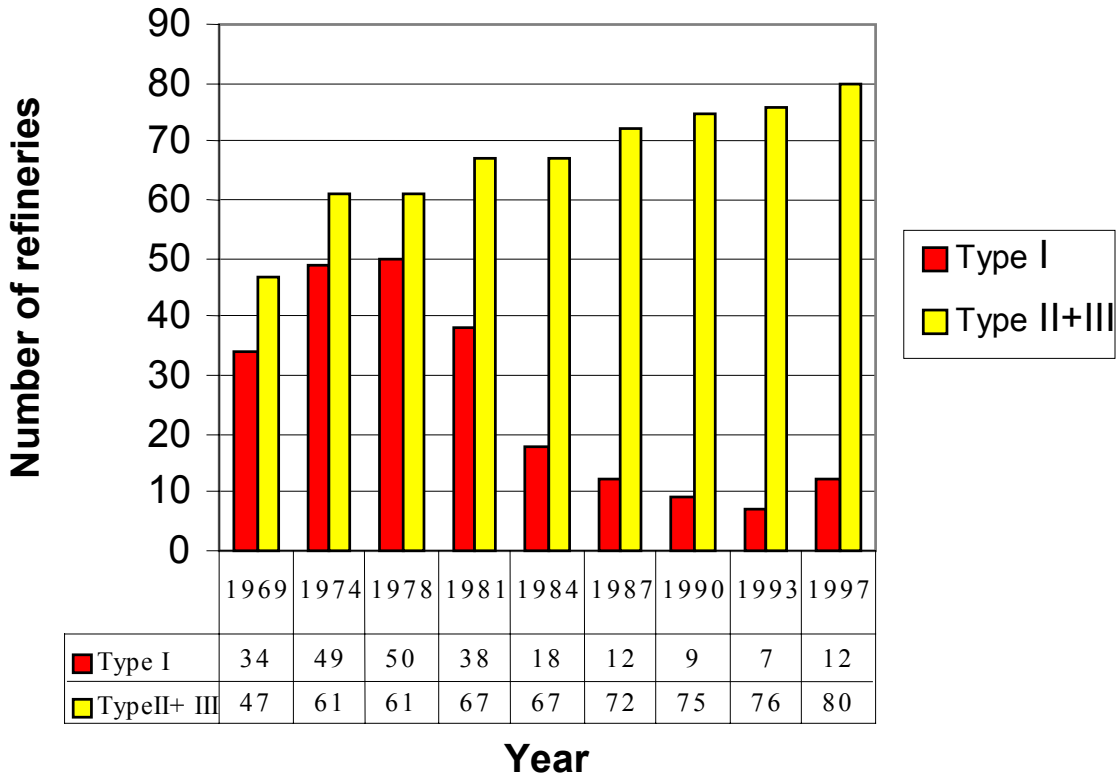


Figure 1.4: Evolution of the complexity of European refineries
Source: [115, CONCAWE, 1999]
Notes:
Type I: Simple or non-conversion refinery. Composed of crude oil distillation, reforming, treatment of distillate products, including desulphurisation and/or other quality improvement processes (e.g. isomerisation or speciality manufacturing).
Type II: Mild conversion (Type I plus thermal cracking or visbreaking).
Type III: Complex (Type II plus fluidised catcracking and/or hydrocracking).
Any of above types may have bitumen or luboil production, which clearly increases the relative complexity. No lubricating or bitumen refinery is included in this figure

1.3.2 Employment in the European refinery sector

It has been estimated that in 1998, there were 55000 direct employees of the refinery operators and 35000 contract workers (based on the numbers of man-hours worked reported to CONCAWE for their annual safety statistics report). These figures were calculated by dividing the reported man-hours by 1840 to give man-years. For the contractors, some of these will be employed full time at refineries, others will have been working there only during the duration of the contract. The number of actual people will therefore be larger.

In order to gain a rough idea of the employment generated by a single refinery, the number of employees (annual average employment) for different EU+ refineries is shown as a function of the complexity of the refineries (Figure 1.5) and as a function of the crude capacity of the refineries (Figure 1.6). Indirect or induced employment has also been plotted in both graphs where the data is available. As can be seen, the employment generated increases as the complexity or the crude capacity increases.

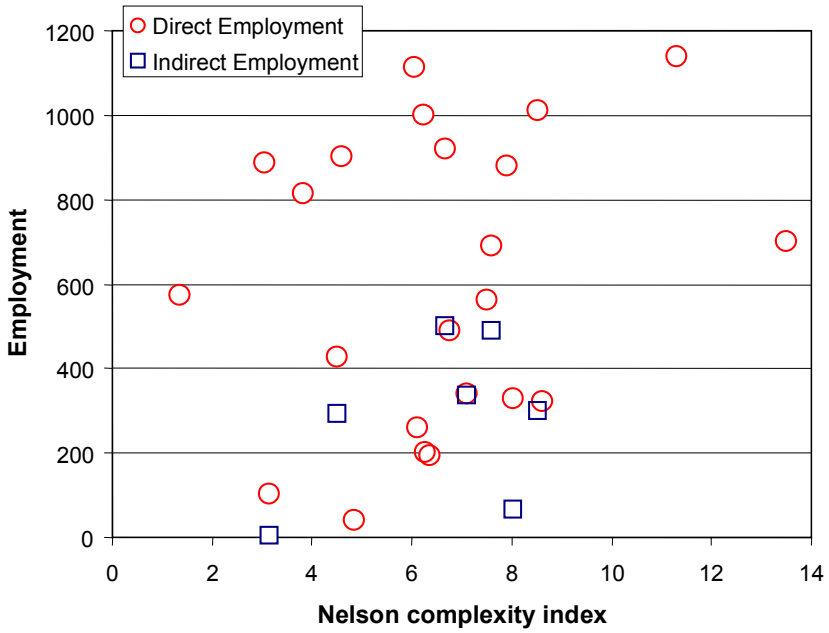


Figure 1.5: Employment in European refineries as a function of the complexity of the refinery

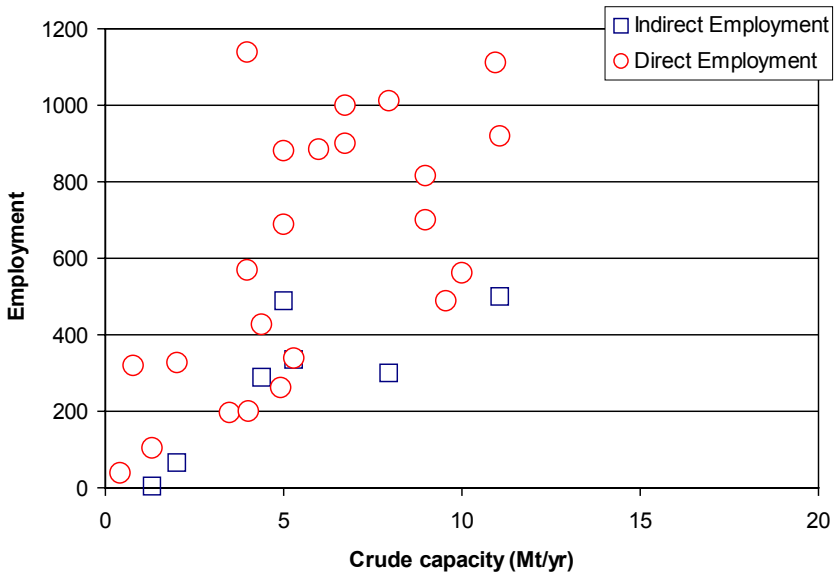


Figure 1.6: Employment in the European refineries as a function of the crude capacity

Big differences in employment are found for refineries with the same capacity or same complexity. For instance, employment at refineries with a capacity of 5 million of tonnes per year ranges from less than 300 to almost 900. Bigger differences can be found in the plot with the Nelson complexity index.

1.4 Main environmental issues in the refining sector

Refineries are industrial sites that manage huge amounts of raw materials and products and they are also intensive consumers of energy and water used to carry out the process. In their storage and refining processes, refineries generate emissions to the atmosphere, to the water and to the soil, to the extent that environmental management has become a major factor for refineries. The refining industry is a mature industry and pollution abatement programmes have been carried out in most refineries for a long time to different extends. As a result, the emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.

It is important to know, with respect to the quality and quantity of refinery emissions, that on a macro scale the crude oils vary only to a certain extent in their composition. Moreover, refineries are often limited to a comparatively narrow range of crude oil diets. Normally, when switching from one crude oil to another within this range, large variations in refinery emissions are not usually expected. Consequently the type and quantity of refinery emissions to the environment are well known during normal operations. However, from time to time, processing of crude oils previously unknown to the refinery can have unforeseen impacts on the performance of refinery processes; leading to an increase in emissions. This is particularly likely to affect aquatic emissions and to a lesser extent air emissions.

1.4.1 Emissions to the atmosphere

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NO_x), particulates, and sulphur oxides (SO_x) to the atmosphere. Refinery processes require a lot of energy; typically more than 60 % of refinery air emissions are related to the production of energy for the various processes. Sulphur recovery units and flares also contribute to those emissions. Catalyst changeovers and cokers release particulates. Volatile organic compounds (VOCs) are released from storage, product loading and handling facilities, oil/water separation systems and, as fugitive emissions, from flanges, valves, seals and drains. Other emissions to the atmosphere are H_2S, NH_3, BTX, CS_2, COS, HF and metals as constituents of the particulates (V,Ni and others). Table 1.10 shows a very brief summary of the main pollutants emitted by a refinery, with their main sources.

Main air pollutants	Main sources
Carbon dioxide	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Flare systems Incinerators
Carbon monoxide	Process furnaces and boilers Fluidised catalytic cracking regenerators CO boilers Sulphur recovery units Flare systems Incinerators
Nitrogen oxides (N_2O, NO, NO_2)	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Incinerators Flare systems
Particulates (including metals)	Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators CO boilers Coke plants Incinerators
Sulphur oxides	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Sulphur recovery units (SRU) Flare system Incinerators
Volatile organic compounds (VOCs)	Storage and handling facilities Gas separation units Oil/water separation systems Fugitive emissions (valves, flanges, etc.) Vents Flare systems

Table 1.10: Main air pollutants emitted by refineries and their main sources

Carbon dioxide (CO_2) is the greenhouse gas which receives most attention in the debate about global climate change. The main source of CO_2 emissions is the production of energy. Since the first oil crisis in 1973, refineries have made a concerted effort to enhance energy efficiency. Despite these energy conservation measures, refinery energy demand has increased due to tightened product specifications and a shift over the years from producing heavy fuel oils to transport fuels.

Carbon monoxide (CO) always appears as an intermediate product of the combustion processes and in particular in understoichiometric combustion conditions. However, the relevance of CO releases from refineries is not very high compared to CO_2.

Oxides of nitrogen (NO_x), when emitted to the air, can combine with water and form a component of 'acid rain'. Further, NO_x in combination with volatile organic compounds and sunlight, can lead to the formation of ground-level ozone. The source of NO_x is mainly the combustion processes; during the combustion of fuel, nitrogen (mainly originating from the combustion air itself) is transformed to a mixture of NO_2 and NO. Combustion conditions play an important role here. N_2O (laughing gas) is a powerful greenhouse gas that contributes to the stratospheric ozone depletion.

Particulate emissions have become a focus of attention because of their potential adverse health effects. Particulate emissions are caused by combustion of fuel oils, especially when there is sub-optimal combustion. Another source is the catcracker.

Sulphur oxides (SO_x), when emitted to the air, can combine with water and form a component of 'acid rain'. The main source of SO_x is the production of energy; during combustion, the sulphur in the fuel is transformed to a mixture of SO_2 and SO_3. Another source, typically smaller, is the flue gas from the sulphur recovery units. There is a direct relation between the sulphur in the feed to a combustion process and the sulphur oxides in its flue gas. Generally speaking the sulphur content of the refinery fuel pool is a careful balance between energy required, the type of crude processed, the emission limits and economic optimisations.

Volatile organic carbons (VOC), as mentioned above, can react with NO_x in the presence of sunlight to form low-level atmospheric ozone. Furthermore, emissions of VOC can give rise to odour problems, which may result in complaints from nearby residents. The source of VOC emissions is the evaporation and leakage of hydrocarbon fractions during storage and distribution. Hydrocarbons may also be emitted during non-optimal combustion conditions, but these give only a small contribution.

Given the progress that refineries have made in the abatement of sulphur emissions to air, the focus has started to shift towards VOC (including odour), particulates (size and composition) and NO_x, as it has in the environmental debate generally. When the carbon dioxide emissions debate gathers momentum, it will also strongly affect refineries.

1.4.2 Emissions to water

Water is used intensively in a refinery as process water and for cooling purposes. Its use contaminates the water with oil products mainly increasing the oxygen demand of the effluent. Refineries discharge waste water which originates from:

- Process water, steam and wash water. These waters have been in contact with the process fluids, and apart from oil, will also have taken up hydrogen sulphide (H_2S), ammonia (NH_3) and phenols. The more severe the conversion processes, the more H_2S and NH_3 are taken up by the process water. The process water is treated in several, well-known steps before discharge to the environment.

- Cooling water, once-through or circulating systems. This stream is theoretically free of oil. However, leakage into once-through systems, even at low concentrations, can result in significant mass losses because of the large volume of water involved.
- Rainwater from process areas. This type of water has not been in contact with the process fluids, but it comes from rainfall on surfaces which are possibly oil-polluted. It is often referred to as 'accidentally oil-contaminated' water and is typically treated prior to discharge to the environment.
- Rainwater from non-process areas. This stream is oil-free.

Oil and hydrocarbons are the main pollutants found in waste water generated by refineries. Other pollutants found in waste water generated by refineries are hydrogen sulphide, ammonia, phenols, benzene, cyanides and suspended solids containing metals and inorganic compounds (e.g. halides, sulphates, phosphates, sulphides). Table 1.11 gives a summary of the main water pollutants as well as their main sources.

Water pollutant	Source
Oil	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)
H_2S (RSH)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic
NH_3 (NH_4^+)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, sanitary/domestic
Phenols	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water
Organic chemicals (BOD, COD, TOC)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary/domestic
CN^-, (CNS^-)	Visbreaker, catalytic cracking, spent caustic, ballast water
TSS	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary/domestic

Table 1.11: Main water pollutants (parameters) generated by refineries
Source: [115, CONCAWE, 1999]

Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted to prevention and reduction. Reduction of water use and/or the concentration of pollutants in the water, can have effects in reducing the final emission of pollutants.

1.4.3 Waste generation

The amount of waste generated by refineries is small if it is compared to the amount of raw materials and products that they process. Oil refinery waste normally covers three categories of materials:

- *sludges*, both oily (e.g. tanks bottoms) and non-oily (e.g. from waste water treatment facilities),
- *other refinery wastes*, including miscellaneous liquid, semi-liquid or solid wastes (e.g. contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash, spent caustic, spent clay, spent chemicals, acid tar) and,
- *non-refining wastes*, e.g. domestic, demolition and construction.

Table 1.12 shows a summary of the main types of solid wastes generated in a refinery and their sources.

Type of waste	*Category*	Source
Oiled materials	*oily sludges*	tank bottoms, biotreatment sludges, interceptor sludges, waste water treatment sludges, contaminated soils, desalter sludges
	solid materials	contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon
Non-oiled materials	*spent catalyst (excluding precious metals)*	Fluid catalytic cracking unit catalyst, hydrodesulphurisation / hydrotreatment) catalyst, polymerisation unit catalyst, residue conversion catalyst
	other materials	resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes
Drums and containers		metal, glass, plastic, paint
Radioactive waste (if used)		catalysts, laboratory waste
Scales		leaded/unleaded scales, rust
Construction/demolition debris		scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood
Spent chemicals		laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/di-ethanol amine), TML/TEL (tetra methyl/ethyl lead)
Pyrophoric wastes		scale from tanks/process units
Mixed wastes		domestic refuse, vegetation
Waste oils		lube oils, cut oils, transformer oils, recovered oils, engine oils

Table 1.12: Main solid wastes generated by refineries
Source: [108, USAEPA, 1995]

Oil retained in sludges or other type of wastes represents a loss of product and, where possible, efforts are made to recover such oil. Waste disposal depends very much on its composition and on the local refinery situation. Because of the high operating costs of waste disposal, much priority has been given to waste minimisation schemes.

Waste generation trends during the last ten years show that oily sludge production is declining, mainly through housekeeping measures, whereas biological sludge generation has increased as a result of increased biotreatment of refinery effluent. Spent catalysts production is also increasing through the installation of new hydrocrackers, hydrotreatment facilities and catalytic cracker dust collectors. For all these waste categories increased use is made of third party waste contractors for off-site treatment and disposal.

1.4.4 Soil and groundwater contamination

Most refineries have some areas that are contaminated by historical product losses. Current refinery practices are designed to prevent spillages and leaks to ground. In the past, the awareness of the potential risks of these contaminated areas was low. The two main topics here are prevention of new spills and remediation of historic contamination. As mentioned within the scope, soil remediation is not included in the scope of this document. Most oil fractions are biodegradable, given time. The thinking about the cleaning-up of those contaminated areas has changed over the years. Increased knowledge about soil sciences and the difficulty of soil remediation on a site that is still in operation, has lead to the pragmatic approach of managing the risks of these contaminated sites to ensure their fitness for use and ensuring that pollution does not spread beyond the site. There are a number of ongoing research initiatives for improving the performance of on-site remediation techniques.

The main sources of contamination of soil and groundwater by oil are typically those places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground. These are commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon-containing water. The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists.

1.4.5 Other environmental issues

Besides the environmental issues mentioned in the above sections, especially for refineries situated near residential areas, nuisance has become an issue of discussion with both local authorities and with representatives of the local population in so-called neighbourhood councils. Topics such as noise, light and smoke emission (flaring) and smell which directly impact the residents receive much more emphasis in these neighbourhood councils than the above-mentioned 'major' emissions which tended to receive more attention historically.

Nuisance by light can be caused through flaring at night by refineries and petrochemical plants located near densely populated areas.

Since the 1970s refineries have devoted considerable resources to increasing process safety, both in design and operation by training, procedures and personal protection equipment. Increased attention, training, safe design and adequate tools and personal protection equipment has resulted in a steady decrease in the number of unsafe acts, accidents, incidents and near misses [242, CONCAWE, 1998].

Occupational health is included in the operational safety procedures aimed at protecting workers from exposure to toxic materials and providing them with all necessary facilities which contribute to their well-being and their sense of security and safety. Instructions, information exchange and training of personnel, the provision of personal protection equipment as well as strict adherence to stringent operational procedures have contributed to a steady decrease in accidents and health incidents. Typical refinery pollutants and products with a health risk include hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NO_x and SO_x, for which legally binding Maximum Acceptable Concentrations values prevail.

The design of the refinery installations and the process control systems needs to include provisions for a safe shut-down with minimum emissions from the unit involved. During unplanned operational upsets, these provisions should guarantee that feed supply is terminated followed by subsequent pre-programmed automated activation of pumps, relief systems, purging systems, flares and other equipment. Examples of such occurrences are utility failure, breakdown of equipment, a fire or an explosion. Emergency situations leading to direct spills occurring in parts of the plant which are neither fully contained nor fully automated, such as pipeline and tank bottom rupture, have to be addressed with standing emergency procedures. These are directed to minimisation and containment of the spills, followed by rapid clean-up in order to minimise the environmental impact.

2 APPLIED PROCESSES AND TECHNIQUES

This section describes the major activities and processes that may be found within the natural gas plant sector and petroleum refining industry, including the materials and equipment used and the processes employed. This chapter is designed for those interested in gaining a general understanding of the processes and activities that can be found in these two industrial sectors, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent chapters of this document - emission, consumption and best available techniques for the different processes. This section does not attempt to replicate published engineering information that is available for this industry in the general literature.

The major production unit operations and activities typically involved at petroleum refineries are described briefly, in alphabetical order, in the current chapter. For many of these production operations, a number of different techniques and or unit operations are used in the industry. While the major techniques used for each process/activity are described, it is not intended to discuss and describe all of the different processes currently in use. This chapter specifically contains the purpose and principle of the process, feed and product streams, a brief process description of commonly used production processes/activity and operability. This information, coupled with schematic drawings of the identified processes, provides a concise description of the process/activity.

The first section is dedicated to a general technical description of refineries and the following 22 sections cover all the processes and activities within the scope of the BREF. Natural gas plants processes are included in one independent section (Section 17). These sections do not pretend to be of equal importance from the environmental impact point of view. Some sections have more relevance than others, but this structure is considered a good way to tackle the BAT assessment for the mineral oil and gas refinery sectors. No pollution abatement technique is include in this chapter. However, some of the processes (e.g. hydrotreatments) have an environmental aspect. Environmental implications of production techniques can be found in Chapter 3. Discussion on good environmental practices (prevention techniques) of production techniques can be found in Chapter 4. As consequence of that, no information about emissions can be found in Chapter 2. Information on, for instance, flares, sulphur recovery units, waste water systems and waste management is not included in this chapter because they are not considered production activities. They are security or environmental techniques that are applied in both sectors.

2.1 General overview of the refinery processes

Crude oil and natural gas are mixtures of many different hydrocarbons and small amounts of impurities. The composition of those raw materials can vary significantly depending on its source (see Section 10.3 for type of crude oils). Petroleum refineries are complex plants, where the combination and sequence of processes is usually very specific to the characteristics of the raw materials (crude oil) and the products to be produced. In a refinery, portions of the outputs from some processes are fed back into the same process, fed to new processes, fed back to a previous process or blended with other outputs to form finished products. One example of that can be seen in Figure 2.1, which also shows that all refineries are different regarding their configuration, process integration, feedstock, feedstock flexibility, products, product mix, unit size and design and control systems. In addition, differences in owner's strategy, market situation, location and age of the refinery, historic development, available infrastructure and environmental regulation are amongst other reasons for the wide variety in refinery concepts, designs and modes of operation. The environmental performance can also vary from refinery to refinery.

The production of a large number of fuels is by far the most important function of refineries and will generally determine the overall configuration and operation. Nevertheless some refineries can produce valuable non-fuel products such as feedstocks for the chemical and petrochemical industries. Examples are mixed naphtha feed for a steam cracker, recovered propylene, butylene

for polymer applications and aromatics manufacture covered under the Large Volume Organic Chemical BREF. Other speciality products from a refinery include bitumen, lubricating oils, waxes and coke. In recent years the electricity boards in many countries have been liberalised allowing refineries to feed surplus electricity generated into the public grid.

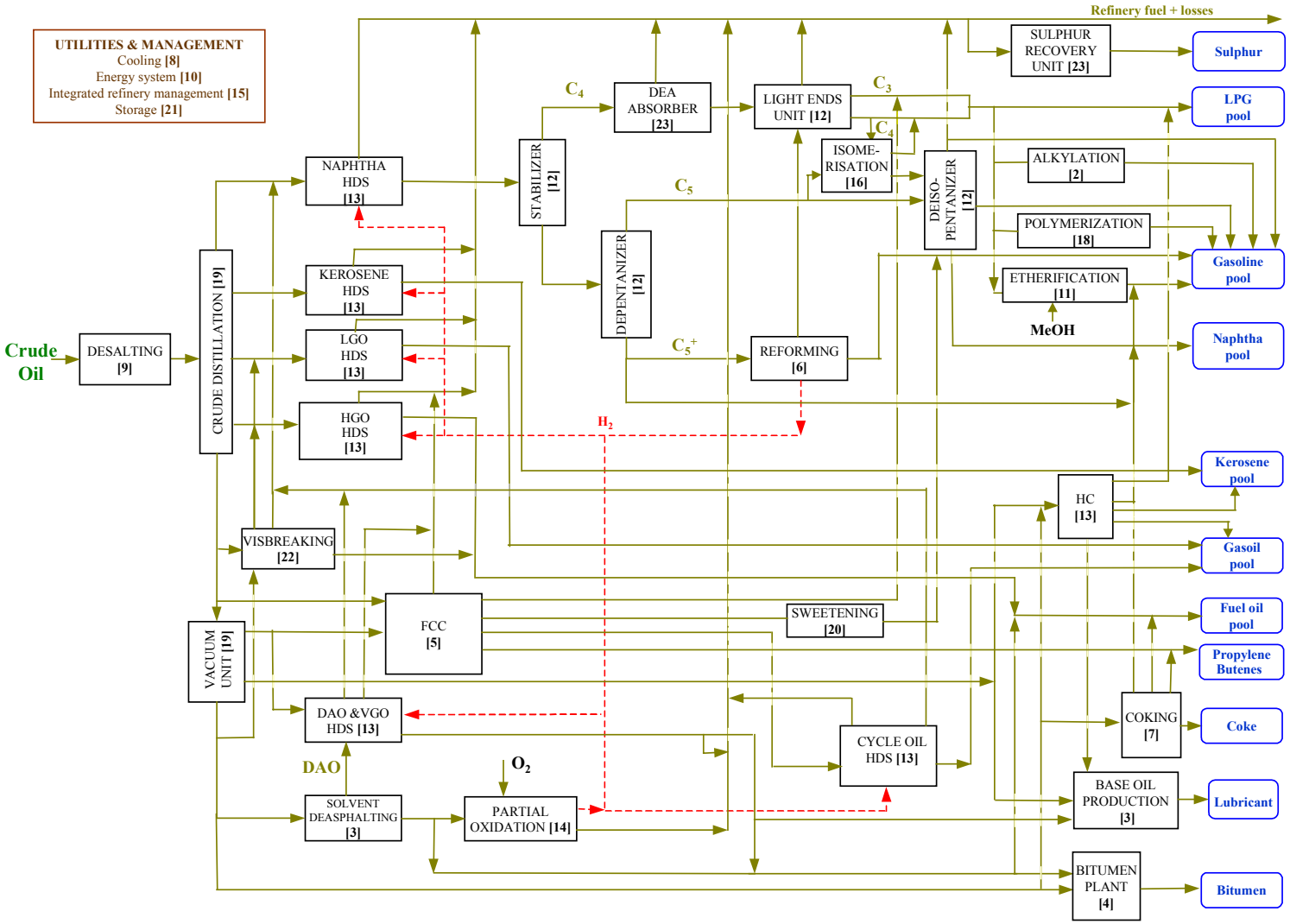
Refining crude oil into usable petroleum products can be separated into two phases and a number of supporting operations. The **first phase** is desalting of crude oil (Section 2.9) and the subsequent distillation into its various components or "fractions" (Section 2.19). A further distillation of the lighter components and naphtha is carried out to recover methane and ethane for use as refinery fuel, LPG (propane and butane), gasoline blending components and petrochemical feedstocks. This light product separation is done in every refinery.

The **second phase** is made up of three different types of "downstream" processes: combining, breaking and reshaping fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. The goal of those processes is to convert some of the distillation fractions into marketable petroleum products (see Section 10.3) through any combination of downstream processes. Those processes define the various refinery types, of which the simplest is the 'Hydroskimming', which merely desulphurises (Section 2.13) and catalytically reforms (Section 2.6) selected cuts from the distillation unit. The amounts of the various products obtained are determined almost entirely by the crude composition. If the product mix no longer matches the market requirements, conversion units have to be added to restore the balance.

The market demand has for many years obliged refineries to convert heavier fractions to lighter fractions with a higher value. These refineries separate the atmospheric residue into vacuum gasoil and vacuum residue fractions by distillation under high vacuum (Section 2.19), and then feed one or both of these cuts to the appropriate conversion units. Thus by inclusion of conversion units, the product slate can be altered to suit market requirements irrespective of the crude type. The number and the possible combinations of conversion units are large.

The simplest conversion unit is the thermal cracker (Section 2.22) by which the residue is subjected to such high temperatures that the large hydrocarbon molecules in the residue convert into smaller ones. Thermal crackers can handle virtually any feed, but produce relatively small quantities of light products. An improved type of thermal cracker is the coker (Section 2.7), in which all the residue is converted into distillates and a coke product. In order to increase the degree of conversion and improve product quality, a number of different catalytic cracking processes have evolved, of which fluid catalytic cracking (Section 2.5) and hydrocracking (Section 2.13) are the most prominent. Recently, residue gasification processes (Section 2.14) have been introduced within refineries, which enable refineries to eliminate heavy residues completely and to convert them into clean syngas for captive use and production of hydrogen, steam and electricity via combined cycle techniques.

Supporting operations are those not directly involved in the production of hydrocarbon fuels but serving in a supporting role. They may include energy generation, waste water treatment, sulphur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and storage of products.



DAO: Deasphalted oil **DEA:** Diethylamine **FCC:** fluid catalytic cracker **HC:** Hydrocracking **HDS:** Hydro desulphurisation **HGO:** Heavy gas oil **LGO:** Light gas oil **VGO:** Vacuum gas oil

Figure 2.1: General scheme of a complex oil refinery
Note: Numbers in the figure are the section numbers given to each type of process in this chapter.

As it has been mentioned in Section 1.3.1, there are various approaches to compare refineries due to the difference in complexity that they have. This can be done defining refinery complexity indexes as they have been explained in Section 1.3.1. The Nelson refinery complexity index was used for the construction of Figure 1.3 [287, Johnston, 1996]. In Dutch notes [118, VROM, 1999] EU refineries are grouped by configuration, as shown in Table 1.9. CONCAWE [115, CONCAWE, 1999] has grouped refineries by types (that differ in definition from the configurations of Table 1.9) in Figure 1.4 as they existed in the period 1969 - 1997. Other definitions are used in the industry, such as FCC equivalent (used by CEC DG Transport reports on the refining industry) or the Equivalent Distillation Capacity as used by Solomon Associates. Some of those parameters will be used in the document.

Table 2.1 summaries the main products obtained from the main refinery processes. As can be seen, many of the products are obtained from different units and consequently it gives an idea of the technical complexity and the modes of operation that may be found in a refinery.

PRODUCTS → REFINERY UNITS ↓	Section	LPG	Gasoline	Kero/ naphtha	Heating oil/diesel	HFO	Base Oil	Coke/ bitumen	Special
Carbon n° range		C_3-C_4	C_4-C_{12}	C_8-C_{17}	C_8-C_{25}	>C_8	>C_{15}	>C_{30}	
Alkylation	2		▨						
Base Oil production	3						▨	▨	wax
Bitumen production	4							▨	
Catalytic cracker	5	▨	▨	▨	▨	▨			
Residue cracking	5	▨	▨	▨	▨	▨			
Catalytic reforming	6	▨	▨						H_2
Delayed coking	7			▨	▨	▨		▨	
Flexicoker	7			▨	▨	▨			low joule gas
Gasification	10								syngas
Etherification	11								MTBE
Gas separation processes	12	▨							Refinery fuel gas
Hydrogen plant	14								H_2
Residue Hydroconversion	14			▨	▨	▨			H_2
Hydrocracker	15		▨	▨	▨	▨			
Hydrodesulphurisation	15		▨	▨	▨				
Isomerisation	17		▨						
Crude atmospheric distillation	19	▨	▨	▨	▨	▨			
Vacuum distillation	19				▨	▨	▨	▨	
Thermal cracking/Visbreaking	22	▨	▨	▨	▨	▨			
Sulphur recovery unit	23								S

Table 2.1: Refinery units and their main products

2.2 Alkylation

PURPOSE AND PRINCIPLE

The purpose of alkylation is to yield high-quality motor fuel blending. The term alkylation is used for the reaction of olefins with isobutane, to form higher molecular-weight isoparaffins with a high octane number. The process involves low-temperature reaction conditions conducted in the presence of strong acids.

FEED AND PRODUCT STREAMS

Low-molecular weight olefins (C_3-C_5) and isobutane are used as alkylation unit feedstocks. The major sources of low olefins are catalytic crackers and cokers. Isobutane is produced by hydrocrackers, catcrackers, catalytic reformers, crude distillation and natural gas processing. In some cases, n-butane is isomerised (see Section 2.16) to produce additional isobutane. The product is alkylate (a high octane gasoline component) with some propane and butane liquids. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range. Dissolved polymerization products are removed from the acid as thick dark oil.

PROCESS DESCRIPTION

In the alkylation unit HF or H_2SO_4 is used as a catalyst. When the concentration of acid becomes low, some of the acid must be removed and replaced with fresh acid.

In the *hydrofluoric acid process*, the slipstream of acid is redistilled. The concentrated hydrofluoric acid is recycled and its net consumption is relatively low. In this process (Figure 2.2), the feed enters the reactor and is mixed with the isobutane recycle and HF from the settler. Both the olefin and isobutane feeds are dehydrated first (not in Figure 2.2), as this is essential to minimise potential corrosion. The reactor, operating at 25 - 45 °C and 7 - 10 barg, is cooled to remove the heat generated by the reaction. In the settler, alkylate and excess isobutane are separated from the HF. The HF is recycled to the reactor, where it is regenerated while the organic phase consisting of the alkylate and unreacted isobutane flow to the isostripper. There, the isobutane and some other light components are stripped from the alkylate. This is routed as product to storage after treating with potassium hydroxide. The decomposition of any organic fluoride formed is promoted by the high tube wall temperatures. The butane feed (n and iso) is normally fed to the isostripper. The isostripper overhead, essentially isobutane, is returned to the reactor. A small overhead slipstream is sent to a depropaniser, where propane is removed. The bottoms of the depropaniser, isobutane, are routed to the isobutane circulation stream, while the depropaniser overhead stream, propane, passes through a HF stripper to remove traces of HF and is sent to storage after final KOH treating. From the unit feed stream, n-butanes are drawn off as a side-stream from the isostripper, treated with KOH and sent to storage.

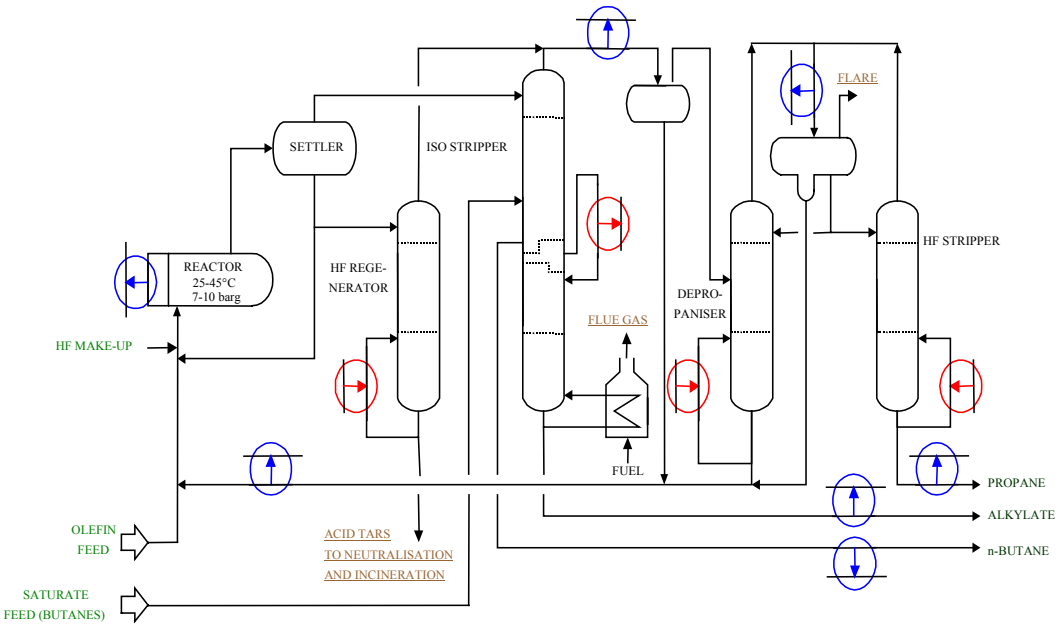


Figure 2.2: Simplified process flow scheme for HF alkylation unit

In the *sulphuric acid process*, units operate at 4 - 15 °C, which requires chilling. Spent sulphuric acid generation is substantial and the sulphuric acid removed must be regenerated in a sulphuric acid plant (not considered as part of the alkylation unit). In this process, the olefin feed and recycled isobutane are introduced into the stirred, autorefrigerated reactor. Mixers provide intimate contact between the reactants and the acid catalyst and the reaction heat is removed from the reactor. The hydrocarbons that are vaporised from the reactor are routed to the refrigeration compressor where they are compressed, condensed and returned to the reactor. A depropaniser, which is fed by a slipstream from the refrigeration section, is designed to remove any propane introduced to the plant with the feeds. The reactor product is sent to the settler where the hydrocarbons are separated from the acid that is recycled. The hydrocarbons that are sent to the deisobutaniser, together with make-up isobutane and the isobutane rich overhead, are recycled to the reactor. The bottoms are then sent to a debutaniser to produce alkylate product.

2.3 Base oil production

Although only 20 % of EU+ refineries produce base oil, some actually specialise in it. Figure 1.2 (Chapter 1) identifies the refineries specialised in production of lubricant and bitumen. More extensive information about the processes can be found in the general literature (e.g. [319, Sequeira, 1998]).

PURPOSE AND PRINCIPLE

Lubricants are a blend of different grades of base oils and special additives. To produce a suitable lubricant, certain properties of the base oil are very important: viscosity, viscosity index (high V.I. means that the viscosity changes very little as temperature changes, and vice versa), high resistance to oxidation, low pour point and good dope susceptibility or compatibility. The principle of base oil production is to separate the desired boiling range components from the atmospheric residue by vacuum distillation (Section 2.19); unwanted components are subsequently removed by different processes and optional hydrofinishing. Base oil is a speciality product and consequently not all crudes are suitable. Heavy crudes are frequently used as feedstock to conventional base oil complexes.

FEED AND PRODUCT STREAMS

The feedstocks to a conventional base oil complex are waxy distillate side-streams from vacuum distillation units (Section 2.19) and the extract from deasphalting units. Atmospheric residue feedstock to the vacuum distillation unit consist of various types of hydrocarbon compounds with different suitability for base oils: a) **Aliphatic or paraffinic:** Normal (n-)paraffins and iso (i-)paraffins form this group. The n-paraffins have a high V.I. and melting points and at ambient conditions form crystals, which must be removed to reduce the pour point of lubricating. i-paraffins have lower melting points, very high V.I. but lower viscosity; b) **Naphthenic:** The naphthenic rings lend high viscosity, low melting point and a good V.I. (less than paraffins) to lubricant oils; c) **Aromatic:** The aromatic rings lend high viscosity and low melting point to compounds but a low V.I to the oils. For this reason they are considered the least satisfactory type of compounds for lubricants. The ratio in which the three groups are present varies from crude to crude.

In the various processes of the base oil production, significant quantities of by-products such as bitumen, extracts and wax are produced. Based on a total feedstream to the vacuum distillation unit, on average some 20 - 25 % ends up as final base oil product.

PROCESS DESCRIPTION

A base oil complex consists typically of a vacuum distillation tower (Section 2.19), a deasphalting unit, an aromatic extraction unit, a dewaxing unit and optional high-pressure hydrogenation unit and hydrofinishing unit to improve colour and stability, meet product specifications and remove impurities. Figure 2.3 shows a simplified block diagram of a base oil manufacturing plant.

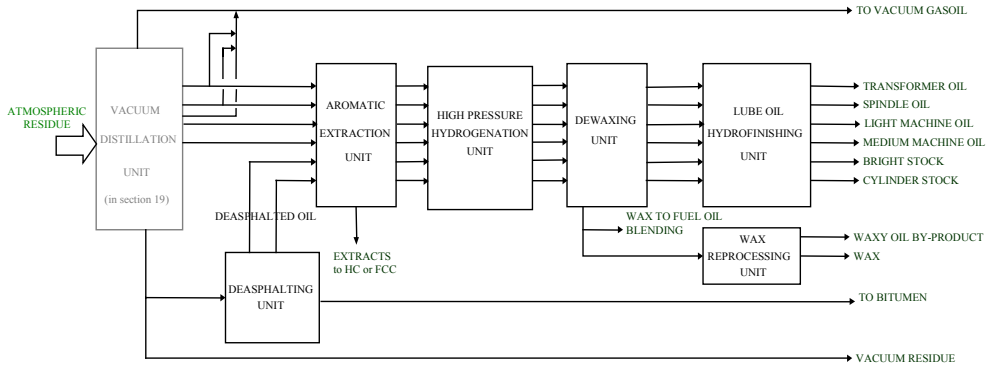


Figure 2.3: Block scheme of a lubricating oil manufacturing plant

A conventional base oil complex is very labour intensive mainly due to its batch operation, the many grades of base oil normally produced and the associated intensive product handling operations.

Deasphalting
Solvent deasphalting produces lubricating oil base stocks by extracting high-boiling lighter paraffinic and naphthenic hydrocarbons (asphaltenes and resins) from the vacuum residue of the vacuum distillation unit. This process makes the deasphalted oil extract light and paraffinic and the bitumen raffinate heavy and aromatic. Propane or propane-butane mixtures are usually used as solvents. At specific operating conditions, 37 - 40 bar and 40 - 70 °C, lower boiling paraffinic and naphthenic hydrocarbons are very soluble in propane. At higher temperatures (100 ºC) all hydrocarbons are almost insoluble in propane. The solvent deasphalting process is a typical extraction process consisting of an extractor and recovery sections, flash evaporation and stripping, to separate the propane solvent from the oil and bitumen phase. The deasphalted oil product stream is run down to intermediate storage; the bitumen product stream can be blended to heavy fuel, used as feedstock for the coker or used for the bitumen product.

More recently, solvent deasphalting has been adapted for the preparation of catalytic cracking, hydrocracking, hydrodesulphuriser feeds and hard bitumen (deep deasphalting). For these purposes, heavier-than-propane solvents (butane to hexane mixture) are used together with higher operating temperatures. This maximises the yield of valuable deasphalted oil and minimises the yield of hard bitumen with a softening point usually over 150 ºC.

Aromatic extraction
Aromatic extraction uses solvents to remove aromatics from base oil feedstocks, improving viscosity, oxidation resistance, colour and gum formation. A number of different solvents can be used (furfural, N-methyl-2-pyrrolidone (NMP), phenol or liquid sulphur dioxide). These processes are typical extraction processes consisting of an extractor and recovery sections, flash evaporation and stripping, to separate the solvent from the oil-rich raffinate and aromatic-rich extract stream. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor. Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The raffinate stream is rundown to intermediate storage. The extract, after solvent recovery, is likely to contain high concentrations of sulphur, aromatics, naphthenes and other hydrocarbons, and is often fed to the hydrocracker or catcracker unit.

High pressure hydrogenation unit
Hydrogenation process is used to reduce aromatics and olephinic compounds found in the base oil streams.

Dewaxing
Dewaxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures. This process is used when paraffinic-rich crudes are processed. *Solvent dewaxing* is more prevalent. In these units the high pour point constituents (mainly paraffins) are removed from the raffinate streams. The oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallized, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK), toluene or chlorinated hydrocarbons. Solvent is recovered from the oil and crystallised wax through heating, two-stage flashing, followed by steam stripping. The wax is removed from the filters, melted and subsequently fed to a solvent recovery unit to separate the solvent from the wax. The wax is either used as feed to the catalytic cracker or is de-oiled and sold as industrial wax.

Hydrofinishing
In this unit the colour and colour stability is improved and the organic acid components are removed. The need for hydrofinishing depends on the crude oil processed and to a certain extent on the licensor and the design of the preceding units. The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).

2.4 Bitumen production

Bitumen is a residue derived from certain crude oils (e.g. Middle East, Mexico or South America) after vacuum distillation has removed waxy distillates. Bitumen is normally mixed with other components (e.g. gravel) to produce asphalt that is used in road paving, roof coating and pipe sealing or coating. Bitumen production only appears in some refineries (45 % of the EU+ refineries). There are also some refineries that specialise in producing those components. Figure 1.2 (Chapter 1) identifies the lubricant and bitumen specialised refineries.

PURPOSE AND PRINCIPLE

The desired properties of bitumen may be achieved either by adjusting distillation conditions or by "blowing". In the latter process, air is blown into hot bitumen causing dehydrogenation and polymerisation reactions and giving a harder product with higher viscosity, higher softening point and a reduced 'penetration' (The penetration, often used as the main criterion, refers to the depth of penetration by a standard needle in a bitumen sample at standard conditions.). The properties of the blown bitumen are determined by the residence time in the oxidation vessel, the air rate and the liquid temperature. If any of these parameters is increased, the penetration is reduced and the softening temperature is raised.

FEED AND PRODUCT STREAMS

In most applications the hydrocarbon feed stream to a bitumen blowing unit (BBU) is the bottom residue stream from a vacuum unit (Section 2.19) and in some instances the residue (extract) from a deasphalting unit (Section 2.3).

Normally, a number of different grades of bitumen are produced in campaigns and these are further modified by blending with other high-boiling components such as vacuum residue, heavy gas oil or synthetic polymers. In this way a single blowing unit is able to cater for a wide range of bitumen grades for various applications.

PROCESS DESCRIPTION

The BBU will either operate on a continuous basis or in batch mode depending on the quality of the vacuum residue feedstock and the required bitumen product specification. Continuous processes are more spread in refineries. A simplified process flow diagram of the BBU is shown in Figure 2.4 which represents a typical continuously operated BBU receiving its hot feed directly from the vacuum distillation unit. Where the bitumen feed is received from storage, an additional fired heater may be required to preheat the feed to a temperature of about 200 - 250°C, but can be up to 550 ºC. With a batch-operated BBU, a feed buffer vessel is usually included to store the hot feedstream from the vacuum unit.

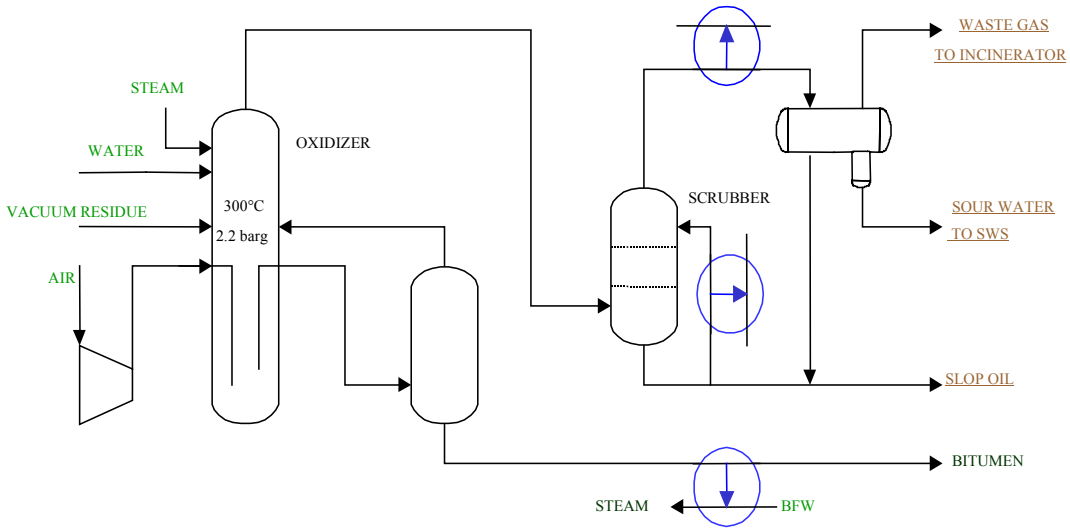


Figure 2.4: Simplified process flow scheme of a bitumen blowing unit

The residue feedstream is pumped into the top of the oxidation vessel. Operating pressure in the top of the oxidation vessel is normally around 1 barg and in the bottom around 2 barg, depending on the height of the vessel. As air is sparged into the base of the vessel, oxidation of the residue takes place, resulting in heat. The temperature in the oxidation vessel, which determines to a certain extent the bitumen grade, is normally controlled between 260 – 300 °C. Different options are applied, taking in colder feed to the oxidation vessel, recirculation of cooled bitumen product from the bitumen rundown cooler, and in older units even direct water quenching is applied. The blown bitumen is removed from the bottom of the oxidation vessel and cooled by raising steam before being sent to storage.

The air rate is normally well in excess of stoichiometric requirements and so a considerable quantity of oxygen is present in the upper vapour space of the oxidation vessel. To avoid an explosion in the vapour space, in most units steam is injected at a rate necessary to keep the oxygen concentration below the lower flammable limit (5 - 6 % vol.). In some units a small amount of water is also injected into the vapour outlet of the oxidation vessel to reduce the vapour temperature. This is sometimes considered necessary to prevent afterburning in the overhead system that could lead to severe coke formation.

The overhead vapours are first passed through a vent gas scrubber to remove oil and other oxidation products. In most cases gasoil is used as once-through scrubbing liquid. The vent gas from the scrubber is subsequently cooled to condense light hydrocarbons and sour water, sometimes in a water spray contact condenser or scrubber. The remaining gas, consisting mainly of light hydrocarbons, N_2, O_2, CO_2 and SO_2, is incinerated at high temperature (~800 °C) to ensure complete destruction of minor components such as H_2S, complex aldehydes, organic acids and phenolics, which have a highly unpleasant odour.

The majority of the BBUs produce the higher grades of bitumen (roof and pipe coatings) and normally operate continuously throughout the year. The BBUs which are used to produce road bitumens operate only when the demand for road asphalt is high.

2.5 Catalytic cracking

PURPOSE AND PRINCIPLE

Catalytic cracking is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons. It uses heat and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Unlike the hydrocracker process, no hydrogen is used and consequently, limited desulphurisation takes place. Compared to other heavy oil catalytic conversion processes the FCC process is superior in being able to handle larger quantities of metals, sulphur and asphaltenes. One drawback is the minimal flexibility in changing the product yields.

FEED AND PRODUCT STREAMS

Normally the main feed stream to a catalytic cracking unit (catcracker) is the heavy vacuum distillate stream from the vacuum distillation unit. Other process streams may be blended into the catcracker feed such as heavy gasoil from the atmospheric distillation unit, coker or visbroken gasoil, deasphalted oil and extracts from lube oil units and sometimes a small quantity of atmospheric residue. Those streams may be hydrotreated to make them suitable for the catcracker. Compared to other conversion processes the catalytic cracker process is characterised by a relatively high yield of good quality gasoline and relatively high quantities of C_3 and C_4. Both products are highly olefinic and therefore ideal feedstreams for the alkylation, etherification and petrochemical industries. One drawback of the FCC process is the very low quality of the mid-distillate products in terms of sulphur, olefins, aromatics and cetane index. The *residue catalytic cracking (RCC)* unit is a catcracker unit used to upgrade heavier fractions such as atmospheric residue. The majority of products need further treatment prior to storage.

PROCESS DESCRIPTION

A number of different catalytic cracking designs are currently in use in the world, including fixed-bed reactors, moving-bed reactors, fluidized-bed reactors and once-through units. The fluidized- and moving-bed reactors are by far the most prevalent in world refineries.

Fluid catalytic cracking (FCC) units are by far the most common catcracking units. The FCC unit consists of three distinct sections, the reactor-regenerator section including air blower and waste heat boiler, the main fractionator section including wet gas compressor and the unsaturated gas plant section. A simplified flow scheme is shown in Figure 2.5. In the FCC process, oil and oil vapour preheated to 250 to 425°C is contacted with hot catalyst (zeolite) at about 680 - 730°C in the riser reactor. To enhance vaporisation and subsequent cracking, the feed is atomised with steam. The cracking process takes place at temperatures between 500 and 540°C and a pressure of 1.5 - 2.0 barg. Most catalysts used in catalytic cracking are zeolites (some 15% w/w) supported by amorphous synthetic silica-alumina with metals. The catalyst is in a fine, granular form which mixes intimately with the vaporised feed. The fluidised catalyst and the reacted hydrocarbon vapour separate mechanically in a (two-stage) cyclone system and any oil remaining on the catalyst is removed by steam stripping. The amount of lost catalyst as fines in the cyclone system is balanced by the addition of fresh catalyst. The catalytic cracking processes produce coke which collects on the catalyst surface and diminishes its catalytic properties. The catalyst therefore needs to be regenerated continuously or periodically, essentially by burning the coke off the catalyst at high temperatures. The method and frequency with which catalysts are regenerated are a major factor in the design of catalytic cracking units. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration by burning off the coke deposits with air. However, in time the catalyst deactivates gradually and irreversibly due to high temperature exposure and metal poisoning (mainly vanadium). The hot regenerated catalyst flows back to the base of the reactor riser, where it is cooled by vaporisation of the feed and by the heat required for cracking reactions. The cracked oil vapours are then fed to a fractionation tower where the various desired fractions are separated and collected. The streams are steam-stripped to remove volatile hydrocarbons prior to cooling and sending to storage. Slurry oil is taken from the bottom of the column and part of it is cooled with the reactor feed stream and steam generation and is returned to the column. The recycled slurry oil is used as wash oil and as a quench for the hot reactor overhead vapours to prevent

aftercracking. The rest of the slurry oil is filtered or decanted to remove catalyst fines, cooled and sent to storage. The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate it into three phases: gas, liquid and sour water streams. The liquid and gas streams are both fed to the gas plant (Section 2.12) for further separation and the sour water stream is sent to the sour water stripper for purification (Section 2.23).

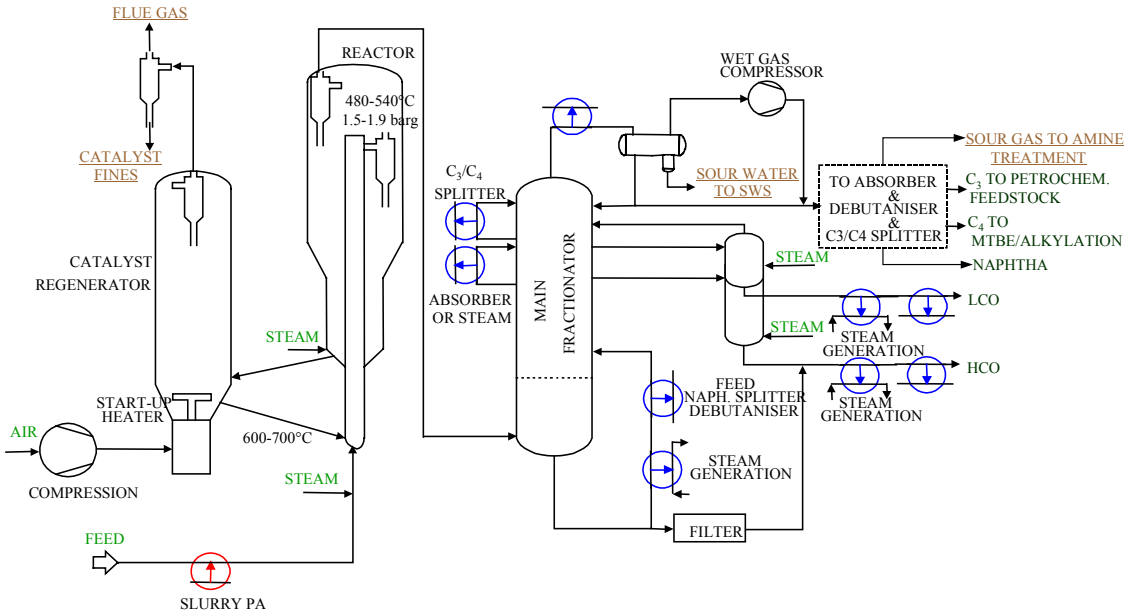


Figure 2.5: Simplified process flow scheme for fluid catalytic cracker

The flow sheet of a **residue catalytic cracker (RCC)** is basically the same as for a FCC with the difference that it often has a CO boiler and a catalyst cooler. Sometimes FCC units are equipped with both a CO boiler and a catalyst cooler and can consequently be used as RCC unit. Due to the higher coke lay-down on the catalyst as a result of the heavier feeds, the heat balance around the regenerator may require additional measures as catalyst coolers. As the heavier feed normally has a higher metal content, especially Ni and V, the catalyst deactivation rate is so fast that the catalyst needs to be removed continuously, to be replaced by fresh catalyst.

In the **moving-bed process**, oil is heated to 400 - 700 ºC and is passed under pressure through the reactor, where it comes into contact with a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated. The catalyst is regenerated in a continuous process. Some units also use steam to strip remaining hydrocarbons and oxygen from the catalyst before catalyst is fed back to the oil stream. In recent years moving-bed reactors have largely been replaced by fluidized-bed reactors.

2.6 Catalytic reforming

PURPOSE AND PRINCIPLE

The heavy naphtha leaving hydrotreating units is a very poor gasoline blend component. So the purpose of a catalytic reformer is to upgrade these streams for use as a gasoline blendstock. The burning characteristics (octane number) of heavy naphtha are improved significantly by catalytic reforming. The most important characteristic of the reformate product is the octane number. Octane numbers are very low for n-paraffins, slightly better for naphthenes, quite high for iso-paraffins and highest for aromatics. There are four major types of reactions which occur during the reforming processes: 1) dehydrogenation of naphthenes to aromatics; 2) dehydrocyclisation of paraffins to aromatics; 3) isomerisation; and 4) hydrocracking. Because the recently reformulated gasoline specifications have limited the allowable amount of benzene in gasoline (e.g. Auto-Oil I see Table 1.4), and possibly in the future the aromatics content, catalytic reformer operation may be driven by hydrogen production needs more than to produce additional aromatic which has been traditionally been the case.

FEED AND PRODUCT STREAMS

The typical feedstocks to catalytic reformer units are the hydrotreated straight-run heavy naphtha stream from the crude distillation unit and, if applicable, the hydrotreated heavy naphtha stream from the hydrocracker unit and medium catcracked naphtha stream. A catalytic reformer produces hydrogen, which is essential for use in hydrotreaters (Section 2.13) and may be used in the hydrocracking processes. Products from a reformer includes, additionally to the hydrogen, refinery fuel gas, LPG, isobutane, n-butane and reformate. The reformate may be blended to gasoline or further separated into components as chemical feedstocks like benzene, toluene, xylene, and naphtha cracker feeds.

Some catalytic reformers operate under more severe conditions, resulting in increased aromatics content in the reformate product. Some catalytic reformers operate for the production of aromatics as a (chemical) product (see Large Volume Organic Chemical BREF).

PROCESS DESCRIPTION

Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulphur, nitrogen and metallic contaminants. The catalysts used in catalytic reforming processes are usually very expensive (containing Pt) and extra precautions are taken to ensure that catalyst is not lost. There are several catalytic reforming processes in use today. In general they can be classified in three categories: continuous, cyclic or semi-regenerative, depending upon the frequency of catalyst regeneration. The fixed-bed or moving-bed processes are used in a series of three to six reactors.

Continuous catalytic reformer (CCR)

In this process the catalyst can be regenerated continuously and maintained at a high activity. The ability to maintain high catalyst activities and selectivities by continuous catalyst regeneration is the major advantage of this type of unit. Figure 2.6 shows a simplified process flow diagram of a continuous catalytic reformer.

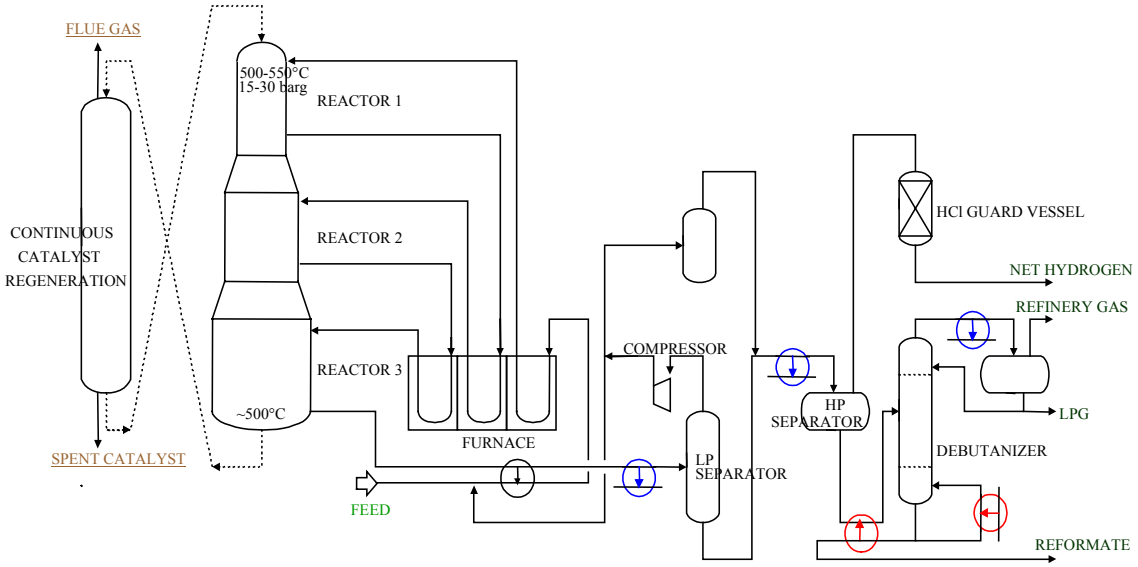


Figure 2.6: Simplified process flow scheme for a continuous catalytic reformer

Interheaters are needed between the reactors to provide the heat required for the endothermic dehydrogenation reaction. As the naphtha feed charge proceeds through the reactors, the reaction rates decrease and the reheat needed becomes less. Freshly regenerated catalyst is introduced at the top of the first reactor and flows by gravity from top to bottom. From here it is passed on to the next reactor. Partially aged catalyst is removed from the bottom of the lowest reactor and sent to an external regenerator where the carbon is burned from the catalyst. The catalyst is reduced and acidified before being returned to the upper reactor. The reaction mixture from the last reactor is used to preheat the fresh feed and further cooled down prior to being fed to the low-pressure separator. There the hydrogen-rich gas is separated from the liquid phase. The gas is compressed and partially recycled to the naphtha feed. The remaining vapour is then further compressed, recontacted with the liquid from the low-pressure separator, cooled and fed to the high-pressure separator. The recompression and recontacting is included to maximise recovery of the C_3/C_4 fraction from the hydrogen rich gas stream. Any excess of this hydrogen rich gas is bled to the refinery fuel gas grid. The selection of the reformer operating pressure and the hydrogen/feed ratio form a compromise between maximum yields and stable operation.

Cyclic process

The cyclic process is characterised by having a swing reactor in addition to those on-stream, in which the catalyst can be regenerated without shutting the unit down. When the activity of the catalyst drops below the desired level, this reactor is isolated from the system and replaced by the swing reactor. The catalyst in the replaced reactor is then regenerated by admitting hot air into the reactor to burn the carbon from the catalyst. Typically, one reactor is always being regenerated.

Semi-regenerative process

In this process, regeneration requires the unit to be taken off-stream. Depending upon the severity of operation, regeneration is required at intervals of 3 to 24 months. High hydrogen recycle rates and operating pressures are utilised to minimise coke laydown and the associated loss of catalyst activity.

2.7 Coking processes

PURPOSE AND PRINCIPLE

Coking is a severe thermal cracking process used primarily to reduce refinery production of low-value residual fuel oils and transform it into transportation fuels, such as gasoline and diesel. As part of the process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities.

FEED AND PRODUCT STREAMS

As the coking process is a thermal destruction process, the quality of the feed in terms of metal content, Concarbon number and other contaminants is not critical. As a matter of fact, coking is predominantly used when the feed has a high Concarbon number and contains high quantities of impurities which cannot be handled in catalytic conversion processes. All this gives high feedstock flexibility. The feed to a delayed coking unit can consist of atmospheric residue, vacuum residue, shale oils, tar sands liquid and coal tar, which results in a petroleum coke used for fuel applications. Aromatic oils and residues such as heavy cycle oils from a catalytic cracking unit and thermal tars are suitable feed stocks for the production of needle coke and anode coke. The feed to a fluid coker is the vacuum residue, sometimes mixed with refinery sludges, tarsands, bitumen and other heavy residues.

The products from the coking fractionator are refinery fuel gas, LPG, naphtha and light and heavy gas oils. Petroleum coke is another product, with the type depending upon the process used, operating conditions and feedstock used. Coke produced by the coker is called “green” coke and still contains some heavy hydrocarbons left from incomplete carbonisation reactions. More information about the properties of the coke can be found in Section 10.3.2.

PROCESS DESCRIPTION

Two types of coking processes exist: the *Delayed and fluid* coking processes that produce coke and the *Flexicoking* process that gasifies the coke produced in a fluid coking process to produce coke gas.

Delayed and fluid coking

The basic process is the same as thermal cracking (Section 2.22), except that feed streams are allowed to react for longer without being cooled. Figure 2.7 shows a simplified process flow diagram of delayed coking unit.

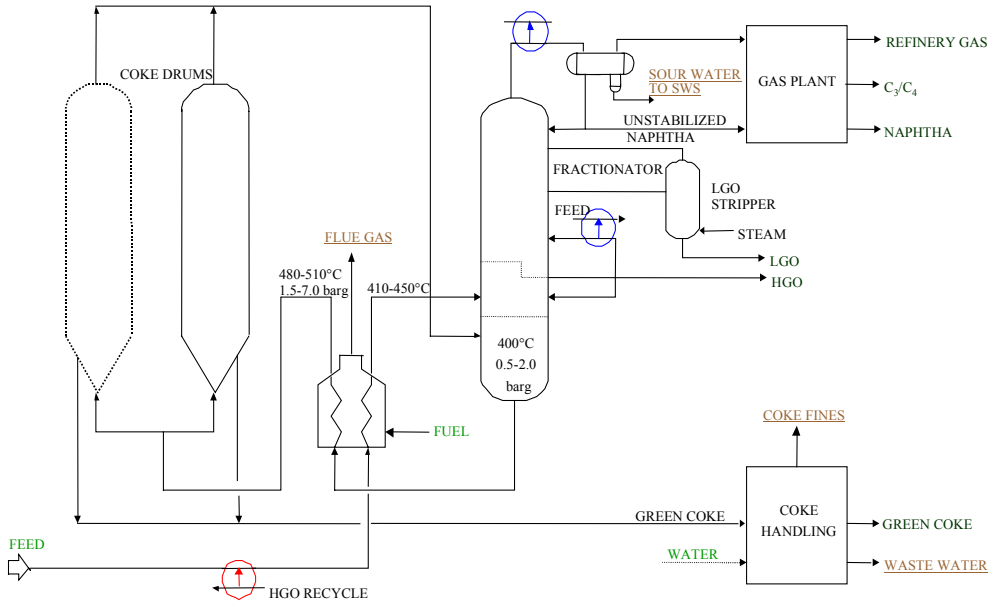


Figure 2.7: Simplified process flow scheme for delayed coking unit

The delayed coking feed stream of residual oils is first introduced to a fractionating tower, where residual lighter materials are drawn off and the heavy ends are condensed (not shown in Figure 2.7). The heavy ends are removed, heated in a furnace and then fed to an insulated vessel called the coke drum, where the cracking takes place. In the case of fluid coking, a fluidised bed is used. Temperature (440 - 450°C), pressure (1.5 - 7.0 barg) and recycle ratio are the main process variables which contribute to the quality and yields of delayed coking products. When the coke drum is filled with product, the feed is switched to an empty parallel drum (dotted drum in Figure 2.7).

When the coke drum is full, steam is then injected to remove hydrocarbon vapours. The coke bed is then quenched with water and the cokes are cut out with high pressure water. The cutting water passes to dedicated settlement where coke solids settle out and the clarified water is re-cycled. The wet green coke is conveyed to designated open stock piles, where water drains out and is recycled. Green coke can already be sold and used for energy production. The yield of delayed coking is usually above 80 % conversion of feed to products. The production of petroleum coke is of the ratio of 0.13 tonnes of petroleum coke produced per each tonne of feedstock.

Hot vapours from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulphide and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products. Condensed hydrocarbons are re-processed and collected water is re-used for coke drum quenching or cutting. Any remaining vapours commonly pass to the flare system. Normally, products such as naphtha are totally fed to the naphtha hydrotreater for further processing. The heavier products are suitable feedstock for catalytic reforming after proper hydrotreatment. Light oil needs further treatment before being sent to the gasoil blending pool. The heavy gasoil is preferably sent to a hydrocracker unit (Section 2.13) for further conversion into light components. When no cracking units are available it is blended in the heavy fuel oil pool.

For certain applications, green coke should be *calcinated* before being used or sold. The incinerator kilns are direct fuel gas or coke fine fired at the discharge end and calcinate the coke at up to 1380 ºC, driving off volatile matter and burning it within the kiln. Exhaust gases discharge from the feed end and are incinerated to burn off residuals and coke fines. Hot flue gases pass through a waste heat boiler and gas cleaning by multi-cyclones. Collected fines from the cyclones are pneumatically conveyed to a silo with exit air filters. The calcined coke discharges to a rotary direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and water scrubber. Collected cyclone fines may be re-cycled to product, which is oil sprayed as a dust suppressant, or may be incinerated or sold as a fuel.

Flexicoking

The flexicoking process typically converts 84 - 88 %w/w of the vacuum residue to gaseous and liquid products. Virtually all metals in the feed are concentrated in the 2 % solids purged from the process. Flexicoking is a very robust process in which coking and gasification are fully integrated. The process is advanced compared to the classic delayed coker in terms of operation and labour intensity.

The flexicoking process uses three major vessels: the reactor, the heater and the gasifier. As auxiliary facilities the system includes a heater overhead cooling system and fines removal system, a coke gas sulphur recovery unit and reactor overhead scrubber (Figure 2.8). The preheated vacuum residue feed is sprayed into the reactor, where it is thermally cracked, typically at 510 - 540 °C. The freshly formed coke is deposited on the surface of the fluidised recirculated coke particles. In the gasifier, the coke is reacted at elevated temperatures, typically 850 - 1000 °C, with air and steam to form coke gas, a mixture of hydrogen, carbon monoxide and dioxide and nitrogen. Sulphur in the coke is converted in the gasifier primarily to hydrogen sulphide, plus traces of carbonyl sulphide (COS). Nitrogen in the coke is converted to ammonia and nitrogen. Unlike normal gasifiers which are fed with pure oxygen, the flexicoking gasifier is

fed with air, resulting in a coke gas with a relatively low calorific value, as it contains a high quantity of nitrogen inerts.

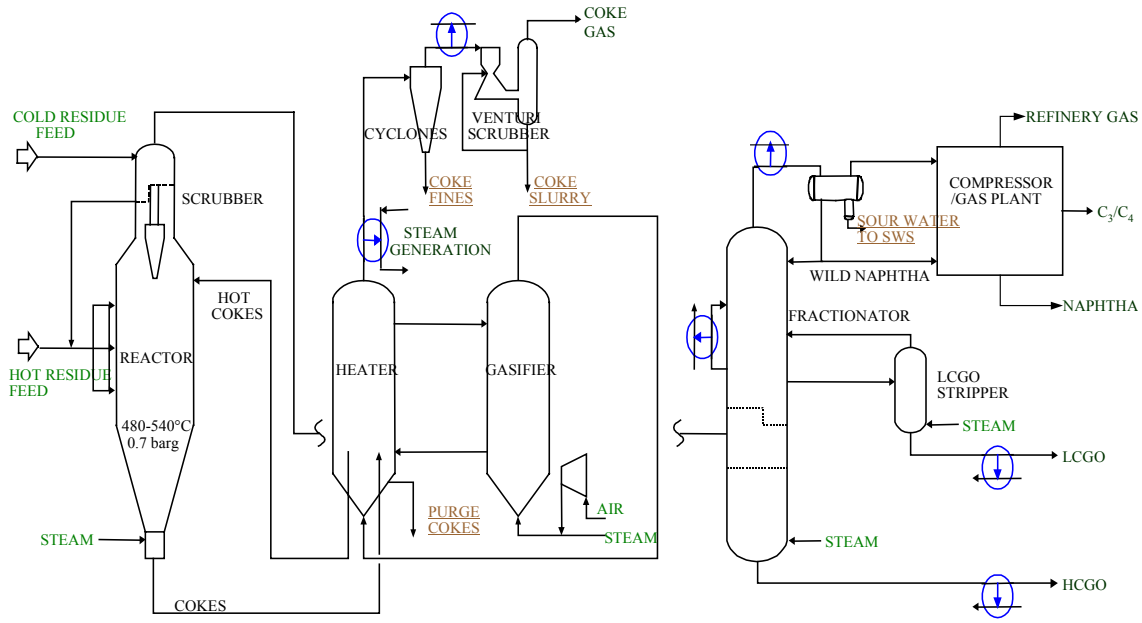


Figure 2.8: Simplified process flow scheme for a flexicoker

The cracked hydrocarbon vapour product from the reactor is passed through cyclones to remove coke particles and is subsequently quenched in a scrubber section located at the top of the reactor. Material boiling above 510 – 520 °C is condensed in the scrubber and recycled to the reactor. The lighter material goes overhead to conventional fractionation, gas compression and light ends recovery sections. The treatments and use of the products are very similar to the ones already described in the delayed coker. Pressure relief from the fractionator of the coking processes passes to flare and from the coke drums to the quench tower system.

2.8 Cooling systems

Under the IPPC process, a horizontal BREF on industrial cooling systems has been produced that covers many topics of relevance to the refineries sector. To avoid repetition, therefore, this section on cooling addresses only topics not covered by that horizontal BREF. Moreover, some cooling water pollution issues have already been studied in the OSPAR (North Sea) and HELCOM (Baltic) processes.

PURPOSE AND PRINCIPLE

In a refinery, cooling of feed and product streams is required to allow refinery process operations to take place at the right temperatures, and to bring products to their appropriate storage temperature. Even though heat integration of process systems ensures that significant cooling can be achieved by exchanging heat between streams to be cooled and streams to be heated, additional cooling is still required. This additional cooling should be provided by an external cooling medium: water and/or air.

PROCESS DESCRIPTION

A wide range of techniques is used for cooling purposes in oil refineries. Most refineries use a combination of the techniques available. The selection of a cooling system depends on required cooling temperature, cooling capacity, contamination risk (primary or secondary cooling loop) and local circumstances. Simplified diagram of the cooling techniques are shown in Figure 2.9 and briefly described below:

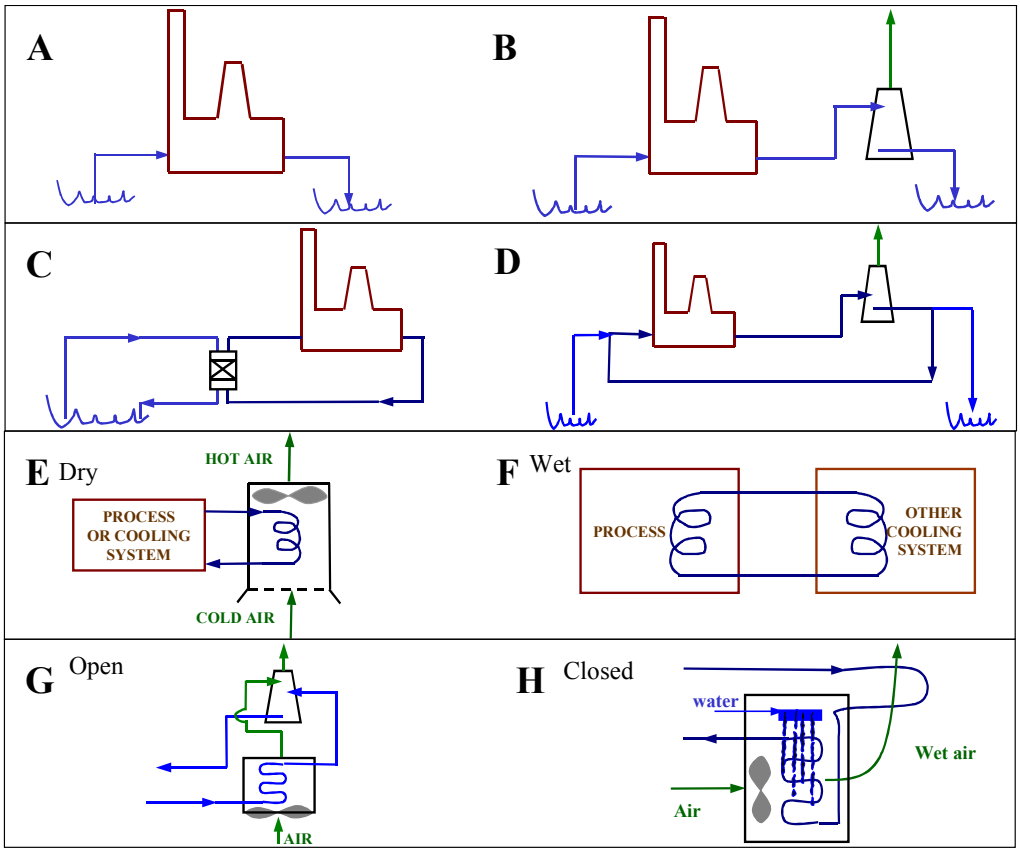


Figure 2.9: Simplified diagrams of the cooling systems used in refineries
A: Once-through cooling, B: Direct cooling with cooling of water cooling effluent, C: Indirect/Secondary system, D: Recirculating, E,F: Closed circuit, G,H: Hybrid system

Air cooling

In an air cooler (forced or induced draught), the process stream in the tubes is cooled against air delivered by a fan. An induced draught air cooler is illustrated in Figure 2.9E.

Water cooling

(1) *Direct cooling* (i.e. quenching)

Because the high contamination generated by this type of cooling, nowadays, quenching is only used in cokers (Section 2.7), in gasifiers and in some sludge incinerators.

(2) *Once-through system* (seawater, river water, etc.)

In a typical once-through cooling system, water is extracted from a surface water body, filtered if necessary and sometimes treated with biocide to inhibit fouling. It is then passed around the refinery to enable cooling through heat exchangers. The cooling water is passed through a process unit once and is then discharged directly without treatment in the waste water treatment plant. There are several ways to use water for once-through cooling in refineries that carry a different risk of contamination by process streams:

- Once-through cooling water used for cooling non-polluting streams, e.g. in power generation. A cooling tower system is generally applied when the thermal loading of the surface water is too high. Figure 2.9A&B
- Once-through cooling water used for heat exchange with a recirculating water system which then cools the process streams. Figure 2.9C.
- Once-through cooling water is used to cool process streams directly (via heat exchangers) Figure 2.9A&B.

(3) *Circulation system* (tempered water, cooling water).

In this system, most cooling water is repeatedly recycled through cooling towers using ambient air. In order to control the concentration of contaminants and the solids content in the cooling water, a blowdown stream is used – which is sent to the waste water treatment unit – and make-up water is added. A certain amount of water also exits the system through evaporation. Figure 2.9D

(4) *Wet closed system* (normally water)

Tempered water is used when process streams to be cooled should not be exposed to the (low) cooling water temperatures, (see Figure 2.9F).

(5) Hybrid systems

In these cases, both air and water are used as cooling media. These systems normally maximise the use of air cooling and the rest is done by water cooling. Two types of systems are available and they are shown in Figure 2.9G&H.

(6) Refrigeration systems

In specific cases when process streams have to be cooled below ambient temperatures, refrigeration systems are applied. This can be either a direct refrigeration system, i.e. using the refrigerant (propane or ammonia) in the process, or an indirect system (Figure 2.9F) using a circulation system (e.g. brine, glycol) where the refrigerant cools the circulating liquid.

2.9 Desalting

PURPOSE AND PRINCIPLE

Crude oil and heavy residues can contain varying quantities of inorganic compounds such as water soluble salts, sand, silt, rust and other solids, together characterised as bottoms sediment. The salt in the crude is primarily in the form of dissolved or suspended salt crystals in water emulsified with the crude.Those impurities, especially salts, could lead to fouling and corrosion of heat exchangers (crude preheaters) and especially the crude distillation unit overhead system (Section 2.19). Salts are detrimental to the activity of many of the catalysts used in the downstream conversion processes and sodium salts stimulate coke formation (e.g. in furnaces). Some inorganic impurities are chemically bound, such as vanadium and nickel, often referred to as oil-soluble salts. These cannot be eliminated in a desalter. Moreover, water should preferably be removed if the water content of the crude is relatively high. Therefore desalting of the incoming crude oil is generally applied before separation into fractions (in Section 2.19).

The principle of desalting is to wash the crude oil or heavy residues with water at high temperature and pressure to dissolve, separate and remove the salts and solids.

FEED AND PRODUCT STREAMS

Crude oil and/or heavy residues (oily feedstock) and re-used and fresh water are the feedstreams to the desalter and washed crude oil and contaminated water are the outputs of desalting processes. The water phase from the overheads crude distillation unit and other used water streams are normally fed to the desalter as washwater. Efforts are made in the industry to minimise water content of the crude to less than 0.3 % and bottoms sediments to less then 0.015 %. The concentrations of inorganic impurities in the cleaned stream are highly dependent on the design and operation of the desalter as well as the crude source.

PROCESS DESCRIPTION

After preheating to 115 - 150 °C, the oily feedstock is mixed with water (fresh and pre-used water) in order to dissolve and wash out the salts. Intimate mixing takes place by contacting the wash water in a globe valve mixer, a static mixer or a combination of both. The water must then be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The separation efficiency depends on pH, density and viscosity of the crude oil, as well as the volume of wash water used per volume of crude. Either AC or DC fields may be used and potentials from 15 to 35 kV are used to promote coalescence. Many refineries have more than one desalter. Multiple stage desalters also exists. The wash water containing dissolved hydrocarbons, free oil, dissolved salts and suspended solids is further treated in an effluent treatment plant (Section 4.24). Where bottoms sediments are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids. Figure 2.10 shows a simplified process flow diagram of a modern design crude desalter.

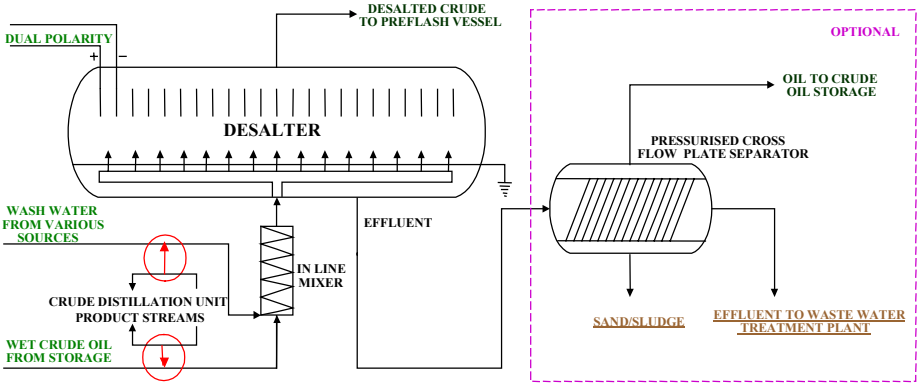


Figure 2.10: Simplified flow diagram of a crude desalter

2.10 Energy system

Although heat-producing plants are an essential and integral part of most refining processes/activities, the systems tend to be very similar and they are therefore dealt within this horizontal section. As consequence of that, energy management issues, fuel management, energy production techniques (e.g. boilers, furnaces, gas turbines) and steam management are included in this section.

PURPOSE AND PRINCIPLE
Heat and electricity are needed to run a refinery. The fairly extensive heat requirement is generally satisfied by fuel combustion. Heat can be provided to process streams and unit operations directly (by heaters) or indirectly (e.g. steam). Electricity can be generated in the refinery (e.g. CHP, gas/steam turbines, IGCC) and it can be bought from the grid. Moreover, energy (steam and power) is recognised by refiners as another output that can be produced in-house and be sold.

FUELS AND FUEL SYSTEMS
The fuel required for the production of steam and power or for the firing of the furnaces originates either from fuels that are produced by the refinery itself (refinery fuels) or from natural gas that is bought outside, or a combination of both. Normally, most or all of the gaseous and liquid refinery fuels used are by-products of refinery processes. The composition and quality of these fuels vary with the crude oils processed. Generally speaking, the refinery fuel pool is a careful balance between energy required, type of crude processed, emission limits and economics.

Refinery fuel gas (RFG)
The majority of the fuel used in a refinery is gas (methane, ethane and ethylene in combination with excess hydrogen) which is internally generated in the different refinery processes and collected in the refinery gas system, but has to be used quickly and cannot normally be sold as a valuable product. RFG, if properly treated, is a low-polluting fuel. Most of the refinery fuel gas systems have two or three alternative sources of supply: refinery gas, imported gas (normally natural gas) and liquified petroleum gas (LPG). These gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking, coking and all hydrodesulphurising processes). In the latter case the gas streams are normally treated by amine scrubbing to remove H_2S before being released to the refinery fuel gas system and dust removal and COS conversion if necessary (Section 4.23). Coke gas forms a main refinery gas source if coking takes place in the refinery. Sulphur content in the form of H_2S is normally below 100 mg/Nm^3, but levels of 20 - 30 mg/Nm^3 are possible for gas treated at high pressure (20 bars). The nitrogen content is negligible.

Fuel gas system
Figure 2.11 shows a schematic diagram of a typical fuel gas system. The fuel gas is supplied from the different refinery units. In this diagram, back-up supply is provided by imported natural gas and by internally produced LPG, which is vaporised and routed into the fuel gas header. The condensation of heavier hydrocarbons and/or water is critical for the fuel gas system. Normally all units have their own fuel gas knock-out drum, in which condensate formed in the fuel gas distribution system is separated. The fuel gas lines from this drum need to be steam-traced to avoid condensation in the supply lines to the individual burners. Liquids from the fuel gas knock-out drum are drained to a closed slops system.

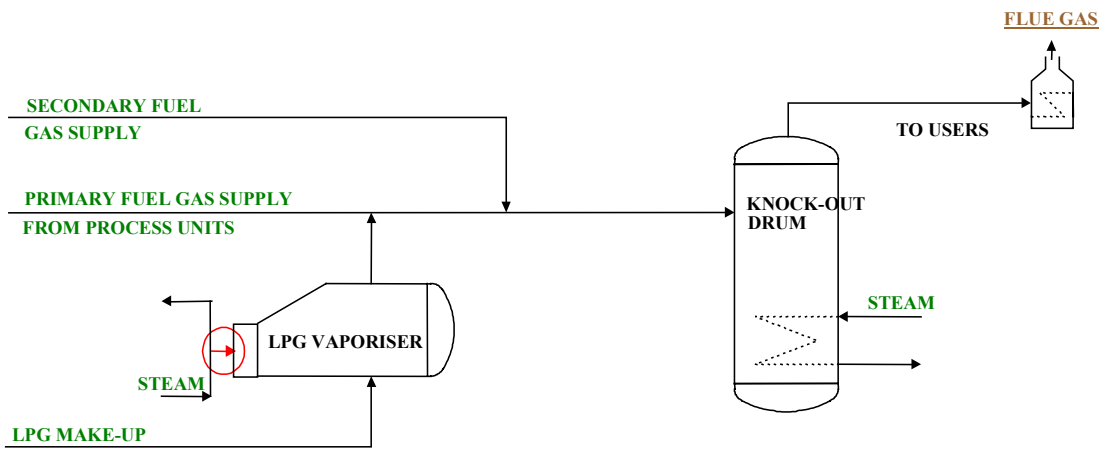


Figure 2.11: Simplified flow diagram of a fuel gas system

Liquid refinery fuel (heavy fuel oil, HFO) used in the refinery is normally a mixture of the residues from atmospheric and/or vacuum distillation and conversion and cracking processes. Liquid refinery fuels are available in various grades, viscosity being the main parameter. The lower the viscosity the more expensive the fuel. The heavier (more viscous) grade fuels require heating to reduce their viscosity before combustion. They contain sulphur (<0.1 - 7%), particle promoters (eg. V, Ni) and nitrogen (0.1 - 0.8 %) resulting, after direct combustion, in high SO_2, particulates and NO_x emissions. They can also be gasified in the IGCC plant where virtually any refinery residue (visbroken or thermal tars, etc.) can be converted to heat and power.

Provided that the crude oil is properly desalted, ash content of the fuel will be directly related to the total solids, the amount being proportional to the sum of the nickel and vanadium present (Ni-V value: 0.03 - 0.15 % w/w depending on the residue source and crude origin). To arrive at the metal content of the HFO, the metal content of the crude is multiplied by a factor of 4 - 5 (dependent on the yield of residue and the residue content of the crude). The metal content of the HFO can vary between 40 and 600 ppm for HFO from a North Sea crude and Arabian Heavy crude respectively, generating particulate concentration in the flue gas of 150 - 500 mg/Nm^3. The most prominent metals indigenous to the crude are vanadium and nickel. Other metals as cadmium, zinc, copper, arsenic and chromium have been detected [43, Dekkers and Daane, 1999]. Next table shows the metal content of residual fuel oil typically used in refineries.

Metal	Concentration range (ppm)	Average concentration (ppm)
V	7.23 - 540	160
Ni	12.5 - 86.13	42.2
Pb	2.49 - 4.55	3.52
Cu	0.28 - 13.42	2.82
Co	0.26 - 12.68	2.11
Cd	1.59 - 2.27	1.93
Cr	0.26 - 2.76	1.33
Mo	0.23 - 1.55	0.95
As	0.17 - 1.28	0.8
Se	0.4 - 1.98	0.75

Table 2.2: Metal content of residual oil
Source: [322, HMIP UK, 1995]

Liquid refinery fuel system

As has already been stated, liquid refinery fuels are heavy residues that should be stored in a separate storage tank at an elevated temperature to reduce the high viscosity. A typical refinery fuel oil system (schematic diagram, see Figure 2.12) includes a dedicated mixing tank (normally off-site), a circulation pump and heater (when required). The system discharges fuel oil at a constant pressure and at the required condition of temperature and viscosity, so that atomisation and efficient combustion are possible. If the fuel consumption is low, the cost of installing heated storage, preheat, etc., may not be justified for the use of heavy fuels and then a light fuel oil will be used. Liquid refinery fuels are normally used for process start-ups.

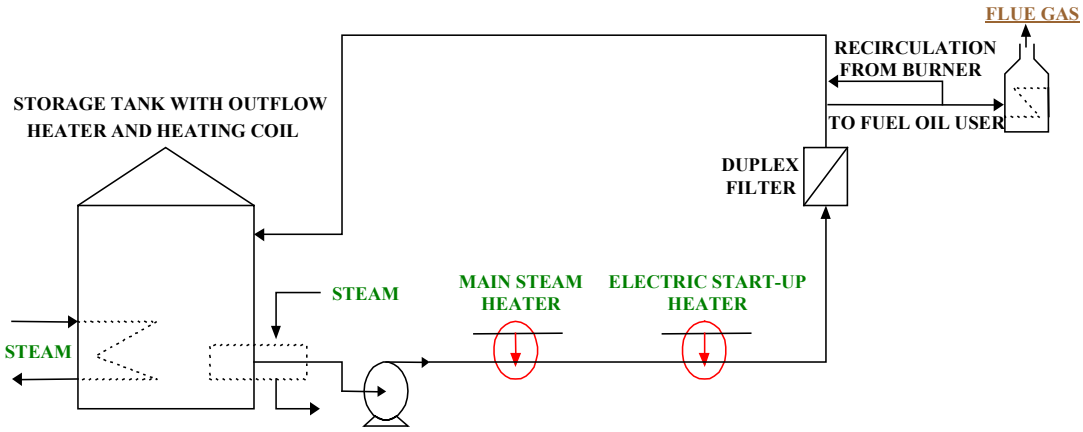


Figure 2.12: Simplified flow diagram of a heavy fuel oil system

Solid fuels such as petroleum coke can be gasified as a refinery fuel gas source for refineries (Flexicoking, Section 2.7). Coke is burnt in the catalytic cracking regenerator (Section 2.5) and coking process (Section 2.7) and represents a heat production source in the refinery. Coal, as imported fuel, is not applied in European refineries.

ENERGY PRODUCTION TECHNIQUES

It is not the intention of this section to include a detailed description of energy production techniques (steam and power), since one can be found in the Large Combustion Plant BREF [317, EIPPCB, 2002].

Furnaces and boilers

Many of the individual refinery processes and utility systems combust fuel (gas and/or liquid) in dedicated furnaces and boilers to supply the *heat* necessary for the process. Fired process heaters and boilers are the main heat producers. The former transfer the heat released in the combustion process directly to the process stream and the latter produce steam that will be used somewhere in the refinery. The principle of steam generation is the heating of boiler feed water, under pressure in, a dedicated fuelled boiler or a waste-heat boiler consisting of heat exchanger bundles (economisers and superheaters). In this document no distinction is made between furnaces and boilers except when relevant.

A variety of furnaces and burner types are used in refineries, largely determined by the heat release characteristics required by a particular process. Many, but not all, furnaces are dual (oil/gas) fired to allow flexibility in the refinery fuel system. Refinery process heaters are typically rectangular or cylindrical enclosures with multiple fired burners of specialised design using mainly low combustion intensity. Boilers (fixed or fluidised bed) are generally fairly standard steam-producing units of medium or high combustion intensity. Waste heat boilers may also be present in the furnaces of stacks. Direct-fired heaters and boilers normally achieve thermal efficiencies of over 85 %. If air preheat is applied and the combustion products (flue

gas) are cooled close to their dew point, the thermal efficiency can be as high as 93 %. Boilers consume about 10 - 20 % of refinery energy requirements.

Gas and steam turbines

Gas turbines work as follows: Fresh air at ambient conditions is drawn into the compressor where its temperature and pressure are raised. The high-pressure air proceeds into the combustion chamber, where the fuel is burned at constant pressure. The resulting high-temperature gases then enter the turbine, where they expand to atmospheric pressure, thus producing power. Steam turbines are used to transform the steam pressure to power. Combined-cycle processes combine the gas and steam turbine processes to produce power at higher efficiency than is reached with open-cycle turbines (steam and gas). More information about gas and steam turbines as well as combined cycles can be found in the LCP BREF.

Cogeneration plants (CHP)

These systems are designed for the co-production of heat and power. The fuel for this type of facility is usually natural gas. It is, however, also possible to fire refinery gas as part of the fuel slate, thus potentially reducing the amount of refinery gas available for combustion in boilers and furnaces. The steam and power cogeneration concept can also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Integrated gasification combined cycle (IGCC)

Integrated gasification combined cycle is a technique for producing steam, hydrogen (optional) and electric energy from a variety of low-grade fuel types with the highest conversion efficiency possible. During the gasification of the oil with oxygen and/or air, syngas is produced that it is lately used in a combined cycle for the production of heat and electricity. Hydrogen can also be separated from the syngas for use in the refinery (Section 2.14).

The principle is based on the high-temperature and high-pressure reaction of organic carbons or coke with steam and under-stoichiometric amounts of oxygen (partial oxidation) to produce syngas ($CO+H_2$). After the combustion chamber the system contains a number of sophisticated energy recovery systems to produce steam and electricity. Figure 2.13 shows a block flow diagram of an IGCC plant. In the partial oxidation of hydrocarbons the product gas contains a certain amount of free carbon (soot). The soot particles are removed from the gas together with the ash in a two-stage water wash.

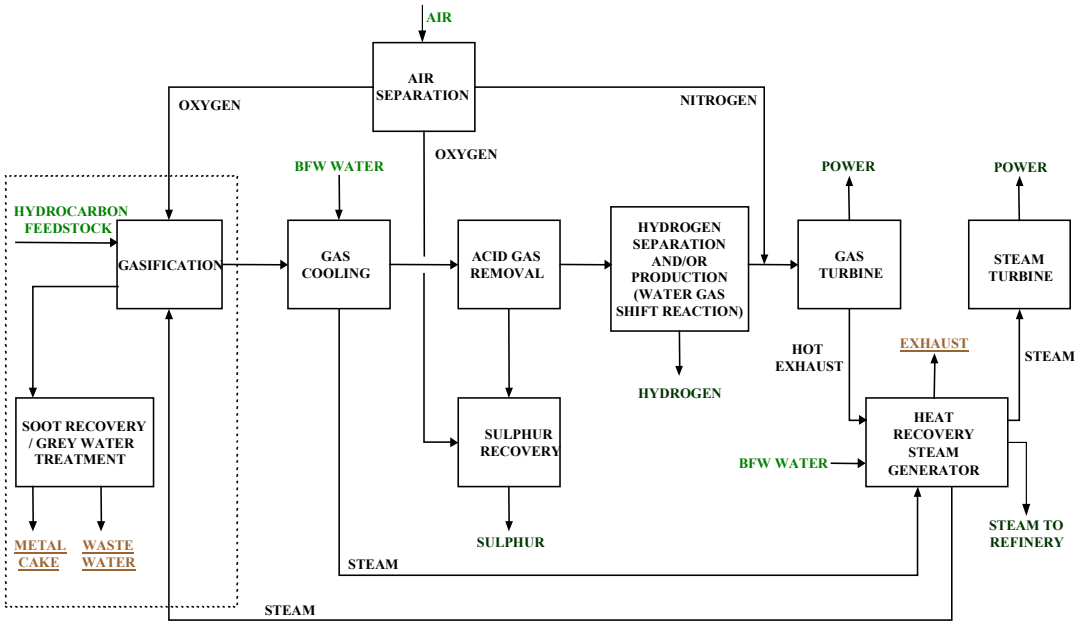


Figure 2.13: Block flow scheme for IGCC

The gasification plant consists of two integrated complex units. In the first, syngas manufacturing process plants (SMPP), the gasification of heavy fractions takes place and the syngas is produced and purified. In the second, the combined cycle power plants, the syngas is fed to a combined cycle thermoelectric unit. The SMPP includes the following two sections:

- *Gasification and carbon extraction:* In the gasification section the feedstock is gasified through a non-stoichiometric reaction with pure oxygen and water; the reaction occurs in the gasifier, a non-catalytic vessel internally coated with refractory, operating at high temperature (about 1300 °C) and pressure (about 65 bar).

- *Gas cooling and purification:* In the gas-cooling section the waste heat from syngas is recovered by generation of steam at three pressure levels. A small quantity of carbon, formed in the gasifiers, is removed from the gas by direct contact with water in a scrubber. Water is then treated in the grey water treatment and then sent to the existing refinery biotreatment plant. A solid effluent in the form of a filter cake is discharged from this unit and sent to external plants for the recovery of the metals. In addition, a COS hydrolysis reactor is provided to convert the small amount of COS produced in the gasifier to H_2S. This section also includes a gas expander for the recovery of the pressure energy of the syngas (pressure in gasifiers is about 65 bar). This system contains an *acid gas removal*. In this unit, a circulating amine stream is used to selectively absorb the H_2S formed in the gasifier and in the COS hydrolysis. It also contains an *air separation unit*. This unit produces the oxygen required for the gasification and the Claus plant, and the nitrogen for syngas conditioning. It is based on conventional cryogenic air fractionation. And finally contains a *sulphur recovery unit*. Claus units recover elemental sulphur from the H_2S recovered in the acid gas removal section and a tail gas treatment section, that maximise the overall sulphur recovery.

After the cooling and purification sections, the purified syngas is sent to the *combined cycle power plant,* for power generation. It mainly consists of a conventional cycle with a gas turbine, a heat recovery steam generator and a steam turbine.

PRODUCTS FROM THE ENERGY SYSTEM

As mentioned at the beginning of this section, the energy system of a refinery (or any other industrial complex) is there to provide the heat and power necessary to carry out the process. A short description of the types of products (steam and power) produced by the energy system of a refinery is given below.

Steam

The different steam qualities generated in the boilers of the refinery have the following general characteristics (the heat content ranges from about 2700 MJ/t for low pressure steam to 3200 MJ/t for super heated high pressure steam at 50 bar):

- High pressure (HP) steam net (>30 bar, 350 – 500 °C), generated in waste heat boilers (cooling of hot off-gases and/or hot products at catalytic processes and hydrocrackers) and in fired boilers. HP-steam is mainly used in turbines to produce electrical power (and MP steam);
- Medium pressure (MP) steam net (7 - 20 bar, 200 – 350 °C), generated by pressure reduction of HP steam, is used within the refinery for stripping, atomisation, vacuum generation and heating (e.g. reboilers, tanks);
- Low pressure (LP) steam net (3.5 - 5 bar, 150 – 200 °C), generated in heat exchangers by cooling of hot products, and by pressure reduction of MP steam. LP steam is used for heating, stripping and tracing.

Steam is produced by heating demineralised water, so called boiler feed water (BFW), under pressure in a steam boiler. Steam raising plants are normally fuelled with refinery fuel gas or liquid. The refinery is equipped with dedicated steam boilers in virtually all process units, containing a HP-, MP- and LP-steam distribution network and with HP-, MP- and LP-condensate collection networks, which are connected with the BFW preparation unit and the

condensate storage tank. (Reference is made to Figure 2.14 and to the LCP BREF [317, EIPPCB, 2002]).

Steam used in turbines and heaters after cooling is usually recovered as condensate. BFW is therefore a mixture of fresh demineralised make up water (quality dependent on steam pressure) and recovered condensate. BFW make up can be bought in but can also be prepared at the refinery using drinking water, filtered ground water, seawater distillation, surface water or even treated effluent by using a combination of treatment operations, such as sandfiltration or microfiltration (to remove suspended solids) and demineralisation which is accomplished by subsequent cation and anion exchange (see dotted area in Figure 2.14). Reverse osmosis (to remove ions, colloids and large organic molecules) is usually applied in new plants and is followed in some cases by mixed bed ion exchange and active carbon filtration for final polishing. The condensate tank is generally equipped with an oil detection system and an oil skimming device. To avoid corrosion in the steam and condensate systems, oxygen and carbon dioxide are removed in de-aerators, and oxygen scavengers and corrosion inhibitors are added. After conditioning, the BFW is pumped to the boilers. In boilers the hot flue gases and BFW flow in countercurrent; BFW is preheated in the economiser and further heated in the first and second superheater. In order to keep the concentration of dissolved compounds and suspended solids in the steam drum constant, a condensate blown down of 1 - 2 % is normally required.

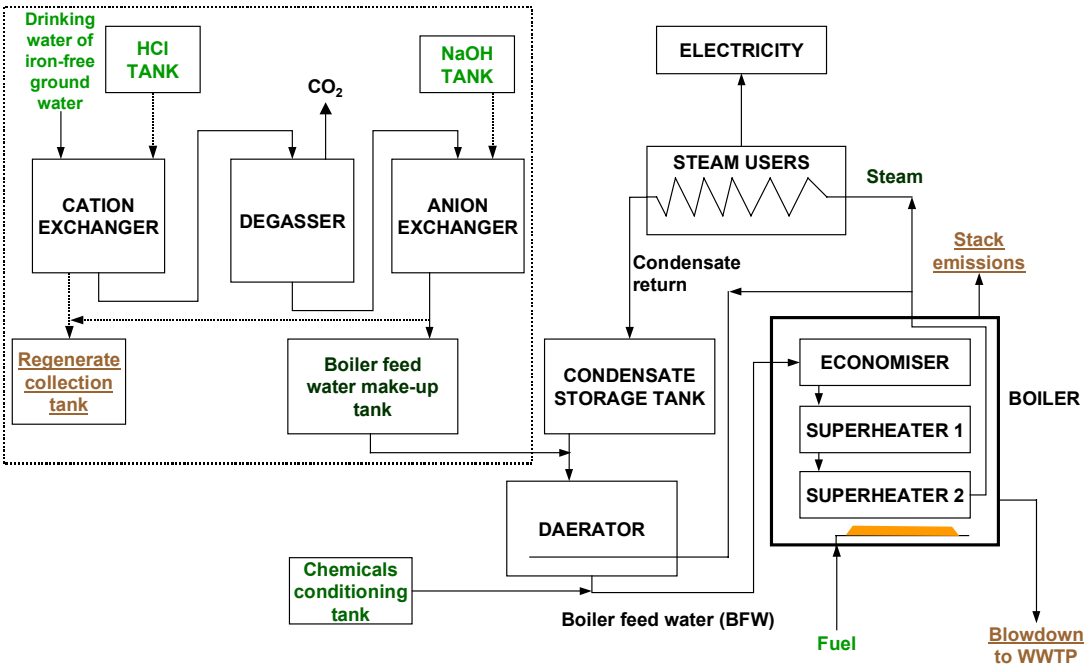


Figure 2.14: Typical layout of a boiler feed water preparation unit and a steam boiler

Electrical power is mainly generated in turbines with high-pressure steam but can be also be produced in gas turbines. Electricity is necessary to run pumps, compressors, control systems, valves, etc. Refinery electrical systems are therefore extensive.

ENERGY MANAGEMENT

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal aim is to match continuously the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This issue is also analysed in this document and in Section 2.15 the integration of all the techniques that may be used in a refinery is examinated. This section is included here because the energy efficiency of a refinery can be increased not only by improving the energy efficiency of the individual processes (which is addressed in each section) or energy efficiency of the

energy production system but also by improving energy management, energy conservation and heat integration/recovery within the refinery as a whole.

Energy management has long been an important issue for refineries. For example, management techniques such as the ISO 14000 system series or EMAS can provide an appropiate framework to develop suitable energy management system and can increase the energy efficiency of the refinery as a whole. Energy conservation techniques such as reporting and incentivating the energy savings, carrying out combustion improvements or reviewing the energy integration of the refinery are some of the techniques that may have a big impact in reducing energy consumption and consequently in increasing the energy efficiency of a refinery. Other technical tools to increase that efficiency are the heat integration/recovery techniques, of which examples are: the installation of waste heat boilers, the installation of expanders to recuperate power and increasing the insulation of buildings and process units to reduce heat losses. Steam management is another good tool for increasing energy efficiency.

2.11 Etherification

PURPOSE AND PRINCIPLE

A number of chemicals (mostly alcohols and ethers) are added to motor fuels either to improve performance or to meet environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels, reduce carbon monoxide generation and reduce atmospheric ozone due to the lower reactivity of resulting VOC emissions. These additives replaced the lead additives which were being phased out as required by the Auto-Oil I. As a result, a number of different ethers are currently added to the gasoline and are better able to meet both the new oxygen requirements and the vapour pressure limits. The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME). Some refineries (~30% of EU+ refineries) manufacture their own supplies of those ethers.

FEED AND PRODUCT STREAMS

Isobutylene and/or isoamylene and methanol (or ethanol) are necessary to produce MTBE (or ETBE) and/or TAME. Isobutylene is obtained from a number of refinery sources including: the light naphtha from the FCC and coking units; the by-product from steam cracking of naphtha (processes described in LVOC) or light hydrocarbons during the production of ethylene and propylene (also in LVOC); catalytic dehydrogenation of isobutane (also in LVOC) and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides (within LVOC). Methanol (ethanol) is bought in.

PROCESS DESCRIPTION

Multiple variations of commercial processes are available. Most processes can be modified to react isobutylene or isoamylene with methanol or ethanol to produce the corresponding ether. All use an acidic ion exchange resin catalyst under controlled temperature and pressure conditions. Temperature control of the exothermic reaction is important to maximise conversion and minimise undesirable side reactions and catalyst deactivation. The reaction is usually carried out in two stages with a small excess of alcohol to achieve isoolefin conversions of over 99 % and the methanol consumption is essentially stoichiometric. The basic difference between the various processes is in reactor design and the method of temperature control.

MTBE production process

Figure 2.15 shows an example of a simplified process flow diagram of a MTBE plant. The feed stream is cooled prior to entering the top of the primary reactor. The resin catalyst in the primary reactor is a fixed bed of small beads. The reactants flow down through the catalyst bed and exit the bottom of the reactor. Effluent from the primary reactor contains ether, methanol and unreacted isoolefin and usually some paraffins from the feed. A significant amount of the effluent is cooled and recycled to control the reactor temperature. The net effluent feeds to a fractionator with a section containing catalyst or to a second reactor. Ether is withdrawn as the bottom product, and unreacted alcohol vapour and isoolefin vapour flow up into the catalyst reaction to be converted to ether. The process usually produces an ether stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling. The excess methanol and unreacted hydrocarbons are withdrawn as net overhead product, and fed to a methanol recovery tower. In this tower the excess methanol is extracted by contact with water. The resultant methanol-water mixture is distilled to recover the methanol, which is then recycled to the primary reaction.

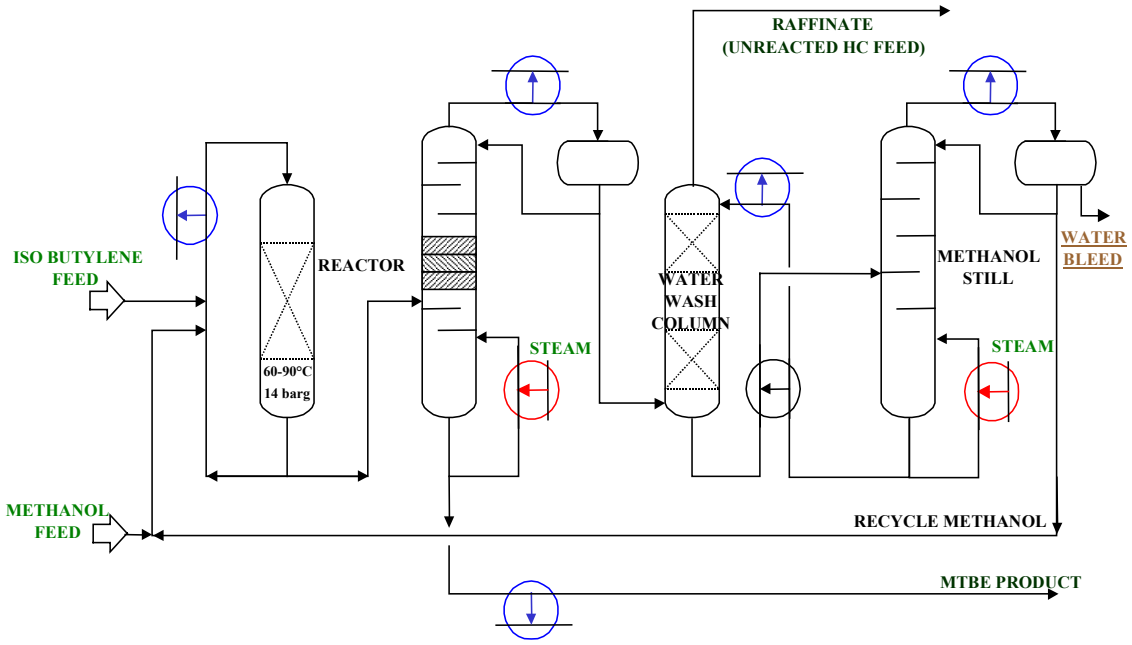


Figure 2.15: Simplified process flow scheme for a MTBE production process

TAME production process

In this process, C_5 isoamylenes are separated from the light catcracked spirit stream (LCCS) from the FCC unit and catalytically reacted with methanol in the presence of hydrogen to produce TAME. The main stages for TAME production are pentane removal, scavenging, reaction and purification. Figure 2.16 shows a simplified scheme for the TAME production.

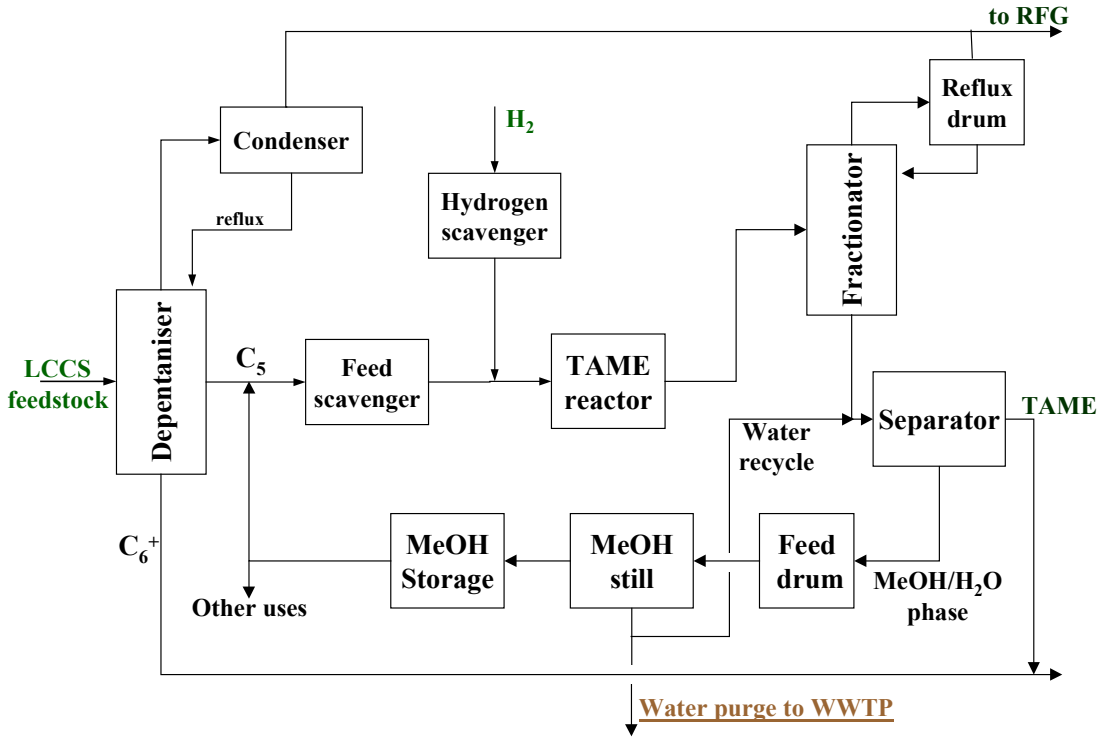


Figure 2.16: Simplified process flow scheme for TAME production

C_5 removal is achieved by distillation (dependentaniser) of the LCCS feedstock. Overheads are condensed and the hydrocarbons are returned as reflux while gases go to the refinery flue gas system. A C_5 side-stream is withdrawn from the column as feed to the TAME unit. Column bottom liquids (C_{6+}) are routed to re-blending with the eventual product from the TAME unit.

The C_5 stream is then scavenged to remove catalyst poisons by passing it through an ion exchange resin to remove basic nitrogen compounds, eg. ammonia, and any metallic contamination. A hydrogen feeds is also scavenged to remove any acidic components. The feedstock, containing injected methanol and hydrogen, is fed to the reactor section. Hydrogen is used to convert di-enes into monoolefins and prevent gum formation during the reaction. This takes place over a palladium-impregnated ion-exchange resin and the isoamylenes are converted to TAME.

The TAME product stream is purified by fractional distillation, washing and phase separation. Fractionator overheads pass to a reflux drum with the gas phase of low boiling hydrocarbons (C_1, C_2, C_4, etc.) plus unreacted hydrogen being vented to refinery fuel gas or flare. The bottom product of TAME gasoline with some methanol is cooled and mixed with recycled water from the methanol recovery plant, then routed to a settler for phase separation. The TAME gasoline fraction from this is blended with the dependentaniser bottoms C_{6+} stream and passed to storage. The methanol/water fraction is recycled to the methanol recovery plant feed drum.

Methanol is recovered by distillation in a common still with the overheads methanol being condensed and passed to buffer storage for recycling to the TAME plant or other uses. The bottoms are essentially water with some contaminants and are mainly recycled but with a purge to effluent treatment to avoid formic acid build up.

2.12 Gas separation processes

PURPOSE AND PRINCIPLE

Low boiling hydrocarbons are usually treated in a common separation plant operating at elevated pressures. The purpose of a gas plant is to recover and to separate C_1 - C_5 and higher compounds from various refinery off-gases by distillation. In mineral oil refineries, one (or more) gas plant is present to handle different gas streams from different processes. (eg. cat reformers, catcrackers, distillation units). Those systems are the core for installations refining natural gas (Section 2.17) where the different components are separated. Depending on application of the products, some refineries remove mercury from LPG, tops and naphtha.

FEED AND PRODUCT STREAMS

The feed of the gas plant consists of gas and liquid streams from crude distillation, catcrackers, catalytic reformer, alkylation, desulphurisation and similar units. Pretreatment of some feedstocks may be necessary, typically by hydro-desulphurisation (Section 2.13) or amine treating (H_2S removal, see Section 4.23.5.1). The compounds recovered depend on the composition of the feed and the market requirements. The gas streams are normally separated into C_1 and C_2 fractions for sale or use as refinery fuel gas, LPG (propane and butane) and a light gasoline (C_5 and higher) stream. Olefins, isoparaffins and n-paraffins can be also separated in the process.

PROCESS DESCRIPTION

As a minimum, the gas plant consists of two columns, an absorber/stripper column (de-ethaniser) to strip all light C_2-minus components and to maximise recovery of C_3-plus components from the feed streams. Figure 2.17 shows a simplified process flow diagram of a gas plant.

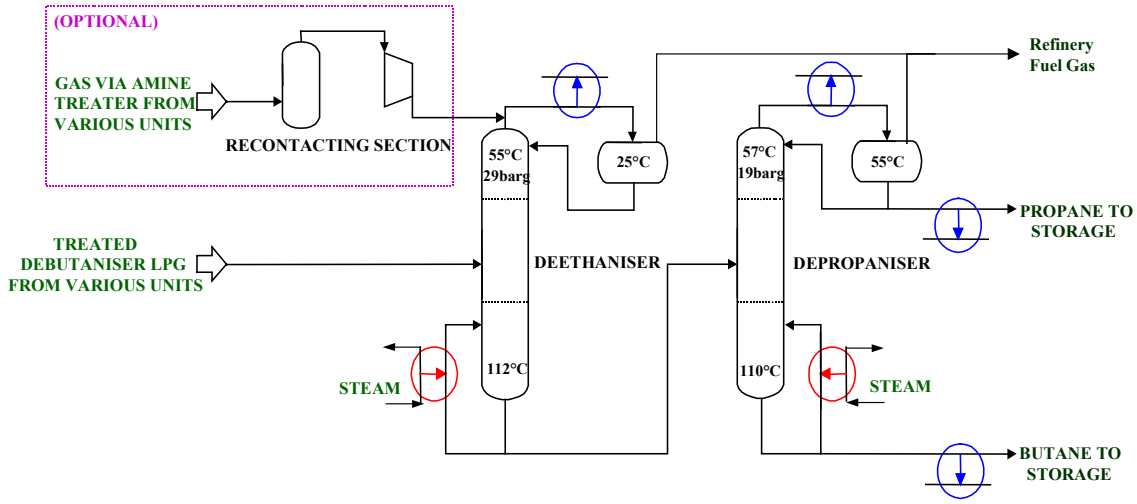


Figure 2.17: Simplified process flow scheme for a part of a gas plant

The feed stream to the gas plant is cooled and chilled, the residual vapour phase from this being routed to a refrigerated absorber, meeting chilled re-cycled light gasoline absorbent. Absorber overhead is the C_1, C_2 fraction. The bottoms are combined with the liquid stream from chilling and pass to the first fractionator or de-ethaniser. The first fractionator overheads (essentially C_2-ethane) are combined with the absorber overheads while the bottoms pass to the second fractionator to produce a C_3/C_4 overheads stream and debutanised gasoline bottoms. A recontacting section, where vapours from various units are compressed and recontacted with the de-ethaniser overhead can be installed to maximise the C_3/C_4 recovery. The bottoms of the de-ethanizer column, mainly C_3/C_4 compounds, are fed to the depropaniser column. This overheads stream is routed to a third fractionator to split the C_3 and C_4 streams as overheads (propane) and bottoms (butane) respectively. Products pass to pressurised storage via any final sweetening by

selective molecular sieve adsorption. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the refinery fuel gas system.

The gasoline bottoms stream passes to a fourth fractionator to produce a depentanised fraction for use as chilled, recycle gasoline on the absorber. The net output is blended to form the gasoline product. A drying step before sending to storage can be necessary (not shown). Also, a vessel containing a bed of caustic pellets (not shown) can be installed in the butane system as an additional guard, although water and H_2S should have been removed in the top of the de-ethaniser and depropaniser column. If no (or insufficient) upstream treatment has taken place, this can also be done in the unit itself, e.g. with an amine H_2S absorber followed by a mercaptan oxidation/extraction of the de-ethaniser bottoms with amine H_2S absorption of the de-ethaniser net overhead gas.

If thermal and/or catalytic cracking units are present, recovery of olefinic components may also be worthwhile. It is also possible to separate isobutane from n-butane. The iso-butane can be used as feed to an alkylation unit, while the n-butane (or part of it) can be used as a blending component in the gasoline pool or isomerisation.

2.13 Hydrogen consuming processes

Two types of process are included in this section: hydrocracking and hydrotreatments. Both processes take place over a metal catalyst in a hydrogen atmosphere. Many of those processes are found in a refinery, normally named according to the type of feed to treat and the reaction conditions. The common denominator to those processes is that all rely on hydrogenation processes and consequently consume hydrogen. Isomerisation processes of alkanes or olefins also consume some hydrogen, but those processes are included in a separate section (Section 2.16).

PURPOSE AND PRINCIPLE

Hydrotreating and hydroprocessing

They are similar processes used to remove impurities such as sulphur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts. *Hydrotreating* also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. *Hydroprocessing*, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter, more saleable products. Both processes are usually placed upstream of those processes in which sulphur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units. The processes use catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen.

The hydrotreating process can be divided into a number of reaction categories: hydrodesulphurisation, hydrodenitrification, saturation of olefins and saturation of aromatics. A hydrotreater unit specifically employed to remove sulphur is usually called a hydrodesulphurisation unit (HDS). In this section the standard hydrotreating of naphtha, mid-distillate and residue type feed streams is discussed:

- A *naphtha hydrotreater* unit normally serves three purposes, desulphurisation, denitrogenation and stabilising the naphtha feed stream to the downstream isomerisation and reformer units. Stabilising the naphtha streams usually requires the conversion of unsaturated hydrocarbons produced in thermal and catalytic cracking processes into paraffins. The selective hydrogenation of light dienes that are contaminants of many light olefin streams may also be partially hydrogenated. Hydrogenation of aromatics is a variant of either naphtha or of distillate processed.
- A *mid-distillate hydrotreater* unit normally has two purposes, desulphurisation and hydrogenation of the mid-distillate stream. Stabilising mid-distillate streams is required when large quantities of cracked components are blended to the mid-distillate pool, and usually requires partial saturation of aromatics and olefins and reduction of the N-content. The saturation of aromatics may be required to saturated in naphtha, kerosene, and diesel feedstocks. Among the applications of this process are smoke-point improvements in aircraft turbine fuels, reduction of the aromatic content of solvent stocks to meet requirements for air pollution control, production of cyclohexane from benzene (LVOC) and cetane number improvement in diesel fuels.
- *Diesel Oil deep desulphurisation* (Hydrofining) is normally done to heating and diesel oils to meet product sulphur specifications. Other reasons are to improve colour and sediment stability.
- *Residue hydrotreating* is mainly applied to improve the residue feed quality (normally atmospheric residue) to a residue catalytic cracker (RCC) unit. RCCs are restricted to process residue streams by their metal content and Concarbon number.

Hydroprocessing may also be designed to remove low levels of metals from the feed. The metals to be removed include nickel and vanadium, which are native to the crude oil, as well as silicon and lead-containing metals that may be added elsewhere in the refinery.

Hydrocracking

It is one of the most versatile of all refining processes, capable of converting any fraction from atmospheric gasoils to residual (deasphalted) oil into products with a lower molecular weight than the feed. The hydrocracking reactions occur under high hydrogen partial pressure in the presence of a catalyst with a two-fold function, hydrogenation and cracking. Hydrocracking may also be used for the cracking of superior fuels and the production of lubricants (Dewaxing in Section 2.3). The type of catalyst maximises the production of naphtha, mid-distillates or lube production. The presence of hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products, giving net products, which are a mixture of pure paraffins, naphthenes and aromatics. Hydrocracking produce mid-distillates with outstanding burning and cold flow properties as follow:

- Kerosene with low freezing points and high smoke points.
- Diesel fuels with low pour points and high cetane numbers.
- Heavy naphthas with a high content of single-ring hydrocarbons.
- Light naphthas with a high isoparaffin content.
- Heavy products that are hydrogen-rich for feed FCC units, ethylene plants (LVOC), or lube oil dewaxing and finishing facilities (Section 2.3).

When hydrocracking is applied to heavy residues, a pretreatment is needed to remove high metal content before the hydrocracking reaction is produced. Residue hydroconversion is type of hydrocracking applied to convert low-value vacuum residue and other heavy residue streams to lighter low-boiling hydrocarbons by reacting them with hydrogen.

FEED AND PRODUCT STREAMS

Hydrotreating and hydroprocessing

These processes are applied to a wide range of feedstocks from LPG up to residue and mixture thereof. Table 2.3 summarises the feeds, products and process objectives for each type of hydrotreatment.

Feedstocks	Desired products	Process aim: Removal or concentration decrease of
LPG	Clean LPG	S, olefins
Naphthas	Catalytic reformer feed (S:0.05 - 0.5 % w/w)	S (< 0.5 ppm), N, olefins
LPG, naphthas	Low diene contents	dienes (25 - 1 ppm) in product
Cat. cracked naphtha	Gasoline blending component	S
Atmospheric gas oils	Ethylene feedstock (LVOC)	S, aromatics
	Jet	S, aromatics
	Diesel	S, aromatic and n-paraffins
Vacuum gas oils	Ethylene feedstock	aromatics
	Kerosene/jet (S:0.05 to 1.8 % w/w)	S, aromatics
	Diesel (S:0.05 to 1.8 % w/w)	S, aromatics
	FCC feed	S, N, metals
	Low-sulphur fueloil	S
	Lube oil base stock	aromatics
Atmospheric residue	FCC feedstock	S, N, CCR, and metals
	Low-sulphur fueloil	S
	Coker feedstock	S, CCR, and metals
	RCC feedstock	CCR, and metals
CCR=Conradson carbon residue		

Table 2.3: Feedstocks, desired products and process objectives of hydrotreatments

Hydrocracking
Hydrogen in substantial quantities is consumed in those processes, making the hydrogen manufacturing unit mandatory (Section 2.14) in those refineries that contain hydrocracking. In addition to the treated products, those processes produce a stream of light fuel gases containing hydrogen sulphide, ammonia and water.

As is reflected in Table 2.4, the main feed stream to a hydrocracker is the heavy vacuum distillate stream from the High Vacuum unit. Those feedstocks are fractions very difficult to crack and cannot be cracked effectively in catalytic cracking units. Other process streams such as heavy cycle oil from the catcracker unit, heavy gasoils from the coker or visbreaker unit, extracts from lube oil units, mid-distillates, residual fuel oils and reduced crudes may be blended to the main heavy vacuum distillate stream. The main products are LPG, gasoline, jet fuel and diesel fuel, all practically sulphur-free. The production of methane and ethane is very low, normally less than 1 %.

Feedstocks	Desired products
Naphthas	LPG
Atmospheric gas oils	Naphtha
Atmospheric residue	Diesel
Vacuum gas oils	LPG
	Naphtha
	Ethylene feedstock (LVOC)
	Kerosene/jet
	Diesel
	Lube oil base stock
Vacuum residues	LPG
	Naphtha
	Kerosene
	Gasoil
	Fuel oil
Tars and derived bitumens (metal content <500 ppm)	Diesel

Table 2.4: Feedstocks and desired products of hydrocracking processes

PROCESS DESCRIPTION

Types of reactor technologies applied in hydroconversion and hydrotreatment
There are several residue hydrotreating and hydroconversion technologies in use today. They can be classified in four categories: fixed bed; swing reactor; moving bed and ebullated bed. The selection of the type of process is predominantly determined by the metal content in the feed. *Fixed bed* residue hydroconversion is applied for 'low' metal-containing feeds (100 ppm) and the required conversion is relatively low, moving bed or ebullated bed technology is used for 'high' metal-containing feeds. To overcome metal poisoning of the catalyst in fixed beds and maintain the concept, some licensors propose the *swing reactor* concept: one reactor is in operation whilst the other one is off-line for catalyst replacement. The concept and layout of the fixed bed hydroconversion technology is identical to long residue hydrotreating. *Moving bed* technology or ebullated bed technology is selected when the metal content in the residue feed is typically above 100 ppm but below 500 ppm. Normally this concentration of metals in the feed is found in vacuum residue streams from heavier crudes, bitumen streams from tar sands and heavy atmospheric residue streams. Both technologies allow withdraw and replacement of the catalyst during operation, the main difference is the reactor configuration.

Hydrotreating and hydroprocessing
Naphtha hydrotreater. Naphtha feed is mixed with a hydrogen-rich gas stream, heated and vaporised in the reactor feed/effluent exchanger and the furnace, and fed into the hydrotreater reactor with a fixed bed cobalt/nickel/molybdenum catalyst. The reactor conditions can vary but

are typically 30 to 40 bar and 320 to 380 °C. The reactor effluent is cooled in the feed/effluent exchanger and reactor cooler and flashed into the high-pressure separator. The flashed vapours, consisting mainly of unreacted hydrogen, are compressed and recycled to the reactor. The fractionation part is very similar to the one explained in hydroconversion process.

*Distillate hydrodesulphurisation***.** Figure 2.18 provides a simplified flow diagram of a typical distillate HDS unit. The distillate feed may range from kerosene up to long vacuum gas oil or mixtures thereof. The reactor system is in principle the same as for the naphtha hydrotreater. The main difference is that the feed does not fully vaporise and the reactor operating conditions are more severe, 40 - 70 barg and 330 - 390 °C. Further it is normal practice that wash water is injected in the reactor effluent stream when nitrogen-rich feedstocks are desulphurised. Solid deposits like $(NH_4)_2S$ and NH_4Cl are formed in the cooler parts of the unit and must be removed by water wash. The liquid from the low-pressure separator is fed to a stripper column to stabilise and strip off the light hydrocarbons and H_2S. The stripping steam and light hydrocarbons are taken overhead, condensed and separated into a sour water phase and a hydrocarbon phase. The water phase is sent to the sour water stripper, the light hydrocarbon phase is normally recycled to the crude unit or naphtha hydrotreater distillation section for further fractionation. Any water dissolved and dispersed in the distillate should be removed to avoid the formation of haze and ice when stored. The wet distillate is therefore either fed to a vacuum column, where the total water content is lowered to 50 ppm, or sometimes a combination of coalescer and molecular sieve beds is used, where water is selectively adsorbed on the bed.

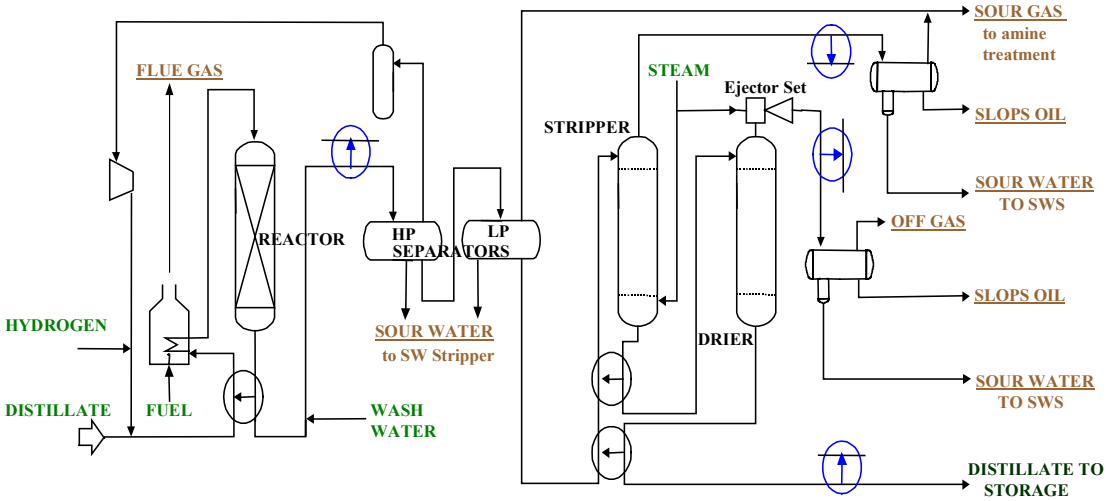


Figure 2.18: Simplified process flow scheme of a distillate hydrodesulphurisation unit

Diesel Oil deep desulphurisation (Hydrofining). Because this technique operates at low pressures, efficient hydrogen utilisation can be achieved within an overall refinery context. Very low sulphur contents can be achieved (8 ppm) in the raffinate. The unit usually operate at 45 bars and consumes very low amounts of hydrogen. Gasoline deep desulphurisation techniques with a comparatively low hydrogen consumption are currently under development.

The principle process scheme for *residue hydrotreating* is the same as normal distillate. The main difference is the reactor systems which normally consists of two or three reactors in series. Removal of the metals from the residue feed normally occurs in the first reactor(s) and uses a low-activity coarser Co/Mo catalyst. Further hydrotreating and hydrogenation occur in the tail reactor(s), resulting in a higher hydrogen-to-carbon ratio and a lower Concarbon number of the residue. Since the catalysts operate in a H_2S and NH_3 rich environment the Nickel/Molybdenum or Nickel/Tungsten catalysts are usually applied in the tail reactors.

Next table shows the typical hydrotreatment operating conditions for the different feedstocks:

Operating conditions	Naphtha	Mid distillate	Light gas oil	Heavy gas oil	Residuum
Liquid hourly space velocity	1.0 - 5.0	1.0 - 4.0	1.0 - 5.0	0.75 - 3.0	0.15 - 1
H_2/HC ratio, Nm^3/m^3	50	135	170	337	300
H_2 partial pressure, kg/cm^2	14	28	35	55	55
Reactor temperature, °C	260 - 380	300 - 400	300 - 400	350 - 425	350 - 425

Table 2.5: Typical hydrotreating operating conditions
Source: [166, Meyers, 1997]

Hydrogenation of light dienes. This process is a highly selective catalytic process that can hydrogenate acetylenes and dienes to the corresponding monoolefin without affecting the valuable olefin content of the feedstock. In addition, those processes can be designed to provide hydroisomerization of some of the olefins. (e.g. conversion of 1-butene to 2-butene). Hydrogenation takes place in a liquid-phase fixed-bed reactor. Unless the hydrogen purity is low, no separation step is required for the removal of light ends from the product. Thus, reactor effluent can be charged directly to downstream units.

Saturation of aromatics. The use of highly active noble-metal catalysts permits the reactions to take place under mild conditions. Because of the mild conditions and the very selective catalyst, the yields are high, and hydrogen consumption is largely limited to just the desired reactions. The process is carried out at moderate temperatures (205 - 370 ºC) and pressures (3500 to 8275 kPa) over a fixed catalyst bed in which aromatics are saturated and in which hydrogenation of olefins, naphthenic ring opening and removal of sulphur and nitrogen occur.

Hydrocracking

Hydrocracking normally use a fixed-bed catalytic reactor with cracking occurring under substantial pressure (35 to 200 kg/cm^2) in the presence of hydrogen at temperatures between 280 and 475 ºC. This process also breaks the heavy, sulphur-, nitrogen- and oxygen bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated and dewatered to remove impurities (H_2S, NH_3, H_2O) before being sent to the hydrocracker. If the hydrocracking feedstocks are first hydrotreated to remove impurities, sour water and sour gas streams will contain relatively low levels of hydrogen sulphide and ammonia in the fractionator.

Depending on the products desired and the size of the unit, hydrocracking is conducted in either single-stage or multi-stage reactor processes. Hydrocrackers can be classified in three categories, single-stage once-through, single-stage recycle and two-stage recycle:

- Only fresh feed is processed in the single-stage once-through hydrocracker. The conversions achieved are around 80 - 90 % depending on catalyst and reactor conditions. The heavy residue is either sent to the fuel oil pool or further processed in a catcracker or coking unit.
- In the single-stage recycle configuration, the unconverted oil is recycled to the reactor for further conversion, increasing the overall conversion to around 97 - 98 %. A small bleed stream of about 2 - 3 % on fresh feed is required to avoid a build-up of polyaromatics (PAH) in the recycle loop. Figure 2.19 shows a simplified process flow diagram of the single-stage hydrocracker with recycle configuration. In the first reactor beds, conversion of N and S compounds, saturation of olefins and partial saturation of PAH takes place. In the following beds the actual cracking will take place. The vapour from the low-pressure (LP) separator is used as refinery fuel after amine treating. Many different fractionation section configurations are found. A common fractionation section is illustrated in Figure 2.19. The product stream is fed to the debutaniser column to separate the LPG. The LPG stream is washed in an amine wash and then fractionated into a propane and a butane stream. The bottom stream from the debutaniser column is fed to the first fractionator. In this column, a

light naphtha stream is taken as overhead product, heavy naphtha and kerosene are taken as side-streams and the bottom stream is fed to a second fractionator. In the second fractionator, operating at mild vacuum, the diesel product is taken as the overhead product and the bottom stream, the unconverted oil, is recycled to the reactor section.

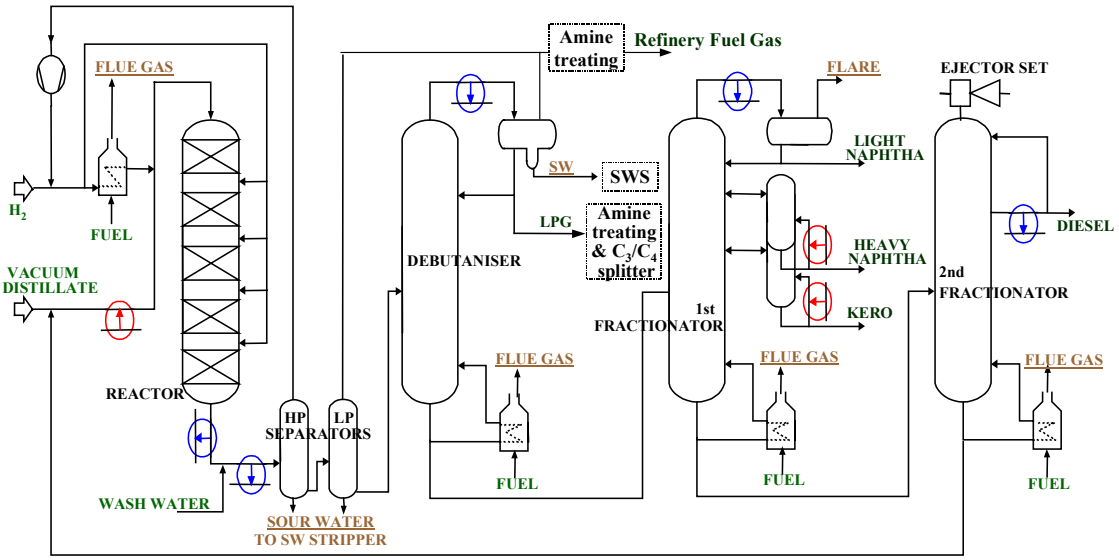


Figure 2.19: Simplified process flow scheme for hydrocracker (single stage with recycle)

- In the two-stage recycle configuration, the first hydrocracker reactor operates in a once-through mode with a typical conversion of around 50 %. The unconverted oil from the first hydrocracker reactor is fed to a second hydrocracker reactor for further conversion. The unconverted oil from the second stage hydrocracker is recycled to achieve an overall conversion of around 97 - 98 %. A small bleed stream of about 2 - 3 % on fresh feed is also required here. This concept is normally applied when a very heavy high refractory feed stock such as deasphalted oil is processed.

Next table shows the typical operating conditions of hydrocrackers

	High-pressure hydrocracking	Moderate-pressure hydrocracking
Conversion, % w/w	70 - 100	20 - 70
Pressure, barg	100 - 200	70 - 100
Liquid hourly space velocity	0.5 - 2.0	0.5 - 2.0
Average reactor temperature ºC	340 - 425	340 - 425
Hydrogen circulation, Nm^3/m^3	650 - 1700	350 - 1200

Table 2.6: Typical hydrocracker operating conditions
Source: [166, Meyers, 1997]

Hydroconversion

In principle, three reactions are taking place: hydro-demetallisation, hydrotreating/ hydrogenation and hydrocracking. Removal of the metals from the residue feed predominantly occurs in the first reactor(s) and uses a low activity Co/Mo catalyst. Hydrotreating, hydrogenation and hydrocracking occur in the following reactor(s) where the quality is mainly improved by increasing the hydrogen-to-carbon ratio. Conversion levels to products in a hydroconversion process are typically 50 - 70 % but depend significantly on the type of hydroconversion process and the quality of the feedstock.

Figure 2.20 shows a simplified process flow diagram of a moving bed process. The process comprises 5 reactors in series, catalyst handling facilities and a work-up section. The reactors operate at high pressure and relatively high temperatures. The first three reactors are bunker hydrodemetallisation (HDM) reactors. The Ni+V conversion typically exceeds 60 % for the first 60 days of operation and then gradually trends towards the expected equilibrium conversion level, 50 to 70 percent. This way, high-metal feeds can be treated. The last two reactors are fixed bed desulphurisation and conversion reactors. The moving bed technology employs a bunker flow/moving bed technology to replenish the HDM catalyst continuously. Catalysts are transported through a slurry transport system in which the rate of catalyst replenishment is controlled in accordance with the rate of metal deposition. The catalyst in the HDM reactors flows concurrently downward with the process fluids. Screens separate the catalysts from the process fluids before leaving the reactor. Sluice systems are present at top and bottom of the reactors to enable catalyst addition and withdrawal. The following conversion section consists of two fixed-bed reactors in series, containing catalysts, that are highly active for sulphur removal and conversion. The ebullated bed reactor operates as a fluidised-bed three-phase system with back mixing of the unconverted liquid and the catalyst.

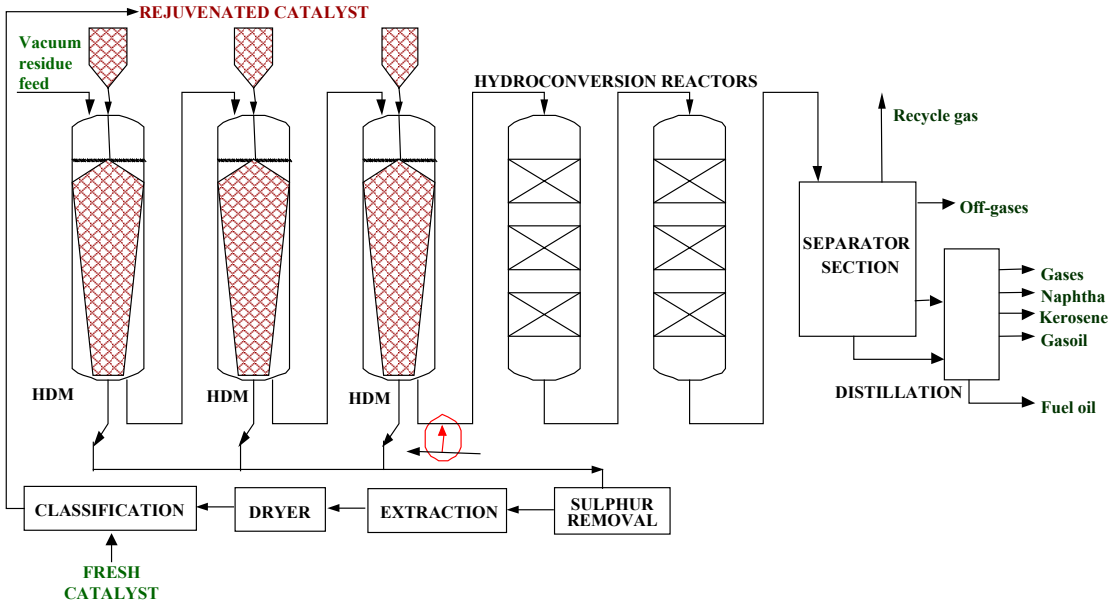


Figure 2.20: Sample of simplified process flow scheme for hydroconversion process (moving bed)

The concept of the fractionation section is also very licensor-dependent as it depends on the configuration of the separator system and the resulting temperatures. Typically it consists of a main fractionator, a vacuum distillation column and some form of a gas plant to fractionate and stabilise the lighter fractions. Products from the fractionation section are normally refinery fuel gas, LPG, naphtha, kerosene, light gasoil, vacuum distillate and a low-sulphur/ metal vacuum residue (bottoms) stream. The refinery fuel gas and LPG streams are amine washed to remove H_2S. The naphtha product is normally fed to a naphtha hydrotreater for further processing identical to the straight run naphtha product. The kerosene and light gasoil products are normally fed to a hydrotreater for further purification. The vacuum distillate is converted further in a hydrocracker or FCC unit. The bottoms stream is normally blended into the heavy fuel oil pool or used as delayed coker feedstock.

2.14 Hydrogen production

PURPOSE AND PRINCIPLE

The purpose of a hydrogen plant is to produce hydrogen for use in hydrocracking and other hydrogen-consuming refinery process units (Sections 2.13 and 2.16). Many refineries produce sufficient quantities of hydrogen at reforming operations (Section 2.6) for hydrotreating. More complex plants with extensive hydrotreating and hydrocracking operations however require more hydrogen than is produced by their catalytic reforming units. This extra hydrogen can be provided by one of the following processes: partial oxidation (gasification) of heavy oil fractions (IGCC in Section 2.10) to produce syngas where hydrogen can be separated; steam reforming of light ends or natural gas. The reliable operation of a hydrogen plant is critical for the hydrogen consuming processes. In those processes the following reactions occur:

Steam Reforming Process

$C_nH_m + n\ H_2O \ ===> \ n\ CO + (n+m)/2\ H_2$	Steam reforming (endothermic)
$CO + H_2O <===> CO_2 + H_2$	Shift (Exothermic)
$CO + 3\ H_2 <===> CH_4 + H_2O$	Methanation (Exothermic)
$CO_2 + 4\ H_2 <===> CH_4 + 2\ H_2O$	

Partial oxidation

$C_xH_y + O_2 \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

Gasification

$C + H_2O \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

FEED AND PRODUCT STREAMS

The feed of the hydrogen plant consists of hydrocarbons in the range from natural gas to heavy residue oils and coke. The conventional steam reforming process produces a hydrogen product of maximum 97 - 98 % v/v purity and higher if a purification process is applied (99.9 - 99.999 % v/v). The partial oxidation process requires oxygen if oxygen-blown gasification is used instead of air-blown gasification.

In steam reforming, light hydrocarbons are reacted with steam to form hydrogen. In principle, all products of a refinery could be used for hydrogen production by partial oxidation. However the most interesting option from the economic point of view is to use products with a low market value. In some refineries, heavy oil residues are transformed to petroleum coke and subsequently gasified (Section 2.7) to produce syngas.

PROCESS DESCRIPTION

Steam reforming

This is the most commonly used method for hydrogen production. The best feedstocks for steam reforming are light, saturated, and low in sulphur; this includes natural gas (the most common), refinery gas, LPG, and light naphtha. This is usually combined with a hydrogen purification process to produce very pure hydrogen (>99 % v/v). A simplified scheme of a steam reforming process is shown in Figure 2.21. The process is carried out in the presence of a catalyst which is very sensitive to poisoning. Desulphurisation of the feedstock is required in order to protect the catalyst in the reformer furnace against poisoning and deactivation. The reaction is typically carried out at 760 - 840°C and a pressure of 20 - 30 barg over a fixed catalyst bed. It is common practice to operate at excess steam-hydrocarbon ratios to prevent carbon formation. Heat for the endothermic reforming reaction is provided by the furnace burners. The reformed gas, a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and steam, is cooled down to about 350°C by raising steam. After reforming, the CO in the gas is reacted with steam to form additional hydrogen (shift reaction). The oxidation of the CO to CO_2 is done in a two-step shift converter, reducing the CO content to less than 0.4 %. The product gas passes to a CO_2 absorber after being cooled, where the CO_2 concentration is reduce to 0.1 % v/v by a suitable regenerable liquid absorbent (e.g. MEA, hot potassium carbonate or sulfinol). The solvent, enriched with CO_2, is stripped in a solvent regenerator. Residual CO and CO_2 in the absorber overhead gas is

methanated, reducing the CO and CO_2 content to about 5 - 10 ppm. Unlike CO, a small amount of CH_4 is usually not objectionable in hydrocracking units and other hydrotreating.

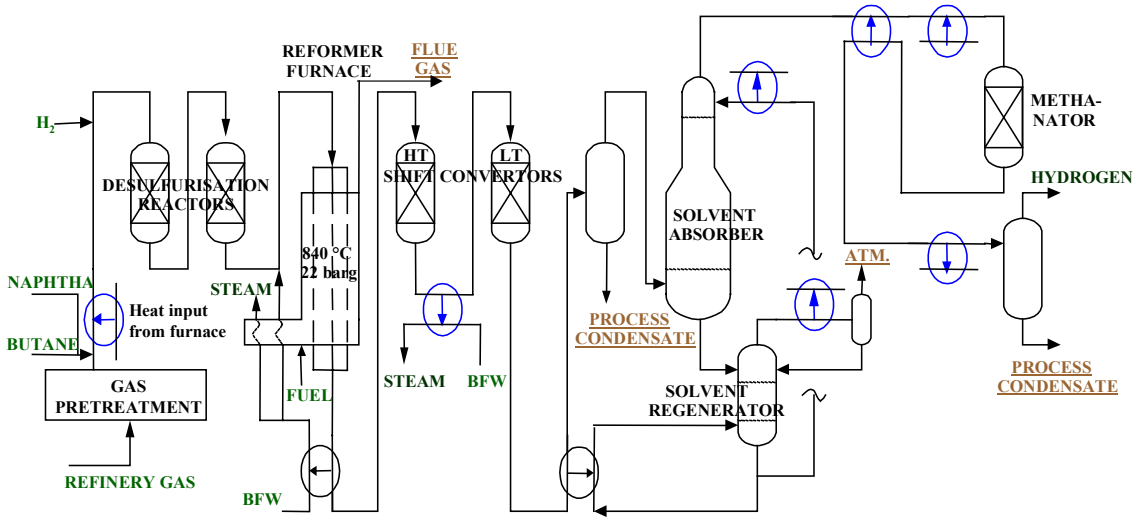


Figure 2.21: Hydrogen production by steam reforming and pressure-swing recovery

Gasification of coke

The processes used for the gasification of petroleum coke are the same as those used in the gasification of coal and they are integrated in the Flexicoker (Section 2.7). In an oxygen-blown operating mode of a gasifier, the gas produced can be processed to recover hydrogen or synthesis gas, or can be used as a medium-calorific value fuel. The gasifier product gas (syngas, CO, H_2, CO_2, CH_4 and H_2O) after it has passed the cyclones, contains hydrogen sulphide (H_2S) and carbonyl sulphide (COS). With a sulphur adsorbent such as limestone ($CaCO_3$) or dolomite (Mg, $CaCO_3$) in the gasifier, the sulphur content of the gas can be drastically reduced. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. The particulates in product gas are removed in the barrier filter. Volatile metals and alkali tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burned and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas.

Analysis of petroleum coke used in gasification		**Composition of gas produced by gasification at 980 - 1135 °C**	
Ultimate analysis	% w/w		% v/v
Carbon	87.1 – 90.3	CO	34.3 - 45.6
Hydrogen	3.8 – 4.0	CO_2	27.3 - 36.4
Sulphur	2.1 – 2.3	Hydrogen	13.5 - 16.8
Nitrogen	1.6 – 2.5	Water	8.7 - 13.9
Oxygen	1.5 – 2.0	Methane	0.1 - 0.9
Proximate analysis		Nitrogen	0.4 - 0.7
Fixed carbon	80.4 – 89.2	H_2S	0.3 - 0.6
Volatiles	9.0 – 9.7		
Moisture	0.9 – 10.2		
Ash	0.2 – 0.4		

Table 2.7: Example of composition of petroleum coke used as well as the composition of the syngas produced in a oxygen-blown fluidised bed gasification process
Source: [166, Meyers, 1997]

Gasification of hydrocarbons (Partial oxidation)
In partial oxidation, hydrocarbon feed reacts with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide (also covered in IGCC in Section 2.10). Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the light, clean feedstocks required for steam reforming.

Hydrogen processing in this system depends on how much of the gas is to be recovered as hydrogen, and how much is to be used as fuel. Where hydrogen production is a relatively small part of the total gas stream, a membrane is normally used to withdraw a hydrogen-rich stream. That stream is then refined in a purification unit.

Purification of hydrogen
A wide variety of processes are used to purify hydrogen streams. Since the streams are available at a wide variety of compositions, flows, and pressures, the method of purification will vary. They are wet scrubbing, membrane systems, cryogenic separation and pressure-swing adsorption (PSA). This last technique is the most commonly used. In the PSA plant, most impurities can be removed to any desired level. An adsorbent (molecular sieves) removes methane and nitrogen from the out-stream. Nitrogen is the most difficult to remove of the common impurities, and removing it completely requires additional adsorbent. Since nitrogen acts mainly as a diluent, it is usually left in the product if the hydrogen is not going to be used in a very high-pressure system such as a hydrocracker. Hydrogen purity is 99.9 - 99.999 % v/v after the PSA unit. The residual constituents of the product gas are mainly methane and less than 10 ppm CO. Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is normally accumulated in a vessel and used as fuel at a convenient location.

2.15 Integrated refinery management

Refineries contain processes and activities that are integrated in different ways. Because this integration, this section tries to analyse the following groups of activities:

- Process/activities that are so common in all parts of the refinery that has no sense to deal it in each single process/activity section. Some of those issues are already treated in other sections as for example energy issues (including management), cooling systems, storage and handling of materials and sulphur management (Section 4.23.5). So, no mention to those activities is done in this section.
- Evaluate the implications for the environment of the process integration. All refinery process units, systems and activities are typically operated in an integrated way, aimed to optimize the production in a way that is economic, sustainable and acceptable to society. This requires a concerted well managed approach in the execution and planning of all activities. This aspect has a great implications in the impact of the refinery into the environment.

Techniques to prevent air emissions, such as fugitive emissions, odour and noise that are relevant to the whole refinery are included in Sections 23. Soil contamination prevention techniques are also included in Sections 25.

Sections 15 within Chapters 2 to 4 have been structured according to two categories:

1. Refinery management activities including environmental management tools and good housekeeping techniques.Within this section activities as maintenance, cleaning, good design, production planning (including start-ups and shutdowns), training, information system process supervision/control systems and safety systems have been included.
2. Utilities management within a refinery not covered by other sections, such as water management, blowdown systems, compressed air generation and distribution and electricity distribution systems.

REFINERY MANAGEMENT ACTIVITIES

1. Environmental management tools

An Environmental Management System is a system for managing all activities (including energy) in a refinery that lays down the purpose of the refinery as a whole, the responsibilities of employees/management and procedures to be followed. An intrinsic aim of many systems is to achieve continuous improvement, with a refinery learning, in particular, from its own operationed experience as well as that of others.

The development of Environmental Management Systems (EMS) started by building upon the experience gained with other business parameters. Quite often, management responsibility for Safety is combined in one person with responsibility for the Environment (and Health, and sometimes Quality). Environmental Management is also named Environmental Care. In this section the importance of Good housekeeping and Management is highlighted. It is remarked that systems exist for improving performance in many fields such as Safety, Maintenance, Product Quality. Environmental Management Systems have also been developed for the improvement of refinery performance in environmental matters.

2. Good housekeeping activities

Good housekeeping techniques refers to the proper handling of the day-to-day aspects of running a refinery. Numerous examples of this nature can be given for refinery activities that have an impact on its performance. Other activities that may have an impact on the environmental performance of a refinery can be the maintenance, cleaning, good design, production planning (including start-ups, shut downs), information system process supervision/control systems, training and safety systems. The Council Directive on the control of major-accident hazards (Directive 96/82/EC) plays an important role in the safety management of refineries.

Heat exchanger cleaning

Heat exchangers are used throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream. The bundles are cleaned periodically to remove accumulations of scale, sludge and any oily wastes.

UTILITIES MANAGEMENT

Energy management including steam management and cooling are included in other Sections (8 and 10).

1.- Water management

Water is used within a refinery as process water and cooling water. Rainwater (clean or contaminated) is another type of water that should be also considered. Sanitary waste water, ballast water and blowdown water are other sources of waste water. Water masterplans are normally applied to refineries in order to optimise the consumption of water. Water inventories are sometimes a great help in the management of water, matching the quantity and quality of the effluents. Water integration and management is dependent on the refinery configuration, the crude quality and the level of desalting required, the cost of potable water, the availability of rainwater and the quality of the cooling water. Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available as well as a number of standard possibilities for water reduction and re-use. In most refineries a number of these options have already been implemented to some extent, either in the original design or by retrofit. Segregation of process water discharges and other types of water are also points to consider in the water management system. Sewerage systems also play an important role in the water management system within refineries.

Ballast water is relevant to those refineries that have crude receipt facilities from ships or handle big product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and heavily polluted with oil. However, volumes of ballast water to be treated are declining with the gradual introduction of segregated ballast tankers.

Water and drainage applies to any industrial site. It entails the complete system of fresh water supply, rainwater, ballast water, process water, cooling water and ground water as well as effluent collection, storage and the various (primary, secondary and tertiary) waste water treatment systems. The design is based on local factors (rainfall, receiving water bodies, etc.), effluent segregation, source reduction, first flush philosophies, flexible routing and re-use options.

Recirculated process water streams and cooling water streams are often manually purged to prevent the continued build up of contaminants in the stream (blowdown system).

2.- Purge/vents systems

Most refinery process units and equipment are manifolded into a collection unit, called the purge/vent system. Those systems provide for the safe handling and disposal of liquid and gases as well as for shutdown, cleaning and emergency situations. Purge/vents systems are either automatically vented from the process units through pressure relief valves, or are manually drawn from units. Part or all of the contents of equipment can also be purged prior to shutdown before normal or emergency shutdowns. Purge/vents systems use a series of flash drums and condensers to separate the blowdown into its vapour and liquid components.

3.- Compressed air generation

Compressed air is necessary as a utility within a refinery. It is normally generated by electric compressors and is distributed round the refinery.

4.- Heating of pipes

Current practices are to apply steam heating (low-pressure steam), electric heating or hot oil heating of lines, if it is required. Electric heating normally generates less corrosion and consequently is easier to maintain compared with heating using steam. Hot oil heating is used when high temperatures are needed.

2.16 Isomerisation

PURPOSE AND PRINCIPLE

Isomerisation is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, low molecular weight paraffins (C_4-C_6) are converted to isoparaffins having a much higher octane index. Isomerisation of olefins is also included in this section.

FEED AND PRODUCT STREAMS

Typical feedstocks to isomerisation units are any butane- or a pentane- and hexane-rich feedstream. Those streams are hydrotreated naphtha, straight run light naphtha, light naphtha from hydrocrackers, light reformate, coker light naphtha and the light raffinate stream from an aromatic extraction unit. The feedstream to C_5/C_6 isomerisation unit is normally fractionated so that it includes as much of the C_5/C_6 as possible, while minimising heptanes and heavier compounds.

PROCESS DESCRIPTION

Figure 2.22 shows a simplified process flow diagram of a low temperature isomerisation unit. The isomerisation reactions occur in the presence of hydrogen and catalyst. The atmosphere of hydrogen is used to minimise carbon deposits on the catalyst, but hydrogen consumption low.

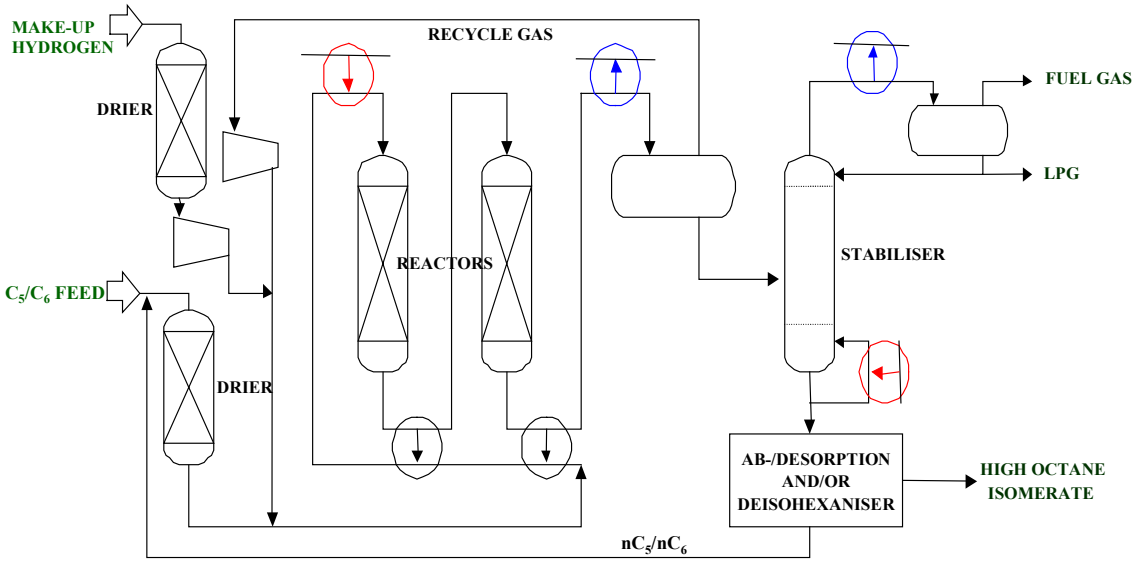


Figure 2.22: Simplified process flow scheme for an isomerisation unit

The reactions normally take place in two reactors in series. This allows replacement of the catalyst during operation. A further advantage of the two-reactor scheme is that the first reactor may operate at higher temperatures to kinetically drive the reactions, while the tail reactor may be operated at lower temperatures to push the desired products closer to equilibrium conversion. There are several isomerisation processes in use today. In general they can be classified in two categories, 'once-through' or recycled.

- In 'once-through' isomerisation, only fresh feed is processed in the isomerisation unit. The octane number which can be achieved is only around 77 - 80 RON when using a zeolite based catalyst and 82 - 85 RON using a chloride promoted catalyst. Conversions of 80 % can be expected.
- In recycle isomerisation, the unconverted, lower octane paraffins are recycled for further conversion. Depending on the recycle option, the recycle may be normal paraffins or methylhexanes and n-hexane. The octane number obtained can be up to 92 RON, dependent on the feedstock composition, configuration and catalyst used. The yield in isomerate is around 95 to 98 % depending on the targeted octane number of the final stream.

There are three distinctly different types of catalysts currently in use: chloride promoted, zeolitic, and sulphated zirconia catalysts. The zeolite catalyst operates at significant higher temperatures (250 – 275 °C and 28 barg) and is more tolerant to contaminants though resulting octane improvements is lower. The zeolite catalyst is mainly used when higher octane isomerate product does not justify the additional capital required to reduce feed contaminants for the chlorided alumina catalyst or is a better match for a retrofit unit. The highly active chloride promoted catalyst, operates at a relatively low temperature (190 – 210 °C and 20 barg) and gives the highest octane improvement.This type of catalyst requires the addition of small amounts of organic chlorides converted to hydrogen chloride in the reactor to maintain the high activity. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. Furthermore, this catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to 0.5 ppm is required. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to the desired isomers is enhanced at lower temperatures.

After isomerisation, the light ends are stripped from the product stream leaving the reactor and are then sent to the sour gas treatment unit. In a once-through isomerisation unit the bottom stream from the stabiliser is, after product cooling, sent to the gasoline pool. In a recycle stream, the bottom stream from the stabiliser is fed to a separation unit, which is either a de-isohexaniser column or an adsorption system.

In the de-isohexaniser column, a split can be made between the higher octane dimethylbutanes and the lower octane methylpentanes. The dimethylbutanes and lower boiling C_5 components (isomerate product) are taken overhead from the column and are sent to the gasoline pool. The methylpentanes and normal hexane are taken as a side-stream close to the bottom, and are recycled to the reactor. The bottom stream from the de-isohexaniser is a small quantity of heavy by-product which is sent with the isomerate product to the gasoline pool or to a catalytic reformer if the refinery recovers benzene as chemical feed. The principle of adsorption is that the unconverted normal paraffins are adsorbed on the molecular sieve whereas the iso-paraffins pass the adsorbent. Desorption takes place with heated hydrogen-rich gas from the separator or a butane mixture. The desorbent is separated from the net hydrogen-rich recycle stream in a separator vessel.

2.17 Natural gas plants

Gas in Europe has been typically found in the North Sea. Natural gas is also obtained from a small number of on-shore oil fields, where it is co-produced with crude oil and separated at local facilities before being treated, brought up to specification and exported. The off-shore gas production consists of a number of central platforms with satellite platforms. The satelite platforms deliver gas to the central platform, where gas is dried (removal of water). Also condensates are partially removed, but these are re-injected again in the produced gas. Chemicals are added to the gas stream either at the well-head or prior to transmission to prevent solid hydrate formation and to limit corrosion in the underwater pipeline. Off-shore platforms are not included in the scope of this document. Subsequently, the central platforms deliver through one main gas pipeline to the on-shore natural gas plants for the final treatment.

PURPOSE AND PRINCIPLE

The overall objective of natural gas processing is to remove the treatment chemicals and to remove any contaminants from the well-head stream in order to produce a methane rich gas which satisfies statutory and contractual specifications. The main contaminants to be removed fall into the following categories:

- solids: sands, clay, sometimes scale like carbonates and sulphates (including naturally occurring radioactive metals (e.g. lead or radium)), mercury
- liquids: water/brine, hydrocarbons, chemicals added at well-head
- gases: acid gases, carbon dioxide, hydrogen sulphide, nitrogen, mercury and other gases (e.g. mercaptans).

FEED AND PRODUCT STREAMS

Feedstock is natural gas and the products that may be separated within the natural gas plants are methane reach gas, C_2, C_3, C_4 fractions and condensates (C_{5+}).

PROCESS DESCRIPTION

As it is shown in Figure 2.23, the purification plant consists on a gas sweetening plant where acid gases as CO_2, H_2S, SO_2 are separated. Natural gas is considered "sour" when contains significantly greater amounts of hydrogen sulphide than those quoted for pipeline quality or when contains such amounts of SO_2 or CO_2 to make it impractical to use without purification. The H_2S must be removed (called "sweetening" the gas) before the gas can be utilized. If H_2S is present, the gas is usually sweetened by absorption of the H_2S in an amine solution. Amine processes are the most common process used in the United States and Europe. Other methods, such as carbonate processes, solid bed absorbents, and physical absorption, are employed in the other sweetening plants.

Natural gasoline, butane and propane are usually present in the gas, and gas processing plants are required for the recovery of these liquefiable constituents (see Figure 2.23). The type of processes found are very similar to those described in Section 2.12. As summary, they are physical separations at very low temperatures (typically distillation).

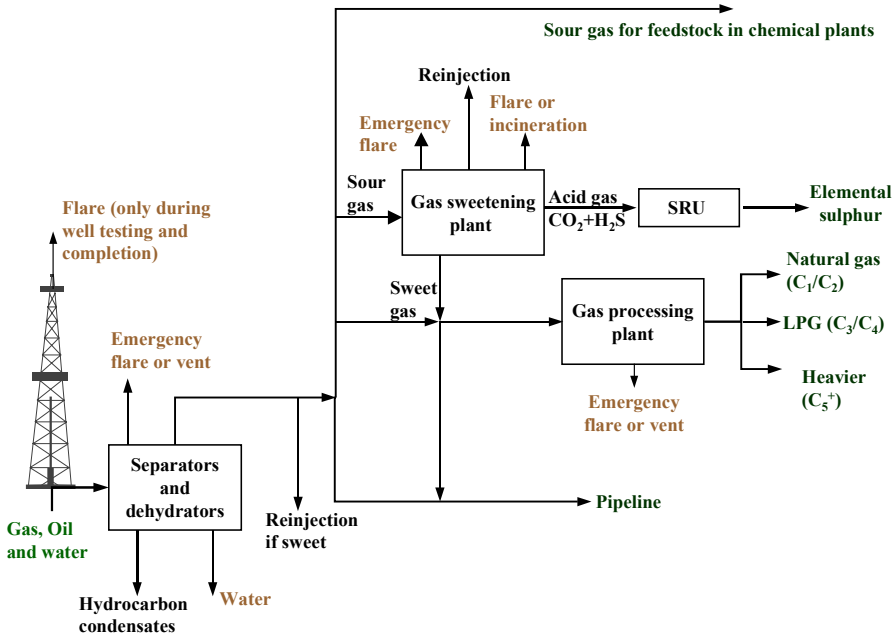


Figure 2.23: General flow diagram of the natural gas industry

2.18 Polymerisation

This section covers up the polymerisation, dimerisation and condensation of olefins.

PURPOSE AND PRINCIPLE

Polymerization is occasionally used to convert propene and butene to high octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. Prevailing chemical reactions may vary according to olefin type and concentration but can be described in the general terms shown below:

$2\ C_3H_6$	→	C_6H_{12}	Dimerisation
$2\ C_4H_8$	→	C_8H_{16}	Dimerisation
$C_3H_6 + C_4H_8$	→	C_7H_{14}	Condensation
$3\ C_3H_6$	→	C_9H_{18}	Polymerisation

FEED AND PRODUCT STREAMS

Propene and butene contained in the LPG stream from the FCC are the most used feedstreams for this unit.

PROCESS DESCRIPTION

The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst adsorbed onto natural silica and extruded in pellets or small cylinder form. All reactions are exothermic, and therefore the process requires temperature control. The feed must be free of: sulphur, which poisons the catalyst; basic materials, which neutralize the catalyst and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans, then with an amine solution to remove hydrogen sulphide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer. A simplified scheme of a polymerisation unit is shown in Figure 2.24.

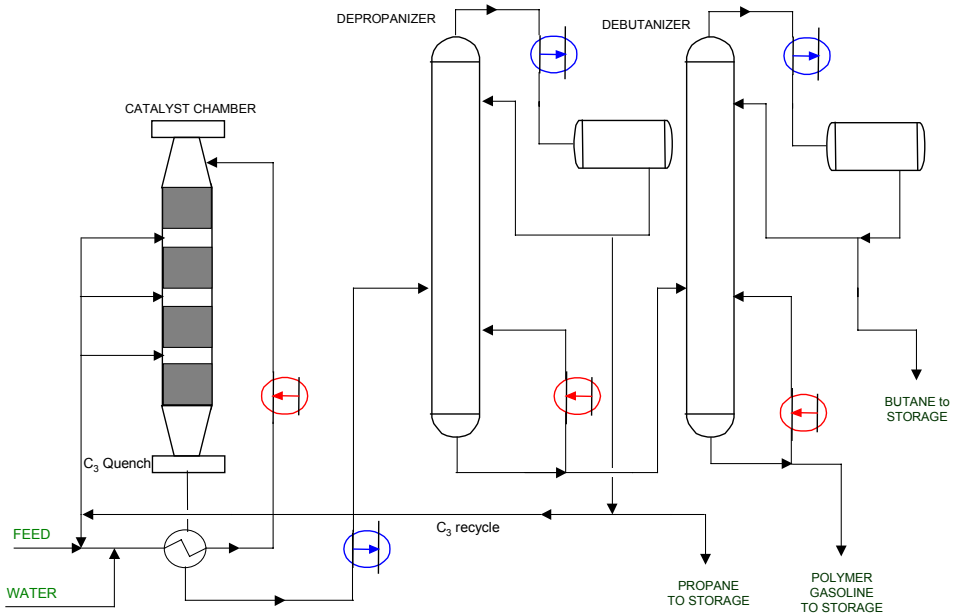


Figure 2.24: Simplified scheme of a polymerisation unit

When the polymerisation yield drops, the catalysts need to be replaced. After nitrogen purging, the polymerisation unit is opened and the catalyst removed by means of a high-pressure water jet. It can also be removed using steam (compression dumping). The phosphoric acid goes in the water medium, while the natural silica pellets break down to form a slurry, which is usually pumpable.

2.19 Primary distillation units

This section includes atmospheric and vacuum distillation. Those two primary distillations are preceded by crude oil desalting and they are the first and fundamental separation processes in a refinery.

PURPOSE AND PRINCIPLE

The Atmospheric Crude Oil Distillation Unit (CDU) is the first important processing step in a refinery. Crude oil is heated to elevated temperatures and then generally subjected to distillation under atmospheric pressure (or slighly higher) separating the various fractions according to their boiling range. Heavier fractions from the bottom of the CDU, which do not vaporise in this column, can be further separated later by vacuum distillation.

Increased demand for light products and a reduced demand for heavy fuel oil have resulted in refiners upgrading the atmospheric residue in more valuable lower boiling fractions such as naphtha, kerosene and middle distillates. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure to increase volatilization and separation whilst avoiding thermal cracking. The *high vacuum unit* (HVU) is normally the first processing step in upgrading atmospheric residue followed by downstream refining units. HVU produces feedstocks for cracking units, coking, bitumen and base oil units. The contaminants from the crude oil stay predominantly in the vacuum residue.

FEED AND PRODUCT STREAMS

The crude oil feed to the crude distillation unit is supplied from the crude oil storage tanks after desalting. Normally all crude oil entering a refinery passes through a crude distillation unit. In addition to that, it is common practice that off-specification product streams are reprocessed in the CDU. The products from the crude distillation unit, ranging from the lightest to the heaviest cut are; naphtha and light components (boiling <180 °C / C_1-C_{12}- lights, naphtha and gasoline), kerosene (boiling range 180 - 240 °C - C_8-C_{17}), light gasoil (boiling range approximately 240 - 300 °C / C_8-C_{25}), heavy gasoil (boiling range approximately 300 - 360 °C / C_{20} - C_{25}) and atmospheric residue (boiling >360 °C / >C_{22}). The overhead of this column is the light fraction, noncondensable refinery fuel gas (mainly methane and ethane). Typically this gas also contains hydrogen sulphide and ammonia gases. The mixture of these gases is known as “sour gas” or “acid gas”. A certain amount of it passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide.

The main feed stream to the HVU is the bottom stream of the crude oil distillation unit referred to as atmospheric or long residue. In addition the bleed stream from the hydrocracker unit (if applicable) is normally sent to the HVU for further processing. The products from the HVU are light vacuum gasoil, heavy vacuum gasoil and vacuum residue. Light vacuum gasoil is normally routed to the gasoil hydrotreater(s), heavy gasoil is normally routed to a fluid catcracker and/or hydrocracker unit. The vacuum residue can have many destinations such as visbreaking, flexicoking or delayed coking, residue hydroprocessing, residue gasification, bitumen blowing or to the heavy fuel oil pool.

PROCESS DESCRIPTION

Atmospheric distillation

Distillation involves the heating, vaporisation, fractionation, condensation, and cooling of feedstocks. The desalted crude oil is heated to about 300 - 400 ºC and fed to a vertical distillation column at atmospheric pressure where most of the feed is vaporised and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected towards the top of the column. The overhead hydrocarbon vapours are condensed and accumulated in the overhead reflux drum of the main fractionator. In this drum sour water, light fractions (about 0.5 % on crude charge) and stripping steam (1.5 % on crude), are separated from the hydrocarbon liquid. The overhead hydrocarbon liquid, the so-called naphtha minus stream, is

commonly fed directly to the downstream naphtha treater. Within each atmospheric distillation tower, a number of side-streams of low-boiling point components are removed from different trays in the tower. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side-streams are each sent to a different small stripping tower containing four to ten trays with steam injected under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side-stream draw tray. Most of these fractions generated in the atmospheric distillation column can be sold as finished products after a hydrotreatment, or blended with products from downstream processes. In Figure 2.25 a simplified process flow diagram of a crude distillation unit is shown. Many refineries have more than one atmospheric distillation unit.

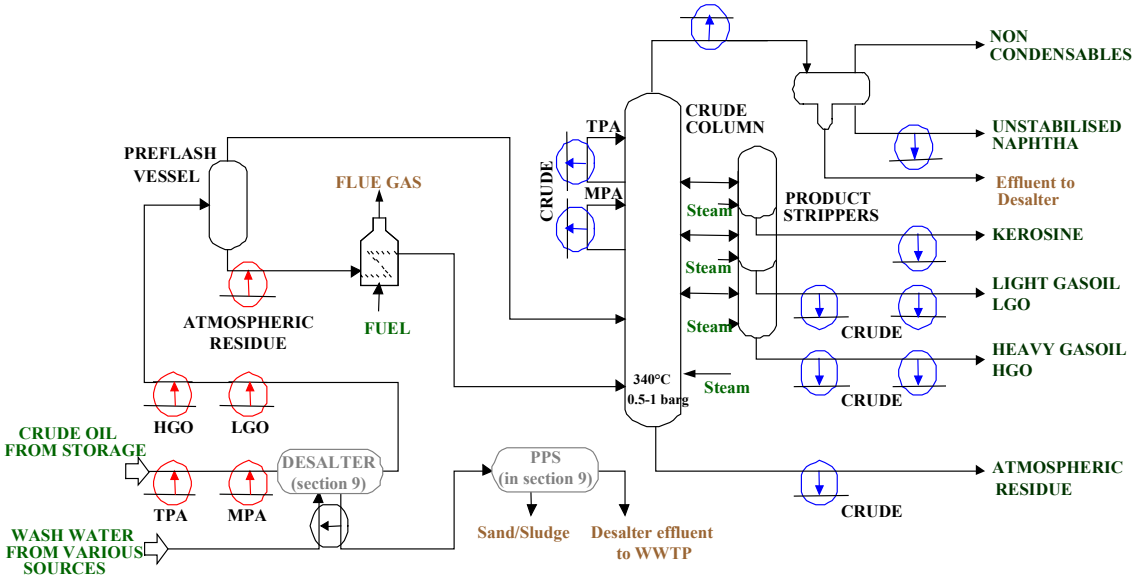


Figure 2.25: Simplified process flow diagram for a crude distillation unit

The operating conditions of the tower are based on the properties of the crude oil and the desired products yield and quality. To maximise the yield of distillates, the pressure is minimised, but the temperature is increased to the maximum. Every refinery has a crude distillation unit designed for a selected crude (mix). There are therefore many different crude distillation configurations with varying product cuts and heat integration.

Vacuum distillation

Figure 2.26 shows a simplified process flow diagram of the high vacuum unit. Atmospheric residue is heated up to 400 °C, partially vaporised (30 - 70 % by weight) and flashed into the base of the vacuum column at a pressure between 40 and 100 mbar (0.04 to 0.1 kg/cm^2). The vacuum inside the fractionator is maintained with steam ejectors, vacuum pumps, barometric condensers or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporisation and separation. The unvaporised part of the feed forms the bottom product and its temperature is controlled at about 355°C to minimise coking. The flashed vapour rising through the column is contacted with wash oil (vacuum distillate) to wash out entrained liquid, coke and metals. The washed vapour is condensed in two or three main spray sections. In the lower sections of the column the heavy vacuum distillate and optional medium vacuum gasoil are condensed. In the upper section of the vacuum column the light vacuum distillate is condensed. Light (non-condensable) components and steam from the top of the column are condensed and accumulated in an overhead drum for separating the light non-condensables, the heavier condensed gasoil and the water phase. Figure 2.26 shows a simplified process flow diagram of a crude distillation unit. The most important operational aspect of a vacuum unit is the quality of the heavy vacuum gasoil, especially when this is fed to a hydrocracker unit. The

Concarbon level and/or metal content is very critical for a hydrocracker unit and depends very much on the operation and performance of, especially, the wash oil section in the vacuum distillation unit as well as the desalter in the crude distillation unit.

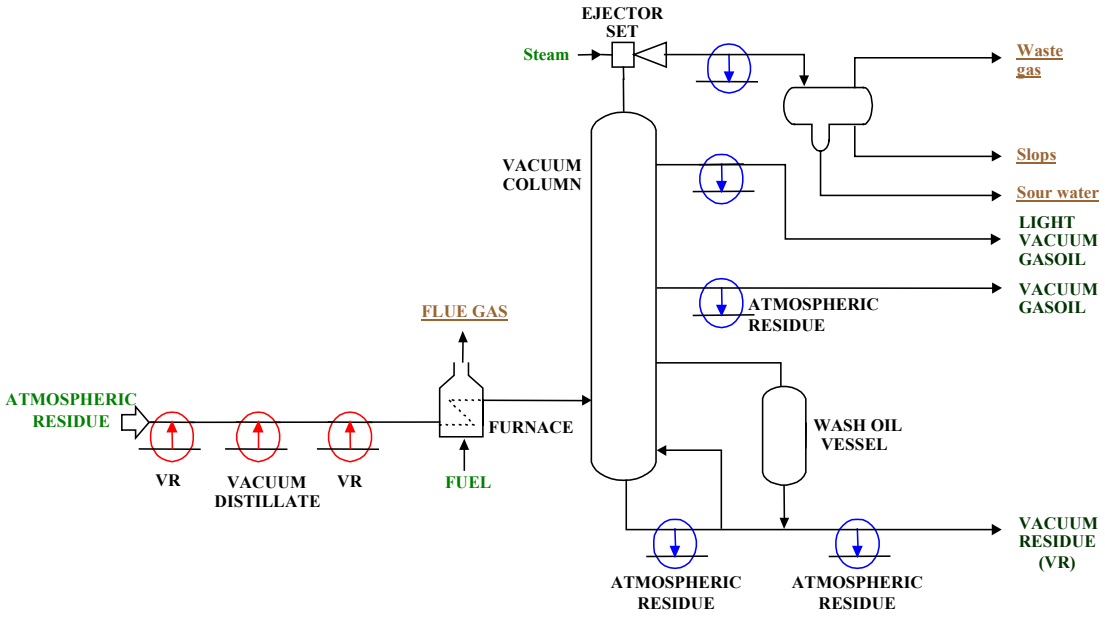


Figure 2.26: Simplified process flow scheme for high-vacuum distillation unit

2.20 Product treatments

The treatments used in a refinery to achieve certain product specifications are included in this section, in which two types of processes can be identified. The first group of processes corresponds to extraction or removal techniques where the component to treat is removed from the stream to be treated. Under this category, mention can be made of molecular sieve extraction for removal of carbon dioxide, water, hydrogen sulphide or mercaptans (Section 4.23.5.3), amine scrubbing for removal of hydrogen sulphide (included in Section 4.23.5.1) or caustic washing for the removal of acids or mercaptans. The second group is composed of those systems where the chemical to be treated is not removed from the stream to be treated.

PURPOSE AND PRINCIPLE

In petroleum refining, chemical treating is used to remove or change the undesirable properties associated with sulphur, nitrogen, or oxygen compound contaminants in petroleum products. Some of those systems (so called mercaptan oxidation) are designed to reduce the mercaptan content (organic sulphur compounds) of hydrocarbon streams to improve product odour and to reduce corrosivity. Those treatments are accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. The extraction process removes the mercaptans by caustic extraction, resulting in a lower sulphur content. The following reaction takes place at low temperatures:

$$R\text{-}SH + NaOH \rightleftharpoons NaSR + H_2O$$

Mercaptan oxidation-sweetening is another version of the mercaptan oxidation process in which the mercaptans in the hydrocarbon products are converted to less odorous and less corrosive disulphides which remain in the product. The reaction is:

$$NaSR + \tfrac{1}{4}\,O_2 + \tfrac{1}{2}\,H_2O \rightleftharpoons NaOH + \tfrac{1}{2}\,RSSR$$

As a result no reduction in the total sulphur content takes place during sweetening and consequently it is only applied to those streams where sulphur content is not a problem.

FEED AND PRODUCT STREAMS

The mercaptan oxidation-extraction process entails the removal of mercaptans from LPG, naphtha and gasoline and kerosene streams. Oxidation or *"sweetening"* is used on gasoline and distillate fractions. It should also be stressed that mercaptans are also removed by hydrotreatment (Section 2.13).

PROCESS DESCRIPTION

Mercaptans are removed from light hydrocarbon streams by a concentrated alkaline wash in an extraction column under elevated pressure (5 barg). If H_2S or acids are present a caustic prewash is required. The treated and odour-free hydrocarbon stream leaves the reactor as an overhead stream. The aqueous bottom phase is heated to 50 °C, mixed with air and fed to the oxidation reactor. The dissolved NaSR is now converted into disulphides (which are insoluble in caustic soda water solution) at 4.5 barg. By using an excess of air and adding catalyst, a high rate of reaction is maintained. In this way the alkaline solution is regenerated. The liquid from the reactor is routed to a vessel where spent air, the disulphide fraction insoluble in the caustic solution and the caustic solution are separated. The spent air is routed to an incinerator or process furnace, the disulphides are usually recycled to the crude and the regenerated caustic is circulated to the extraction column. Figure 2.27 shows a simplified process flow diagram of an extraction process.

Another oxidation process is also a mercaptan oxidation process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic ("mini-alky" operation) are injected into the hydrocarbon stream and the caustic cannot regenerated. As the hydrocarbon passes through the mercaptan oxidation catalyst bed, sulphur mercaptans are oxidized to disulphide.

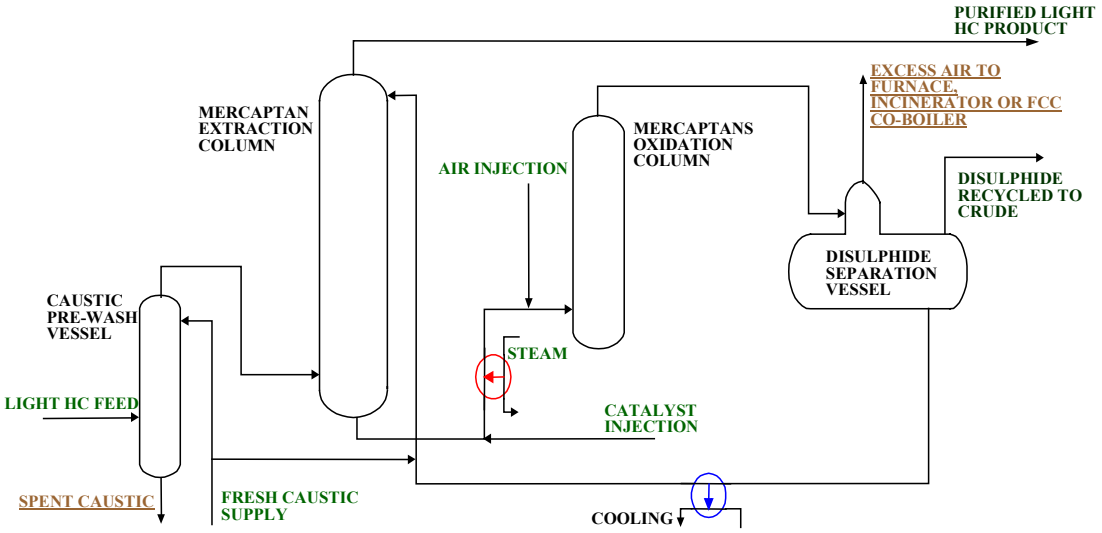


Figure 2.27: Simplified process flow diagram of the mercaptan oxidation extraction process

Both processes can be integrated in a so-called caustic cascading system to achieve the desired product quality improvements at minimum caustic make up and spent caustic disposal costs. Figure 2.28 shows a simplified process flow diagram of the mercaptan oxidation extraction process.

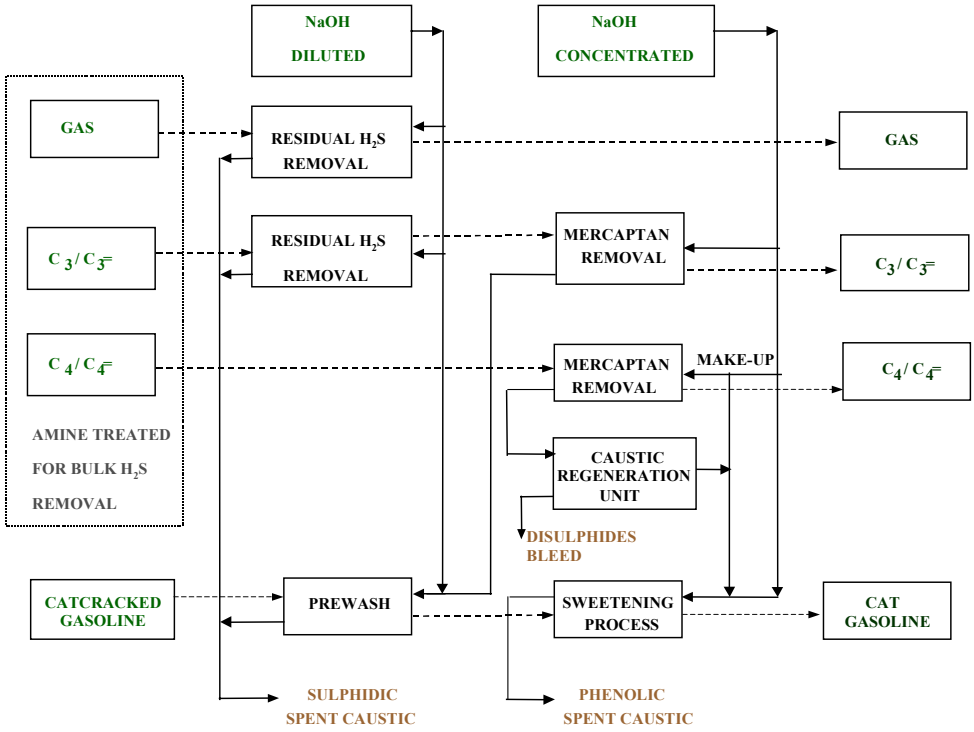


Figure 2.28: Simplified process flow diagram of the caustic cascading system (mercaptan oxidation extraction and mercaptan oxidation sweetening)

Another process that can be found in refineries is the *selective hydrocracking* (hydrofiner), where one or two zeolite catalysts are used to selectively crack the wax paraffins (n- and near-to-n-paraffins). This technique can be used for the dewaxing of middle-distillate components that may be blended into products for extreme winter conditions. A variation of this is the use of *isodewaxing* catalyst that isomerizes the n-paraffin wax to desirable isoparaffin lube molecules, while co-producing low quality middle-distillate transportation fuels. The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).

2.21 Storage and handling of refinery materials

Storage and handling of refinery materials are not covered exhaustively in this document, because the storage and handling of oil products are within the scope of the horizontal BREF on storage, to which reference will be made as appropriate. This section also covers activities related to feed and product blending, piping and other small techniques used for the handling of materials. Storage of specific products, such as base oils, bitumen and petroleum coke, is included in their respective production sections.

PURPOSE AND PRINCIPLE

Crude oil, petroleum intermediates and final products are transferred to, in and from refineries, through marine terminals, via pipeline or rail/road vehicles. Between these movements, the products are stored in tanks. *Storage* tanks or caverns are used throughout the refining process to store crude oil, other raw materials and intermediate process feeds. Finished petroleum products are also kept in storage tanks before transport off site. Tanks are also needed to accommodate blocked-out operation of processing units, to link continuous refinery processes with discontinuous ones. Consequently, storage is an essential part of a refinery. Blending systems are also used in refineries to prepare feed streams to individual refinery units and to produce finished products to be sold.

Feed blending may be applied to prepare the optimum feed stream to a refinery unit, thereby ensuring the optimum performance of the refinery unit. For example, a refiner processes a mixture of four different low-sulphur crudes in his atmospheric distillation unit. The feed blend is selected so that the throughput in the distillation unit and further downstream units are optimised/ maximised with the objective of maximising overall profit. Alternatively, it also happens that the different quality crudes are processed separately for a short period (a few days) in so-called “blocked-out” operations.

Product blending is applied to produce the optimum mix of finished refinery products. The majority of the product streams as produced in different refinery units, normally identified as an intermediate product stream, can be blended into more than one finished product stream. For example (hydrotreated) kerosene product is normally blended into diesel oil, light heating oil and even heavy fuel oil, with the remainder blended into the jet fuel oil. The amount of kerosene allocated to the different products is selected so that product demands and specifications are met with the objective of maximising overall profit. Blending products involves mixing the products in various proportions to meet specifications such as vapour pressure, specific gravity, sulphur content, viscosity, octane number, cetane index, initial boiling point and pour point and to add distinctive smells (LPG).

PROCESS DESCRIPTION

The crude oil storage systems can be located either at a separate oil terminal or within the refinery complex. More than 50 % of the refinery area is occupied by oil movement facilities. Storage tanks can be divided into four main types: Pressure vessels, fixed roof tanks, fixed roof tanks with floating cover and floating roof tanks. Figure 2.29 shows a drawing of the different types of storage systems found in a refinery.

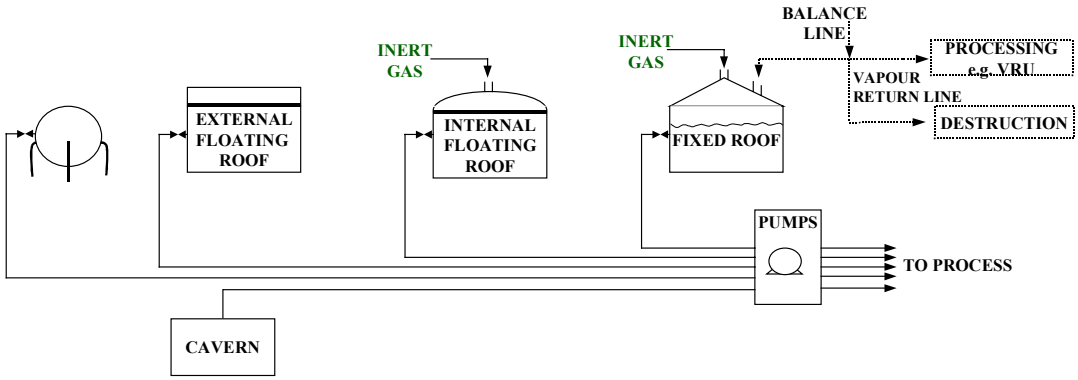


Figure 2.29: Different type of storage tanks

Pressure vessels are normally used to store gases at high pressures (>91 kPa, e.g. LPG). *Fixed roof tanks* can be open to atmosphere, or designed as a pressure tank, with several classes of allowed pressure build-up, from 20 mbarg (low pressure) to 60 mbarg (high pressure). The pressure tanks are provided with Pressure/Vacuum Relief Valves to prevent explosions and implosions, the vacuum setting being -6 mbarg. *Floating roof tanks* are constructed in such way that the roof floats on the liquid, and moves with the liquid level (>14kPa to < 91 kPa).

Above-ground storage tanks (ASTs) are used at refineries for holding either the raw feedstock (crude oil) or end-products generated by the refinery processes (gasoline, diesel, fuel oils etc.). Underground storage tanks are used much less frequently (if at all) at refineries - primarily for storing fuel for onsite boilers and vehicles, or for capturing liquids at low level drain points. Storage of crude oil and products in caverns is also applicable in some European countries.

Blending can be carried out in-line or in batch blending tanks. An in-line blending system consists of a manifold where individual streams are blended on flow control, and the blend ratio is normally controlled and optimised by a computer. When a certain volume of a given quality product is specified, the computer uses linear programming models to optimise the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost. To ensure that the blended streams meet the desired specifications, in-line stream analysers for flash point, RVP, boiling point, specific gravity, research and motor octane number (RON and MON), sulphur, viscosity, cloud point and others are inserted to provide feedback to the computer which in turn corrects blending ratios where necessary.

Batch blending involves mixing the feed streams in a blend tank, from where the relevant process units are fed. The same applies to intermediate product streams, which are first sent to intermediate storage tanks, from where they are batch blended into the final product tanks.

Additives and odorants. The odorant is stored as a liquid, normally in fixed tanks. The odorant is not added to the gas stream prior to liquefaction but is usually added to the LPG whilst the LPG is being loaded into the delivery tankers, although in-tank odorising is also carried out. Allowance may be made for any residual mercaptans already present in the LPG. The pump addition rate is carefully controlled. In the case of liquid propane, methanol may be added with the odorising agent in order to prevent hydrate icing in propane evaporators.

Pipes, valves and auxiliary systems, such as vacuum recovery units are found throughout a refinery. Gases, liquids and even solids are transferred from unit operation to unit operation by pipes. Process pipes are normally overground but some pipes are underground.

2.22 Visbreaking

PURPOSE AND PRINCIPLE

Visbreaking is a well-established noncatalytic thermal process that converts atmospheric or vacuum residues to gas, naphtha, distillates and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules.

When vacuum residue is directly blended to the heavy fuel oil pool, significant quantities of cutter stock (normally high-value gasoil) need to be blended to the residue to meet the viscosity specifications of the heavy fuel oil. By thermally cracking the vacuum residue at relatively mild conditions, about 10 - 15 % of the feed is cracked to lighter fractions and, more importantly, the viscosity of the vacuum residue is reduced significantly. For this reason, the thermal cracker unit is normally called the “visbreaker” gas oil unit.

FEED AND PRODUCT STREAMS

The atmospheric residue from the crude distillation unit, the vacuum residue from the high vacuum unit, heavy gas oils or vacuum gasoils or mixtures are typically the feedstocks. In this process, only part of the feedstock is converted and a large amount of residue remains unconverted. As no catalyst is involved in the thermal cracking process, the quality of the feedstock in terms of metals and sulphur is not critical. A significant quantity of gas is produced and all distillate products need further treatment and upgrading prior to running them to storage.

PROCESS DESCRIPTION

Thermal cracking is one of the oldest conversion processes to upgrade heavy oil fractions. At present it is mainly used to upgrade vacuum residue. Figure 2.30 shows a simplified process flow diagram of the Visbreaker unit. The most important factor in controlling the cracking severity should always be the stability and viscosity of the visbroken residue fed to the fuel oil pool. In general, an increase in the temperature or residence time results in an increase in severity. Increased severity produces higher gas-plus-gasoline yield and at the same time a cracked residue (fuel oil) of lower viscosity. Excessive cracking, however, leads to an unstable fuel oil, resulting in sludge and sediment formation during storage. Thermal cracking conversion is maximum 20 % of the feed. Thermal cracking units to upgrade atmospheric residue have conversion levels significantly higher (35 - 45 %) and the viscosity of the atmospheric residue is reduced.

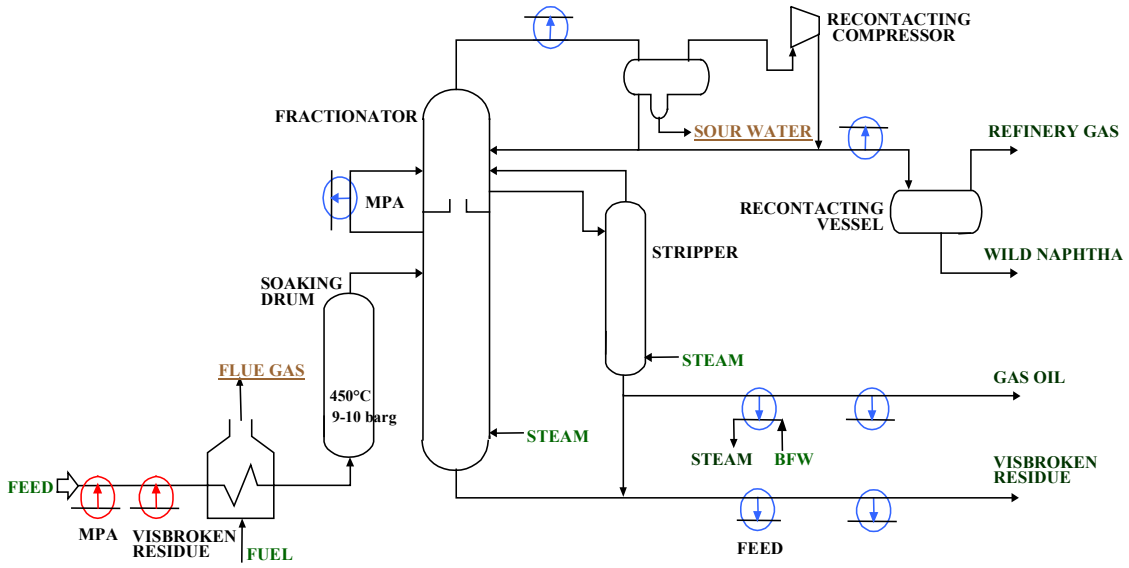


Figure 2.30: Simplified process flow scheme for visbreaking unit

The feedstock is heated above 500 ºC and then fed to a reaction chamber which is kept at a pressure of about 9.65 barg. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporise and are drawn off. The lighter products are fed to a fractionating tower, where the various fractions are separated. The "bottoms" consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel.

There are two types of visbreaker operations, “coil or furnace cracking” and “soaker cracking”. Coil cracking uses higher furnace outlet temperatures (470 – 500 °C) and reaction times from one to three minutes, while soaker cracking uses lower furnace outlet temperatures (430 - 440 °C) and longer reaction times. The product yields and properties are similar. Run times of 3 - 6 months are common for furnace visbreakers and 6 - 18 months for soaker visbreakers.

2.23 Techniques for the abatement of emissions

There are many non-production techniques in use in a refinery. In particular, for this document are relevant those techniques used to control and abate emissions to air, water and soil. Descriptions of many of those techniques can be found in the BREF on Waste Gas and Waste Water in the Chemical Industry and in Chapter 4 (Section 4.23 to 4.25). Those techniques are not described in this chapter because they are typically techniques that might be considered in the determination of BAT and consequently are going to be described and analysed in Chapter 4, Sections 23-25.

Pollutants such as NO_x, particulates, H_2S, SO_2, other sulphur compounds and VOC, among others, are typically abated by end-of-pipe techniques. One of the largest systems within a refinery is the abatement of H_2S produced across the refinery. These systems typically contain an amine scrubbing system and a sulphur recovery unit to convert H_2S into sulphur, a by-product produced within refineries. Flares are also another technique used within the refinery for safety and environmental reasons. Techniques for the abatement of odour and noise are also relevant for refineries.

Refineries also contain waste water plants with different unit operations. Oil separators, flotation, floculation and biological treatment are typical within refineries. Biological treatment is required when biodegradation of some organic chemicals that may be present within the waste water stream is necessary. Final water cleaning systems can also be present.

Refineries also generate solid wastes. Some of them are recycled within the refinery, others are recycled by specialist companies (e.g. catalysts) and others are disposed of. Soil contamination prevention techniques that are also relevant to the whole refinery.

3 CURRENT EMISSION AND CONSUMPTION LEVELS

This chapter provides data and information about current emission and consumption levels in existing installations at the time of writing. Because it covers many types and sizes of refinery, the data are very wide-ranging. The goal of the chapter is to bring together, as far as possible, the emission and consumption levels of the refinery as a whole and for each specific process. The data quoted will, in most cases, enable an estimate of the concentration and load of emissions, in turn enabling a competent authority issuing a permit to verify the information provided in the permit application.

Section 3.1 gives an overview of the main emissions and consumptions of European refineries as a whole. It is not a simple aggregation of the emissions and consumptions in the other sections: most of them cannot be aggregated because of the integration of processes in refineries.

Section 2 to 22 cover the emissions and consumptions from the various processes/activities covered by this document. Sections 23-25 covers the emissions generated by the techniques used to abate emissions, including the emissions from sulphur recovery units. The chapter ends with a section on monitoring, which covers the monitoring systems typically applied in refineries and provides some discussion on their application.

3.1 Current emission and consumption levels in refineries as a whole

Refineries are industrial sites that manage huge amounts of raw materials and products and they are also intensive consumers of energy and water. From storage and from the refining process, they generate emissions to the atmosphere, to the water and to the soil.

This chapter addresses those three media in turn, and the pollutants that affect them, and is a summary of the emissions from all refinery processes. The main environmental problems were mentioned in Chapter 1 (Section 1.4), but without figures. This section aims to quantify refinery emissions.

Although the principal raw material input to petroleum refineries is crude oil, they use and generate an enormous number of chemicals, some of which leave the facilities as discharges of air emissions, waste water or solid waste. Pollutants generated typically include ammonia (NH_3), carbon dioxide (CO_2), carbon monoxide (CO), hydrogen sulphide (H_2S), metals, nitrogen oxides (NO_x), particulates, spent acids (e.g. HF, H_2SO_4), sulphur oxides (SO_x), volatile organic compounds (VOC) and numerous organic compounds (some very toxic). Figure 3.1 shows a simplified example of what it is consumed and emitted by a refinery.

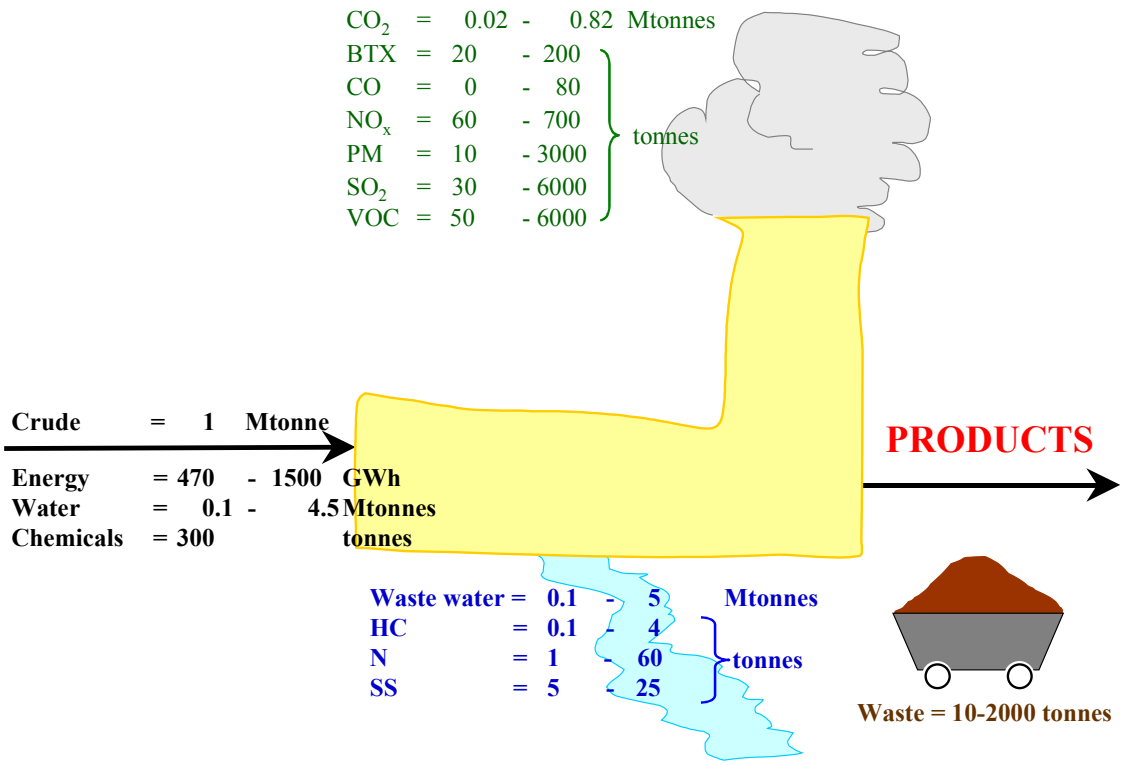


Figure 3.1: Example of specific emissions and consumptions found in European refineries
Note: European refineries range from 20 to less than 0.5 Mt of crude oil per year. Low values in the ranges normally correspond to refineries with abatement techniques and good environmental performance, whereas high values typically correspond to refineries without abatement techniques.

Figure 3.1 shows only the main pollutants generated by refineries, but more than 90 specific compounds have been identified [108, USAEPA, 1995]. The great majority are pollutants to air. The next table shows the environmental account of refinery processes. Next table shows a summary of the impact on the different media from the different activities found within refineries.

Process/Functional unit	Environmental compartment						
	Air	Waste water	Waste	Substances and energy	Waste heat	Noise	Safety
Fundamental processes							
Delivery	—	—	—	—	—	0	X
Loading	X	—	—	—	—	X	X
Storage	X	0	X	0	0	—	X
Process furnaces	X	—	0	X	X	0	X
Separation processes							
Crude oil atmospheric distillation unit	X	X	0	X	X	0	X
Vaccum distillation unit	X	X	0	X	X	0	X
Gas separation unit	X	0	0	0	0	0	X
Conversion processes							
Thermal cracking, visbreaking	X	X	0	X	X	0	X
Delayed coking	X	X	X	X	X	X	X
Catalytic cracking	X	X	X	X	X	0	X
Hydrocracking	X	X	X	X	X	0	X
Bitumen blowing	X	X	X	X	X	0	X
Reforming	X	X	X	X	X	0	X
Isomerisation	X	X	X	X	X	0	X
MTBE production	X	X	X	X	0	0	X
Alkylation	X	0	X	X	0	0	X
Refining processes							
Hydrodesulphurisation	X	X	X	X	X	0	X
Sweetening	X	X	X	X	0	0	X
Gas washing	X	0	X	X	0	0	X
Lubricating oil production	X	X	X	X	0	0	X
Extractions							
- with solvents	X	0	0	X	0	—	X
- with molecular sieves	X	—	X	X	0	—	X
Other processes							
Sulphur plant	X	X	0	0	0	0	X
Flare	X	X	0	0	0	X	X
Cooling tower	X	X	0	0	0	0	0
Waste water treatment	X	X	X	X	0	—	0
Blending units	X	X	0	0	0	—	X
Off-gas clean up (Exhaust gas recovery unit)	X	X	X	0	0	0	X
X: high account		0: small account		—: very small or no account			

Table 3.1: Environmental account of refinery processes
Source: [302, UBA Germany, 2000]

3.1.1 Present consumption levels in refineries

The capacity of the combustion plants in a refinery varies widely from less than 10 to up to 200 megawatts thermal input (MW_{th}). The total installed capacity ranges from several hundred to more than 1500 MWh_{th} in the largest refineries (equals 1.7 to 5.4 GJ per tonne crude processed). This capacity equals to an overall power installation from 20 to 1000 MW. These ranges depend strongly on the degree of energy integration of the refinery, its complexity and the integration of units such as cogeneration and petrochemical and lubricant oil plant.

Water and steam are used in the various refinery processes, e.g. to assist the distillation process or the cracking of hydrocarbons and in scrubbing, quenching or (steam) stripping. Petroleum refineries use relatively large volumes of water: in the processes; in steam generation and, especially, in cooling systems. Wash water is used in a number of processes, of which the desalter is the biggest user and therefore also the main producer of waste water in oil refineries

(exceptions are base oil refineries). Wash water is also used in the overhead systems of many processes. Tank and flare seal drains and cleaning water all contribute to the amount and quality of process water streams. The amount of water used depends on the type of refinery and the cooling system used. It ranges from 0.01 up to 5 tonnes per tonne of crude oil processed.

The amount of chemicals used in a refinery is around 300 tonnes per each million of tonnes of crude oil processed.

3.1.2 Emissions to air

The main air emissions from a refinery are CO_2, SO_x, NO_x, VOC and particulates (dust, soot and associated heavy metals (mainly V and Ni)). However, noise, odour, H_2S, NH_3, CO, CS_2, benzene, toluene, dioxins, HF and HCl also contribute to the air emissions. They emerge typically from sources such as stacks of process furnaces and boilers, regenerators (FCC), individual items such as valves and pump seals and to a lesser extent from flares and incinerator stacks. Some documents have already been published that establish emissions factors for the calculation of air emissions from refineries [208, USAEPA, 1996] [136, MRI, 1997].

Carbon dioxide emissions
Almost all the carbon present in crude oil, once produced from the oil well, will be converted into CO_2 sooner or later. A small portion (< 3 - 10 %) of the CO_2 will be converted in the refinery during the processing of crude oil into marketable products. The remainder will be converted into CO_2 once the refined oil products are sold and subsequently consumed by the various sectors of industry and private consumers. The main emission sources for CO_2 are the process furnaces and boilers, gas turbines, FCC regenerators, flare system and incinerators. The range of CO_2 emissions is very wide (28500 - 1120000 t/yr for a single refinery) and specific emissions range from 0.02 to 0.82 tonnes of CO_2 per tonne of crude processed. Next figure gives the plot of the specific CO_2 emissions from some European refineries as a function of the Nelson complexity index. As it can be seen, the figure shows that specific emissions of CO_2 depend on the refinery complexity. More complex refineries tend to consume more energy and consequently emit more CO_2.

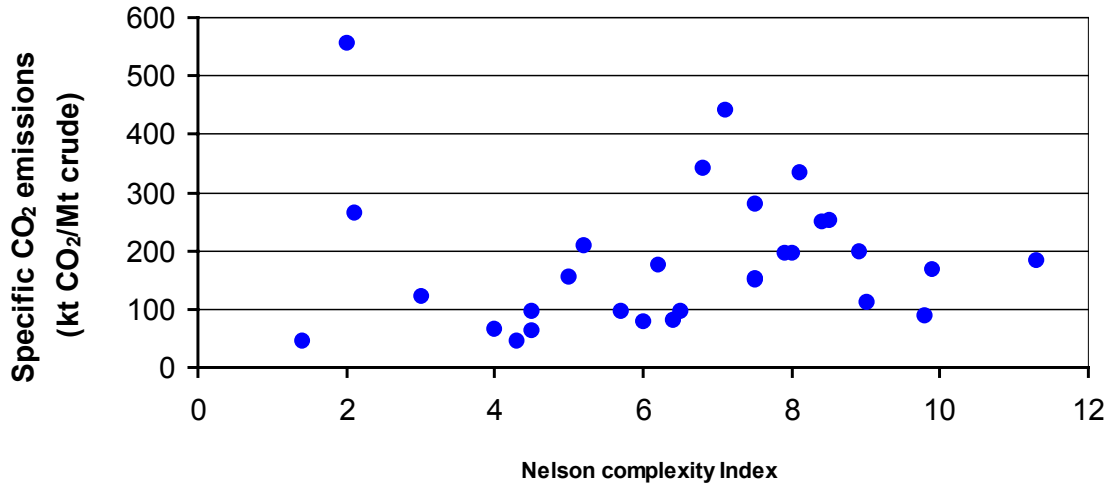


Figure 3.2: Specific CO_2 emissions from some European refineries as function of the Nelson complexity index
Source: [268, TWG, 2001]

Nitrogen oxides emissions

The term NO_x - by convention - only refers to NO (nitric oxide) and NO_2 (nitrogen oxide). N_2O can be also found in flue gases from FCCs and some SCR. In most combustion processes NO contributes over 90 % of the total NO_x. It is rapidly oxidised to NO_2 in the atmosphere. Hence, emissions of NO are expressed as NO_2.

Combustion processes are the main source of NO_x. The main emission sources for NO_x are process furnaces/ boilers, gas turbines, FCC regenerators, incinerators, gas turbine and the flare system. Roughly 60 - 70 % of the NO_x of a refinery derives from the use of fuels in furnaces, boilers and gas turbines. 16 % relates to the FCC, 11 % to engines and the rest to gas turbines and combined cycle systems. NO_x emissions from refineries depend on the fuel type, fuel nitrogen or hydrogen content, combustor equipment design, and operating conditions. Accordingly, large differences in the NO_x emission level can be expected between refineries and even between different combustion installations at the same refinery at different times. The range of NO_x emissions in refineries is from 50 to 5000 tonnes per year. The specific emission range of NO_x varies from 60 to 500 tonnes of NO_x per million tonnes of crude oil processed [101, World Bank, 1998]. Next figure gives the plot of the specific NO_x emissions from some European refineries as a function of the Nelson complexity index. As it can be seen, the figure does not show that specific emissions of NO_x depends on the refinery complexity.

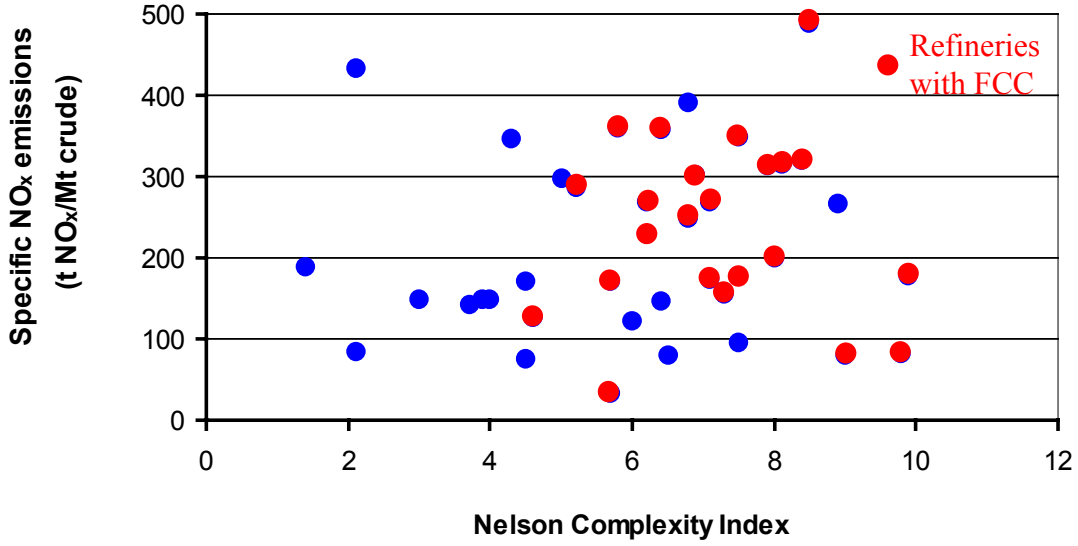


Figure 3.3: Specific NO_x emissions from some European refineries as function of the Nelson complexity index
Source: [268, TWG, 2001]

As it has been mentioned above, FCC generates NO_x emissions and they represent around 16% of the NO_x emissions in refineries. As consequence, it is possible that FCC refineries may emit more NO_x than the ones that they do not have. In the graph, refineries with FCC have been plotted with red points. As it can be seen, the figure does not show that specific emissions of NO_x depends on having or not having a FCC.

Specific emissions may be transformed to concentrations if a factor is calculated. Data from some European refineries have been compiled with the idea to analyse the factor between specific emission with concentration values. The data compiled is summarised in the next table:

Refinery capacity (Mt)	Total flue gas volume (10^9 Nm^3/yr)	Specific volume of flue gas (10^9 Nm^3/yr per Mt)	
15	22.173	1.48	
12.4	10.171	0.82	
10	11.9	0.84	gas fired refinery
9.6*	6.2	1.55	More liquid fuel
9.6*	6.6	1.46	
9.6*	7.4	1.30	
9.6*	9.9	0.97	Less liquid fuel
9	8.28	0.92	
9.0	9.2	0.98	
5	5.098	1.02	
4.5	5.535	1.23	
4.2	1.996	0.48	
2.5	0.866	0.35	
1.2	0.288	0.24	
Range in a EU+ country		1 – 1.5	
* Values that correspond to the same refinery but for different years. The proportion of RFG increases as you go down in the table.			

Table 3.2: Volume of flue gas generated by EU refineries
Source: [268, TWG, 2001]

As it can be shown in this table, the specific volume of flue gas is very variable. However, it has been found a correlation that speciality refineries (last two raws in the table) tend to give lower values. The average for other nine refineries is around 1 and it varies between 0.48 and 1.55. This factor depends on fuel distribution (gas/liquid ratio as shown in the asterisk example within the table), fuel composition, oxygen content of the flue gas, etc. and consequently the range is wide. However, it may be calculated, considering those values, that a refinery emitting 200 tonnes of NO_x/Mt of crude processes may emit flue gases with a NO_x concentration of 130-420 mg/Nm^3 (average: 200 mg/Nm^3).

Particulate emissions

The concern with particulate emissions (including of heavy metals) stems from health effects. The main emission sources are process furnaces/ boilers (mainly those fired with (liquid) heavy fuel oil), catalytic cracker regenerators, coke plants, incinerators, decoking & sootblowing of furnaces and the flare. The range of emissions found in European refineries is from 100 to 20000 tonnes of particulates emitted per year. The specific emission range found is from 10 to 3000 tonnes of particulates per million tonnes of crude oil processed. The lower emission value can be achieved in simple refineries burning substantial amounts of gas or when effective dedusting devices (ESP, bag filters) are installed.

Important heavy metals in crude oils are arsenic, mercury, nickel and vanadium (See Section 10.3). Nickel and vanadiun are enriched in the residues during distillation and are removed with the particulate matter by ESP or fabric filters after combustion in the furnaces or after regeneration of catalysts by burning off. Next table shows data on air emissions of Nickel and Vanadium from two EU+ refineries:

	Nickel		Vanadium	
Refinery capacity (Mt)	Specific load (t/Mt)	Range of concentration (mg/Nm^3)	Specific load (t/Mt)	Range concentration (mg/Nm^3)
15.3	0.196	0.2 – 1.2	0.327	0.3 – 2.1
12.3	0.772	0.02 – 2.35	1.666	0.05 – 5.1

Sulphur oxides emissions

Sulphur emission to the atmosphere has long been an issue for refineries. All crude oils contain sulphur compounds. Consequently, when firing refinery fuels, SO_2 and SO_3 will be emitted. There is a direct relation between the sulphur content of the fuel and the amount of SO_x emitted (for example, a fuel with 1% sulphur generates a flue gas with 1700 mg/Nm^3). The sulphur, which is not extracted from the products in the refinery, will remain in the various products and will be combusted to SO_x by the various end-users. The refinery as consumer of fuel for its energy use, similarly emits SO_x. Natural gas normally contains only traces of sulphur compounds.

There are both continuous and non-continuous sources of SO_x emissions. The number of sources may vary from refinery to refinery. The main emission sources of SO_2 are the process furnaces/ boilers, gas turbines, sulphur recovery units, FCC regenerators, flare system, incinerators, decoking operations and the treating units. CONCAWE [49, CONCAWE, 1998] gives an average distribution of the SO_x emissions of some 70 refineries studied. Mainly as a result of the use of liquid refinery fuels in boilers and furnaces, 59.4 % of refinery SO_x emissions stem from combustion processes. FCC units account for 13.5 %, sulphur recovery units for 10.7 % and other miscellaneous sources for 11.4 %. Next table shows the ranges found for those refineries.

	SO_2 discharged expressed as sulphur (kt/yr)	**Percentage of refinery SO_2 emissions (%)**
Fuel fired in furnaces/boilers	257	59 - 69
FCC units	58	7 - 14
Sulphur recovery units	46	10 - 11
Flares	22	5 - 9
Miscellaneous	49	5 - 12
TOTAL	432	

Table 3.3: SO_2 discharged to atmosphere as an average from 70 European refineries and a split of total refinery emissions as an example for SO_2 emissions.
Sources: Corinair W-Europe and CONCAWE report 3/98

The same report mentioned above shows that, in 1995 the average SO_2 concentration in European refineries amounted to 1350 mg/Nm^3; concentrations ranged from 226 – 2064 mg/Nm^3 flue gas. Some data on average bubble calculations have been included in Section 3.15. The range of annual emissions is from 49 to 10000 tonnes per year and specific emissions range from 30 - 6000 tonnes of SO_2 per million of tonne of crude processed. That report also shows that, despite similar sulphur levels in the crude oil, major differences exist between average refinery SO_x emissions. In order to complement this information the next three figures relating SO_x emissions from EU+ refineries are plot. Next figure gives the plot of the SO_2 emissions from some European refineries as a function of the crude capacity. Figure shows that bigger refineries tend to emit more SO_2.

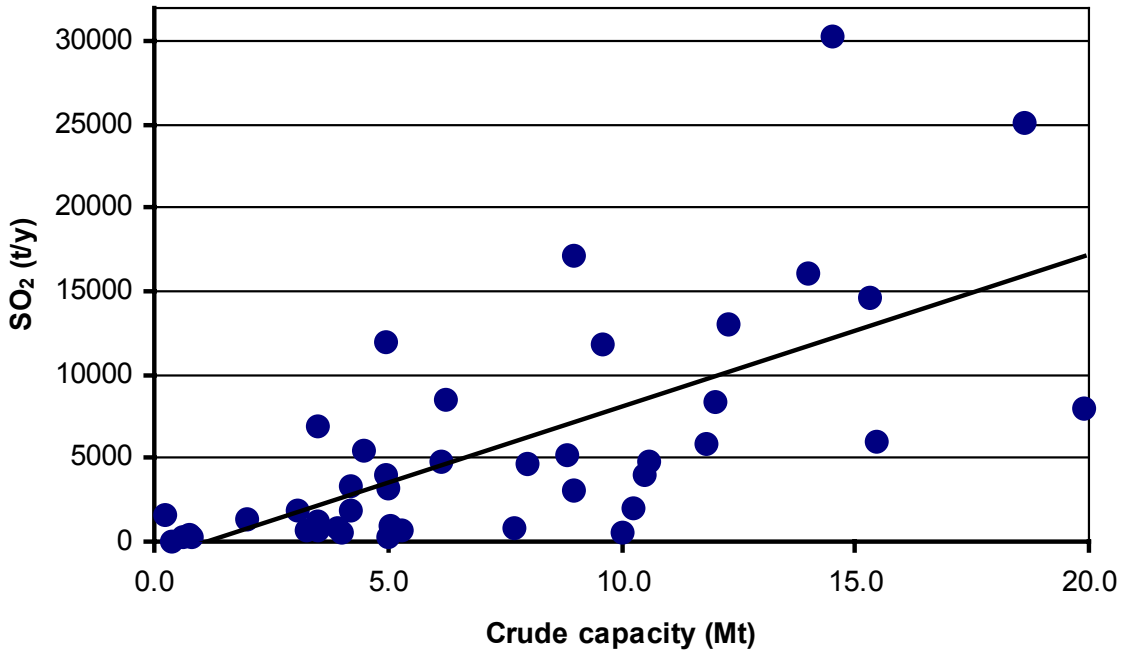


Figure 3.4: SO_2 emissions from some European refineries as function of the crude capacity
Source: [268, TWG, 2001]

However, if the emissions of SO_2 are divided by the capacity of the refinery, the figure does not show that specific emissions of SO_2 depends on the crude capacity. The following figure shows the results for the same refineries of the picture above.

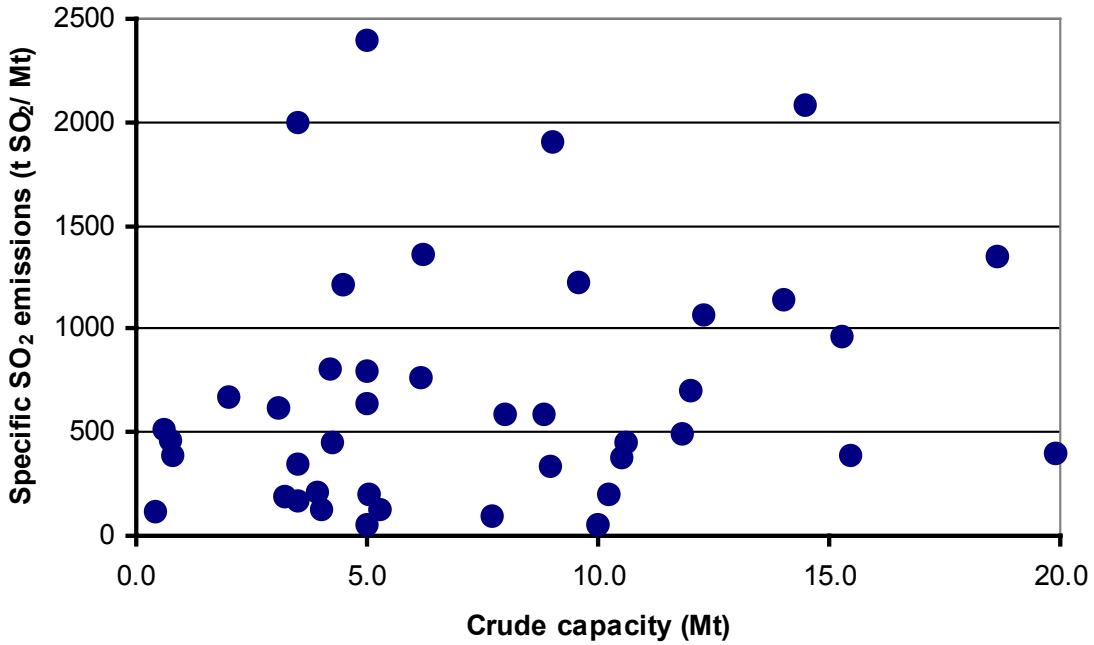


Figure 3.5: Specific SO_2 emissions from some European refineries as function of the crude capacity
Source: [268, TWG, 2001]

No correlation is also found when the specific SO_2 emissions are plotted against Nelson complexity index. As it can be seen, the figure does not show that specific emissions of SO_2 depend on the refinery complexity.

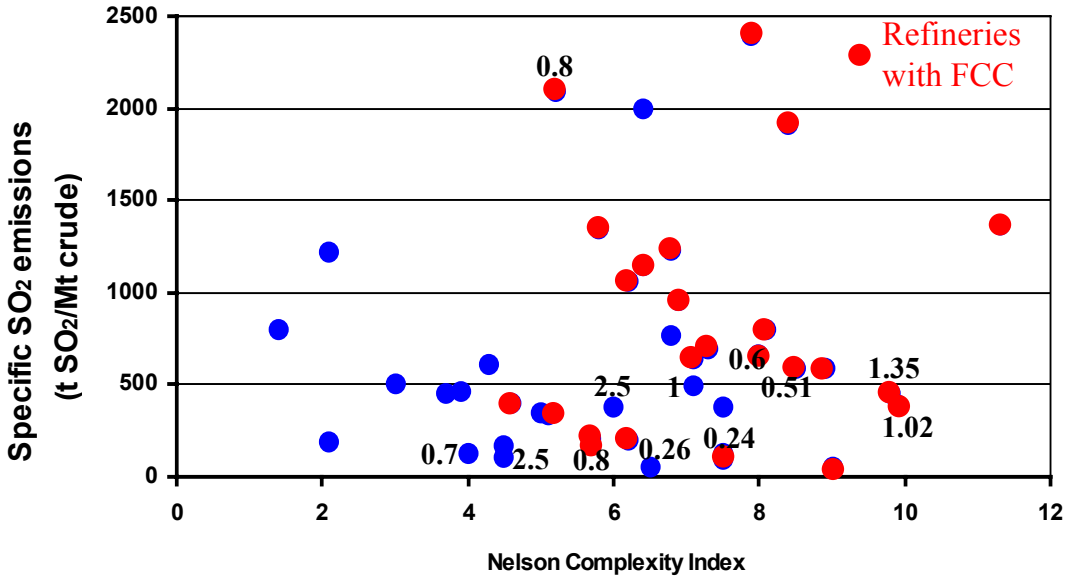


Figure 3.6: Specific SO_2 emissions from some European refineries against the Nelson complexity index
Source: [268, TWG, 2001]

As it was mentioned in the beginning of this section FCC contribute between 7 to 14 % of the SO_2 emissions within a refinery. Then possibly, refineries with FCC may tend to emit more SO_2 than refineries without FCC. However, red points in the above graph do not show that refineries with FCC tend to emit more SO_2. Another variable that typically is refer to to explain behaviour of SO_2 emissions in refineries is the content of sulphur in the crude oil processed. Figures in the above figure, show that refineries with similar sulphur content in the crude oil that they process (e.g. 0.8 %) can have very high differences in specific emissions. Moreover, it is shown in the figure that no correlation is demonstrated with this figure. This also reinforces the conclusion of the Concawe report that shows that, despite similar sulphur levels in the crude oil, major differences exist between average refinery SO_x emissions.

Table 3.4 shows the historic development in the distribution of sulphur output in European refineries. It also presents the average sulphur recovery percentage in the western European refineries that has grown from about 10 % in the late 70's to more than 36 % now. This table also shows that the sulphur reductions achieved in the oil products (so called S in fuels) sold to customers are not mirrored in direct sulphur emissions from the refineries, which have remained static.

Year	1979	1982	1985	1989	1992	1995
Crude throughput	680000	494000	479000	527000	624000	637000
S in crude % w/w	1.45	1.28	0.98	1.10	1.06	1.03
S in crude	9860	6323	4694	5797	6615	6561
S recovered	1023	1108	1090	1767	1782	2370
S recovered % w/w	10.4	17.5	23.2	30.5	26.9	36.1
SO_x emitted by refineries as S	884	772	526	525	523	563
S in fuels	8945	4786	3439	3380	3364	2625

Table 3.4: Trends of sulphur distribution in western European refineries (data in kt/yr)
Source: [49, CONCAWE, 1998]

Table 3.5 shows that since 1985 the sulphur recovered in refineries has increased, which reflects the steady increase in sulphur recovery capacity of European refineries. This is also demonstrated in the decrease in the sulphur content of the oil products leaving the refineries. However, Table 3.5 also shows that since 1985 direct SO_x emissions from European refineries have been stable. It demonstrates that on average the reductions in SO_2 emissions have clearly lagged behind the sulphur reductions achieved in the oil products sold to the customers of the refineries.

Sulphur output category	% S intake 1979	% S intake 1982	% S intake 1985	% S intake 1989	% S intake 1992	% S intake 1995
S emitted by refinery as SO_2	9 [1)]	12.2	9.1	8.0	7.9	8.6
S in distillate S in fuel oil S in BFO	} 75 [1)]	} 63.5	9.9 } 41.5 } 60.0 8.6 }	10.7 } 30.3 } 51.5 10.5 }	14.2 } 25.8 } 51.1 11.1 }	11.5 } 16.8 } 40.1 11.8 }
S emitted as SO_2	**84 [1)]**	**75.7**	**69.1**	**59.5**	**59.0**	**48.7**
S fixed in special products [2)]	6 [1)]	10 [1)]	11.9	13.2	13.5	14.6
S recovered	10	14.7	19.0	26.9	27.1	36.3
S retained	**16**	**24.7**	**30.9**	**40.1**	**40.6**	**50.9**
TOTAL	100.0	100.0	100.0	99.6	99.6	99.6

Notes: (%w/w of total)
[1)]: Figures for the year 1979 from the first CONCAWE report (1979) are not accurate
[2)]: Chemical feedstock (naphtha), bitumen, coke, lube oil
Total sulphur intake in 1995 was 6.56 Mt.

Table 3.5: Historical trend sulphur output distribution European refining industry
Source: [115, CONCAWE, 1999]

Table 3.5 depicts the development of the sulphur balance in European refineries from 1979 to 1995. It shows that in 1995 36.3 % of the 6.56 million tonnes of sulphur intake is recovered as elementary sulphur and 8.6 % is emitted as SO_2 by the refinery. About 50 % w/w is emitted as SO_2 via the combustion of the oil products, while 14.6 % w/w is accumulated in non-fuel products, such as bitumen, lube oils, coke and chemical feed stocks. Those last compounds may be burnt to some extent or can finish their life as solid or liquid waste and consequently might contribute to emissions to the air, water and soil. The historic trend is clearly one of a steady decrease in the sulphur levels in oil products and an equally steady increase in the sulphur recovered in the refinery. The decrease of sulphur levels in oil products is partly the result of tighter European and national legislation, especially with respect to middle distillates. A major part of the decrease is the result of changes in the demand for fuel oil.

Volatile organic compounds emissions

Volatile organic compounds (VOC) is the generic term applied to all compounds containing organic carbon, which evaporate at ambient temperature and contribute to the formation of 'summer smog' and odour nuisance. VOC losses can be calculated or directly measured (discrepancies in the emission numbers from both methods are found in many cases. Some data on that can be found in the Monitoring Section, 3.26). The main sources of VOCs from refineries are vents, flares, air blowing, blowdown systems, fugitive emissions from piping systems, waste water systems, storage tanks (tank breathing), loading and unloading systems, storage & handling. Diffuse (fugitive) VOC emission sources such as (single) seals from pumps, compressors, valves and flanges and leaks in pipelines and equipment may contribute 20 - 50 % to the total VOC emissions. The range of emissions found in European refineries (including storage farms) is from 600 to 10000 tonnes of VOC emitted per year. The specific emission range found is from 50 to 6000 tonnes of VOC per million tonnes of crude oil processed.

Some accidental spillages can be of a continuous nature, such as leaking pump seals, leaking valve glands and leaks from pipework or others which are of a one-off nature, can occur from sources such as equipment failures, overfilling of tanks and overfilling of road and rail cars. Fugitive emissions from process equipment are the largest single source of VOCs emitted to the atmosphere in a refinery and can frequently account for 50 % of the total emissions. Fugitive emissions include the emissions that occur from items such as valves, pump and compressor seals, flanges, vents and open ends. Valves are considered to account for approximately 50 - 60 % of fugitive emissions. Furthermore, the major portion of fugitive emissions comes from only a small fraction of the sources (e.g. less than 1 % of valves in gas/vapour service can account for over 70 % of the fugitive emissions of a refinery). Some valves are more likely to leak than others, e.g.:

- valves that are operated frequently, such as control valves, may wear more quickly and will allow emission paths to develop. However, newer, low-leak control valves provide good fugitive emissions control performance.
- valves with rising stems (gate valves, globe valves) are likely to leak more frequently than quarter-turn type valves such as ball and plug valves.

Factors driving these releases of hydrocarbons are equipment design, quality of the sealing system, maintenance programme and properties of the line contents. Poorer designs (with wider tolerances), poor sealing systems (e.g. leak-prone valve packings) and limited maintenance will lead to higher emissions. Those emissions can be estimated using the factors in Table 3.6.

For example it can be estimated, using the USAEPA method, that a pump for light liquid that has an emission measured in the range of 1001 - 10000 ppm, has an emission factor of 33.5 g/h. Other methods have been applied to calculate the fugitive emissions from refineries. They are the adsorption method and DIAL method (see Section 3.26). Emission factors measured with the latest method are presented in Table 3.7.

Emission Source	**Emission factor in (g/(h.source)) for measured values in ppm v/v in the following three ranges**		
Emission range (ppm v/v)	0 - 1000	1001 - 10000	> 10000
Valves for gas or vapour	0.14	1.65	45.1
Valves for liquids with Vp>0.3 kPa (light liquid)	0.28	9.63	85.2
Valves for liquids with Vp< 0.3 kPa (heavy liquid)	0.23	0.23	0.23
Pumps for light liquids	1.98	33.5	437
Pumps for heavy liquids	3.80	92.6	389
Compressors	11.32	264	1608
Safety valves for gases	11.4	279	1691
Flanges	0.02	8.75	37.5
Open-end valves	0.13	8.76	12.0

Table 3.6: Emission factors according to stratified USAEPA-method for the assessment of fugitive emissions

Process	VOC emissions (t/yr)
Crude oil harbour	260
Waste water treatment plant	400
Product harbour	815
Process area	1000
Tank area	1820
TOTAL	4295

Table 3.7 VOC emissions from a refinery with a capacity of 10Mt/yr
Source: [107, Janson, 1999]

Other air emissions
Other pollutants considered are carbon monoxide (process furnaces/ boilers, gas turbines, catalytic cracker regenerators, flare system, incinerators, cold vents), methane (storage & handling (loading), cold vents and leaks) and halon from firefighting equipment. Noise, H_2S, NH_3, CS_2, dioxins and HF also contribute to the air emissions from a refinery.

The mercury and components of arsenic are volatile and are emitted to some extent with the clean gas. A part of these compounds react with plant material or deposit on the catalysts in the reactors of the conversion plants. Therefore protective layers are used for the interception of the catalyst poisons.

Flares, compressors, pumps, turbines and air coolers require particular attention as regards sources of noise.

Odours in a refinery are mainly created by sulphur compounds as H_2S, mercaptanes but also by some hydrocarbons (e.g. aromatics). The main focus of odour in refineries are storage (e.g. sour crudes), bitumen production, desalter water, sewers, dissolved air flotation and biotreatment and flaring.

3.1.3 Emissions to water

Waste waters consist of cooling water, process water, sanitary sewerage water and storm water. The quantity of waste waters generated and their characteristics depend on the process configuration. Waste waters are treated in on-site waste water treatment facilities and then discharged. The water and blowdown streams from refinery operations can become contaminated with dissolved gases, dissolved and suspended solids and hydrocarbons. Water can also become contaminated with dissolved gases in the process, compounds that could be toxic and/or could give to water an unpleasant smell. Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia, hydrogen sulphide and hydrocarbons). Sour water needs stripping prior to further treatment or re-use as wash water.

Depending on the prevailing climate, storm or rainwater can also generate a significant effluent stream in refineries. Rainwater may come into contact with potentially oil-polluted surfaces (‘surface water run-off’). The effect of rainwater on both the amount and the quality of the effluent water and the problems that the water discharges to either fresh continental waters or to the sea are issues to consider. Occasionally, ballast water from crude carriers and from other seagoing vessels or barges transporting oil products is also treated in refineries. Furthermore, sanitary waste water and fire-fighting water are waste water sources which all need attention and quality control prior to deciding on treatment, direct discharge and/or potential re-use.

Some water emission parameters are the pH, dissolved solids, suspended solids, total organic carbon, total nitrogen, total phosphorous, COD, BOD, H_2S, NH_3, oil, aromatics (BTEX), phenols, salt, AOX, mercaptans, cyanides, MTBE, fluoride, PAH, heavy metals, temperature,

conductivity, bacteria and fish toxicity. As a general guide, approximately 0.1 - 5 m^3 of waste water (process waste water, cooling water and sanitary waste water) per tonne of crude is generated when cooling water is recycled.

The resulting discharge of the aforementioned substances depends on the 'in-process' preventive measures (good housekeeping, re-use) and the presence and technical standards of waste water treatment facilities. The main typical process water pollutants and/or waste water parameters relevant to the overall refining process and prior to any purification step are as stated in Table 3.8.

	Oil	**H_2S (RSH)**	**NH_3 (NH_4^+)**	**Phenols**	**BOD COD TOC**	**CN^- (CNS^-)**	**TSS**
Distillation Units	XX	XX	XX	X	XX	-	XX
Hydrotreatment	XX	XX(X)	XX(X)	-	X(X)	-	-
Visbreaker	XX	XX	XX	XX	XX	X	X
Catalytic Cracking	XX	XXX	XXX	XX	XX	X	X
Hydrocracking	XX	XXX	XXX	-	X	-	-
Lube oil	XX	X	X	-	XX	-	-
Spent caustic	XX	XX	-	XXX	XXX	X	X
Ballast water	X	-	-	X	X	X	X
Utilities (Rain)	-(x)	-	-	-	X	-	-
Sanitary/Domestic	-	-	X	-	X	-	XX
Key: X = < 50 mg/l, XX = 50 - 500 mg/l, XXX = > 500 mg/l							

Table 3.8: Representative concentrations of pollutants in typical refinery effluents before treatment
Source: [115, CONCAWE, 1999]

Table 3.9 shows the composition and annual averages of the water effluents from European refineries.

	Composition after pretreatment by API, CPI, SWS		Annual average effluent composition	Specific load
Parameter (in mg/l)	Average	Maximum	of waste water plants	(t/Mt feedstock)
pH-range (pH unit)	7	10	6 - 9	
Temperature range (°C)	25	45	10 – 35	
Oil	40	100	0.05 – 9.8	0.01 – 4.5
COD	300	700	30 – 225	3 - 125
BOD_5	150	400	2 - 50	0.5 - 25
Suspended solids	10 - 20	75	2 – 80	1 - 50
Phenols	12	40	0.03 - 1.0	0.01 - 0.25
Sulphide	5	15	0.01 - 1.0	
Kjendahl nitrogen	25	50	5 - 35	
Total N	25	50	1.5 - 100	1 - 100
Phosphate	5	20	0.1 - 1.5	
MTBE [1)]	0 - 3	15	< 1	
Fluoride [1)2)]	0 - 30	60	1 - 20	
Cyanide [1)]	0 - 3	5	0.03 - 1.0	
PAH (Borneff)	0.1	0.5	0.005 - 0.05	
Benzo-pyrene		0.01 - 0.1	<0.05	
BTEX	5	10	<0.001 - 3	
Benzene		10	<0.001 - 1	
Heavy metals	1	2	0.1 - 1.0	
Chromium		100	0.1 – 0.5	
Lead		10	0.2 – 0.5	

Notes:
[1)] dependent on whether or not relevant units are part of the refinery
[2)] discharge measured at one refinery

Table 3.9: Typical refinery influent/effluent annual average composition and load
Sources: [118, VROM, 1999], [261, Canales, 2000], [101, World Bank, 1998], [293, France, 2000]

The amount of oil discharged is usually expressed in grams of oil per tonne of refinery throughput. Most of the European refineries already meet the standard of the Oslo/Paris Commission of 3 grams oil/tonne of refinery throughput.

3.1.4 Waste generation

Refineries also generate solid wastes and sludges with a range of 0.01 - 2 kg per tonne of crude processed (before waste treatment). According to the World Bank, 80 % of those solid wastes may be considered hazardous because of the presence of toxic organics and heavy metals [101, World Bank, 1998]

The refinery waste generation was covered in a report [82, CONCAWE, 1995] representing the 1993 European refinery waste situation (see Table 3.10). A summary of the waste generated in a refinery is 45 % sludge, 35 % non-refining wastes and 20 % other refining wastes. From the one million tonnes of wastes identified in Europe in 1993, 39.9 % was placed in landfills, 21.4 % was recycled or re-used, 14.9 % was incinerated with energy recovery, 8.4 % was incinerated

without energy recovery, 4.9 % was landfarmed, 1.7 % was used as alternative fuel and the rest (0.6 %) was sent to unidentified disposal routes [82, CONCAWE, 1995].

Sludges originate from various sources such as crude and product tanks bottoms, desalters, alkylation units, boiler feed water preparation, biotreaters, the cleaning of heat exchanger bundles and equipment, oil spills and soil remediation. In terms of volume oily sludges represent the largest waste category from refineries. Partly this is due to the presence of basic sediment and water in the crude, which can vary from crude to crude. Bio-sludge production takes place only if a refinery operates a biotreater.

Other wastes are generated from many of the refining processes, petroleum handling operations and waste water treatment. Both hazardous and non-hazardous wastes are generated. Spent catalysts originate from reformers, catalytic crackers, hydrocrackers, hydrodemetallisation, hydrodesulphurisation and hydrotreating units. The regeneration of catalysts is a well-established technique.

Table 3.10 shows the percentage of wastes categorised in each group.

Type of Waste	Percentage (% w/w)
Sludges	
API/DAF/IAF sludges	41.8
WWTP biosludge	30.2
Boiling fresh water preparation sludge	13.0
Tank bottom sludge	7.1
Miscellaneous sludge	6.7
Desalter sludge	0.8
Acid alkylation sludge	0.3
Non-refining wastes (Construction/Demolition and Domestic Wastes)	
Domestic	43.8
Rubble	41.9
Scrap metal	14.3
Other refining wastes production	
Contaminated soil	26.3
FCCU catalyst	19.4
Other wastes	15.5
Miscellaneous oily wastes	8.9
Incinerator ash	6.0
Spent caustic	6.0
Other catalysts	4.7
Desulphurisation catalyst	3.2
Spent clay	2.7
Tank scales	2.4
Sorbents	1.9
Flue gas desulphurisation	1.3
Spent chemicals	1.2
Reformer catalyst	0.4
Acid tar	0.2

Table 3.10: Percentage of each type of waste in a refinery
Source: CONCAWE

3.2 Alkylation

This section contains data on consumption and emissions generated by alkylation processes.

Consumptions

Table 3.11 gives a summary of the utility and chemical consumptions in the two techniques currently used in the alkylation processes.

	Alkylation technique	
Values per tonne of alkylate produced	**Sulphuric acid**	**Hydrofluoric**
Utilities		
Electricity (kWh)	4	20 - 65
Fuel (MJ)	n.a.	1000 - 3000
Steam (kg)	830	100 - 1000
Cooling water (m^3) (ΔT = 11 ºC)	72	62
Industrial water (m^3)	0.08	
Chemicals		
Fresh acid (kg)	78 - 120	1.15
Caustic (as 100 % NaOH) (kg)	0.41	0.57
Lime	n/a	n.a.
Note: $AlCl_3$ and water-free $CaCl_2$ consumption depend on operating conditions (water content of feed- and side-reactions)		

Table 3.11: Estimated utilities and chemical consumption for the various alkylation techniques
Sources: [166, Meyers, 1997], [118, VROM, 1999], [261, Canales, 2000]

Emissions

Emissions generated by the alkylation processes are summarised in next tables. [108, USAEPA, 1995]

Air pollutant	Sulphuric acid	Hydrofluoric
CO_2, SO_2, NO_x and other pollutants arise from the furnaces *	From column heating furnaces	From column heating furnaces
Hydrocarbons	May be released from pressure reliefs, storage, handling operations, spillages and fugitive emissions and water and waste discharges	May be released from pressure reliefs, storage, handling operations, spillages and fugitive emissions and water and waste discharges
Halogens	n/a	Fluoride compounds may be released from pressure reliefs, vent gas and spillages
Odours	n.a.	Acid-soluble oil may be released from process shut-down ponds during maintenance work, particularly the de-scaling of pipes coveying hydrogen fluoride. This may be odorous
*Emissions from these combustion processes are addressed in an integrated way in Section 3.10.		

Table 3.12: Air emissions generated by the alkylation processes

Water parameter	Sulphuric	Hydrofluoric
Waste water	Waste water produced in the alkylation processes has low pH, suspended solids, dissolved solids, COD, H_2S, and spent acid.	
Hydrocarbons	n.a.	HC from separator drains (surge drum, accumulator, dryer) and spillages, and of acidic effluent containing dissolved and suspended chlorides and fluorides from the settlement pit or the process shutdown ponds.
Acid	Sulphuric acid	Effluents from HF scrubber are 2 - 8 m^3/h with compositions min/max of 1000 - 10000 ppm F; after lime treatment 10 - 40 ppm F.

Table 3.13: Waste water generated by alkylation processes

Solid waste	Sulphuric	Hydrofluoric
Sludge	n.a.	The flow 7 - 70 kg sludge per kg used HF (dry solids content 3 - 30 %)
Hydrocarbons	Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerization products are removed from the acid as a thick dark oil.	HC from spent molecular sieves, carbon packings and acid-soluble oil. Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerization products are removed from the acid as a thick dark oil.
Acid products in the sludge	Sludge generated in the neutralisation process contains sulphuric acid.	Inorganic fluorides (Na/KF) and chlorides from treatment stages. Sludge generated in the neutralisation process contains CaF_2.
Halides	n/a	Composition of sludge is 10 - 40 ppm F^- after lime treatment

Table 3.14: Solid waste generated by the alkylation techniques

3.3 Base oil production

This section gives the consumption and emission values that can be found in European refineries. Those values are given for each base oil production process identified.

Deasphalting

Consumption

A conventional solvent-based base oil lube complex is energy intensive. The main reason is the high amount of heat required to evaporate the solvents and to separate them from the raffinate and extract streams. Solvent losses are usually in the order of 1 % despite extensive solvent recovery. In the tower method, for example, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. As an example, the figures below give the utility requirements of a solvent deasphalting absorption (SDA) unit.

	Data corresponding to 1000 tonnes of feedstock
Fuel	136 - 150 MWh
Power	12.2 - 21 MW
Steam	166 - 900 tonnes
Cooling water	Nil (maximum air cooling)

Table 3.15: Consumption data of deasphalting units
Sources: [166, Meyers, 1997], [261, Canales, 2000]

Emissions

Air	*Waste water*	*Solid waste*
Air emissions may arise from fugitive solvent emissions and process vents. Heater stack gas (in Section 3.10).	The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Oil components	Little or no solid waste generated.

Aromatic extraction

Consumptions

Utilities, typical per m^3 feedstock		
Fuel absorbed	862	MJ
Electricity	5	kWh
Steam	8	m^3
Water cooling (ΔT = 14 °C)	12.5	m^3

Table 3.16: Consumption data of aromatic extraction units
Source: [212, Hydrocarbon processing, 1998]

Emissions

Air	*Waste water*	*Solid waste*
Fugitive solvent VOC emissions can come from the furfural and NMP from its storage tanks. Flue gas from fired heater (in Section 3.10).	The total amount of process water is around 2 - 4 m^3 per tonne of product, containing around 15 - 25 ppm furfural, 10 - 15 ppm NMP. The water stream leaving the fractionator is likely to contain some oil and solvents.	Little or no solid wastes generated.

Source: [118, VROM, 1999]

High pressure hydrogenation unit

Utilities, typical per kt of feedstock		
Fuel	11.5	t
Electricity	26	kWh
Net steam consumption*	200	t
Water cooling (ΔT = 14 °C)	110	m^3
*(50 % is recovered as condensate)		

Table 3.17: Typical utility consumption of high pressure hydrogenation unit

Solvent dewaxing

Consumptions

The utility requirements in this process together with the aromatic extractions are:

Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT=10°C)
1000 - 1300	60 - 160	300 - 800	10 - 20

Table 3.18: Typical utility consumption of solvent dewaxing and aromatic extraction units together
Sources: [118, VROM, 1999], [261, Canales, 2000]

Emissions

Air	*Waste water*	*Solid wastes*
VOC may arise from solvent vapour extraction from the wax filters as well as fugitive emissions. Fugitive solvent VOC emissions can come from the MEK/ Toluene from its storage tanks. Flue gas from fired heater (in Section 3.10).	The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Potential releases into water are hydrocarbons, sulphur compounds and organic compounds from spillages and leaks, and of organic compounds from process waters from solvent recovery operations. Waste water contains 1 - 3 ppm MEK/toluene.	Little or no solid wastes generated.

Hydrofinishing

Consumptions

The utility needs for a hydrofinishing unit are:

Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT=10 °C)
300 - 550	25 - 40	100 - 150	5 - 15

Table 3.19: Typical utility consumption of hydrofinishing units
Source: [118, VROM, 1999]

Emissions

Air	*Waste water*	*Solid wastes*
Pressure relief valves of the hydrofiner, solvent recovery systems and refrigerant systems; Leakages from flanges, glands and seals on pumps, compressors and valves.	Leakages from flanges, glands and seals on pumps, compressors and valves.	n.a.

3.4 Bitumen production

Consumptions

Bitumen blowing is a very low energy consumer. Some electricity is required for the air blower, product rundown pump and overhead condensing system. The electricity utilisation in this process is 15 - 35 kWh/tonne and the steam produced in the process is 100 - 200 kg/tonne. For cooling-water utilisation it is assumed that an aircooler is used as a condenser. If a direct water quench is applied instead of scrubbing, more water is normally used.

Emissions

To air	Flue gas from fired heater (see Section 3.10). Flue gas from overhead vapours incinerator. The overhead vapours from bitumen production, consisting mainly of light hydrocarbons, N_2, O_2, CO_2 and SO_2, are incinerated at high temperature (~800 °C) to ensure complete destruction of components such as H_2S, CO, complex aldehydes, organic acids, PAHs and phenolics, which have a highly unpleasant odour. The flow of the oxidiser overhead is around 0.07 - 0.30 Nm^3 air/kg feed. The main nuisance problems with bitumen production relate to hydrogen sulphide releases from the distilled residues and sour condensates and gas produced in the blowing process. Hydrocarbons and sulphur compounds may emanate from leakages (particularly on overhead systems) and pressure relief valves and in the form of aerosol-containing liquid droplets from the venting of tanker top-loading operations.
Process waste water	Sour water is produced in the oxidiser overhead waste water. Its flow is up to 5 m^3/tonne feed and it contains H_2S, oil, aromatics, PAHs, sulphuric acid, odorous oxidation products (ketones, aldehydes, fatty acids) and particulates. Other potential releases into water are of hydrocarbons and sulphur compounds from spillages and leakages.
Solid waste	Slop oil emulsions are formed in the oxidiser overhead slop oil. It consists of an emulsion of light oil, water and particulates.

3.5 Catalytic cracking

Consumptions
The next table shows the energy and process materials usage in the catcrackers.

	FCC	RCC
Fuel (MJ/t)	120 - 2000	120 - 2000
Electricity (kWh/t)	8 - 50	2 - 60
Steam consumed (kg/t)	30 - 90	50 - 300
Steam produced (kg/t)	40 - 60	100 - 170
Cooling water (m^3/t, ΔT=17 °C)	5 - 20	10 - 20
Catalyst make-up (kg/t)	0.4 - 2.5	2 - 4

Table 3.20: Typical utility consumption of catcrackers
Sources: [261, Canales, 2000], [212, Hydrocarbon processing, 1998], [118, VROM, 1999], [166, Meyers, 1997], [268, TWG, 2001]

Virtually all the heat required in a FCC unit is generated in the regenerator. The catalyst used depends greatly on the type of product required and can be silica-alumina substrate carrying rare earth and/or precious metals or can be based on zeolites.

Emissions

Air emissions
Within a refining complex, one of the sources with major potential for atmospheric emissions is the catalytic cracking unit. Air emissions come principally from the regenerator and are mainly CO, CO_2, NO_x, particulates (mainly catalyst fines) and SO_2. The emissions from catalytic crackers are very variable. The wide variation reflects both the wide variations of feedstocks used in the catcracker units (nitrogen, sulphur, metals contents), and the regenerator and waste heat boiler operating conditions. Emissions from an FCC can be 20 - 30 % of total refinery SO_2 emissions, 15 - 30 % for NO_x and 30 - 40 % of particulates. However, these figures can be subject to wider variation [112, Foster Wheeler Energy, 1999]. Air emissions generated by the combustion of fuels in the FCC furnaces are treated in Section 3.10.

The next table shows a summary of the emission factors and emissions from FCCs

Emissions	PM	SO_x (as SO_2)	CO	HC	NO_x (as NO_2)	Aldehydes	NH_3
Emission factors (kg/m^3 of fresh feed)	0.009 - 0.976	0.19 - 1.50	0.08 - 39.2	0.630	0.107 - 0.416	0.054	0.155
Emission data (mg/Nm^3) @ 3% O_2	10 - 1000	10 - 4000	<50 - 900	n.a.	30 - 2000	n.a.	n.a.
Values attainable in continuous operation. Emissions values as half hourly mean values Note: Lower levels in the range are catcrackers with abatement techniques.							

Table 3.21: Emission data and factors found in catcrackers
Sources: [136, MRI, 1997], [297, Italy, 2000], [261, Canales, 2000], [117, VDI, 2000], [250, Winter, 2000], [269, Confuorto, 2000]

Residue catalytic crackers (RCC) use mainly as feedstock atmospheric residue. Hence the Conradson carbon, sulphur content and nitrogen content is higher. Therefore, RCC are potentially a stronger source of SO_x and NO_x, and contaminated catalyst than normal FCC. As consequence of the type of feedstock used in the RCC, RCC produces more coke and hence more heat should be removed from the regenerators.

Because the catcracker is a significant emitter of pollution in a refinery, there follows a more detailed analysis by type of pollutant.

Carbon dioxide

Carbon dioxide is generated in the catalyst regeneration train and its load depends on the size.

Throughputs (kt/yr)	%S in feed	Flue gas flow (Nm^3/h at 3 % O_2)	CO_2 emissions load (t/yr)	Specific CO_2 emissions (kg/t)
1314	< 0.5	110000	272243	207
2350	0.35	200000	498006	212
Range of emissions			130000 - 600000	160 - 220

Table 3.22: Range and examples of emissions of CO_2 from catcrackers
Sources: [250, Winter, 2000], [136, MRI, 1997]

Carbon monoxide

Relatively high concentrations of carbon monoxide can be produced during regeneration of the catalyst and it is typically converted to carbon dioxide either in the regenerator (total combustion) or further downstream in a carbon monoxide boiler (partial combustion). Incomplete combustion may lead to releases of carbon monoxide in the total combustion. CO ex full burn units ranges typically between 50 and 1200 mg/Nm^3 (depending on temperature, CO promoter level, size of unit). In partial combustion mode, depending on the conditions under which the regenerator is operating, the levels of CO in the regenerator exhaust gases feeding the CO boiler may be in the region of 5 to 10 %. Levels of CO in the exhaust from the CO boiler can be maintained to less than 100 mg/Nm^3 depending on the type of CO boiler used [80, March Consulting Group, 1991].

Throughputs (kt/yr)	%S in feed	Flue gas flow (Nm^3/h at 3 % O_2)	CO concentration (mg/Nm^3)	CO emissions load (t/yr)	Specific CO emissions (kg/t)
1314	0.5	110000	215 - 814	558	0.43
2350	0.5	200000	125	194	0.08
remark: data are related to yearly average, 3 % O_2, dry conditions					

Table 3.23: Examples of CO from catcrackers running
Source: [250, Winter, 2000]

Nitrogen oxides

The wide range in NO_x emissions (levels) from catcracker regenerators (gases) reflects the main effects of different combustion conditions from FCC regenerators or FCC CO-boilers, the spread in unit capacities and the coke (feed) nitrogen contents; these latter depend on crude type and upstream process configuration. Lower emission values can be found when deNO_x treatments are applied. Some examples of NO_x emissions from catcrackers as well as the ranges found are shown in the next table.

Throughputs (kt/yr)	%S in feed	Flue gas flow (Nm^3/h at 3 % O_2)	NO_x concentration (mg/Nm^3)	NO_x emission load (t/yr)	Specific NO_x emissions (kg/t)
1314	0.5	110000	409	280	0.21
2350	0.5	200000	500	775	0.33
1750				45	0.03
Range			30 – 2000 (average continuous monitoring)	56 - 1000	22 – 100 mg/MJ (related to throughput)
remark: data are related to yearly average, 3 % O_2, dry conditions					

Table 3.24: Range and examples of nitrogen oxide emissions from catcrackers
Sources: [250, Winter, 2000], [136, MRI, 1997], [268, TWG, 2001]

Particulates

Generally a FCCU is the biggest single emitter of particulates although the calciner in a coking unit is also a significant emitter. Particulate matter arises from catalyst fines from the catalyst regeneration exhaust gases and catalyst handling and disposal. The emitted catalyst is fine and is produced in catcracker as a result of the constant movement of the catalyst grains. In the absence of moisture or sulphuric acid condensation, the normal cause of stack plume opacity is the presence of the fine catalyst particles. In practice, operating conditions may have a large effect on particulate emissions.

Throughputs (kt/yr)	Flow (Nm^3/h at 3 % O_2)	%S in feed	Concentration (mg/Nm^3)	PM load (t/yr)	Specific emissions (kg/t)
1314	110000	0.5	17	11.6	0.009
2350	200000	0.5	50	44.5	0.033
1750			47	33.8	0.019
Ranges found in European crackers			10 – 500	10 - 50	0.009 - 0.040

Table 3.25: Examples of particulate emissions from catcrackers (lower values correspond to FCC with abatement techniques)
Sources: [250, Winter, 2000] [136, MRI, 1997], [268, TWG, 2001]

Particulates emitted by the catcracker regenerator consist predominantly of catalyst particles with a typical size of 10 µm max. The particle size distribution shows that almost up to 90 % by weight is smaller than 10 µm. Much of this dust consist of silica/alumina and the nickel and vanadium (as well as other metals) present in the feedstock. The deposited coke (including metals) on the catalyst ranges between approximately 4 and 5 % w/w. Metal compounds are enriched in the heavy residues during distillation, and are therefore present in the FCC feedstock. If hydrotreated heavy residues are used as FCC feed, heavy metal concentrations will be small as shown in next table.

Parameter	Actual value	Dimension
Total particulate	23	mg/Nm^3
Mass flow	2.0	kg/h
Total metal content	<0.1	%
Nickel	0.05 0.012	% Ni/PM mg/Nm^3
Vanadium	0.02 0.005	% V/PM mg/Nm^3
Platinum	<0.004 <0.001	% Pt/PM mg/Nm^3

Table 3.26: Example of composition of particulate matter generated by catcrackers when feedstock is hydrotreated
Source: [250, Winter, 2000]

Sulphur oxides

The sulphur in the feed to the catcracker is split between liquid product streams, H_2S in the gaseous products and SO_2 emission from the regenerator in the approximate ratio of 50/45/5. The degree of sulphur dioxide leaving the exhaust gases from the catalytic cracker depends on the sulphur content of the feedstock used as well as the technology used to control these emissions. SO_3 aerosols will also contribute to the catcracker stack plume opacity.

The next table shows some examples of yearly averages of SO_2 emissions from catcrackers.

Throughputs (kt/yr)	Flow (Nm^3/h at 3 % O_2)	%S in feed	SO_2 concentration (mg/Nm^3)	SO_2 load (t/yr)	Specific SO_2 emissions (kg/t)
1750				268	0.15
1300	110000	0.5	360	247	0.19
2300	200000	1.7	700	840	0.36
750	65000	0.5	150	350	0.47
1700	150000	2.0	900	810	0.48
1500	130000	2.5	4000	3100	0.48
800	70000	3.0	1100	470	0.59
2350	200000	0.5	1200	1860	0.79
750	62500		1960	1110	1.48

Table 3.27: Sulphur oxide emissions from catcrackers (with and without abatement techniques) Sources: [261, Canales, 2000], [250, Winter, 2000], [107, Janson, 1999], [112, Foster Wheeler Energy, 1999], [268, TWG, 2001]

Other compounds

Hydrogen sulphide, mercaptans and ammonia may arise from sour waters from reflux condensers. Hydrocarbons (typically 80 % alkanes and typically 15 % of olefins) may be released from pressure reliefs, storage and handling operations, spillages and water discharges. Measured dioxin emission values in two European FCC reported levels of < 0.016 ng TEQ/Nm³ after CO - combustion. [268, TWG, 2001]

Waste water emissions

The typical flow of waste water generated by a catalytic cracking process is around 60 - 90 litres of waste water per tonne of feedstock treated. Generated waste water is typically from sour water drains and spillages from the fractionator containing some hydrocarbons (high levels of oil BOD, COD), suspended solids, sulphur compounds (H_2S), phenols, cyanides, ammonia and high pH. The next table shows the loads and composition of waste water generated in the catcrackers.

Source of waste water	Parameter	Value	Units
Steam used to purge and regenerate catalysts	Metal impurities from the feed oil	n.a.	ppm
Fractionator overhead reflux drum	Percentage of feed intake Flow H_2S HCN COD N-Kj Phenols Free oil	7 - 10 20 – 40 10 – 200 1 - 300 500 - 2000 15 - 50 5 - 30 50 - 100	% v/v m^3/h ppm ppm ppm ppm ppm ppm
Caustic washing of hydrocarbons	Flow Phenolic caustic Cresylic acids	128 n.a. n.a.	m^3/h

Table 3.28: Waste water emissions generated by catcrackers

Solid wastes

Potential releases into land are of catalyst in the form of fines from particulate matter arrestment equipment and intermittent spent catalyst discharge. Those solid residues are enriched in the heavy cycle oil and clarified oil (distillate of FCCU) fractions.

	Source	Flow	Composition min/max
Replacement of old catalyst during turnaround maintenance	Regenerator	50 tonnes/4 yr	Spent Catalyst: Gray, solid powder consisting of Al_2O_3, SiO_2, carbon, refractory material and metals.
Catalyst fines	Regenerator overhead cyclone/ESP		Dust containing high levels of V, Ni, Sb
Tank sludge slurry		Depends on slurry filtration system	10 - 30 % oil, depending on draining for cleaning, PAH

Table 3.29: Solid wastes generated in the catcracking

Catalyst addition rates for resid operation depend on feed metal levels. Addition rates shown are typical values covering a feed metal range of 10 - 20 ppm Ni+V+Na.

3.6 Catalytic reforming

Consumptions

Table 3.30 shows a summary of the utilities and catalyst requirements for the catalytic reforming.

	Reforming	Semi-regenerative process	Continuous regeneration process
Electric power, kWh Specific consumption (kWh/t)	- 25 - 50	246* 55	6142* -
Fuel fired, GJ Specific fuel consumption (MJ/t)	- 1400 - 2900	185* 71.5 t/kt	232*
Cooling water, (m^3/t, ΔT=10 °C)	1 - 3	0.12 - 3	5.5
High-pressure steam generated, kg/t	50 - 90	64 - 90	97
Boiler feed water, kg/t		170	22
Condensate return, t/h Specific value (t/kt)		88 20	113 -
Catalyst(containing Pt) t/(Mt/yr)	1.35		
* Values related to a capacity of 2351 t/d. Specific values related to capacity values Note: First column gives ranges for all types of reformers			

Table 3.30: Typical utilities requirements for catalytic reforming
Sources: [118, VROM, 1999], [166, Meyers, 1997], [261, Canales, 2000]

Emissions

Emissions to the air

Air emissions from catalytic reforming arise from the process heater gas (addressed in Section 3.10), fugitive emissions (hydrocarbons from pressure relief valves and leakages) and regeneration. Hydrocarbons and dust releases may arise from venting during catalyst replacement procedures and during clean-out operations. The next table shows an example of emissions to the air generated by reformers in two European refineries. The table also shows the emissions generated by the heaters.

Installation	Fuel consumption (GWh/yr)	Throughput (t/yr)		SO_2	NO_x	CO	CO_2	Particulates
Platformer			mg/m^3	35	100	100		5
Mider (1)	753.4	1000000	t/yr	24.1	68.7	68.7	146152	3.4
		Naphtha	kg/t feed	0.024	0.069	0.069	146	0.003
Platformer			mg/m^3	18	170	5		1
OMV	494.1	728000	t/yr	8.8	83	2.4	95848	0.5
		Naphtha	kg/t feed	0.012	0.114	0.003	132	0.001
Notes: Data are related to yearly average, 3 % O_2, dry conditions. (1) Emissions from the Mider refinery, only limit values are given. Loads and specific emissions were calculated.								

Table 3.31: Examples of emission to air generated by catalytic reforming
Source: [250, Winter, 2000]

In the regeneration process of the catalyst in a continuous reforming unit, a slipstream of catalyst is withdrawn, the coke (60 - 80 kg coke/tonne feed) is burned off with hot air/steam, trace quantities of a promoter, normally an organic form of chlorine (such as tri- or per-chloroethylene) are added to retain catalyst activity, moisture is removed and the regenerated catalyst is returned to the reformer. In the cyclic or semi-regenerative units, the regeneration of catalyst and the resulting emissions are discontinuous. The off-gas from the regenerator contains steam, air, hydrocarbons, CO_2, HCl, H_2S a small quantity of catalyst fines, traces of Cl_2, CO

(well below 10 mg/Nm^3 [117, VDI, 2000]), SO_2 and dioxins and furans (113 ng/Nm^3 TCDD-eq EADON, 131 ng/Nm^3 TCDD-eq I-TEF [215, Jansson, 1999]). A study from USAEPA [315, USAEPA, 2000] shows that the CDD/CDF emission factors from petroleum catalytic reforming units are 0.196 ng/t for semi-regenerative units and 1172 ng/t for continuous regeneration units. Dioxin emissions measured in four Belgian refineries are <0.1-0.13; 3.3-6.7; <0.01 and <0.01 ng TEQ/Nm^3 (higher values are derived from an installation with a flow of 2000Nm^3/h (ca 1800 h/yr) [268, TWG, 2001]. The regenerator gas is normally treated in a water scrubber to remove dust, chlorine compounds and SO_2 prior to release to atmosphere. The storage and handling of organic chlorides used during the regeneration may also lead to releases.

Waste water

The amount of waste water generated in the catalytic reforming is around 1 - 3 litres per tonne of feedstock. The waste water contains high-levels oils, suspended solids, COD and relatively low levels of H_2S(sulphides), chloride, ammonia and mercaptans. Those compounds may also be found in the stripping tower used to remove light ends from the reactor effluent. Hydrocarbons from spillages and leaks may occur. A study shows that the untreated waste waters and spent caustics from the reformers contain a wide range of CDD/CDF concentrations of 0.1 pg I-TEQ_{DF}/l to 57.2 ng I-TEQ_{DF}/l [315, USAEPA, 2000].

Solid wastes generated

Spent catalyst fines (alumina silicate and metals) may be generated from the particulate abatement techniques. For process units using expensive catalysts, such as catalytic reformers (Pt), contracts with the supplier exist for taking the spent catalyst back for regeneration and/or recycling. Spent catalyst generated is around 20 to 25 tonnes per year for a 5 Mtonnes per year refinery. Table 3.32 gives the typical composition of the sludge generated in the catalytic reformers.

SPECIES	Concentration (ppm)	SPECIES	Concentration (ppm)
Oil	2.4 %	Ethylbenzene	215.8
Solids	97.6 %	Lead	108.6
Carbon	7.7 %	Benzene	92.5
Hydrogen	6.5 %	Naphthalene	79.1
Nitrogen	0.4 %	Chromium	75.1
Carbonate	0.3 %	Sulphate	72.4
Iron	38070	Phenan	40.2
Sulphur	18901	Vanadium	19
Aluminium	6836	Antimony	19
Calcium	6166	Fluorine	17.1
Sulphide	4658	Phenol	13.4
Magnesium	3405	Pyrene	9.4
Sodium	1059	Benzo(A)Pyrene	6.7
Xylene	1056.3	Arsenic	4.8
Nickel	898.1	Selenium	1.9
Nitrate	683	Cyanide	0.6
Toluene	667.6	Mercury	0.02
Note: Figures quoted on a moisture-free basis			

Table 3.32: Example of composition of the sludges generated in the unit separator sludge of an ultraformer
Source: [80, March Consulting Group, 1991]

3.7 Coking processes

Consumptions

Delayed coking
Table 3.33 shows the energy and process materials usage in the delayed coking.

Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Steam produced (kg/t)	Cooling water (m^3/t, ΔT=17 °C)
800 - 1200	20 - 30	50 - 60	50 - 125	6 - 10
Note: Electricity including the electric motor drives for the hydraulic decoking pump.				

Table 3.33: Utility requirements of a delayed coking process

The amount of required make-up water for the coking process depends on the evaporation losses and the bleed to the desalter. Treated effluent can be used for this. The water used for coke cutting during decoking of the drums is highly contaminated with (un)saturated hydrocarbons and coke particles.

Flexicoking
Table 3.34 shows the energy and process materials usage in flexicoking.

Electricity (kWh/t)	Steam consumed (kg/t)	Steam produced (kg/t)	Cooling water (m^3/t, ΔT=10 °C)
60 - 140	300 - 500 (MP)	500 - 600 (HP)	20 - 40

Table 3.34: Utility requirements in the flexicoking process

Calcinator
The calciner specific energy consumption figures are given per tonne of calcined coke produced.

Electricity (kWh/t)	Refinery fuel gas (kg/t)	Steam produced (kg/t)	Steam consumed (kg/t)
13.2	0.03	0.1	2.4

Table 3.35: Typical utility requirements in the calcinating unit

Emissions

The most important health and safety aspect of these processes is the handling of the coke fines.

Emissions to the air
Air emissions from coking operations include the process heater flue gas emissions (see Section 3.10, where emissions from heaters are included) and fugitive emissions. In addition, the removal of coke from the drum (delayed coking) can release particulate and any remaining hydrocarbons to the atmosphere. The main pollutants generated as well as the sources are described below:

- *hydrogen sulphide and sulphur compounds* as mercaptans may be released from the sour water stream from reflux condensers
- *hydrocarbons* may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling operations, spillages and waste and water discharges
- *particulate matter* may be released from the kiln gas cleaning system, the rotary cooker gas cleaning system, coke handling and storage, loading operations and from the calcinator process. The back pressures of the gas discharges from the kiln are critical to maintain the flame front in the kiln. This could mean the cyclone operating conditions are dictated by the requirement of the kiln rather than the optimum conditions for dust removal. Overall particulate emissions of 10 - 460 mg/Nm^3 are currently being achieved [80, March

Consulting Group, 1991] [251, Krause, 2000]. Storage, crushing and handling of green coke takes place in the wet state with no releases to air. Typical size distribution profiles for particulate matter in calciner exhaust gases after passing through a cyclone system is:

99 % w/w below	100 microns
98 % w/w below	45 microns
90 % w/w below	8 microns
60 % w/w below	5 microns
20 % w/w below	2.5 microns
10 % w/w below	1.5 microns

Waste water

Waste water is generated from the coke removal, water bleed from coke handling, sour water from fractionator overhead, cooling operations and from the steam injection and should be treated. The amount of waste water generated in the coking processes is around 25 litres per tonne of feedstock. It contains H_2S, NH_3, suspended solids (coke fines with high metal contents), COD, high pH, particulate matter, hydrocarbons, sulphur compounds, cyanides and phenols. Detailed analysis of the contaminants of such waste waters is not available because they are transferred directly to the refinery main waste water system for treatment.

Solid wastes

Solid wastes generated in the coking processes are coke dust (carbon particles and hydrocarbons) and hot oil blowdown sludges containing hydrocarbons. Table 3.36 shows a typical analysis of those sludges.

SPECIES	Concentration (ppm)	SPECIES	Concentration (ppm)
Solids	91.4 %	Selenium	53
Oil	8.6 %	Antimony	40
Carbon	28.5 %	Nitrate	35.8
Hydrogen	3.5 %	Naphthalene	32.4
Nitrogen	0.3 %	Vanadium	32
Iron	80537	Phenan	20.1
Sulphur	27462	Phenol	11.2
Calcium	8166	Arsenic	10.5
Aluminium	3098	Toluene	7.8
Magnesium	2237	Fluorine	6.7
Sulphide	613.0	Pyrene	6
Sodium	459	Benzo(A)Pyrene	5.6
Lead	272.9	Benzene	2.2
Nickel	230.4	Ethylbenzene	2.2
Chromium	166.7	Mercury	1.0
Xylene	145.4	Cyanide	1.0
Sulphate	115.0		
Figures quoted on a moisture-free basis.			

Table 3.36: Typical chemical characterisation of the sludge generated in the coker
Source: [80, March Consulting Group, 1991]

3.8 Cooling systems

Under the IPPC process, a horizontal BREF on industrial cooling systems has been produced. The information given in this section should be read in conjunction with that BREF, particularly the extensive coverage it gives to the consumption of additives.

The need for cooling in a refinery depends on the processes used and on the degree to which they are integrated but, where water cooling systems are applied, it certainly accounts for the majority of water usage. In a refinery, it is important to maximise heat integration at a plant level and at process/activity level to minimise cooling duty. Therefore, energy requirements for cooling will depend on the cooling system used together with the cooling strategy applied. The next table shows a typical split of the cooling needs in a refinery (Hydrocracking refinery with a throughput of 7 Mt/yr)

	Cooling capacity	
Application	MW	%
Process streams	400	94
Pumps, compressors	10	2
Vacuum systems	15	4
TOTAL	425	100

Table 3.37: Cooling needs in a refinery
Source: [119, Bloemkolk and van der Schaaf, 1996]

The next table gives a distribution of the cooling capacity according to temperature range within a typical refinery. (Hydrocracking refinery with a throughput of 7 Mt/yr)

	Cooling duty	
End temperature (T) process fluid (ºC)	MW	%
T> 43	380	95
43>T>38	15	4
38>T>30	0	0
30>T	5	1
Total	400	100

Table 3.38: Typical cooling duty according to temperature range
Source: [119, Bloemkolk and van der Schaaf, 1996]

Consumptions

Power is consumed by pumps in a water cooling system and by fans in an air cooling system. The water cooling system uses water and requires chemicals as corrosion and bacterial growth inhibitors. For more detailed information and annual consumption figures, reference is made to the IPPC BREF on cooling which can be regarded as the state-of-the-art document on cooling systems. Both recirculating and once-through cooling water systems require additives, to prevent fouling and/or corrosion. Because once-through systems generally use surface water (either fresh or salted), the chances of fouling are higher, compared to recirculating systems. Therefore, in these systems, more anti-fouling additives (i.e. chlorinated biocides) should be used. On the other hand anti-corrosion additives are mainly applied in recirculating systems and not used in once-through systems.

Water utilisation in cooling systems is lower in a recirculating system, compared to a once-through system (up to only 3 %). In the recirculating system a certain amount of water exits the system through evaporation, mist droplets and as bleed or blowdown to the waste water treatment system. Therefore, make-up water in the range of about five percent of the circulation rate is required, a figure equivalent to the use of 0.23 m^3 of cooling water per tonne of crude oil processed.

Emissions

The main "contamination" generated by the cooling systems is the heat, increasing the temperature of the cooling fluid used. In refinery water cooling, the increase of the temperature (ΔT) is around 10 – 15 ºC.

Water consumption (mentioned above), energy consumption (pumps, air-cooler fans) and water pollution are the main environmental issues of cooling systems. Other environment-related effects include noise production (cooling tower, pumps, air-cooler fans (97 - 105 dB(A) at source)) and plume formation (cooling tower).

The main pollutants to be considered in water cooling systems are the chlorinated and/or brominated antifouling additives, and anticorrosion additives containing zinc, chromium, molybdenum etc. Special attention has to be paid to the use of dispersing additives in closed cooling water systems, particularly when the bleed is routed to an oil separating water treatment unit, where they can interfere with the oil-water separation process. A once-through system coupled with a low rate of leaks and a high volume of water mean that cooling water discharges contain between 0.1 and 1 mg/l oil. Hydrocarbon emissions to the air from cooling towers (as a result of leakages and stripping) may occur. The emissions to the air were reported to vary between 0.5 and 85 g hydrocarbons per m^3 cooling water recirculating over the cooling tower [119, Bloemkolk and van der Schaaf, 1996]. Cooling by quenching (only used in delayed cokers within refineries) results in high vapour emissions, significant energy losses, large water use and severe water pollution.

Emission or effect	Once-through	Once-through (closed-loop)	Cooling tower	Cooling tower (closed-loop)	Air coolers	Air-cooled (closed-loop)
Water						
thermal heat (MW)	300	300	Negligible	Negligible		
hydrocarbons (kg/h)	2.6 - 26					
chemical conditioning[a] (kg/h)	2.6	2.6	3 - 25	3 - 25		
water blow-down discharge (m^3/h)	26000	26000	156	156		
Air						
Visible plume			+[c]	+[c]		
Water vapour (kg/h)			468000	468000		
Hydrocarbons (kg/h)			13	(+)[e]		
Energy consumption[d] (kW)	3500	5500	5600	7000	2000	8700
Fresh water consumption (m^3/h)		in closed circuit	624	624		
Noise[b]	+	+	+	+	+	+
Other	entrainment of fish in intake	entrainment of fish in intake				

[a] Hypochlorite in once-through cooling water; anti-corrosives, hypochlorite and anti-scalants in cooling tower make-up water
[b] See text
[c] Suppression of plume possible at extra cost
[d] Process energy losses not included
[e] Possible effect: the leaking of air coolers is not a well-described phenomenon. The absence of water would suggest that corrosion is not an important factor compared to water-cooled systems. Further study would be needed for an accurate assessment
\+ Effect occurs

Table 3.39: Environmental impact of different cooling systems for a typical refinery
Source: [119, Bloemkolk and van der Schaaf, 1996]

3.9 Desalting

The quantity of inorganic impurities in the crude oil depends very much on both the crude origin and the crude handling during transport from the crude well to the refinery.

Consumptions
The water used in crude desalting is often untreated or partially treated water from other refining process water sources. Table 3.40 shows the typical operating conditions and water consumptions in the desalters, depending on the type of crude oil used.

Crude oil density kg/m^3 (at 15 °C)	Water Wash, % v/v	Temp (°C)
< 825	3 - 4	115 - 125
825 - 875	4 - 7	125 - 140
> 875	7 - 10	140 - 150

Table 3.40: Typical operating conditions of desalting process

For desalting long CDU residue, 10 % w/w water on feed is common. Once the water and the oily phase have been well mixed, the water should be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals (5 - 10 ppm) to assist in breaking the emulsion and/or, more commonly, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The electricity consumption used in the desalting processes varies typically from 0.075 to 0.15 kWh per tonne of crude oil.

Emissions

Air emissions
No major emissions to the air are produced during the desalting processes. Air emissions from the heating processes are expected (in Section 3.10), and fugitive emissions (hydrocarbons) may be expected.

Waste water
The desalter is a big contributor of process waste water (30 - 100 litres / tonne feedstock desalted). The desalting process creates an oily desalter sludge and a high-temperature salt water waste stream (possible the most polluted in the refinery) which is typically added to refinery waste water treatment facilities. The waste water generated is highly contaminated. Table 3.41 shows the ranges to be expected from waste waters from desalters.

Water pollutants	Typical concentration (mg/l)
Temperature (°C)	115 - 150
Suspended solids	50 - 100
Oil/oil emulsions	high
Dissolved hydrocarbons	50 - 300
Phenols	5 - 30
Benzene	30 - 100
BOD	high
COD	500 - 2000
Ammonia	50 - 100
Nitrogen compounds (N-Kj)	15 - 20
Sulphides (as H_2S)	10

Table 3.41: Composition of the waste water generated in the desalting process
Source: [181, HP, 1998], [101, World Bank, 1998]

Solid wastes generated

The quantities of desalter sludge generated depend on the solid content of the crude, the separation efficiency and the applied desludging mode and frequency. Normally a desalter clean-out is done twice a year, yielding from 60 - 1500 t/yr oily sludge, dependent on the throughput and efficiency of the process to capture solids. The sludge generated can contain iron rust, clay, sand, water (5 - 10 %), emulsified oil and wax (20 - 50 % w/w) and metals.

3.10 Energy system

The energy system is an important if not the most important activity from the environmental perspective. The energy (heat and power) necessary to transform the raw materials to products are provided by the combustion of hydrocarbon fractions that generates mainly emissions to the air. As it was mentioned in Section 2.10, this section contains the emissions generated by the energy system as a whole. As consequence of this, the emissions generated by furnaces or boiler of specific processes are integrated here and they are not considered in each of the other Sections.

3.10.1 Energy management

Energy efficiency in refineries
As the name indicates, energy efficiency is an index for calculating a refinery's energy efficiency. There are currently three methodologies in use in refineries briefly described below:

- *specific energy consumption (SEC)*. This is the most simple index. It is calculated as the ratio between the energy consumed by the refinery and the tonnes of feedstock processed. The specific energy consumption of European refineries ranges from 1 to more than 4 GJ per tonne of throughput. Because it is a simple index, this ratio does not take account of the complexity of the refinery (more complex refineries tend to consume more energy).

- *products method.* [318, Phylipsen, Blok et al., 1998] This method considers the products and internal energy products produced in the refinery, giving a specific energy consumption benchmark per tonne of energy product produced. Multiplying those specific energy consumptions by the amount produced within the refinery and adding all those totals gives an energy consumption benchmark for that refinery. Some calculations indicate that the best specific energy consumption figures are between 2.4 and 2.9 GJ/tonnes whereas actual values are from 1 to 4.8. That means that some European refineries are doing better than figures that are considered a good benchmark.

- *energy intensity index (EII)* is a measure used to compare energy consumption in refineries. The standard energy use is based on the energy consumption at about 300 refineries worldwide. The average EII obtained in a worldwide market survey (Solomon study, 1994) was 92, with a range from 62 to 165. [107, Janson, 1999]. More energy efficient refineries correspond to the lower values of EII. So, some refineries are almost three times as energy efficient as others. This index does reflect the types of processes and throughput of each process in the refinery. This data is not available for all refineries and typically is considered confidential by refineries. 10 refineries have reported its figure and the values have been plotted against the complexity index. Lowest EII values are typically achievable under local circumstances where low grade heat can be externally exchanged.

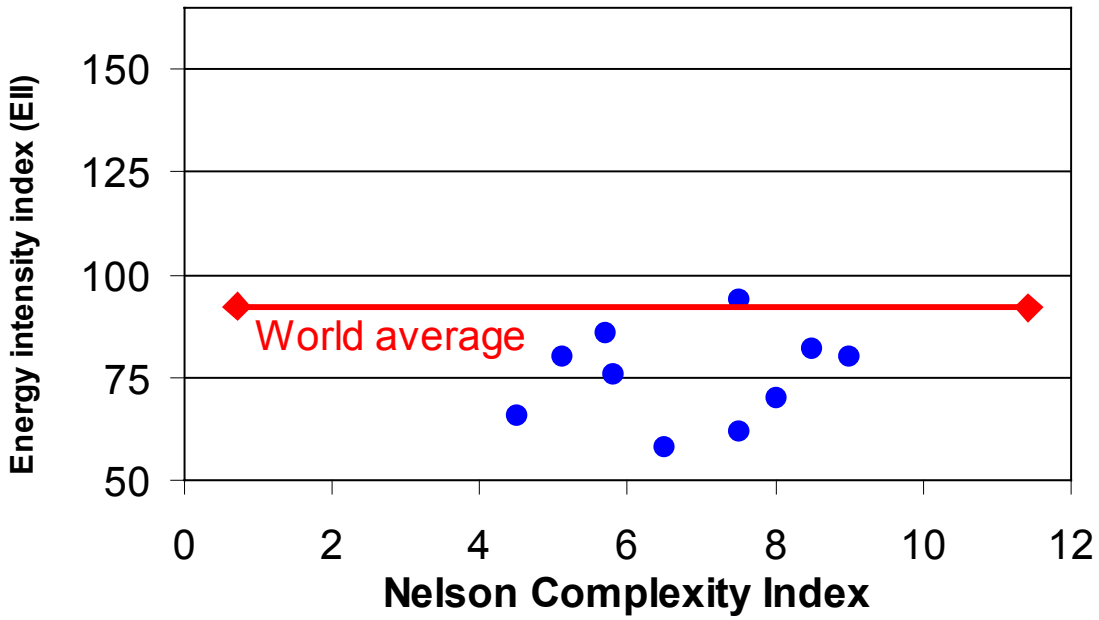


Figure 3.7: Energy intensity index vs. Nelson complexity index for some EU+ refineries
Source: TWG

3.10.2 Energy capacity and consumptions

Capacity of the refinery energy system
The capacity of the individual combustion plants in a refinery varies widely from less than 10 up to 200 Megawatts thermal input (MW_{th}); and the total installed capacity ranges from several hundred to more than 1500 MWh_{th} in the largest refineries. The energy consumed at the combustion plants of the refineries ranges from 200 to more than 17000 TJ per year. Deep conversion refineries in general use more than three times as much energy (10 % of crude intake) as simple hydroskimming refineries (3 %) [101, World Bank, 1998].

Gasification plant
An example of IGCC units produces 130 t/h of syngas mainly composed of CO and H_2 in the ratio 1:1 (calorific values of 9600-10000 kcal/kg) starting from 58 t/h of feedstock (calorific value of the heavy residue varies between 8800 and 9200 kcal/kg, sulphur content: 3.5 - 7 % and metal content: 300-800 ppm). A solid effluent in the form of a filter cake (about 160 - 400 kg/h dry) is discharged and sent to external plants for the recovery of the metals. Two Claus units recover 4 t/h of elemental sulphur from the H_2S recovered in the acid gas removal section. A tail gas treatment section, that permits an overall sulphur recovery of 99.9 %, follows the units [297, Italy, 2000].

Refinery fuels
The baseline ratio of gas to liquid refinery fuel used in a refinery is a function of a number of factors, important amongst which are the size, degree of complexity, LPG recovery efficiency and extent to which refinery fuel gas is processed into other products (e.g. olefins) or exported to adjacent chemicals plants (either directly or as energy from common facilities). It varies from 80/20 or 70/30 (gas/liquid) on a stand-alone, moderately complex refinery to 40/60 on a highly complex site which also services a chemicals complex. However these ratios can be increased when energy conservation measures are applied and the gas availability becomes sufficient for the energy supply of the refinery.

Next table illustrates the calorific value and the sulphur content of the different fuels as well as its calorific value.

Type of fuel	Calorific value (MJ/kg)	Sulphur content
Refinery gas	29 - 49	20 - 1700 mg H_2S/Nm^3
Hydrogen gas	15	20 - 1200 mg H_2S/Nm^3
Catalyst coke from FCC		0.11-0.3 % S
Liquid refinery fuel	40	<0.1 – 7 % S

Table 3.42: Properties of the fuels used within a refinery

There are great differences in the characteristics of the liquid refinery fuel used in European refineries. The data from a CONCAWE report show that in 1995 some 20 % of the total liquid refinery fuel used in the refineries had a sulphur level between 3 and 4 %, another 20 % a sulphur level of 2 to 3 %, some 40 % a sulphur level between 1 and 2 %, and 20 % a sulphur level below 1 %. However, it is worth to mention that some European refineries use heavier liquid refinery fuels (up to 7%). Next table shows the chemical characteristics of three different liquid fuels.

Property	High sulphur	Intermediate sulphur	Low sulphur
Sulphur % by weight	2.2	0.96	0.50
Carbon % by weight	86.25	87.11	87.94
Hydrogen % by weight	11.03	10.23	11.85
Nitrogen % by weight	0.41	0.26	0.16
Ash %	0.08	0.04	0.02
Vanadium (ppm)	350	155	70
Nickel (ppm)	41	20	10
Sodium (ppm)	25	10	<5
Iron (ppm)	13	9	<5

Table 3.43: Chemical properties of several typical heavy liquid oils
Source: [345, Molero de Blas, 2000]

The nitrogen and sulphur contents are two of the most important chemical parameters and responsible amongs other to the emissions of NO_x and SO_x. The following graph shows the distribution of nitrogen and sulphur contents in various types of vacuum residues according to their geographical origin.

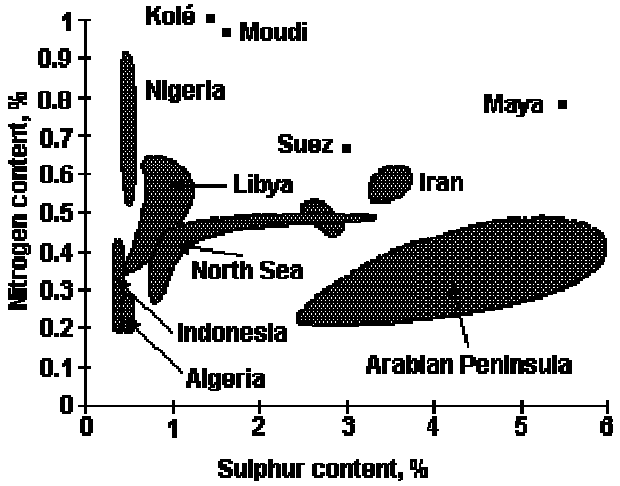


Figure 3.8: Sulphur and nitrogen contents in HFO (vacuum residues) according to their geographical origin
Source: [345, Molero de Blas, 2000]

Steam generation
Steam generation requires a energy input of 2700 - 3200 MJ per tonne of steam produced. Conditioning chemicals are dosed to the BFW in low concentrations and comprise the following groups of chemicals: anti scaling agents, corrosion inhibitors and anti foaming agents. A 100 t/h steam generation system requires approximately 1.5 - 3 t/yr corrosion inhibitors and 2 - 4 t/yr anti-scaling agents. Those conditioning chemicals are:

- *corrosion inhibitors* (mainly oxygen scavengers and alkaline compounds). Sulphite (< 60 bar), oximes, hydroxyl amines, and hydrazine (declining use due to safety issues) etc. are commonly applied as oxygen scavengers for deaerated boiler feed water prior to pumping into the boiler. Commonly applied alkaline compounds are sodium phosphates (which are also hardness binders), caustic, ammonia and neutralising amines.
- *anti-scaling agents* such as polyacrylates and phosphonates that are rest hardness binders and dispersing agents
- *anti-foaming agent*, in general intermittently dosed, to combat foaming in case the condensate contains oil or organics.

3.10.3 Emissions

Emissions to the air
Since emissions to water are minimal and very little is generated in the way of solid waste, emissions to air are the major ones, both from the energy system and from a refinery as a whole. The flue gas flows generated from combustion processes in a refinery range from 100000 to more than 700000 Nm^3/h at 3 % O_2.

The main releases to air from combustion processes are stack gases containing oxides of sulphur, oxides of nitrogen, oxides of carbon (carbon monoxide and carbon dioxide) and – particularly important when liquid refinery fuel or coke is combusted – particulate matter (including PM_{10} and metals (e.g. V, Ni)). When operating properly and when burning cleaner fuels such as refinery fuel gas, low-sulphur fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significantly higher. Incomplete combustion may lead to releases of carbon monoxide, smoke and, if heavy fuel oils are used, particulate matter. As a result of that, combustion plants are major contributors to the release of air emissions from refineries. The level of pollutants emitted will depend on the quality of the fuels burnt, which can vary considerably. There are conflicting factors in a combustion process which contribute to emission levels. For example, combustion conditions which favour low particulate emissions for liquid refinery fuel, i.e. excess air, high temperature, good air/fuel mixing and good fuel-atomisation, are not favourable for low- NO_x emissions.

Refinery fuel gas, if properly treated, is a low polluting fuel. Liquid refinery fuels generate more emissions to the air than refinery fuel gas. Gas-fired heaters and boilers generate little dust and lower SO_2 emissions, as the refinery fuel gases are usually cleaned in amine scrubbers. NO_x emissions are also much lower than those of liquid-fired boilers and heaters. By way of example, tables 3.44 to 3.46 show, respectively, the air emissions generated by gas and liquid refinery fuels in two power plants used in European refineries.

Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	CO_2	CO	NO_x	Particulates	SO_2
		mg/m^3		42	135	1	132
561.4	41000	t/yr	108917	23.6	75.7	0.6	74
		kg/t feed	2657	0.58	1.85	0.014	1.81
Data in table yearly average, 3 % O_2, dry							

Table 3.44: Air emissions from a power plant fired with refinery fuel gas
Source: [247, UBA Austria, 1998]

Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	CO_2	CO	NO_x	Particulates	SO_2
		mg/m^3		20	551	20	700 (1)
3741.4	323841	t/yr	1036439	76.2	2099	76.2	2666
	RFG. Residues	kg/t feed	3200	0.24	6.5	0.24	8.2
Data in table yearly average, 3 % O_2, dry. Flue gas is treated in a FGD unit (Wellman Lord)							

Table 3.45: Air emissions from a power plant fired with heavy fuel oil (primarily visbreaker residue, up to 7 % S)
Source: [247, UBA Austria, 1998]

	Raw gas	Clean gas
Volume, wet (m^3/h, 7 % O_2)	171690	188249
Gas temperature (°C)	180 - 200	up to 72
Particulates (mg/m^3, 3 % O_2)	220	< 10
NO_2 (mg/m^3, 3 % O_2)	800	< 150
SO_2 (mg/m^3, 3 % O_2)	6500	
SO_3 (mg/m^3, 3 % O_2)	650	< 10
SO_x as SO_2 (mg/m^3, 3 % O_2)		< 400
Note: It includes a FGD process. Liquid refinery fuel contains 7 % of sulphur.		

Table 3.46: Air emissions from the power plant of the Mider refinery buring refinery liquid residue
Source: [247, UBA Austria, 1998].

These follows an analysis of the air emissions produced by the energy system, pollutant per pollutant.

CO_2
Combustion processes of fossil fuels produce CO_2 as a result of the combustion of hydrocarbons. The amount of CO_2 emitted to the atmosphere by European refineries varies from 20000 to 20 Mtonnes per year (range depending on the type of refinery and the energy integration). The specific CO_2 emissions range from 0.02 to 0.82 tonnes of CO_2 per tonne of crude oil processed. CO_2 emissions from power plants in the refineries correspond to around 42 % of the CO_2 emitted by the refinery. The use of liquid fuels results in lower thermal efficiencies and higher CO_2 emissions than the use of gaseous fuels.

Table 3.47 shows the sources (type of fuels) of the CO_2-emissions of the refining industry. The table also includes the calculated emission factors for CO_2 for various refinery fuels

Fuel Type	Typical Composition (% w/w)	kg CO_2 / kg fuel	kg CO_2 / GJ
Refinery fuel gas	30 H_2/ 35 C_1/ 35 C_2 % v/v	2.83	43
Natural gas	100 % methane	2.75	56
LPG	50 C_3/ 50 C_4	3.02	64
Distillate Fuel oil	60 P/ 10 O/ 30 A	3.22	74
Residual Fuel	50 P/ 50 A	3.26	79
Coke	90 C/10 ash	3.30	117
(abbreviations: Carbon, Hydrogen, Paraffins, Olefins, Aromatics)			

Table 3.47: CO_2 emission factors for different types of fuels
Sources: [115, CONCAWE, 1999] [259, Dekkers, 2000]

CO

One of the products of partial combustion processes is carbon monoxide. The CO emissions, which range from 20 - 42 mg/Nm^3 @ 3 % O_2, are very dependent on the type of fuel used and the completeness of the combustion process. Specific emission values for CO are 0.58 kg CO per tonne of refinery fuel gas and 0.24 kg CO per tonne of liquid fuel. [247, UBA Austria, 1998]

NO_x

NO_x emissions from a refinery energy system depend on the fuel type, fuel nitrogen or hydrogen content, combustor equipment design and operating conditions. The formation and release of NO_x from combustion processes arises from the oxidation of nitrogen present in the fuel source and/or the air used. Accordingly, large differences in the NO_x emission level can be expected between refineries and even between different combustion installations at the same refinery at different times. Differences in temperature, residence time and oxygen concentration result in varying levels of thermally formed NO_x. The influence of temperature is most important, with NO_x emissions increasing exponentially with temperature.

Gaseous fuels typically release less NO_x per unit of energy compared to liquid fuels, especially liquid refinery fuels. Oil burning normally leads to higher levels of NO_x releases for several reasons, especially the problem of fuel NO_x arising from the nitrogen content (0.03 - 1 %), the way in which plant is often operatied so as to balance NO_x and particulate releases and the frequent design requirement for firing in combination with gas. However, the latter statement is only true for non-abated emissions, since the inclusion of secondary measures can reduce both NO_x and particulate emissions. One refinery in 1996 found that fuel oil can generate about three times more NO_x than gas fuels. NO_x factors (NO_x produced per tonne of fuel combusted), used by some refiners to report NO_x emissions, indicate NO_x from oil firing to be 2 to 3 times that from gas firing. However data from other refiners, particularly those based on stack monitoring, indicate that NO_x from oil can be as much as 5 or 6 times that from gas (e.g. see Table 3.44 and Table 3.45)

	Gas*	Liquid refinery fuel (HFO)
Process furnaces	70 - 1300	280 - 1000
Boilers	100 - 1100	300 - 1000
Turbines (@15 % O_2)	15 - 1050	200-450#
All figures are NO_x as NO_2 (@ 3 % O_2, mg/Nm^3) *The lower range relates to natural gas firing # for gasoil/jet oil		

Table 3.48: NO_x emissions ranges for existing installations
Source: [45, Sema and Sofres, 1991], [115, CONCAWE, 1999]

The fired heaters, boilers and gas turbines running on refinery blend gas produce lower NO_x emissions than FCCs. Specific NO_x emissions related to energy consumption range from 15 - 200 mg/MJ for furnaces with 100 % gas fuel. Specific NO_x emissions related to the throughput range from 84 to 700 tonnes of NO_x per million tonnes of crude oil processed. The NO_x load ranges from 20 to more than 2000 tonnes per year.

Particulates

Under normal conditions, the solids in the flue gases of a furnace or boiler consist mainly of coke particles with some cenospheres, depending on firing conditions. The particulate emission of oil-fired equipment may vary considerably since they depend on a number of more or less independent parameters such as: fuel type, burner design, oxygen concentration at the outlet of the radiant section, the flue gas outlet temperature of the radiant box, and the residence time of the fuel droplets. The particle size of the particulate matter (PM) from furnaces and boilers on HFO is in the order of 1 µm. The PM in flue gases can take any of the following four forms:

- soot; the particle size is below 1 µm-visible smoke from a stack is caused by all particles but mainly those with a particle size between 0.5 and 5 µm.
- cenospheres: they originate from the liquid phase wastes of combustion of heavy oil droplets at relatively low temperature (< 700 °C). The size is equal to or larger than that of the original oil droplets
- coke particles, formed through liquid phase cracking in combustion at high temperatures (>700 °C). The particle size is generally from 1 to 10 µm
- fine particles (< 0.01 µm): their contribution to the total mass emission is negligible.

The PM in the flue gas of furnaces and boilers fired with heavy fuel oil is a mix of metal compounds and soot/coke. Metals (mainly V and Ni) are a natural constituent (indigenous) of the crude. Soot and coke result from imperfections of the combustion process. Contaminants such as sand, rust and other metals, and coke particles of the fuel itself, may also contribute to the formation of particulates. The indigenous metal content of the heavy fuel oils (see Section 2.10, and which can be calculated from the metal content of the crude oil from which the HFO is made) is the basis for calculating the minimum ash content of the HFO and therefore also the basis for the PM in the flue gas. Ash contents are higher than the metal content itself (as the metal compounds are in the ash), and generally lie in the range 500 – 1500 ppm (0.05 - 0.15 % w/w). In practice the PM content is normally higher by a factor of 2 - 4, because unburnt fuel (soot) adheres to the metallic PM, and because aerosols of SO_3 are also monitored as PM.

The range of the unabated PM (150 - 500 mg/Nm^3) is typical for the burners applied nowadays (steam atomization and low- NO_x), assuming all measures are taken to achieve good combustion (optimum oxygen content and lowest practicable NO_x in the flue gas) and directly related to the ash content of the fuel. For older furnaces, liquid refinery fuel-fired flue gas levels may range from 500 to 1000 mg/Nm^3. For boilers, all these figures are on average lower. For a new optimal burner design with steam atomisation this can be well below 200 mg/Nm^3. The range of 150 - 500 mg/Nm^3 represents the current typical range with liquid refinery fuels employed (ash contents) and burners installed (low-NO_x with steam atomisation). Table 3.45 shows the particulate emission range found in current European refineries.

	Refinery fuel gas	Liquid refinery fuel
Process furnaces	< 5	5 – 1000
Boilers	< 5	5 – 500
Turbines (@15 % O_2)	n.a.	n.a.
All figures in mg/Nm^3 @ 3 % O_2		

Table 3.49: Particulate emissions ranges for existing installations
Sources: [45, Sema and Sofres, 1991], [247, UBA Austria, 1998]

Sootblowing is an operation that is carried out at regular intervals to remove soot from the furnace that is accumulating on the furnace equipment and hampers proper functioning. During this operation the PM content of the exhaust gas can reach values of 2000 mg/Nm^3.Abatement techniques installed for normal operations will be effective to reduce the PM emissions from this operation.

SO_x

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Heavy fuel oil residues normally contain significant proportions of sulphur and nitrogen, depending mainly on their source and the crude origin. Data from CONCAWE show that the average SO_2 content in the flue gas of refineries (from oil/gas firing) is 1350 mg/Nm^3. 55 % of the flue gas from oil/gas that is burnt, is at less than 1000 mg/Nm^3.

SO_x (mg/Nm^3) @ 3 % O_2	Refinery fuel gas (*)	Liquid fuel oil (#)
Process furnaces	3 - 1700	50 - 7000
Boilers	3 - 1700	50 - 7000
Turbines (@15 % O_2)	3 - 1700	n.a.
* The lower range relates to natural gas firing. Higher value corresponds to untreated refinery fuel gas without sulphur abatement. # The lower range relates to combustion process of very low sulphur liquid refinery fuel with abatement technique. Higher value corresponds to liquid sulphur fuel (4.1 %) without abatement.		

Table 3.50: Sulphur dioxide emissions ranges for existing European refineries
Sources: [45, Sema and Sofres, 1991], [247, UBA Austria, 1998], [198, (Hellas), 1999; 197, Hellenic Petroleum, 1999; 199, Petrola Hellas, 1999]

In air-blown gasification of coke, the sulphur content will be about 4000 mg/Nm^3 per percent sulphur in the feed.

VOC
Fugitive VOC emissions may occur from storage of fuels as well as uncombusted fuels. No data have been made available on that.

Waste water
Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. The waste water generated in the energy processes comes mainly from the boiler feed water (BFW) system. The main streams are the boiler blowdown (1 to 2 % of the BFW intake) and the BFW preparation regeneration wash (2 - 6 % of the BFW produced). The main pollutants and composition of the first stream are COD: 100 mg/l N-Kj; 0 - 30 mg/l PO_4; 0 - 10 mg/l. The BFW preparation regeneration stream is combined with NaOH/HCl for pH neutralisation. Normally no biotreatment is required.

Solid wastes generated
Releases to land may result from routine collection of grit and dust and arisings during cleaning procedures. The composition is 0.5 - 1 % w/w Ni and 2 - 3 % w/w V in furnaces and 1 - 3 % Ni/V for boilers. The amount depends on the furnace design and the liquid fuel quality, but in boilers varies from zero to 10 tonnes per year. Liquid refinery fuel tank bottom sludge and bundle cleaning sludge are generated in the storage tanks. The flow depends on the liquid refinery fuel quality and the presence of fuel tank mixers. Dependending on the mode of draining, 20 - 80 % is oil.

3.11 Etherification

Consumptions

The etherification reaction is exothermic and cooling to the proper reaction temperature is critical in obtaining optimal conversion efficiency. Methanol is needed for the production of those ethers. The utility consumptions in Table 3.51 are specified per tonne of MTBE processed in an oxygenate unit.

Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT=10°C)
12 - 20	1000 - 2000	2 - 8

Table 3.51: Utility requirements in the etherification processes

Emissions

Air emissions

Potential releases into air are of hydrocarbons from pressure reliefs on vessels, depentaniser column overheads drum and distillation column reflux drum, methanol plant, steaming vents on scavengers and reactor catalyst.

Waste water

Potential releases into water are of hydrocarbons, methanol and ethers from spillages and water bleed from methanol recovery. The water bleed is generated at a flow of 1 - 2 m^3/t and with a composition of COD: 50 - 200 mg/l and a N-Kj: 5 - 20 mg/l. Some components that can be found in this waste water are methanol (ethanol), ethers and formic acid (acetic acid).

Solid wastes generated

Waste generated is the spent catalyst/resin with no possibility of regeneration. Every 2 years, it should be changed and steamed to flare before recycling. The catalyst is recycled for recovery of its palladium content. Some efforts in the recycling of the resin have not successful.

3.12 Gas separation processes

Consumptions
The electricity demand of a gas separation process varies from 15 to 20 kWh per tonne of feedstock processed. Those processes also consume between 300 and 400 kg of steam per tonne of feedstock and between 1 and 2 m^3/t of cooling water ($\Delta T=10°C$).

Emissions
Air emissions
Potential releases into air are of hydrocarbons from pressure reliefs on vessels, regeneration vent gas from molecular sieves, C_1/C_2 refinery fuel gas, refrigeration system leaks, storage and handling operations.

Mercury if present in the feedstock of the refinery, will concentrate in overhead sections, particularly coolers. LPG, tops and naphtha coolers are most likely involved. Steaming that contaminated equipment may give mercury emissions to atmosphere. Upon opening equipment for inspection and maintenance mercury is sometimes found.

The final process in LPG production is the addition of some odorants. The odorants used are typically volatile organic sulphur compounds, i.e. mercaptans and sulphides. Potential releases into air include leaks or spillages of odorant and vapours displaced during tank filling or from thermal expansion of blanket gas. Also the products of incinerating or flaring displaced vapours if these techniques use used, including a small release of sulphur dioxide from combustion of the odorant.

Waste water
Potential releases into water are spillages of hydrocarbons, H_2S, NH_3 and amines.

Solid wastes generated
Potential releases into land are of hydrocarbons from contaminated spent molecular sieves and from odorant addition including solid waste such as materials used to absorb odorant spillage.

3.13 Hydrogen-consuming processes

Consumptions

In this section, two groups of processes have been included: hydrocracking and hydrotreatments. Both types of processes are catalytic and consume hydrogen. Table 3.52 shows approximate hydrogen consumption for hydrotreatment and hydrocracking of various feedstocks.

Process (Chemical consumption data)	% S w/w in crude	% S w/w in feed	Nm^3 of H_2 per tonne of feed
Deep atmospheric residue conversion	1 - 2	2 - 3.5	260 - 500
Hydrocracking vacuum gas oil	0.5 - 0.8	2 - 3	260 - 400
Cycle oil hydrogenation	0.3	3	370
Hydrotreating			
FCC naphtha/coker naphtha	0.05 - 0.01	1	110
Kerosene	0.1 - 0.02	0.1	11
Straight-run naphtha	0.01	0.05	4
Hydrodesulphurisation			
FCC gas oil/coker gas oil	0.1	1	130
High-sulphur gas oil to 0.05 % S	0.05	0.35	200
High-sulphur gas oil to 0.2 % S	0.04	0.3	44
Low-sulphur gas oil to 0.05 % S	0.04	0.15	17
Low-sulphur gas oil to 0.2 % S	0.03	0.1	13
Hydroconversion		metal content < 500 ppm	

Table 3.52: Hydrogen consumption data
Source: [166, Meyers, 1997], [118, VROM, 1999]

HYDROTREATMENTS

Consumptions of hydrotreatment units

The H_2 consumption, and consequently the energy requirement, significantly increase in the order naphtha (0.05 % H_2), distillate (0.3 % H_2) and residue hydrotreating (1.8 % H_2). Next table shows the utility requirements for different hydrotreatments.

	Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT=10°C)	Wash water (kg/t)	H_2 (kg/t)
Naphtha processed	200 - 350	5 - 10	10 - 60	2 - 3	40 - 50	1 - 15
Distillate processed	300 - 500	10 - 20	60 - 150	2 - 3	30 - 40	1 - 15
Residue processed	300 - 800	10 - 30	60 - 150	2 - 3	30 - 40	10 - 100
Hydroconversion	600 - 1000	50 - 110	200 – 300 (steam produced)	2 - 10	-	-
Note: Hydroconversion is an exothermic reaction and the heat generated in the reactor system is partially recovered in the feed product exchanger.						

Table 3.53: Utility requirements for different hydrotreatments
Sources: [45, Sema and Sofres, 1991], [118, VROM, 1999]

Process	Composition	Cycle lengths / average consumption (t/Mt feedstock)
Hydrodesulphurisation	$CoO/MoO_3/Al_2O_3$	1 year / 46
Denitrification	Ni/Mo catalyst	1 year / 46
Demethalisation	n.a.	< 1 year / n.a.
Saturation of olefins and aromatics	Ni/Mo catalyst	1 year / n.a.
Hydrogenation of light dienes	n.a.	2 years / n.a.

Table 3.54: Catalysts used in hydrotreatments

Emissions from hydrotreatment units

Emissions to air

Air emissions from hydrotreating may arise from process heater flue gas (dealt with in Section 3.10), vents, fugitive emissions and catalyst regeneration (CO_2, CO, NO_x, SO_x). The off-gas stream may be very rich in hydrogen sulphide and light fuel gas. The fuel gas and hydrogen sulphide are typically sent to the sour gas treatment unit and sulphur recovery unit. Hydrocarbons and sulphur compounds from pressure relief valves; leakages from flanges, glands and seals on pumps, compressors and valves, particularly on sour gas and sour water lines; venting during catalyst regeneration and replacement procedures or during cleaning operations. The following tables show two examples of emissions from hydrotreating processes. These air emissions include the emissions generated by the combustion of fuel required in those processes.

Installation *OMV Schwechat*	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates
Naphtha		1160000	mg/m^3	700 (1)	74	10		20
Hydrotreater	205.9	Naphtha	t/yr	142	15	2	40152	4.1
			kg/t feed	0.13	0.013	0.002	36	0.004
Middle		1780000	mg/m^3	59	242	5		1
distillate	135.8	Kerosene. GO	t/yr	8.1	33	0.7	26341	0.1
			kg/t feed	0.005	0.019	0	15	0
Vacuum		1820000	mg/m^3	700 (1)	442	10		20
distillate	72.4	VGO	t/yr	51.6	32.6	0.7	19466	1.5
			kg/t feed	0.028	0.018	0	10.7	0.001

(1) Raw gas was treated in a flue gas desulphurisation (Wellman Lord)
Data are related to yearly average, 3 % O_2, dry conditions.

Installation Mider	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates
Naphtha		1500000	mg/m^3	35	100	100		5
Hydrotreater	205.9	Naphtha	t/yr	7.1	20.3	20.3	39937	1
			kg/t feed	0.005	0.014	0.014	27	0.001
Middle		3000000	mg/m^3	35	100	100		5
distillate	205.9	GO	t/yr	7.1	20.3	20.3	39937	1
			kg/t feed	0.002	0.007	0.007	13	0
Vacuum		2600000	mg/m^3	35	100	100		5
distillate	578.2	VGO	t/yr	18.6	53.2	53.2	164776	2.7
			kg/t feed	0.007	0.02	0.02	63	0.001

Emissions are only limit values. Loads and specific emissions were calculated.
Data are related to yearly average, 3 % O_2, dry conditions.

Table 3.55: Examples of air emission generated by hydrotreatment units
Source: [250, Winter, 2000]

Waste water generated by hydrotreatments

Hydrotreating and hydroprocessing generate a flow of waste water of 30 - 55 l/tonne. It contains H_2S, NH_3, high pH, phenols, hydrocarbons, suspended solids, BOD and COD. This process sour water should be sent to the sour water stripper/treatment. Potential releases into water include HC and sulphur compounds from spillages and leaks, particularly from sour water lines. In distillate hydrotreatments, solid deposits such as $(NH_4)_2SO_4$ and NH_4Cl are formed in the cooler parts of the unit and must be removed by water wash.

Solid wastes generated by hydrotreatments
Those processes generate spent catalyst fines (aluminium silicate and metals Co/Mo and Ni/Mo 50 - 200 t/yr for 5 Mt/yr refinery). For process units using expensive catalysts, contracts with the supplier exist for taking the spent catalyst back for regeneration and/or recycling. This practice is also being adopted for other types of catalysts. During the last 20 years the use of catalytic processes has increased considerably and hence also the regeneration and rework services, particularly for Ni/Mo and Co/Mo hydrotreating catalysts. Molecular sieve beds are sometimes used to capture the water content of some streams (e.g. distillate hydrodesulphurisation).

HYDROCRACKING

Consumptions of hydrocracking units

Hydrocracking is an exothermic process. The heat generated in the reactors is partially recovered in a feed/product heat exchanger. A significant amount of heat is required in the fractionation section. Catalysts used in this process are typically cobalt, molybdenum, nickel or tungsten oxides impregnated on alumina. Fluorided alumina, activated clay, silica-alumina or zeolites are also present. Average consumption of catalysts is 57.4 t/Mt of feedstock. A small amount of coke-like material is formed which accumulates over time on the catalyst. This deactivates the catalyst, requiring regeneration off-site every one to four years by burning off the coke. Water is removed by passing the feed stream through a silica gel or molecular sieve dryer. The utility requirements for hydrocracking are the following:

	Fuel (MJ/t)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m^3/t, ΔT=17°C (*ΔT=10°C))
Hydrocracking	400 - 1200	20 - 150	30 - 300	10 - 300
Hydroconversion	600 - 1000	50 - 110	200 - 300	2 - 10*

Table 3.56: Utility consumption of hydrocracking units
Source: [45, Sema and Sofres, 1991], [118, VROM, 1999]

Emissions from hydrocracking units

Emissions to air
Heater stack gas contains CO, SO_x, NO_x, hydrocarbons and particulates that generate smoke, grit and dust in flue gas (covered in Section 2.10), fugitive emissions (hydrocarbons) and catalyst regeneration (CO_2, CO, NO_x, SO_x, and catalyst dust). Fuel gas and bleed stream will contain H_2S and should be further treated. VOCs are generated by the non-condensable from vacuum ejectors set condenser.

Waste water
Hydrocracking generates a flow of waste water of 50 - 110 l per tonne processed. It contains high COD, suspended solids, H_2S, NH_3 and relatively low levels of BOD. The sour water from the first stage HP separator, LP separator, and overhead accumulator should be sent to the sour water stripper/treatment. Effluents from hydroconversion processes may contain occasionally metals (Ni/V).

Solid wastes
Hydrocracking also generates spent catalysts fines (metals from crude oil, and hydrocarbons). Catalyst should be replaced once per <1 - 3 years generating an average of 50 - 200 t/yr for a refinery of 5 Mt/yr. Hydroconversion normally generates between 100 and 300 t/yr of spent catalysts which contain more heavy metals than hydrocracking catalysts.

3.14 Hydrogen production

Consumptions

Steam reforming

The steam reformer has to supply a large amount of heat at high temperature for the steam reforming reaction by burning fuel, with the result that a large amount of heat is lost in the flue gas. Hydrogen plants are one of the most extensive users of catalysts in the refinery. Typical utility requirements for steam reforming plant feeding natural gas are as follows (no compression is required)

Fuel ($MJ/t\ H_2$)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m^3/t, $\Delta T=10°C$)
35000 - 80000	200 - 800	2000 - 8000	50 - 300

Table 3.57: Utility requirements for steam reforming
Source: [45, Sema and Sofres, 1991]

and on average those processes produce 2600 Nm^3 of hydrogen (210 kg) per tonne of feedstock. Catalyst for reforming is 25 - 40 % nickel oxide deposited on a low-silica refractory base. The catalyst used in the reformer furnace is not regenerable and is replaced every four or five years. A refinery with a capacity of five million tonnes of crude per year will consume 50 tonnes per year.

The composition of the product depends on the purification technique, as shown in Table 3.58.

Parameter	Wet scrubbing technique	Pressure-swing adsorption
Hydrogen purity, % v/v	95 - 97	99 - 99.99
Methane, %v/v	2 - 4	100 ppm v/v
$CO+CO_2$, ppm v/v	10 - 50	10 - 50
Nitrogen, % v/v	0 - 2	0.1 - 1.0

Table 3.58: Composition of product hydrogen in steam reforming
Source: [166, Meyers, 1997]

Coke gasification

Coke gasification produces between 2600 and 3500 Nm^3 of hydrogen (210 - 300 kg) per tonne of coke gasified. Figure 3.9 shows a scheme of the hydrogen production from a coke gasifier and the amount of hydrogen produced per tonne of petroleum coke.

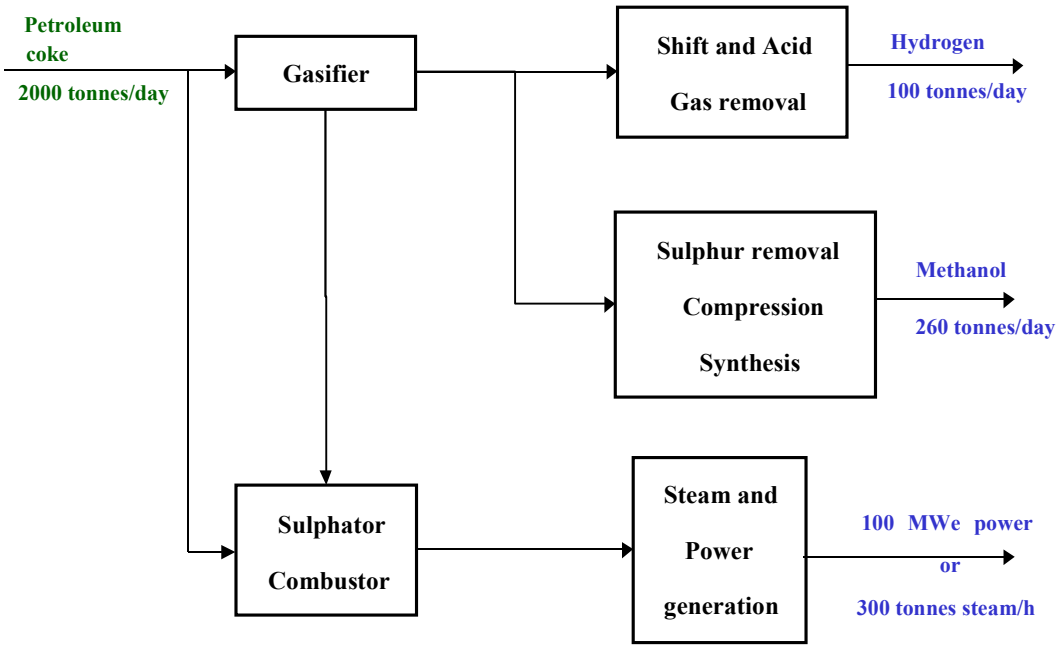


Figure 3.9: Petroleum coke commercial process
Source: [166, Meyers, 1997]

Heavy fuel gasification

Bitumen and heavy fuel can be gasified. Bitumen characteristics that have been used in the gasification are shown in next table

Density at 15 °C	**1.169**	**kg/l**
Carbon	85.05	% w/w
Hydrogen	8.10	% w/w
Nitrogen	0.80	% w/w
Sulphur	6.00	% w/w
Ash	0.05	% w/w
V	600	ppm
Ni	200	ppm

Table 3.59: Bitumen characteristics that can be used as partial oxidation feedstock
Source: [166, Meyers, 1997]

Emissions

Air emissions

Steam reforming

NO_x emissions are the most important to consider. Other emissions such as SO_x or water emissions are minimal, because low-sulphur fuel is typically used and there are few emissions other than flue gas. The choice of heat recovery system can have a major effect on NO_x production, since both the amount of fuel fired and the flame temperature will be affected. NO_x emissions from a steam reforming unit using gas or light gasoline as fuels and with low-NO_x burners are 25 - 40 mg/MJ (100 - 140 mg/Nm^3, 3 % O_2) [107, Janson, 1999]. Other emissions, such as CO_2, originate from carbon in the feed.

Coke gasification

Sulphur sorbents, such as limestone ($CaCO_3$) or dolomite (Mg, Ca carbonate), are normally used in the gasifier, reducing drastically the sulphur content. Sulphur composition in the exhaust gas ranges from 600 to 1200 mg/Nm^3 of H_2S and COS. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. In oxygen-blown gasification, the

sulphur content will be about 10000 mg/Nm^3 per percent sulphur in the feed. Ammonia is formed in the gasifier from the fuel-bound nitrogen. Ammonia in the product gas typically contained less than 5 % of the fuel-bound nitrogen when limestone was present in the gasifier.

Heavy fuel gasification

For the Mider Refinery, data are available concerning air emissions of the partial oxidation unit:

Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates
		mg/m^3	35	158	100		5
2452.8	670000	t/yr	243.4	1099	695.5	475843	34.8
		kg/t feed	0.363	1.64	1.038	710	0.052

For the emissions only limit values are given. Loads and specific emissions were calculated.
Data are related to yearly average, 3 % O_2, dry conditions

Table 3.60: Example of air emissions generated by heavy fuel gasification
Source: [247, UBA Austria, 1998]

Solid waste

Coke gasification

The solid waste from the process consists mainly of spent limestone and metals from the petcoke. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm. Volatile metals and alkalis tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burned and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas. The solid waste from the process consists mainly of spent limestone and metals from the petcoke. After processing in the combustor/sulphator, this material is send to disposal. Vanadium and nickel are found in most petroleum cokes in concentrations far greater than in coals or lignites. They remain in the ash product.

Hydrogen purification

Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is normally accumulated in a vessel and used as fuel at a convenient location.

3.15 Integrated refinery management

Emissions from European Refineries as a whole
Next calculations are based on SO_2 emissions from 76 European refineries (annual figures) in 1998 (CONCAWE). The refinery emissions of 387 ktonnes comprise 7.4 % of the global sulphur intake from feedstock (ranging from 2% to 10 %).

The breakdown of these annual emissions globally for the Western European sites is about:
- 65 % from the combustion, representing a consumption of 28.5 % liquid fuel of 1.7 %S content and 65 % of fuel gas
- 13 % from the FCC units
- 11 % from the sulphur recovery units
- and the 11 complementary % from flare and miscellaneous sources.

Bubble values are based on calculated (*) yearly averages for all refineries participating: total emissions divided by total (calculated stoichiometric required) flue gas emitted. Thus $\sum(S_{unit1} + S_{unit\ 2} + S_{FCC} + S_{SRU} + S_{FLARE})$ divided by $\sum$(Volume flue gas resulting from burning different types of fuels). The results are shown in next table:

Bubble values (mg/Nm^3)	European	ATL area	MED area	NWE area	OTH area
Global average	1600	> 2000	> 2200	< 700	< 400
Combustion weighted average	1000	1290	1540	570	310
Geographical contribution of the areas [3](% FOE)	100 %	26 %	25 %	39 %	10 %
Expressed in term of "Global Average Bubble", the mass of sulphur emitted per volume of flue gas calculated for the reporting sites represents an annual Western European average concentration of 1600 mg/Nm^3, all units of the refineries included for all types of refineries. Expressed in term of "Combustion Bubble" - only due to fuels burned within the refinery site, thus excluding FCC and SRU - the distribution of calculated annual value of each individual site is reported in a graph according to their respective and cumulative contribution to the total fuel use in Europe.					

The geographical splitting in the three major zones confirms variation between areas, representative of these different operational conditions through Europe.

The results of last three surveys from years 1992, 1995 and 1998 are given in Figure 3.10 a weighted average for the annual bubble of 1000 mg/Nm^3 is calculated representing a significant decreases from previous surveys for which the average combustion bubble was 1350 mg/Nm^3.

[3] The four areas are :
- NWE - Northwest Europe (mainland France, United Kingdom, Belgium, the Netherlands, Germany and Denmark)
- ATL - Atlantic (Ireland, Portugal and the Atlantic coasts of France and Spain)
- MED - Mediterranean (Spain, the med coast of France, Italy and Greece)
- OTH - "Others" (Norway, Sweden, Finland, Austria, Hungary and Switzerland).

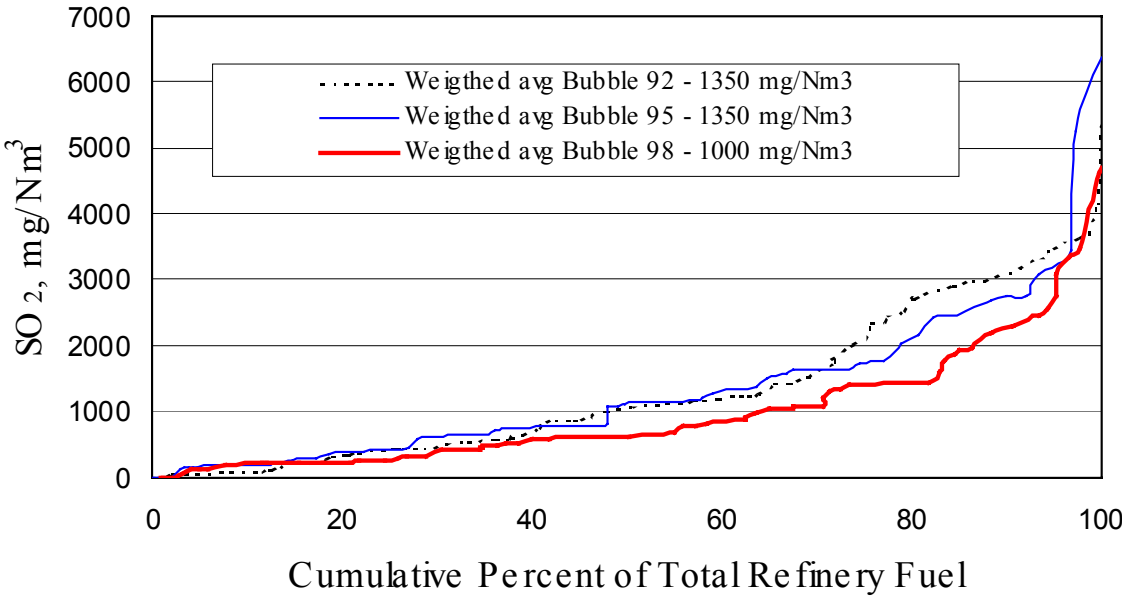


Figure 3.10: Historical and distribution trend of calculated annual SO_2 combustion bubble for EU refineries
Source: CONCAWE surveys

The lower part of the curves represents sites which are combining:
- burning more gas than liquid fuels
- lower sulphur content in liquid fuel used
- high sulphur content marketed products
- and/or control techniques of SO_2 emissions.

Then it is a combination of what kind of operating window they have been running in (crude/feedstock, supply and demand situation, plant design limitations, etc.) and the local availability of refinery fuels and natural gas for burning in the refinery. It is only in this complex context that any reference to "good" performance should be seen.

REFINERY MANAGEMENT ACTIVITIES

Emission integrated management
Some of the air emissions issues are by its nature refer to many processes or activities than consequently can be considered as a refinery as a whole issue. Under those issues, we can include sulphur emissions and VOC emissions.

Emissions in abnormal circumstances
Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard. Emergency situations are normally regulated in the refinery permit. Quantification of these emissions is difficult.

Start-up and shutdown
Conditions such as start-up and shutdown operations occur fairly infrequently, and are normally of short duration. Modern designs include fully automated fail-safe start-up and shutdown systems with interlocks to maximise safety and to minimise risk and emissions. Start-up and shutdown of a full refinery or part of the installation may result in substantial emissions to atmosphere, mainly VOC, SO_2, CO_2 and particulates. Effluent drainage and treatment facilities could also be temporarily overloaded. Refinery design and operational constraints call for safe and environmentally acceptable management and disposal of emissions, discharges and waste in upset conditions. Start-up and shutdown procedures, and hence emissions and discharges, vary

according to the type of unit and the purpose of the shutdown. If a particular unit is only to be depressurised and heavy components flushed out for a temporary stop, the emissions will be far less than if all equipment must be purged, steamed out and filled with air to allow workers to enter. Stringent safety and health care procedures are normal practice in present-day refineries. Not only own personnel but also contractors have to adhere to these procedures. Nevertheless, occasional accidents take place and safety precautions have to be practised regularly. Shut-down or blowdown can also have an impact on neighbouring dwellings (noise and light flaring).

Heat exchangers cleaning
The bundles of heat exchangers are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities. The sludge generated (oil, metals and suspended solids) may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents. Oily waste water is also generated during heat exchanger cleaning. VOC emissions may occur during those processes.

UTILITIES MANAGEMENT

1.- Water management
Surface water run-off is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Run-off surface water also includes water coming from crude and product storage tank roof drains.

The daily *sanitary waste water* production of an individual is about 120 litres, so the total sanitary effluent of the refinery can be easily calculated. Normally this domestic effluent is collected in a septic tank and then treated in the waste water treatment plant.

Ballast water is relevant to those refineries that have crude receipt facilities or handle big product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and heavily polluted with oil. It can easily lead to an upset of existing effluent treatment systems. The use of ballast water tanks is therefore an important equalisation tool for feeding the water in a controlled way to either the process water system or the continuously oil-contaminated system, if the COD is lower than 100 ppm. As more and more tankers are equipped with segregated ballast tanks, the ballast water problem is slowly phasing out.

Water used in processing operations also accounts for a significant portion of the total waste water. Process waste water arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Because process water often comes into direct contact with oil, it is usually highly contaminated.

The water usage depends both on purpose and complexity of the refinery. While there are usually opportunities to economise on waster use, the scope for major reductions in existing refineries is sometimes limited. Data from 63 European refineries gave the following data on water usage (data in annual averages).

Annual average fresh water usage:	4.2	million tonnes/year
Range	0.7 to 28	million tonnes/year
Average refinery throughput:	6.9	million tonnes/year
Average water usage per tonne throughput	0.62	tonne/tonne throughput
Range	0.01 to 2.2	tonne/tonne throughput

The fresh water consumption recorded is that taken from:
- Potable (mains) water
- River water
- Privately extracted groundwater (including in some cases contaminated groundwater extracted for purposes of treatment)

It does not include:
- Recycled final effluent
- Storm water
- Ship's ballast water
- Waste water from adjoining facilities
- Seawater

2.- Blowdown system

The gaseous component of the blowdown system typically contains hydrocarbons, hydrogen sulphide, ammonia, mercaptans, solvents and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulphur oxides when flared. The liquid is typically composed of mixtures of water and hydrocarbons containing sulphides, ammonia and other contaminants, which are sent to the waste water treatment plant.

Seal drum blowdown generates an effluent of 1 - 2 m^3/h and 10 times as much in case of emergency, with a composition of: COD, 500 - 2000 mg/l, H_2S, 10 - 100mg/l, phenol, 5 - 30 mg/l, NH_3, oil and suspended solids, 50 - 100 mg/l

3.16 Isomerisation

The main environmental problems, for this process, apart from the energy consumption are the catalyst promotion and the reduction of side-effects.

Consumptions

The total energy requirement depends mainly on the configuration (recycle operation 2 - 2.5 times higher than once-through), and the facilities to separate the n- from the iso-paraffins; absorption/desorption process or a de-isohexaniser column. The isomerisation processes require an atmosphere of hydrogen to minimize coke deposits but the consumption of hydrogen is negligible. The utilities requirements for an isomerisation process are:

Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT=10°C)
20 - 30	300 - 600	10 - 15

Table 3.61: Utility requirements in the isomerisation processes

Catalyst life can range from 2 to 10+ years depending on unit operation. The chloride promoted catalyst, chlorinated alumina containing platinum, requires the addition of very small amounts of organic chlorides to maintain high catalyst activities, to avoid catalyst deactivation and potential corrosion problems. See Section 2.16 for further information about the type of catalysts used.

The next table shows the utility and chemical requirements for the adsorption process for a feed rate of 600 tonnes per day.

Utilities & chemical requirements of the adsorption process	
Fuel consumed (90 % furnace efficiency) MW	9
Water (ΔT = 17 ºC), m^3/day	2159
Power, kWh	1455
Steam at 10.5 kg/cm^2, saturated, kg/h	2.8
Hydrogen consumption, Nm^3/day	17.7
Soda consumption (kg)	8.4
Hydrogen chloride (kg)	6
Catalyst consumption (kg)	0.12

Table 3.62: Utilities and chemical requirements of an adsorption process
Source: [166, Meyers, 1997], [337, Journal, 2000]

Emissions

Air emissions

Air emissions may arise from the process heater, vents and fugitive emissions. Emissions from process heaters are analysed in Section 3.10. Other emissions are HCl (potentially in light ends from organic chloride added to increase catalyst activity), vents and fugitive emissions, pressure reliefs on surge drum, separators and column reflux drum, regeneration vent gas from dryers, storage and handling operations, spillage (hydrocarbons). Releases of hydrogen may occur from pressure relief on the hydrogen system. Product stabilisation, however, does result in small amounts of LPG (C_3+C_4, rich in i-C_4) and in stabilizer vent (H_2+C_1+C_2) products. The stabilizer vent products are usually used as fuel. Fuel gas is normally caustic-treated to remove HCl.

Process waste water

Potential releases into water are of hydrocarbons from reflux drum boot drain and spillages and of spent sodium hydroxide from the scrubber system. The process waste water contains chloride salts, caustic wash, relatively low H_2S and NH_3 and has high pH. Brine from feed dryer

(desiccant, water free $CaCl_2$) contains dissolved $CaCl_2$ and hydrocarbons**.** Its flow depends on moisture content and is usually drained to the effluent treatment plant.

Residual wastes generated

Potential releases into land are of hydrocarbons from spillages/contaminated molecular sieves and catalyst. Calcium chloride sludge (or other desiccants) is the waste generated in this process. Catalyst used in these processes normally is regenerated by the catalyst manufacturers. Platinum is then recovered from the used catalyst off-site. Molecular sieves can be used as feed drying agent. The flow and composition are plant-specific and the spent molecular sieves are disposed of as non-regenerable solid waste.

3.17 Natural gas plants

Consumptions

Water and energy consumption within a natural gas plant is shown in the following table:

Water and Energy consumption	Existing plant (Statpipe and Sleipner Plant)	New plant (Åsgard Plant)
Capacity	22 MSm^3/day of rich gas	39 MNm^3/day of rich gas
Fuel gas	29 tonnes/h	14 tonnes/h (design)
Power (gas power))	30 MW	16 MW (design)
Water (steam production)	30 m^3/h	15 m^3/h
Seewater cooling	22400 m^3/h (average energy flux 274 MW)	14000 m^3/h (including the Ethane Plant) (energy flux 200 MW)

Table 3.63: Example of utility consumption in natural gas plants
Source: [290, Statoil, 2000]

Emissions

Emissions to the air

The major emission sources in the natural gas processing industry are compressors, boilers and furnaces, acid gas wastes, fugitive emissions from leaking process equipment and, if present, glycol dehydrator vent streams. Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethylbenzene and xylene, as well as a wide range of less toxic organics.

Potential release routes for prescribed substances and other substances which may cause harm are shown in Table 3.64.

	H_2S	SO_2	NO_x	CO, CO_2	Organic compounds	Oily waters	N_2	Spent catalysts/ adsorbents	Sand/ corrosion products	Acids/ alkalis/salts, etc.
On-shore reception	A*				AW	W			L	
Gas treatment processes	A*		A	A	AW	W		L		L
Acid gas processes	A*	A*	A	A	AW	W		L		
Nitrogen removal	A*				A		A			
Hydrocarbon removal					AW	W				
Gas compression			A	A	A					
Condensate treatment			A	A	AW			L		W
Field water treatment					W	W				
Flares/vents	A*	A*	A	A	A					
Gas storage sites	A	A	A	A	AW	W		L		
* if sour gas is being processed Source releases: A: air, W: water, L: land										

Table 3.64: Releases to the environment commonly associated with the natural gas processes
Source: [144, HMIP UK, 1997]

Emissions of SO_2 will result from gas sweetening plants only if the acid waste gas from the amine process is flared or incinerated. Most often, the acid waste gas is used as a feedstock in nearby sulphur recovery (see Section 4.23.5.2) or sulphuric acid plants. When flaring or incineration is practised, the major pollutant of concern is SO_2. Most plants employ elevated smokeless flares or tail gas incinerators for complete combustion of all waste gas constituents,

including virtually 100 percent conversion of H_2S to SO_2. Little results from these devices in the way of particulates smoke or hydrocarbons and, because gas temperatures do not usually exceed 650 ºC, no significant quantity of nitrogen oxides is formed. Emission factors for gas sweetening plants with smokeless flares or incinerators are presented in Table 3.65. Factors are expressed in units of kilograms per 1000 cubic meters. Emission data for sweetening processes other than amine types are very meagre, but a sulphur mass balance will give accurate estimates for sulphur dioxide (SO_2)

Amine Process	**kg/10^3 Nm^3 gas processed**	
Particulate	Negligible	
SO_x (as SO_2)	26.98	Assumes that 100 % of the H_2S in the acid gas stream is converted to SO_2 during flaring or incineration and that the sweetening process removes 100 % of the H_2S in the feedstock.
CO	Negligible	
Hydrocarbons	-	Flares or incinerator stack gases are expected to have negligible hydrocarbon emissions.
NO_x	Negligible	

Table 3.65: Emission factors for gas sweetening plants
Source: [136, MRI, 1997]

Emissions to water
Routine process-derived liquid effluent produced by natural gas plants is normally derived mainly from formation water arising from the drying of the gas and associated condensate. The effluent principally occurs as condensed steam from the glycol or methanol regeneration plants and usually contains a number of organic contaminants which may include glycol, methanol, aliphatic and aromatic hydrocarbons, amines and mercaptans. The presence of these contaminants typically causes the effluent to have a very high biochemical and chemical oxygen demand. The process of natural gas containing mercury can generate waste water containing that metal.

Solid waste
Natural gas refining gives rise to relatively small quantities of process wastes. These typically include occasional disposal of spent catalysts, activators, corrosion inhibitors, absorbents, adsorbents, filter cartidges, separator dusts, etc.; they may be contaminated with trace amounts of hydrocarbons. Some natural gas sources contain traces of Hg which should be collected (generating spent adsorbent) and safely disposed off. For every 1000 kg of sludge treated, 12 kg of metallic mercury is produced. Total sludge production within some Dutch natural gas plants is on average 250 tonnes/year with a maximum of 400 tonnes/year. This corresponds to 3-5 tonnes of mercury annualy.

3.18 Polymerisation

Consumptions
The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. Typically 0.2 gr. of phosphoric acid are consumed to produce 1 tonne of polymer or 1.18 kg of catalyst (phosphoric acid + support) per tonne of product. Catalyst life is normally limited to 3 to 6 months, depending on unit size and operating conditions. A typical unit, capable of producing 25 tonnes of polymerised gasoline per day, is customarily filled with 12 tonnes of catalyst.

Caustic solution is used to remove mercaptans from the propene/butene feed, then amine solution to remove hydrogen sulphide, then water to remove caustics and amines. It is finally dried by passing through a silica gel or molecular sieve dryer.

Next table shows the typical utility consumption of polymerisation process

Electric power	20 – 28	kW/t of product
Steam	0.7 – 1.1	t/t of product
Cooling water	4.4 – 6.0	t/t of product

Table 3.66: Utility consumption in polymerisation process
Source: [166, Meyers, 1997]

Emissions
Emissions to air
Potential releases into air are of hydrocarbons from pressure reliefs, storage and handling operations, spillages and water and waste discharges, and of particulate matter from catalyst fine from handling and disposal of spent catalysts. Sulphur dioxide and H_2S may arise during the caustic washing operation.

Process waste water
Potential releases into water are of hydrocarbons from sour water purge from the washtower, condenser drains and spillages, and of particulate matter from spillages of catalyst fines. Waste water streams will contain caustic wash and sour water with amines and mercaptans. Its more important parameters are H_2S, NH_3, caustic wash, mercaptans and ammonia, and low pH (2 - 3) due to the phosphoric acid.

Solid waste generated
Spent catalyst containing phosphoric acid, which typically is not regenerated, is occasionally disposed of as a solid waste. Potential releases into land are of acids in solid form and hydrocarbons from spent catalyst. Typically, 0.4 grams of used silica is disposed of per tonne of polymer gasoline produced.

3.19 Primary distillation units

Consumptions

Despite the high level of heat integration and heat recovery that is normally applied, crude distillation units are among the most intensive energy-consuming units in a refinery, because the total volume of crude oil being processed has to be heated to the elevated processing temperature of 350 ºC. The overall energy consumption of a refinery is normally dominated by a few processes. Atmospheric and vacuum distillation accounts for 35 - 40 % of the total process energy consumption followed by hydrotreating with approx. 18 - 20 % [195, The world refining association, 1999]. The various processes downstream of the CDU make use of the elevated temperatures of the product streams leaving the CDU. The number of side-streams in a high vacuum unit is chosen to maximise heat integration of producing streams at different temperatures, rather than to match the number of products required. The utility requirements for the atmospheric and vacuum distillation units are:

	Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT=17 °C)
Atmospheric	400 - 680	4 - 6	25 - 30	4.0
Vacuum	400 - 800	1.5 - 4.5	20 - 60	3 - 5
Note: Replacement of the steam ejectors by vacuum pumps will reduce steam consumption and waste water generation but increase the electricity consumption.				

Table 3.67: Utility requirements for atmospheric and vacuum distillation units
Sources: [118, VROM, 1999], [261, Canales, 2000], [268, TWG, 2001]

Emissions

Air Emissions

Potential releases into air are from:

- Flue gases arising from the combustion of fuels in the furnaces to heat the crude oil. Those emissions are treated in Section 3.10.
- Pressure relief valves on column overheads; relief from overhead accumulator are piped to flare as well as the vent points.
- Poor containment in overhead systems, including barometric sumps and vents.
- Glands and seals on pumps, compressors and valves.
- De-coking vents from process heaters. During furnace decoking (once or twice a year) some emission of soot can occur if operation is not properly controlled in terms of temperature or steam/air injection.
- Venting during clean-out procedures.
- Some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of non-condensable light hydrocarbons and hydrogen sulphide passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide. The quantity of these emissions depends on the size of the unit, the type of feedstock and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated. Oily sour water is also generated in the fractionators. The emissions of non-condensables from vacuum ejector set condensor are between 50 and 200 kg/h, depending on furnace design and type of crude and throughput. They are hydrocarbons and H_2S.
- Fugitive emissions from atmospheric and vacuum distillation units account for 5 - 190 t/yr for a refinery with a crude capacity of 8.7 Mt/yr [79, API, 1993].

The following table gives some examples of the air emissions generated by the atmospheric and vacuum distillation units by two European refineries. Those tables include the emissions from combustion of fuels in the furnaces.

Installation	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates
CDU		8200000	mg/m^3	46	107	6		1
OMV Schwechat	1536.9	Crude oil	t/yr	71	165	9.3	298149	1.5
			kg/t feed	0.009	0.02	0.001	36	0
CDU		8500000	mg/m^3	35	100	100		5
Mider	1138.8	Crude oil	t/yr	35.2	100.4	100.4	220927	5
			kg/t feed	0.004	0.012	0.012	26	0.001
Vacuum		2485000	mg/m^3	700[1)]	264	10		20
distillation	289.9	Atm. Res.	t/y	205	78	2.9	76170	5.9
OMV Schwechat			kg/t feed	0.083	0.031	0.001	31	0.002
Vacuum		4500000	mg/m^3	35	100	100		5
distillation	639.5	Atm. Res.	t/yr	19.8	56.6	56.6	182252	2.8
Mider			kg/t feed	0.004	0.013	0.013	41	0.001

(1) Raw gas was treated in a flue gas desulphurisation (Wellman Lord)
Note: Data are related to yearly average, 3 % O_2, dry conditions
For the emissions from the Mider refinery, only limit values are given. Loads and specific emissions are calculated.

Table 3.68: Examples of air emissions generated by crude oil and vacuum distillation units
Source: [250, Winter, 2000]

Process waste water

Process waste water generated in the atmospheric distillation units is 0.08 - 0.75 m^3 per tonne of crude oil processed. It contains oil, H_2S, suspended solids, chlorides, mercaptans, phenol, an elevated pH, and ammonia and caustic soda used in column overhead corrosion protection. It is generated in the overhead condensers, in the fractionators and can also become contaminated from spillages and leaks. The overheads reflux drum (gasoil dryer condensator) generates 0.5 % water on crude + 1.5 % steam on feed with a composition of H_2S 10 - 200 mg/l and NH_3 10 - 300 mg/l. Sour water is normally sent to water stripper/treatment.

Waste water (sour water) is generated in the vacuum distillation units from process steam injection in furnace and vacuum tower. It contains H_2S, NH_3 and dissolved hydrocarbons. If steam ejectors and barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated (± 10 m^3/h) containing also H_2S, NH_3.

Residual wastes generated

Sludges can be generated from the cleaning-out of the columns. The amount depends on the mode of desludging and the base solid and water content of the crude processed. The range of solid waste generation from a crude unit of 8.7 Mt/yr ranges from 6.3 - 20 t/day.

3.20 Product treatments

Consumptions
Utility requirements in the gasoline sweetening process are:

Electricity (kWh/t)	Steam consumed (kg/t)	Caustic (kg/t)
1 - 10	10 - 25	0.02 - 0.15

Sources: [261, Canales, 2000], [118, VROM, 1999]

Catalytic dewaxing
Catalytic dewaxing catalysts typically last 6 to 8 years. During that time, they are regenerated as needed. Typical cycles last 2 to 4 years between regenerations. Utilities needed in the catalytic dewaxing process are summarised in the following table.

Utilities for a feed capacity of 3500 tonnes per stream day	
Power, kW	5100
Steam (tracing only)	Minimal
Cooling water, m^3/h	80
Condensate, m^3/h	4
Fuel absorbed, MW	23084

Table 3.69: Typical utility consumption of catalytic dewaxing units
Source: [166, Meyers, 1997]

Emissions
Air emissions
Potential releases into air from oxidation-extraction processes are of hydrocarbons, sulphur compounds (e.g. disulphides) and nitrogen compounds from sour water drains, pressure relief valves, vents from feed vessels, spillages and leakages from flanges, glands and seals on pumps and valves – particularly from overhead systems and fugitive emissions. Emissions may occur from the spent air from the disulphide separator that contains less than 400 ppm of disulphides and is normally incinerated.

Process waste water
Those treating processes does not generate much waste water. The potential releases into water are from spillages and leakages (hydrocarbons), and the sulphur and nitrogen compounds arising from inadequate stripping performance.

Residual wastes generated
In the extraction process, a waste oily disulphide stream leaves the separator. Most refineries are able to regenerate their spent caustic, but sometimes they have to dispose of some excess quantities of spent caustic, mainly from caustic pre-wash activities. Usually these quantities are small and can be managed within their effluent treatment system or they are disposed of externally via contractors or may be re-used elsewhere. From the extraction process, the disulphide recovered can be sold as product, or be recycled to a hydrotreater or incinerator. The amount of spent caustic generated varies between 0.05 - 1.0 kg/tonne feed and contains sulphides and phenols. Concentration of organic compounds in spent caustic solutions is typically higher than 50 g/l.

Catalytic dewaxing processes

Air	*Waste water*	*Solid wastes*
Flue gas from fired heater (in Section 3.10). VOC may arise from venting during catalyst regeneration/replacement procedures and cleaning.	none	Potential releases into land are from disposal of spent catalytic dewaxing catalyst. (50 t/yr for a 50000 t/yr hydrofining process). Spent Ni-W catalysts containing sulphur and carbon sent to specialised off-site regeneration companies. After 2 - 3 regenerations catalyst is disposed of and subjected to metal reclaiming.

3.21 Storage and handling of refinery materials

Consumptions
No energy or process material is required for balancing lines, double seals, floating roofs on tanks. However, some tanks need mixers (a heavy user of power) and some need heating too. Handling refinery materials also needs electricity for the pumps that move the materials through the pipes.

Emissions
Air Emissions
Air emissions, and more specifically VOC emissions, are the main emissions that occur during the storage and handling activities of refinery materials. Emissions from hydrocarbon liquids in storage occur because of evaporative loss of the liquid during storage and as a result of changes in the liquid level. Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. Moreover, fugitive emissions in storage systems are mainly from imperfect seals or from tank fittings. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks [108, USAEPA, 1995]. However, it is generally the case that the amount of emissions depends much more on the vapour pressure of the product (higher vapour pressure tend to produce higher VOC emissions) than on the type of tank.

VOC emissions from storage represent more than 40 % of the total VOC emissions and are normally the biggest emitter in a refinery. The emissions from tanks have been estimated by using API estimations [245, API, 1983/1989/1990]. These estimations suggests an annual emission of 320 tonnes per year from the storage systems, a much lower figure than the one calculated from the DIAL measurements: 1900 tonnes per year for a refinery processing 11 million tonnes per year [107, Janson, 1999]. However, API methods have been updated and storage losses can be predicted with acceptable accuracy [259, Dekkers, 2000]. A CONCAWE study [229, Smithers, 1995] which was the only trial of DIAL where measurements were conducted over a reasonably long period showed that there was good agreement between DIAL and the latest API estimation methods when the test times were long enough.

When transferring liquids to vessels at atmospheric pressure, the vapour phase (often air, but also inerts) in the receiving vessel is often emitted to atmosphere. Such loading operations are recognised as having an impact on the environment due to the presence of VOC. VOC emissions from blending come from blending tanks, valves, pumps and mixing operations. The amount depends on design and maintenance of the systems. Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities. One of the largest sources of VOC emissions identified during the Amoco/USAEPA study was fugitive emissions from loading of tanker barges. It has been estimated that during loading of products with high partial pressure, 0.05 % of the throughput can be emitted to the air.

VOC emissions to the air from cavern storage of hydrocarbon materials can be prevented connecting the gas spaces of several caverns. So the breathing gases when filling one cavern are leaded to the other caverns. In case of only one cavern the breathing gases must be leaded to the air. However the VOC-emissions in this case are low because the temperature of storage is low (5 - 10 ºC).

Waste water
Leaking flanges and valves may contaminate rainwater. The amount depends on the maintenance service. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued build up. That waste water is contaminated with tank product. Oil levels up to 5g/l in tank water bottoms can be found [101, World Bank, 1998]. However, if the draw off rate of the water is too high, oil can be entrained with the water, thereby giving a false high reading of oil in the water.

The groundwater leaking into underground storage systems (caverns) should be pumped out and led to the waste water treatment system of the refinery. The amount of the water depends on the solidity of the rock and how carefully the fractures in the rock are sealed by injection of concrete [256, Lameranta, 2000]. The quality of waste water depends on the product (or crude) wich is stored in the cavern. Typically the waste water contains hydrocarbons as emulsion and water soluble components of stored liquid. Some examples of waste water generated by cavern storage is given in the next table:

Cavern	Volume of the cavern (m^3)	Product	Seeping water removed (m^3/yr)	Amout of hydrocarbons discharged after oil separation (kg/yr)
A	40000	light fuel oil	22300	49
B	2x75000	heavy fuel oil	25800	104
C	50000	light fuel oil	36900	40
D	105000	light condensate	140	n.a.
E	52000	propane/butane	80	n.a.
F	150000	propane/butane	150	n.a.
G	430000	heavy fuel oil	50000	76
H	100000	car fuel (diesel)	5000	n.a.
I	100000	car fuel (petrol)	3000	n.a.

Table 3.70: Examples of waste water generated by caverns
Source: [256, Lameranta, 2000]

Wastes and soil contamination

The primary subsurface (soil and groundwater) contamination threats posed by above-ground storage tanks include the disposal of sludges from the bottoms of the tanks during periodic cleaning of tanks for inspections, loss of product from the tanks during operations such as tank water drainage, and product leakage to the ground caused by tank or piping failures or overfilling accidents. Spills may result contamination soil from handling processes, especially in loading processes, mainly due to human errors. Storage tank bottom sludge contains iron rust, clay, sand, water, emulsified oil and wax, phenols and metals (lead for leaded gasoline storage tanks). Table 3.71 shows some analyses of sludges taken from the sewerage system around tank storage facilities. The analyses are unique to that site and are reproduced to show what may occur.

SPECIES	TANK FIELD SEWERS (two different sources)		GASOLINE TANK FIELD SEWERS	DISTILLATE TANK FIELD SEWERS
	1	2		
Solids	92.7 %	91.2 %	81 %	97.0 %
Oil	7.3 %	8.8 %	19 %	3.0 %
Carbon	26.9 %	27.1 %	44.9 %	58 %
Hydrogen	10.2 %	15.1 %	7.8 %	7.3 %
Nitrogen	1.2 %	< 0.6 %*	0.4 %	0.6 %
Sulphur	64441	70034	58222	13514
Iron	25000.0	174024.0	62222.0	105326.0
Magnesium	9317.0	2695.0	4430.0	1331.0
Sulphide	8327.0	3624.8	4325.9	4238.9
Aluminium	4193.0	3969.0	8148.0	3180.0
Nitrate	2290.4	10.8	91.9	8.9
Sodium	1180.0	772.0	770.0	445.0
Sulphate	1037.3	165.5	19.3	39.7
Xylene	746.9	< 4.2*	1121.5	4.0
Toluene	478.3	< 4.2*	794.1	4.0
Ethylbenzene	158.4	< 4.2*	106.8	4.0
Nephthalene	130.4	27.6	-	25.8
Benzene	80.7	< 4.2*	35.6	4.0
Phenan	71.4	129.5	-	69.6
Nickel	68.3	106.1	500.7	190.8
Lead	55.9	492.4	308.1	234.5
Chromium	35.4	70.5	154.1	81.5
Pyrene	30.0	< 105.0*	-	39.0
Carbonate	29	2.0	0.3	0.3
Vanadium	27.0	72.0	49.0	25.0
Antimony	19.0	42.0	15.0	20.0
Phenol	18.6	< 105.1*	-	39.3
Fluorine	15.5	< 105.1*	-	39.3
Benzo(A)Pyrene	< 7.8**	< 105.1*	-	39.3
Selenium	7.0	< 4.0*	4.3	5.0
Arsenic	5.0	16.1	14.5	15.9
Mercury	4.0	1.6	9.5	0.2
Cyanide	0.6	1.0	0.5	0.7
Calcium	< 0.3*	39261.0	13185.0	11725.0

* Below Detection Limit Shown
** Estimated Value Below Detection Limit
Note: Figures quoted on a moisture free basis, all units mg/kg unless otherwise stated. Figures do not sum to 100 % because of double counting.

Table 3.71: Composition of the sludge taken from four different sewer systems close to the storage tanks
Source: [80, March Consulting Group, 1991]

3.22 Visbreaking

Consumptions
The following represents typical utility consumptions for a visbreaker:

Fuel (MJ/t)	400 - 800
Electricity (kWh/t)	10 - 15
Steam consumed (kg/t)	5 - 30
Cooling water (m^3/t, ΔT=10°C)	2 - 10
Note: the power consumption given is for "furnace" cracking.	

Table 3.72: Utility consumptions fo a visbreaker
Sources: [118, VROM, 1999], [261, Canales, 2000]

For visbreaking, fuel consumption accounts for about 80 % of the operating costs with a net fuel consumption of 1 - 1.5 %w/w on feed. Fuel requirements for soaker visbreaking are about 30 - 35 % lower.

Emissions
Air Emissions
Air emissions from visbreaking include emissions from the combustion of fuels in the process heaters (discussed in Section 3.10), vents and fugitive emissions. A sour water stream is generated in the fractionator. The gas produced contains H_2S and should be further treated. Hydrogen sulphide and mercaptans are released from the sour water stream from reflux condensers. Hydrocarbons are released from pressure reliefs on reflux drums and vessels, storage and handling operations, spillages and discharges of waste/water. Particulate emissions occur during furnace decoking and cleaning operations about twice a year.

The next table shows the air emissions from visbreaking processes in two European refineries.

Installation	Fuel consumption (GWh/yr)	Throughput (Mt/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates
OMV Schwechat	87.9	1.02 Atm. Res.	mg/m^3	47	183	5		1
			t/yr	4.2	16.5	0.5	17057	0.1
			kg/t feed	0.004	0.016	00	16.7	00
Mider refinery	306.6	1.20	mg/m^3	35	100	100		5
			t/yr	13	50.6	1.4	59480	0.3
			kg/t feed	0.011	0.042	0.001	50	0
For the emissions from the Mider refinery, only limit values are given. Loads and specific emissions were calculated. Data are related to yearly average, 3 % O_2, dry conditions.								

Table 3.73: Example of air emissions generated by visbreaking processes
Source: [247, UBA Austria, 1998]

Process waste water
The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate into three phases, a hydrocarbon gas stream, a hydrocarbon liquid stream and a sour water stream. The sour water stream should be sent to the sour water stripper for purification.

The flow of waste water generated in the visbreaking process from the sour water drain is around 56 litres per tonne of feedstock. It represents between 1 and 3 percent volume on feed intake. Table 3.74 shows the range of composition of the visbreaker waste water.

Substance or parameter	Concentration (mg/l)
PH	high
Free oil	50 - 100
COD	500 - 2000
H_2S	10 - 200
NH_3 (N-Kj)	15 - 50
Phenols	5 - 30
HCN	10 - 300

Table 3.74: Composition of the waste water produced in visbreaking

Solid wastes generated

The waste generated in visbreaking comes from the cleaning and turnaround of the process. It is generated discontinuously at a rate of 20 to 25 tonnes per year for a 5 million tonnes per year refinery. It contains between 0 and 30 % of oil/sludge.

Next sections cover the emissions arising from refinery processes that are used for the treatment of waste gas, waste water and solid waste. Those techniques are described in Chapter 4 (Sections 4.23 to 4.25). The main objective of those processes is to reduce the concentration of pollutants in the effluents. Obviously the loads and concentrations of pollutants in those streams will be reduced by those processes, but some pollutants will remain in the streams and other may be generated. That is the purpose of the following next three sections. Emissions from the refinery as a whole are included in Section 3.1.

3.23 Emissions from waste gas treatment techniques

Under this section, end-of-pipe or abatement techniques of CO, CO_2, NO_x, particulates, sulphur compounds, VOC, combined techniques for the abatement of air pollutants, odour and noise are included.

Sour gas treatments

The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. The area of the amine treating unit poses health risks because of the presence of H_2S, possibly by inadvertent leakages.

Sulphur recovery units(SRU)

In 1995, the average percentage of sulphur recovered in the SRU represented 42.6 of the sulphur entering the refinery with the crude oil. All that sulphur is recovered in those units socalled sulphur recovery units, extensively described in Section 4.23.5. They represent around the 10% of the SO_2 emissions from refineries (see Section 3.1.2). The fuel gas from SRU represent around 1.5 % of the total flue gas emitted by a refinery. The sulphur recovery of SRUs is in the range of 95 to 99.99 %. SO_2 emissions ranges from 40 – 25000 mg/Nm^3. Emissions from those units typically contain some H_2S, SO_x and NO_x. They also generate process waste water that contains H_2S, NH_3, amines and Stretford solution. Residual wastes are spent catalysts. The next table shows two examples of emissions from European refineries.

Installation	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates
SRU			mg/m^3	700[1)]	70	100		20
OMV	27.2	63900	t/yr	92.9	9.3	13.3	5268	2.7
Schwechat		Sulphur	kg/t feed	1.5	0.15	0.21	82.4	0.042
SRU			mg/m^3	4322	200	100		50
Mider	131.4	90000	t/yr	1125.6	52.1	26.0	25492	13
Refinery		Sulphur	kg/t feed	12.5	0.58	0.29	283.2	0.15

(1) Raw gas was treated in a flue gas desulphurisation (Wellman Lord)
Data are related to yearly average, 3 % O_2, dry conditions.
For the emissions from the Mider refinery, only limit values are given. Loads and specific emissions were calculated.

Table 3.75: Examples of air emissions generated by sulphur recovery units
Source: [247, UBA Austria, 1998]

Flares

Consumptions

The main utilities that flare systems will use are refinery fuel gas or nitrogen for purging the flare headers, fuel gas for the pilot burners and steam for heating purposes. However, the consumption of these utilities is very low under normal operating conditions.

Emissions

They emit CO, CO_2, SO_2 and NO_x. The composition depends on the system being relieved and combustion efficiency at the flare tip. Flares are a very important point source of refinery emissions. Some plants still use older, less-efficient waste gas flares. Because these flares

usually burn at temperatures lower than necessary for complete combustion, larger emissions of hydrocarbons and particulate, as well as H_2S, can occur. No data are available to estimate the magnitude of these emissions. Emissions of VOC and soot are also present and they depend on the system being relieved and combustion efficiency at the flare tip.

3.24 Emissions from waste water treatment techniques

Large volumes of waste water are produced by the petroleum refining industry. Waste water treatment plants are advanced environmental protection systems for the control of surface water pollution. Waste water treatment plants are a significant source of refinery air emissions, water emissions and solid wastes. Sources of contamination of water with hydrocarbons are desalters (40 %), storage tanks (20 %), slop systems (15 %) and other processes (25 %).

Process effluent volume can be compared to the volumes of process effluent discharged (excluding once through cooling water). Although related, the values are not identical given that there are other sources of water to the effluent system including rainwater on plant surfaces, water separated from crude, ballast water etc. On the other hand, some water will evaporate, be used in chemical reactions, etc. Figures for effluent for 63 European refineries are (all in annual averages):

▪ Annual average effluent volume	3.6	million m^3/year
▪ Range	0.07 to 21	million m^3/year
▪ Average effluent per tonne throughput	0.53	m^3/tonne throughput
▪ Range	0.09 to 1.6	m^3/tonne throughput

Emissions

Air emissions

The air emissions from waste water treatment plants stem from evaporation (hydrocarbons, benzene, H_2S, NH_3, mercaptans) from the numerous tanks, ponds and sewerage system drains that exposes its surfaces into air. The sewerage system and the waste water treatment in a refinery may be sources of odour nuisance, particularly from open drains and from oil separators. VOCs are also emitted during air stripping in flotation units and in the biotreater. The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [117, VDI, 2000]:

- 20 g/m^2 per hour for open oil separator
- 2 g/m^2 per hour for covered oil separator
- 2 g/m^2 per hour for flotation
- 0.2 g/m^2 per hour for biological treatments

Emissions to water

Potential releases into water consist of the residual substances contained in the effluent after treatment. Depending on the nature of the refinery and the treatment efficiency, these include hydrocarbons (dissolved and suspended), organic compounds (notably phenols), sulphur compounds (notably sulphides), ammonia/ammoniacal compounds and their derivatives after treatment. Traces of heavy metals are also likely to be present, arising from the desalting of crude oil feedstock and from caustic soda if this contains trace contaminants, notably mercury. More information in this subject is included in Section 3.1.3.

Solid wastes generated

Solid wastes are generated in the form of sludges from a number of the treatment units. Primary treatments generate API separator sludge (phenols, metals and up to 10 % oil), chemical precipitation sludge (chemical coagulants, oil), DAF floats (up to 30 % oil), biological sludges (metals, < 0.5 % oil, suspended solids) and spent lime. Secondary treatment generates biomass waste which is typically treated anaerobically and then dewatered. Flotation units and biotreaters generate the largest quantities of sludges in the waste water treatment plants. DAF units produce significant quantities of sludges. The limited information reported in the survey (for three units [115, CONCAWE, 1999]) indicated an annual sludge production of about 2400 tonnes per year for a throughput of 600 m^3/h. The induced air flotation generates 600 tonnes per

year with a unit operating at 600 m^3/h. Table 3.76 shows the composition of the different sludges generated in the waste water treatment plants.

Species	API Separator	Activated Sludge	Settling Basin Plant
Solids	90.4 %	94.3 %	99.7 %
Oil	9.6 %	5.7 %	0.3 %
Carbon	25.8 %	13.1 %	1.7 %
Hydrogen	13.1 %	51.8 %	6.3 %
Nitrogen	0.6 %*	1.7 %	0.5 %
Sulphur	40733	9479.0	4214.0
Carbonate	0.3 %	0.2 %	0.1 %
Iron	48269.0	10900.0	7131.0
Aluminium	43177.0	2322.0	4878.0
Calcium	11609.0	4692.0	8104.0
Sulphide	6180.2	2165.9	103.7
Magnesium	4878.0	1351.0	1767.0
Sodium	1711.0	3981.0	3971.0
Xylene	469.5	9.5	3.2
Naphthalene	288.2	46.9	16.0
Lead	279.0	49.3	15.2
Phenan	265.0	46.9	16.0
Nickel	252.5	37.9	8.8
Nitrate	228.1	2066.4	194.5
Toluene	138.5	9.5	32
Flyrene	134.4	47	16.0
Vanadium	99.0	18.0	24.0
Ethylbenzene	82.5	9.5	3.2
Chromium	80.0	8.1	11.2
Fluorine	59.1	46.9	16.0
Antimony	49.0	14.0	5.0
Benzo(A)Pyrene	42.6	46.9	16.0
Phenol	40.3	46.9	16.0
Selenium	35.4	26.0	9.0
Benzene	13.2	9.5	3.2
Sulphate	12.2	2767.8	285.3
Arsenic	6.5	15.2	5.2
Mercury	3.0	1.0	0.0
Cyanide	1.0	7.0	0.7

* Below Detection Limit Shown
Figures do not sum to 100 % because of double counting.
Figures quoted on a moisture-free basis, all units mg/kg unless otherwise stated.

Table 3.76: Examples of analysis of refinery sludges
Source: [80, March Consulting Group, 1991]

3.25 Waste generation

An important issue when considering refinery wastes is that there are still many differing definitions between countries, which makes comparisons of waste difficult.

The amount of sludge generated depends on the types of processes and the availability of incineration. As a common figure, the generation rate of solid waste and sludges is normally less than 0.5 % of crude processed, but in some refineries is less than 0.3 %. Annual sludge generation was 1250 kt per year (in 1993), some 0.2 % of refinery intake.

In 1993, CONCAWE carried out a survey of waste in Western European refineries [82, CONCAWE, 1995]. In this survey 89 refineries reported their sludge production from all sources as one million tonnes. That means an average of 11000 t per year per refinery. This figure represents a 0.20 % of the crude oil processed by those refineries. However, a variation range from 2.5 % to less than 0.02 % was found in European refineries, with the value being independent of the type of refinery. From that million tonnes of waste, 45 % was sludge, 20 % other refining wastes and the rest non-refining wastes. *Sludges* come from stabilisation processes (4.7 % of the total sludge generated after treatments), waste water sludges (39.8 %) and sludges with no treatment (55.5 %). The total amount of identified *other refining wastes* which are specific to the refining process (e.g. spent catalysts, tank scales, contaminated soils, etc.) produced in 1993 by the 89 European refineries reporting was 201983 tonnes (i.e. 0.04 % w/w of the total refinery throughput). Data provided by 16 EU+ refineries show that the specific production of waste ranges from 133 to 4200 t/Mt of crude. Next table shows an example of the waste production of a refinery.

	Non-hazardous waste 1997 (t)	Hazardous waste 1997 (t)	Sum 1997 (t)
Landfill	7362	1109	8471
Material recycling and thermal treatment	202	2401	2603
Biological treatment	1003	57	1060
Chem./phys. treatment	21	13	34
Total	8588	3580	12168
Note: Waste includes waste generated by storage tanks			

Table 3.77: Waste generation of an European refinery
Source: [250, Winter, 2000]

Spent catalyst
Hydroprocessing requires the use of catalysts to remove impurities and to convert the oil into more useful products. The catalysts used consist mainly of oxides of nickel, cobalt and molybdenum on an alumina carrier. During hydroprocessing operations the catalysts are loaded with sulphur, vanadium and coke. The porosity of the catalysts decreases and their activity is reduced, which eventually requires replacement of the catalyst in the reactors. Consequently, the catalysts become spent and must be replaced.

Co/Mo catalysts from hydrodesulphurisation, hydrocracking, hydrotreating. For a 5 Mt/yr refinery spent catalyst amounts can vary from 50 - 200 t/yr.

Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. A 5 Mt/yr refinery generates typically 20 - 100 t/yr spent Ni/Mo catalyst.

Ni/W catalysts are used in lube oil hydrofinishing. This category experiences limitations to dispose off in view of the high Tungsten content (24 % w/w). A 50000 t/yr Lube oil plant can generate 50 t/yr of this catalyst waste.

FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries (world production about 0.5 Mt/yr). A 1 Mt/yr FCC unit generates 400 - 500 t/yr predominantly as FCC fines if an ESP is installed. For a RCC this amount can be a factor 5 - 10 higher, depending on the feed as spent catalyst is withdrawn from the regenerator.

Reformer and Isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved. Typical average amounts involve 20 - 25 t/yr for a 5 Mt/yr refinery. If necessary guard beds of HDS catalysts are used for protection and extension of the life-time of the expensive catalysts.

Hydrodemetallisation catalysts typically have high vanadium contents (10 - 20 %) and are currently alumina based (used to be silica). The annual amount for regeneration is in the order of 500 - 1000 t/yr for Hycon (Shell Pernis NL) dependent on the feed quality.

Zn containing beds from H_2 plants are typically recycled to the Zn-industry where ZnS ores are processed. Amounts are some 50 t/yr.

In Hydrodesulphurisation, Hydrotreating and Hydrocracking the world catalyst production (and thus also the generation of spent catalysts) has grown in the last 10 years considerably and is estimated at 100 kt/yr (1998). Current regeneration capacity is estimated at 125 kt/yr. It is estimated that 5 - 10 % of this category of spent catalysts is still being landfilled.

Process	S	C	Mo	V	Ni	Co	Al	Other
FCC, RCC	< 1	< 1		4 - 8000 *	2 - 3000 *		30	
Cat.Reforming & Isomerisation							30	0.5 Pt, Pa, Rh
Hydro processing	6 - 16	10 - 30	4 - 8	2 - 12	1 - 2	1 - 2	20 - 30	
Claus plant	5	5	4 - 8		2 - 3		20 - 30	
Hydrofinish	5	1 - 2			2 - 4		30	24 W
Hydrogen	5 - 15						0	30 Zn
Hydrodemetal.	5 - 15	10 - 30		10 - 20	2 - 5		30	
(*: ppm)								

Table 3.78: Composition of spent catalysts from various sources in % w/w

3.26 Monitoring

There is an IPPC BREF and an expanding series of literature (e.g. HMIP Technical Guidance Notes) on monitoring, containing information on theory and methodology, and providing technical information on monitoring techniques. It should be considered that the requirements and frequency of sampling, analysis and type of monitoring requirements are site and/or process specific, influenced by consideration of the anticipated volume and composition of the waste streams and normally are included in the permits. Monitoring BREF includes guidances to permit writters as compliance assessment and environmental reporting. That document also encorage the comparability and reliability of monitoring data across Europe.

This section aims to give recommendations on the scope and frequency (continuously or discontinuously) of monitoring streams in a refinery. Monitoring should be undertaken during commissioning, start-up, normal operation, and shutdown unless it is agreed that it would be inappropriate to do so.

The monitoring system should allow adequate processing and emission control. Some elements of a monitoring system could include:

- continuous monitoring of pollutants for high volume flows with a high variability in pollutant concentrations
- periodic monitoring or the use of emission relevant parameters for flows with a low variability
- regular calibrating of measurement equipment
- periodic verification of measurement by simultaneous comparative measurements.

In order to have a good idea of the emissions generated by an installation (e.g. a refinery), the emissions need to be quantified. This will give to the refinery and permit writter the possibility to know where the actions to reduce a certain pollutant may be more economical. Typically higher emissions at high concentrations are more economic to be abate that lower emissions at low concentrations. As consequence, a quantification of the emissions for each single refinery is the first starting point in any environmental assessment. This quantification may contain a full mass balance also considering other outpus (e.g. products).

Monitoring air emissions

In many refineries the bubble concept is applied for some air pollutants. The concept is to consider the refinery as a whole and to sum up concentrations and volumes of all the emission sources. From this is calculated the average concentration of the pollutants regardless of the source or stack. This type of concept is applied to sulphur dioxide and other air pollutants in some European countries and in the EU Large Combustion Plant Directive. More information can be found in 4.15.2.

SO_2, NO_x, particulate matter, and CO are typically monitored in continuous (on-line or predictive) in the refineries. Records of the volumes are also required for the calculation of the load (tonnes of pollutant per year) or for the application of the bubble concept. Following table shows the locations where the main air pollutants are typically continuous monitored in a refinery.

Parameter	Location where normally is measured
Particulate matter	Combustion processes burning fuel oil
	FCCU regenerators
	Coking processes and petroleum coke calciners and coolers
	Gasification units
	Catalyst regeneration (e.g. reforming)
Sulphur dioxide	FCCU regenerators
	Sulphur recovery units (i.e. from tail gas incinerators)
	Incinerators or furnaces used to burn sour gas or liquid fuels
	Bitumen production units
	Gasification units
	Coking processes
Oxides of nitrogen	Combustion processes
	FCCU regenerators
	Gasification units
	Coking processes
Carbon monoxide	FCCU regenerators (for partial combustion type units if CO release is significant).
	Combustion processes

Next information gives some good monitoring practices that have been found in European refineries.

Sulphur monitoring
It can be expected from the operators to compute site sulphur balances over appropriate time periods as a part of monitoring their operations; the time period may vary with the circumstances (e.g. how often feedstocks change) but could typically be quarterly. In the case of SO_x, the amount of SO_x emitted by combustion processes may be calculated from the analysis of the fuel being burnt.

Gases coming from combustion processes
Wherever a combustion process (other than flaring) is used for the destruction of hydrogen sulphide or hydrocarbons, its effectiveness can be demonstrated indirectly by continuously monitoring the temperature and oxygen content of the exhaust gas. Visual and olfactory assessments of releases from incinerators, flares, furnaces and other sources liable to cause a nuisance emission can be made when appropriate, particularly during upset/start-up/shut-down conditions.

Additionally, flare systems can be equipped with adequate monitoring and control systems necessary to operate smokelessly and should be observed at all times under non emergency conditions. Such systems can include flow measurement, for which proven non-intrusive systems at the flare base are available, with automatic steam control, luminosity measurement with automatic steam control, remote visual observation using colour TV monitors in relevant plant control rooms with access to steam control, pilot flame detection, etc.

Gaseous releases from gas turbines used for electrical generation or gas compression are typically also monitored.

In order to relate emission concentrations to mass releases, it will be necessary to measure or otherwise determine the gas flow. Additionally, in order to relate measurements to reference conditions, temperature will need to be determined. Determination of oxygen or water vapour content may also be required.

VOC monitoring
VOC emissions come mainly from fugitive emissions. The site may be equipped to monitor all process vents and possible sources of fugitive losses. A Leak Detection and Repair (LDAR) programme can be implemented (see Section 4.23.6.1) in order to prevent those. An assessment of the total hydrocarbon emissions from the site on a regular basis can be made. Records can be kept of the individual contributions to each total.

VOC emissions can be estimated by USAEPA Method 21 (emission factors for different type of equipment) or by mass balance (feedstock – products). Perhaps one should add that another way of monitoring HC emissions from all sources is through the mass balance between feed stock and products.Other methods have been developed and proven in recent years for the monitoring of VOC emissions as well as locating sources of VOC emissions, typically using laser absorption techniques (DIAL) of considerable sophistication. Mobile versions are available which can be used to plot pollutant concentration plumes and calculate pollutant flux, including three-dimensional resolution. Whilst having recognised limitations, they have been used successfully in the oil and gas industries. In most of this monitoring campaigns the measurements have been divided into four areas: Process area, product tank farm, crude oil tank farm and water treatment plant. DIAL method has been used in a number of refineries and in many cases, the results appear to be higher than those derived from the API estimations. However, in these trials, the sampling period was very short. In the only trial where a long-term survey was conducted, the results gave reasonable agreement with the API estimations [229, Smithers, 1995]. Next paragraph gives an example of monitoring of VOC within a refinery as well as the discrepancies that they have found using estimation method and DIAL measurement.

Before the measurements, it was estimated a VOC emissions of about 200 tonnes per year at a certain European refinery. The DIAL measurements and annualisation of the results suggested a yearly emission exceeding 1000 tonnes. Especially emissions from tanks were higher than expected. In all cases, emissions estimates using API methods gave lower emissions than estimates based on the DIAL monitoring. In some cases, the discrepancies are very large. By using the method for estimating fugitive emissions proposed by USAEPA [244, USAEPA, 1992] *the emissions from the process area 1Mtonnes per year refinery have been estimated to 125 tonnes per year. Extrapolations of the DIAL measurements to a yearly emission give emissions of 500 - 600 tonnes per year* [107, Janson, 1999]. *For the total emission from the refinery, the use of estimation methods suggests that the emissions are 600 - 1100 tonnes per year. Extrapolations of DIAL measurements indicate a yearly emission of 1600 - 2600 tonnes for medium refineries. During the same exercise of measurements it was also found that the dominating fraction of fugitive emissions was alkanes within interval* C_8 - C_{10}. *Aromatics contributed to about 9 - 15 % of the total emission* [107, Janson, 1999]. *However, it is important to notice that the composition of the vapour will depend heavily on refinery configuration and what happens to be leaking at the time of the measurement of the VOC.*

Monitoring releases to water
Continuous monitoring and flow proportional sampling for releases to water are always preferable but the use of a fixed interval or time proportional sampler for low flow rates (less than 1 litter per second) may be acceptable.

Monitoring of process effluents released to controlled waters and sewers will commonly be made for the following: flow rate, pH, temperature, TOC (surrogate for COD/BOD). Samples are also being monitored for appropriate other parameters such as COD, BOD, hydrocarbon oil, ammoniacal and total nitrogen, suspended solids, phenols, sulphides, dissolved oxygen, phosphates, nitrates, nitrites, metals (typically Cd, Hg, Cr, Ni, Zn, Cu, As). The periodicity can be typically daily, weekly or monthly depending on risk assessment and on local circumstances.

One problem about water discharge from refineries is analysis and especially analysis of oil. There are a number of different methods (e.g. IR one wave lengths, IR two wave lengths, gravimetric) which give completely different results. Another problem is the toxic substances used in the COD analysis.

Losses of oil through leaks can also be minimised through continuous monitoring of the *cooling water* system. At its simplest, this comprises monitoring of the cooling water separators for oil build-up. If this is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak. A further refinement is to install oil in water monitors at various points in the cooling water system. This allows leaks to be detected rapidly and corrective action taken. For this procedure to be effective, sparing of critical heat exchangers will be required.

In case of a once-through system the cooling fluid outlet system may be divided into *a suspect system*, where the process pressure is higher than the cooling system pressure and a *clean system*, where the cooling system pressure is higher than the process pressure. The suspect system needs to be monitored for contamination.

Monitoring solid wastes

A record of the quantity and composition (including prescribed substances) of residues generated is typically done. In addition the operator typically have written procedures which ensure that releases are handled, treated and disposed of in an approved manner, and specify how the accumulation and storage of waste are controlled. The frequency of analysis of the waste is site and/or process specific.

Soil Monitoring

Quoted costs for installation and operation of monitoring wells was highly variable ranging from 25000 EUR for 100 wells (250 EUR per well) to 140000 EUR for 50 boreholes (2800 EUR per well) but with a minimal operating cost. Costs of groundwater monitoring systems were quoted as 1400 EUR per year for 18 wells (78 EUR per well) in one case to an average of 45000 EUR (including 7000 EUR for analysis) for three surveys at intervals of some years.

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter describes in detail the techniques that are considered to be most relevant for determining BAT. This chapter should be seen as the main background information for the determination of best available techniques in the refinery sector (Chapter 5). Techniques that are generally seen as obsolescent are not included. Moreover, it does not include all the techniques applied in the refinery sector and described in Chapter 2. Only techniques with good environmental performance are included here.

Production, prevention, control, minimisation and re-cycling procedures/techniques are considered in this chapter. This can be done in many ways, such as using production techniques that pollute less than others, changing the operating conditions, reducing material inputs, re-engineering processes to re-use by-products, improving management practices or employing substitution of toxic chemicals. This chapter provides information on some both general and specific pollution prevention and control advances that have been implemented within industry in general and in the refinery industry in particular.

As in previous Chapters 2 and 3, each section of this chapter deals with a refinery process or activity and contains the process and abatement techniques worth considered in the determination of BAT. If different techniques may be applicable for one process/activity, they are discussed there. Sections from 4.2 to 4.22 in this chapter have been structured internally in the same way. Each of those sections contain first the pollution prevention techniques applicable in the process/activity section referred to and secondly the end-of-pipe techniques that may be applicable to reduce the emissions coming from the process/activity. Those end-of-pipe techniques are grouped in media/pollutant bases to clarify the sequence of techniques applicable as, in some cases, the number of EOP techniques that may be use is quite extensive.

At the end of this chapter, three sections appear containing the end-of-pipe (EOP) techniques applied to waste gas, waste water and waste management. Those sections contain the descriptions of the EOP techniques that may be applicable to more than a refinery process/activity as well as some other EOP processes. Consequently, the descriptions of those EOP techniques that may appear in this chapter are included in Sections 4.23, 4.24 and 4.25 and not in the activities/process sections.

Each technique (both preventive (including process techniques) and control) is well documented and includes information on consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Each technique in this chapter is analysed in the same way in order to give a good background for the determination of BAT for the refinery sector. That determination is done in the next chapter. Table 4.1 shows the structure of the information for each technique included in this chapter.

When possible, this chapter provides information from real activities that can be, or are being, implemented by this sector, including associated costs. When possible, information provided gives the context in which the technique can be used effectively.

Name of the type of information	Type of information included
Description	Technical description of the technique
Achieved environmental benefits	Main environmental impact(s) to be addressed by the technique (process or abatement) including emission values (normally a range) achieved and efficiency performance. Environmental benefits of the technique in comparison with others.
Cross-media effects	Any side-effects and disadvantages to other media caused by implementation. Environmental problems of the technique in comparison with others and how to prevent or solve them.
Operational data	Performance data on emissions/wastes and consumption (raw materials, water and energy). Any other useful information on how to operate, maintain and control the technique including safety aspects and operability constraints of the technique.
Applicability	Consideration of plant age (new or existing), plant size (large or small) and factors involved in retrofitting (e.g. space availability).
Economics	Information on costs (investment and operation) and any savings (e.g. reduced raw material consumption, waste charges) related to the capacity of the technique. Values in currencies different than EUR have been converted according to EU conversion factors to EUR of 1999. Annex IV provides some information on cost-effectiveness.
Driving force for implementation	Local conditions or requirements which lead to implementation. Information on reasons other than environmental ones for implementation (e.g. improvement in product quality, increased yield).
Example plants	Reference of the number of plants containing the technique in Europe and in the world. If such technique has not been yet applied in the sector or in Europe, brief explanation of why.
Reference literature	Literature for more detailed information on the technique.

Table 4.1: Information contained in the description of each technique included in Chapter 4

4.1 General overview of activities considered in this chapter

The following table gives a general picture of the number of techniques considered in the document and in each activity, split into four categories. Numbers included in this table are only orientative and they are not the simple counting of the subsections that appear in each sections. As it will be seen some subsections include more than one technique. This table only want to give an overview of the number of techniques considered in each section of the document. That number can be used as a first indicator of what activities/processes are more important from the environmental point of view (e.g. energy system, storage and handling, integrated management systems and catalytic cracking, coking). Following the same rationale, it is also easy to see that air emissions are the ones with more techniques.

		Techniques applied to				
Chapter section	**Activity/Process**	**production and prevention**	**gases and waste gas**	**waste water**	**solid waste**	**TOTAL**
2	Alkylation	3	0	0	0	3
3	Base oil production	14	4	2	1	21
4	Bitumen production	2	5	1	2	10
5	Catalytic cracking	17	13	2	5	37
6	Catalytic reforming	3	3	0	0	6
7	Coking processes	9	19	8	3	39
8	Cooling	3	-	-	-	3
9	Desalting	13	0	4	1	18
10	Energy system	56	22	2	0	80
11	Etherification	1	0	1	1	3
12	Gas separation processes	3	2	0	0	5
13	Hydrogen-consuming processes	8	0	0	2	10
14	Hydrogen production	6	0	0	0	6
15	Integrated refinery management	33	0	24	6	63
16	Isomerisation	3	0	0	0	3
17	Natural gas plants	0	12	5	3	20
18	Polymerisation	1	0	0	2	3
19	Primary distillation units	3	2	3	3	11
20	Product treatments	5	2	4	0	11
21	Storage and handling of refinery materials	21	19	2	12	54
22	Visbreaking	3	1	1	1	6
23	Waste gas treatments	-	76	-	1	77
24	Waste water treatments	-	-	41	-	41
25	Waste management	-	-	-	58	58
	TOTAL	207	180	100	101	588

4.2 Alkylation

The techniques considered in the determination of BAT for the alkylation process are the following:

4.2.1 Hydrofluoric acid alkylation process

Description
A brief description of the process can be found in Section 2.2.

Achieved environmental benefits
The main advantages of the HF-alkylation process in comparison with the sulphuric acid process are the regeneration of HF, which minimises waste formation and disposal, and the lower acid-catalyst consumption as well as the minor consumption of energy and cooling.

Cross-media effects
Effluent gases: Scrubber using alkaline solution (NaOH or KOH) is necessary to remove HF from the incondensable gas stream. The acid relief neutraliser is operated so as to minimise the hydrogen fluoride content of the incondensable gas stream. Emissions levels of <1mg HF/Nm^3 can be achieved. The vent gas should pass to flare not to the refinery fuel gas system; a dedicated flare/stack is normally retained for this. Fugitive emissions are also generated by this process.

HF is a very dangerous compound because of its severe corrosive nature and burning effects of both liquid and fumes to skin, eyes and mucous membranes. Consequently, storage and handling it should comply with all safety rules.

KF (or NaF) is formed during the neutralisation process. The spent solution is stored and then requires regeneration with lime (or alumina). The regenerated KOH (or NaOH) is recycled. CaF_2 is regularly cleaned out and disposed of, usually to a landfill. If alumina is used instead of lime as the neutralising agent, then, recovery of the aluminium is possible by the aluminium industry. Fumes can originate in the unit's neutralising basin. To prevent the discharge of these odorous gases to the surroundings, the neutralising basins are tightly covered and equipped with a gas scrubber to remove any offensive agent.

Water: HF alkylation effluents are a potential cause of acid excursions in refinery effluents and a high standard of control should be exercised on the neutralisation treatment system, e.g. on-line pH monitoring. The effluent containing HF acid can be treated with lime (CaO-$Ca(OH)_2$), $AlCl_3$ or $CaCl_2$ or it can be neutralised indirectly in a KOH system to produce the desired CaF_2 or AlF_3 (insolubles) which is separated in a settlement basin. The supernatant liquor flows to the water treatment process. KOH may be regenerated for re-use. After this treatment, the supernadant contains still 10 – 40 ppm F and some hydrocarbons and is directed to the WWTP. KOH may be regenerated from the aqueous solution for re-use.

Wastes: The HF process also yields tars (polymeric material) but these are essentially free from HF. HF-containing tars are neutralised (with lime or alumina) and disposed of by incineration or blended as a fuel-oil component in small amounts because its pronounced odours. However, technology and special operating techniques such as internal acid regeneration have virtually eliminated this liquid-waste stream.

Bad operation of the system (excessively cold acid, improper acid settler level, low reactor pressure, excessive acid recycle rate, low i-butane or acid concentration, high reactor temperature and improper mixing) increases the amount of waste generated.

Operational data
The potentially corrosive and toxic properties of HF require special engineering design and special construction materials, advanced process controls and stringent safety, personal protection and maintenance requirements. These precautions include:

a) special seals on acid-containing equipment such as pumps and valve stems
b) special safety clothing which must be worn by personnel entering an acid area
c) extensive operator training
d) special facilities (e.g. sprinkler systems, acid-inventory reduction, HF-detection systems, isolation valves, rapid acid transfer systems) should be included in the design of this kind of system to mitigate the effects of an accidental emission of HF vapour clouds. For leak detection, HF sensitive colours on pipes and flanges are suitable as alternative to continuous air analysers and video control. The potential reduction of airborne HF acid has also been demonstrated by the addition of additives. Special care should be taken during maintenance and cleaning of the plant, e.g. for major shut-downs not to release odours from the drainage system and/or ponds.

Same developments (such as additives) have been already tested in order to lower the vapour pressure and to minimise the amount of HF released to the atmosphere in case of accident. On the downside of this is that handling and recyling the additive add to the complexity of the process.

Applicability
Fully applicable.

Economics
The next table shows the investment and production cost summary for HF alkylation. Disposal costs are not included.

	Estimated erected cost (3rd quarter 1995)	**New HF plant (1999)**
Capacity (kt alkylate/yr)	348	160
Investment cost (EUR million)	25.6	35
Operating cost (EUR/tonne alkylate)		
Labour	0.016	
Utilities	0.066	
Chemical consumption, laboratory allowance, maintenance, taxes and insurance	0.056	
Total direct operating costs	0.138	

Driving force for implementation
Alkylation plant is a refinery process used to increase the gasoline octane.

Example plants
Common technique.

Reference literature
[166, Meyers, 1997], [113, Noyes, 1993], [261, Canales, 2000], [330, Hommeltoft, 2000], [268, TWG, 2001]

4.2.2 Sulphuric acid alkylation process

Description
A description of the process can be found in Section 2.2.

Achieved environmental benefits

A sulphuric acid plant is an alternative process for alkylation, but has the drawback of more spent acid to be disposed of or recycled outside. Efficiency of the process is lower than the HF alkylation and more cooling is needed in this process.

Cross-media effects

Technologies using suphuric acid as catalyst produce very large quantities of spent acid (sulphuric and sulphonic acids) that has to be regenerated. The transport of spent and fresh acid to and from the sulphuric acid regeneration has give rise to some concern and increased the pressure on refiners to establish sulphuric acid regeneration plants near the alkylation unit. In some cases this transport to/from the regeneration facility is by pipeline. However, no major new improvements have been introduced in sulphuric acid alylation technology dealing with the spent acid issue. Fugitive emissions from this process is similar to the HF alkylation.

Acid-soluble oil should be recycled to process. Tars from the H_2SO_4 process contain sulphuric and miscellaneous sulphonic acids, which may cause disposal problems. This process generates waste water that should be neutralised before be routed to WWTP, gum, spent acid, caustic solutions from regeneration and fugitive emissions.

Operational data

The product quality from butyplenes (primary feedstock) is higher than in HF alkylation. To produce an equivalent product quality, HF alkylation would require similar energy consumption to sulphuric acid alkylation. This type of alkylation is considered relatively safer when compared to HF catalysed alkylation.

Utilities and chemical consumption (Basis: 716 m^3/d of alkylate plant)	
Power, kW	1779
Compressor	1235
Pumps	303
Mixers	240
Cooling Water, m^3/h (1)	835
Industrial Water, t/d	39
Steam, kg/h	
3.45 barg	13
10.3 barg	3
Chemicals	
Fresh Acid, t/d (2)	40
NaOH (15 Baume), t/d	1.7
Notes: (1) Cooling water supply temperature is 26 ºC and the average ΔT is 15 ºC (2) Includes allowance for feed impurities	

The sulphuric acid removed need to be regenerated in a sulphuric acid plant which is generally not a part of the alkylation unit and is normally located off-site.

Applicability

Fully applicable. This type of process technique is driven by the economics of the proximity of regeneration facility of sulphuric acid.

Economics

Capacity	**Estimated costs**	**Units**
290 kt/yr	*Material* $12.0 million *Labor* $1.7 million	USA Gulf Coast, second quarter 1993. Operational data correspond to this plant.
28300 m^3/d	14.49 M$	
1590 m^3/d	$22000 per m^3/d	USA Gulf Coast, 4th quarter 1998

Driving force for implementation
Alkylation plant is a refinery process used to increase the gasoline octane.

Example plants
Commonly used.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [330, Hommeltoft, 2000], [268, TWG, 2001]

4.2.3 Upgrade feedstock by selective hydrogenation or isomerisation

Description
More information about the processes can be found in Section 2.13, 4.13.5, 2.16 and 4.16.

Achieved environmental benefits
The naphtha hydrotreatment or isomerisation (e.g. hydrogenation of butadiene, isomerisation of 1-butene to 2-butene) helps the alkylation units to reduce the acid losses and consequently the waste generation. As consequence, the amount caustic consumption is decreased. The reduction in acid and caustic consumption depends on the feed diene content, which varies widely at different refineries.

Cross-media effects
Drawbacks for the implementation of such technique is the increased fuel/energy consumption, the increased fugitive emissions and need for spent catalyst handling used in such a processes. More information about those issues can be found in Sections 4.13 and 4.16.

Operational data
It requires hydrogen and consumes energy.

Applicability
No restrictions for application.

Economics
See Section 4.13 and 4.16.

Driving force for implementation
Because of increased demands for higher octane gasoline and the increased conversion of heavier crudes to lighter products, there has been a relative decrease in the quality of alkylation feed throughout the industry.

Reference literature
[113, Noyes, 1993], [268, TWG, 2001]

4.3 Base oil production

As described in Section 2.3, several types of processes can be found in the base oil production. It includes the desaphalting unit, aromatic extraction, high pressure hydrogenation unit, dewaxing, hydrofinishing and wax processing. All these process are covered here and good techniques from the environmental point of view are discussed in this section. Techniques applicable for the storage of the solvents used in base oil production (e.g. furfural, NMP, MEK, MIBK) are also included here. Storage of products and intermediates appearing in base oil production is included here as well.

4.3.1 Multiple-effect extraction process

Description

Solvent based processes used in the manufacture of base oils are energy intensive because large volumes of solvent must be recovered by flash distillation for recycle in the process. Number of stages used for evaporation of the solvents has a significant effect on the energy cost for these processes and as many as five evaporation stages were used in some early liquid SO_2 extraction units in Europe.

Achieved environmental benefits

Heat efficiency can be improved (less water and steam usage) by applying so-called double and triple effect configurations, especially in the deasphalting and aromatic extraction units. Energy saving of a triple-effect evaporation is 30-33 % compared with double-effect evaporation.

Operational data

Utilities needed in the process are listed in the economic section. The energy saving of the triple effect systems is on the low level heat side only (in most cases LP-steam) where refineries often already have a surplus. This means that the actual saving depends on the local circumstances and a retrofit/change should be evaluated for each individual location.

Applicability

Multiple effect evaporation requires both a pressure and a temperature driving force. In some instances, the increase in pressure and temperature required to go from double to triple effect is not feasible and could result in higher emissions and energy consumption because of larger residual amounts of solvent left in the oil leaving the evaporation section and entering the stripping section.

Triple effect systems are typically used for non-fouling feedstocks only (e.g. wax) as they are known to be more vulnerable in this respect, so their application is restricted.

Economics

Investment (basis: 318 - 6360 m^3/d, 4th Q, 1998, US Gulf): 5000 - 18900 $ per m^3/d.

	Single-effect	Double effect	Triple-effect
Conversion investment ($) [1]	0	1300000	1900000
Annual utility cost ($) [2]			
Medium-pressure steam, $8.1/t	91100	91100	91100
Low-pressure steam, $6.8/t	931600	465200	377500
Power, $0.04/kWh	218400	218400	218400
Cooling water, $0.018/$m^3$	87200	47600	39200
Fuel, $1.92/net GJ	44100	44100	44100
Total annual utility costs	1372400	866400	770300
Annual utility reduction	0	506000	602100

Notes: 1. Estimated basis: United States Gulf Coast, third quarter 1995
2. Based on unit cost provided by SRI International, Menlo Park, Calif. December 1994
Note: Large savings are shown for low-pressure steam. In most refineries, low-pressure steam is considered "free" since excess is vented to the atmosphere.

Table 4.2: Deasphalting-Unit Energy-Reduction Economics

Driving force for implementation
The conversion to multiple-effect unit reduces the utility cost.

Example plants
Common technology used in refineries having lubricant oil production. Double effect units are the most predominant type of extraction processes. Units built in 1950-1975 used double effect and a few used single. Because the cost of energy increased rapidly during the 1970, most new units built since about 1980 have been designed (and older units converted to) triple effect evaporation to reduce the cost of energy consumed.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [319, Sequeira, 1998]

4.3.2 Types of solvent used in the aromatic extraction unit

Description
The selection of the type of solvent used in the aromatic extraction has an impact on the energy consumption of the system and the use of a less toxic solvent (furfural and n-methyl pyrrolidone (NMP) can be used in preference to the more toxic selective solvent as phenol and sulphur dioxide).

Achieved environmental benefits
The use of a less polluting solvent (e.g.NMP or furfural) is preferred. As consequence the reduction of emissions of phenols and sulphur dioxide in the refinery effluents is achieved.

The advantage of NMP versus furfural is a higher selectivity leading to a higher raffinate yield and a lower solvent ratio which both result in a lower energy consumption of some 30 - 40 %.

Cross-media effects
Care should be taken to avoid solvent contamination of aqueous effluents by applying efficient solvent recovery techniques. Some contamination of aqueous effluents occurs, so care should be taken not to upset the activated sludge treatment unit of the waste water treatment. NMP is easier to be degraded in the WWTP than furfural however is more corrosive than clean furfural.

Operational data
The performance of NMP and furfural techniques are similar. Well maintained and operated furfural extraction units perform just as well as NMP plants. Similar quantities of furfural, compared to NMP, are required when the plants are run in the correct manner.

Applicability
Some technical dificulties for applicability or change of solvent are the following:

- phenol is easier to recover than furfural. Furfural forms a different ratio azeotrope with water, so a straight switch of solvent of a phenol unit may not possible, much larger quantities of furfural are used per unit throughput
- NMP switching of phenol is also difficult. NMP has a higher boiling point (by 22 ºC), a lower melting point (by 64 ºC) and no azeotrope. Because those reasons, furfural is typically used when producing lower boiling point base oils (e.g. transformer oil distillates)

Major modifications would be required for existing units to change from furfural to NMP as the process conditions are different (change from hot oil heat exchangers to a fired furnace to achieve the required temperatures in the solvent recovery section).

Economics
The change of solvent used does not entail significant extra costs in some cases. In other cases, for instance, the change from a SO_2 aromatic extraction to another solvent needs a completely new unit. Cost comparison of major base oil refining processes is given below

	Furfural	NMP	Phenol
Solvent, relative	1.0	2.3	0.60
Investment	medium	low	high
Maintenance	medium	low	high
Energy	high	low	medium

The switch from furfural to NMP process need economical calculations because major modification may be required. As consequence, the energy saving against the cost of the revamp has to be carried out individually. Changing from furfural to NMP requires significant investment, including, but not limited to the extraction tower, furnaces, metallurgy etc. Cost for conversion of a phenol unit (277 m^3 per operating day) to a NMP unit (563 m^3 per operating day) is estimated in EUR 0.9 million (cost including solp and solvent tankage). Other estimates says that the investment cost of a switch of a phenol units to NMP unit is around 70 % of a completely new unit.

Driving force for implementation
Reduction of energy consumption and the emissions of phenols and SO_2 in the refinery.

Example plants
Common technologies.

Reference literature
[110, HMIP UK, 1993], [319, Sequeira, 1998], [268, TWG, 2001]

4.3.3 Solvent recovery from dewaxing units

Description
Information about the process can be found in Section 2.3. Different prevention techniques may be applied to the solvent dewaxing process:

- vapours from the wax filters are contained in the inert gas system. In this process the inert gas is circulating and solvent vapours are recovered by refrigeration as part of the process. Solvent incineration in furnaces should be minimised. Alternative to refrigeration is pressure absorption of solvents in oil (e.g. fresh feed or finished)
- solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK). Toluene or chlorinated hydrocarbons should be avoided
- the solvent recovery stage results in solvent-contaminated water, which should be sent to the waste water treatment plant
- use of inert gas in place of steam for stripping the last traces of solvent from the dewaxed oil and waxes. When chlorinated solvents are used this procedure is typically applied.

Achieved environmental benefits
Maximise the recovery of the solvents used in the solvent dewaxing processes and reduce the contamination of waste water by toluene or chlorinated hydrocarbons Benefits of inert gas stripping in solvent dewaxing are the reduction of energy requirements in solvent refining units, the increse of dewaxed oil yields, reduction of the dilution ratios, reduction of solvent losses, decrease of dewaxing differential, and maintenance cost reduced.

Cross-media effects
Large refrigeration systems are used and refrigerant losses from these should be minimised. Energy consumption for refrigeration / pressure and heat. Care should be taken to avoid solvent contamination of aqueous effluents because most of the solvent used in solvent dewaxing are problematic for water micro-organisms and waste water plants. VOC fugitive emissions may be generated during the processes.

Operational data

Utilities, typical per m^3 feed		**Units**
Fuel	1856	MJ
Electricity	290	kW
Steam	171	kg
Cooling water (ΔT = 25 ºC)	36	m^3
Solvent make-up	1.7	kg

Applicability
Fully applicable.

Economics
A new solvent recovery unit cost 66000 US$ per m^3/day (basis 44000 m^3/day feed rate capacity, 1998 US Gulf Coast). Data on implementation of inert gas stripping in refineries shown paybacks of 9-14 months.

Driving force for implementation
Those techniques can be used in refineries having solvent dewaxing units in their lubricant oil production to promote reduction of solvent losses.

Example plants
Many refineries having lubricant production contain this type of processes.

Reference literature
[212, Hydrocarbon processing, 1998], [19, Irish EPA, 1993], [319, Sequeira, 1998], [268, TWG, 2001]

4.3.4 Wax reprocessing unit

Description
Hydrofinishing or clay treating can be used in the wax processing.

Achieved environmental benefits
Wax hydrofinishing offers several advantages over clay treating which include lower operating costs and reduction of waste generation.

Cross-media effects
When hydroprocessing is used, hydrogen is necessary. Hydrotreatments consume energy, hydrogen and the nickel, tungsten or even platinum catalyst needed for this process. Spent clay results in a disposal problem.

Operational data
Hydrogen finishing yields approach 100 % whereas the clay treating product yield ranges from 75 to 90 % for the microcrystalline waxes and as high as 97 % for light parafin waxes. Hydrogen consumption is around 15 Nm^3 per m^3 of wax produced. Clay consumption runs from 2 to 45 kg/t of product.

Applicability
Hydrofinishing is fully applicable especially when hydrogen is available. However, in some cases, hydrofinishing processes cannot reach certain very special product quality specifications.

Economics
Investment cost for a wax hidrofinishing process is EUR 1 million for a feed capacity of 20000 t/yr.

Driving force for implementation
Hydrotreating offers a lower operating cost.

Example plants
Many examples exists.

Reference literature
[319, Sequeira, 1998], [268, TWG, 2001]

4.3.5 Lube oil clean-up

Description
A short description of the process can be found in Section 2.3. The use of hydrotreating or sulphuric acid and clay treatments are treatments used in the lube oil clean-up.

Achieved environmental benefits
The use of hydrotreatment intead of the other cleaning techniques reduces waste generation.

Cross-media effects
Hydrotreatments consume energy, hydrogen and the nickel, tungsten or even platinum catalyst needed for this process.

Operational data
In stand-alone luboil refineries, the small amounts of H_2S generated due to hydrotreatment are normally incinerated because the erection of a Claus unit is not justified economically.

Applicability
Fully applicable. However, in some cases, hydrofinishing processes cannot reach certain very special product quality specifications.

Driving force for implementation
Technology that may be used in refineries having lubricant oil production for the production of cleaner lubricants.

Example plants
Sulphuric acid and clay treatments are typically used in old plants.

Reference literature
[19, Irish EPA, 1993], [268, TWG, 2001]

4.3.6 Storage of base oil intermediates and products

Description
Storage of intermediates and products from base oil production is typically found in base oil production units.

Achieved environmental benefits
Reduce risk of leaking and VOC emissions

4.3.7 Storage and benchmarking of solvents

Description
Solvent used in the solvent extraction of aromatics should be stored in blanketed tanks to minimise fugitive emissions of furfural, NMP and MEK/toluene. The practice of internal and/or external benchmarking may reduce the solvent consumption.

Achieved environmental benefits
Reduce VOC emissions, leakage prevention and reduction of solvent consumption. Prevention of leakage of solvents soluble in water reduce the contamination of soil and groundwater.

Applicability
Those tehniques can be seen as part of the VOC abatement programme (4.23.6) or soil contamination prevention programme (4.25.1).

Driving force for implementation
Toluene and MEK should be routinely nitrogen blanketed, mainly to reduce fire hazard rather than to prevent VOC emissions; higher boiling range solvents, such as furfural and NMP are less prone to VOC releases and may be blanketed mainly to prevent oxidative degradation (furfural) or to reduce nuisance odorous.

Example plants
Benchmarking of solvents and leakage prevention is widely applied in refineries.

Reference literature
[297, Italy, 2000], [268, TWG, 2001]

4.3.8 Sulphur treatment from hydrogenation units

Description
Hydrogenation processes generate H_2S. As consequence off-gases containing H_2S are recovered in a sulphur recovery plant (See Section 4.23.5) or incinerated.

Achieved environmental benefits
Reduction of sulphur and H_2S emissions.

Cross-media effects
Amine recovery of H_2S consumes energy and chemicals. Sulphur recovery units consumes energy (see Section 4.23.5). Incineration requires fuel.

Operational data
See Section 4.23.5

Applicability
In stand-alone luboil refineries, the small amounts of H_2S generated in this process are typically incinerated. Sulphur recovery is less commonly applied in those specialised refineries.

Economics
See Section 4.23.5. Data from EU refineries have found that the implementation SRU in stand-alone lubricant refineries producing more than 2 tonnes of sulphur per day is cost-effective.

Driving force for implementation
Reduction of sulphur oxide and H_2S emissions.

Example plants
At least one specialised European refinery has a SRU which recover 99.1 % of the sulphur in the acid gas.

Reference literature
[147, HMIP UK, 1995], [268, TWG, 2001]

4.3.9 Stripping of waste water from aromatic extraction

Description
Stripping of waste water from aromatic extraction prior to sending to waste water treatment plant. Other technique to consider is dehydration/settling.

Achieved environmental benefits
Reduce the content of organic and sulphur compounds of waste water produced in the aromatic extraction. Other benefits are energy requirements reduced, dewaxed oil yield increased, dewaxing differential decreased, dilution ratios reduced, solvent losses reduced and maintenance costs reduced.

Cross-media effects
Stripping consumes energy.

Operational data
Stripping consumes energy.

Applicability
Fully applicable

Driving force for implementation
Energy consumption reduction and reduction of solvent losses.

Example plants
Applied in some refineries.

Reference literature
[147, HMIP UK, 1995], [319, Sequeira, 1998], [268, TWG, 2001]

4.3.10 Hot oil system

Description
When the base oil production units have a single energy system, the introduction of clean-up facilities in the flue gases is more cost-effective.

Achieved environmental benefits
Reduction of SO_x, NO_x, particulates emissions from the energy system.

Cross-media effects
See different cross-media for the abatement of SO_x, NO_x and particulates in Section 4.23

Operational data
See Section 4.23

Applicability
This technique may be very difficult to be applied to existing refineries.

Economics
See Section 4.23

Driving force for implementation
Reduction of SO_x, NO_x, particulates emissions from the energy system.

Example plants
Some stand-alone lubricant refineries have already applied this concept to reduce emissions coming from the burning of liquid fuels.

Reference literature
[268, TWG, 2001]

4.4 Bitumen production

4.4.1 Storage of bitumen products

Description
Bitumen should be stored in proper storage tanks normally under heating conditions and insulated. Bitumen is not handled as a solid because is too difficult and is very intensive in man power. Loading and unloading of the tank is typically done as follow. When the tank is filled, nitrogen does not flow to the tank, and the pressure is lowered by letting part of the gas go to the atmosphere. When the tank is unloaded on a low speed, a little bit nitrogen is led to the tank. However when the speed of unload is higher, higher amounts of nitrogen must be used. If the tank would be equipped with some cleaning system, it must be mechanically very simple and easy to clean.

Achieved environmental benefits
For safety reasons, bitumen tanks are equipped with nitrogen blanketing and pressure/vacuum safety valve. Those valves need maintenance due to the slime.

Cross-media effects
Hydrocarbons and sulphur compounds may emanate from leakages (particularly in overhead systems) and pressure relief valves and in the form of aerosol-containing liquid droplets from the venting of tanker top-loading operations.

Operational data
Electricity hot oil and low pressure steam can be used for heating. The heat exchanger can be inside the tank or outside the tank in which case bitumen is circulated through it. Difference in temperature should not be too high due to the surface temperature and coking.

Applicability
Storage of bitumen products is done in refineries that have bitumen production. Prevention techniques as mentioned are typically applied.

Driving force for implementation
For safety reasons, bitumen tanks are equipped with nitrogen blanketing and pressure/vacuum safety valve.

Example plants
Some refineries in Europe use those techniques mentioned here.

Reference literature
[268, TWG, 2001]

4.4.2 Techniques to control emissions to the air

4.4.2.1 Treatment of the gaseous overheads

Description
Oxidiser overhead can be routed to a scrubber rather than direct water quenching for contaminant removal prior to incineration.

Achieved environmental benefits
Reduction of H_2S, SO_2, SO_3, CO, VOC, particulates, smoke and odour emissions.

Cross-media effects
Additional contaminated water. Scrubber water is dirty and requires oil and solids separation prior to re-use as desalter wash water and/or biotreatment. The sour water from the scrubber is routed to and stripped in a sour water stripper prior to re-use and/or purification.

Applicability
Typically applied to overheads from the bitumen blowing systems

Reference literature
[147, HMIP UK, 1995]

4.4.2.2 Use the heat from incondensable products and condensates

Description
- Both incondensable products and condensates from the separator, hydrocarbon and aqueous, can be burnt in a purpose-designed incinerator, using support fuel as necessary or in process heaters.
- Oxidiser overhead slop oil can also be treated in the sludge processing or recycled in the refinery slop oil system.

Achieved environmental benefits
Reduction of emulsion of light oil, water and particulates. Another environmental benefit is the removal of foul smelling odorous incondensables difficult to treat elsewhere.

Cross-media effects
On scrubbing, aerosols can give rise to plugging. Additional contaminated water streams. In a well operated unit, SO_2 or odour from incineration of bitumen blowing incondensables do not pose any problem.

Operational data
The incinerator should operate at a temperature of at least 800 ºC and the combustion chambers should have a residence time of at least 0.5 second. The oxygen concentration at the combustion chamber outlet should be greater than 3 % v/v. Low-NO_x burners can be fitted in those incinerators.

Applicability
Widely used to get rid of bitumen fumes. Incondensable and/or condensates can be burnt in process heaters. However they should be treated or scrubbed to remove compounds of sulphur or combustion products that may cause odours or other environmental problems.

Driving force for implementation
Reduction of odours, sludge and oily waste.

Example plants
Many bitumen oxidisers have associated facilities to handle gas and liquid wastes.

Reference literature
[147, HMIP UK, 1995]

4.4.2.3 Treatment of vents from storage and handling bitumen materials

Description
Techniques that may be applied to prevent VOC emissions and odours are:

- odorous gases vented during the storage of bitumens and the tank blending/filling operation can be vented to an incinerator
- the use of compact wet-type electrostatic precipitators has been proven capable of successfully removing the liquid element of the aerosol generated during the top-loading of tankers.

Achieved environmental benefits
Reduction of emissions of sulphur compounds, VOC, particulates, smoke and odour emissions.

Cross-media effects
Energy consumption and in case of wet ESP waste generation.

Operational data
In the waste gas of a cleaning unit, a mass concentration of VOC of a total of 150 mg/Nm³ can be complied with. In the waste gas of a incineration plant, a mass concentration of VOC, given as total C, of a total of 20 mg/Nm³ can be complied with (Half-hourly mean values attainable in continuos operation).

Applicability
Fully applicable.

Driving force for implementation
Reduction of emissions and nuissance.

Reference literature
[147, HMIP UK, 1995], [117, VDI, 2000]

4.4.2.4 Sulphur dioxide abatement and sulphur recovery units

Description
SO_x abatement techniques and SRU are techniques to reduce sulphur emissions. Those are extensivelly documented in Section 4.23.5.

Achieved environmental benefits
Reduction of sulphur emission

Cross-media effects
See Section 4.23.5 for the different techniques applicable.

Operational data
See Section 4.23.5 for the different techniques applicable.

Applicability
The implementation of those techniques are extremely linked to the rest of the refinery. In stand-alone bitumen refineries its application is more restricted.

Economics
See Section 4.23.5 for the different techniques applicable.

Driving force for implementation
Reduction of sulphur emissions

Example plants
Those techniques are applied in many refineries. However less applications are found in stand-alone bitumen production refineries.

Reference literature
[268, TWG, 2001]

4.4.3 Techniques to control emissions to the waste water

Description
Oxidiser overhead waste water accumulated in the overhead condensate collection drum can be sent to a sour water stripper prior to sending it to the effluent water treatment facilities.

Achieved environmental benefits
The stripping reduces the H_2S, oil, aromatics, volatile PAHs, sulphuric acid and odorous oxidation products (ketones, aldehydes, fatty acids) in the sour waste water reducing the charge to the central waste water system of the refinery.

Cross-media effects
Increase of oil and particulates load to sour water stripper.

Applicability
Typically applied to waste water from bitumen blowing.

Driving force for implementation
Reduction of the pollutant charge to the refinery waste water treatment.

Reference literature
[147, HMIP UK, 1995], [268, TWG, 2001]

4.4.4 Techniques for prevention of generation of waste

Description
In the bitumen production facilities, including storage, leakages can be produced. Those leakages typically generate waste when mixed with other components as sand.

Achieved environmental benefits
Reduction of waste production

Operational data
This can be seen as a part of a waste management programme described in Section 4.25.1.

Applicability
Fully applicable

Driving force for implementation
Reduction of waste and cleaning

Example plants
Many refineries apply those type of systems.

Reference literature
[268, TWG, 2001]

4.4.5 Hot oil system

Description
When the bitumen production units have a single energy system, the introduction of clean-up facilities in the flue gases is more cost-effective.

Achieved environmental benefits
Reduction of SO_x, NO_x, particulates emissions from the energy system.

Cross-media effects
See different cross-media for the abatement of SO_x, NO_x and particulates in Section 4.23

Operational data
See Section 4.23

Applicability
This technique may be very difficult to be applied to existing refineries.

Economics
See Section 4.23

Driving force for implementation
Reduction of SO_x, NO_x, particulates emissions from the energy system.

Example plants
Some stand-alone bitumen refineries have already applied this concept to reduce emissions coming from the burning of liquid fuels.

Reference literature
[268, TWG, 2001]

4.5 Catalytic cracking

Several types of techniques are considered in this section. The first group of techniques (Sections 4.5.1 to 4.5.3) corresponds to the types of catalytic cracking processes. Those sections give the emission values that can be achieved without use of abatement techniques (where data is available). The remaining sections correspond to end-of pipe techniques applicable to catcrackers.

4.5.1 Full combustion mode in regenerator

Description
This section gives emission information from the FCC when it is run under favourable conditions and the regenerator in total combustion mode. Operational techniques that affect the emissions from the FCC are also discussed. A description of the process can be found in Section 2.5.

Achieved environmental benefits
Some operating modes that can reduce the emission of pollutants from the FCC are the following:

- when operating a FCC in full combustion mode, and with an excess of oxygen greater than 2 %, the amount of CO produced can range from 35 to 250 mg/Nm^3 (Value attainable in continuous operation. Emissions values as half-hourly mean values)
- in full combustion mode, a CO oxidation promoter can be added to the regenerator to catalyse the oxidation of CO. However, this promoter also catalyses the oxidation of the fuel nitrogen in the coke, increasing the NO_x levels (especially NO). Platinum catalyst may promote the generation of N_2O. Consequently, the amount of CO promoter varies the relationship between the NO_x emissions and CO emissions. However; values of 300 - 700 mg/Nm^3 of NO_x (3 % O_2) can be achieved
- minimisation of the use of aeration and purge steam can decrease particulate emissions significantly. Aeration/steam rates are based on achieving a stable catalyst circulation in the catalyst lines between reactor and regenerator
- proper loading and pre-sulphiding procedures, good reactor temperature control and good flow distribution can reduce catalyst losses
- stripping of catalyst before reaction or before regeneration helps to reduce the coke formation
- temperature adjustment in the riser by injection of a recycle stream above the zone of the fresh feed injection.
- modification of the design and operation of regenerator especially to avoid high temperature spots that tend to increase the NO_x formation.

Cross-media effects
The catcracker is the source of SO_2 and NO_x, CO_2, CO, dust (particulates), N_2O, SO_3, metals, hydrocarbons (ex. aldehydes), ammonia emissions, as discussed in Section 3.5. For example, the basic design of a FCC includes two-stage cyclones in the regenerator vessel, which prevent the bulk of the fine catalyst used from escaping from the system. However, smaller catalyst particles, some of which are introduced with fresh catalyst and some created by attrition in the circulating system, are not easily retained by the two-stage cyclone system. Consequently, in many cases, other abatement techniques can be included to complement the process abatement techniques discussed here. Next table gives a summary of the lowest emissions of pollutants to the atmosphere due to an uncontrolled catcracker (No end-of-pipe technology is used to abate air emissions).

PM	SO_x (as SO_2)	CO	HC	NO_x (as NO_2)	Aldehydes	NH_3
0.267 - 0.976	0.286 - 1.505	39.2	0.630	0.107 - 0.416	0.054	0.155

Emission factors in kg/1000 litres of fresh feedstock

A reduction of the regeneration temperatures under the usual conditions (700-750 °C) would not have an significantly impact in the NO_x emissions but could need a CO boiler and increase coke formation. A change in the design or operation of the regeneration may increase the CO concentration.

Operational data

Operational data of the FCC process can be found in Sections 2.5 and 3.5. More operational data about FCCs can be found in [325, Gary and Handwerk, ; 326, Nelson,]. A high-severity FCC process enables higher yields of low olefins (C_3, C_4) that may be used for alkylation, oxygenates production or direct sale to the market. This is carried out increasing the temperature at which the cracking process is done and decreasing the contact time.

Applicability

Total combustion mode is typically applied to vacuum distillate feedstocks. Only low Conradson carbon feeds are typically processed in FCCs.

Economics

Investment cost for FCCs in EUR/(t·yr)	Basis of calculation	
48 – 64	1.5 Mt/yr fresh feed including reaction/regeneration system and product recovery. Excluding offsites, power recovery and flue gas scrubbing. (1998)	
45 – 50	2.4 Mt/yr fresh feed including converter, fractionator, vapour recovery and amine treating but not power recovery battery; battery limit, direct material and labor, (1994)	
Maintenance	2 - 3	% of investment per year

The operating cost for the addition of CO promoter to a 1.5 Mt/yr FCC (flue gas generation of around 10^9 Nm^3/yr) providing an efficiency around 30 % (700 mg/Nm^3) is EUR 0.5 million /yr. A major revamp of a FCC to change the design and/or operation is very expensive and typically is not justified only by environmental reasons.

Driving force for implementation

It is a production process.

Example plant(s)

Common technique. Around 50 FCCs are installed in Europe. Catalytic cracking has largely replaced thermal cracking because it is able to produce more gasoline with a higher octane and less heavy fuel oils and light gases. FCC is a very typical operation in medium-complexity refineries but RCC units are becoming more prevalent.

Reference literature

[212, Hydrocarbon processing, 1998], [113, Noyes, 1993], [117, VDI, 2000], [297, Italy, 2000] [136, MRI, 1997], [247, UBA Austria, 1998], [45, Sema and Sofres, 1991], [268, TWG, 2001]

4.5.2 Residue catalytic cracking (RCC)

Description

This section gives emission information from the RCC when it is run under favourable conditions and the regenerator runs in partial combustion mode. Operational techniques that affect the emissions from the RCC are also discussed. A description of the process can be found in Section 2.5.

Achieved environmental benefits
Possibility to upgrade heavier residues than with the FCC (e.g. vacuum residue or low added value residues). As consequence, the RCC can provide positive environmental benefit to reduce the generation of residue in the refinery that otherwise may go to bunker and other heavy fuels. Those fuels may finally be used in combustion processes generating SO_2, NO_x and metals. Other operational benefits of the RCC over the FCC with environmental consequences are:

- use of two-stage catalyst regeneration as alternative to a catalyst cooler so as to control the heat release due to coke combustion and can process feeds up to 10 % w/w Conradson carbon
- stripping of catalyst before reaction or before regeneration helps to reduce the coke formation
- temperature adjustment in the rise by injection of a recycle stream above the zone of the fresh feed injection
- CO boiler and expander benefits used in RCC are analysed in Section 4.5.5.

Cross-media effects
Some feedstocks may need hydrotreatment.

Applicability
Fully applicable. FCC can be retrofitted to RCC. Medium Conradson carbon feeds would need a CO boiler and higher ones a catalyst cooler. Metal content (Ni, V) should be limited; residue demetallisation/hydrotreating may extend the range of residual feedstocks. It can run with carbon Conradson index lower than 6 - 8 % and the total metal content less than 20 ppm.
Example plants
Several examples in Europe.

Reference literature
[212, Hydrocarbon processing, 1998]

4.5.3 Partial combustion mode in the regenerator

Description
FCC regenerators are operated either in a complete (considered in this document as the basis operational mode) or partial combustion mode. In the partial combustion mode considerable CO is present in the flue gas and it is consumed downstream of the regenerator in a CO boiler, both to recover the energy produced in a CO boiler and to meet environmental requirements. This system can be seen as two stage regeneration in comparison with the total combustion mode, where a single regeneration step is present. Another technique to consider is the modification of the design and operation of regenerator especially to avoid high temperature spots that tend to increase the NO_x formation.

Achieved environmental benefits
The use of partial combustion mode together with a CO boiler generates less CO and NO_x emissions compared with full combustion. The use of a CO boiler or high-temperature regeneration technology can significantly reduce the CO emissions. CO achieved emissions are from less than 50 - 400 mg/Nm^3 (3 % O_2 daily average). In the CO boiler, refinery fuel gas addition is required to incinerate CO (~900 °C). The advantage of partial combustion coupled with a CO boiler is lower NO_x (100 - 500 mg/Nm^3 (3 % O_2, daily average, standard conditions)), ammonia and hydrocarbons emissions. Emissions of SO_x and particulates are not affected by this mode of operation.

The emission factors for a cracking unit with an electrostatic precipitator and a CO boiler are shown below.

Process	PM	SO_x (as SO_2)	CO	HC	NO_x (as NO_2)	Aldehydes	NH_3
FCC with ESP and CO boiler	0.020 - 0.428	0.286 - 1.505	Neg	Neg	0.107 - 0.416	Neg	Neg
Neg: Negligible							

Table 4.3: Emission factors for cracking (units in kg/1000 litres of fresh feed)

Cross-media effects
Fuel gas is needed for the incineration of CO. If fuel contains sulphur, emissions of SO_2 may occur. Other benefits are greater throughputs and heat/power recovery.

Operational data
Where a CO boiler is installed it should be carefully designed and operated to minimise CO and NO_x releases.

Applicability
This mode of combustion is fully applicable. In general it can be said that feed having a Conradson carbon figure up to 2 - 3 % can be processed in a 'standard' FCC without CO boiler as well as partial-burn FCC. A Conradson figure from 2 - 5 % would require a CO boiler and from 5 - 10 % a cat cooler would be needed. It should be noted that the above figures are only indicative and depend also on the severity of cracking.

Economics
Investment cost necessary to convert a FCC from total to partial combustion mode is around EUR 2.5 - 4 million. A major revamp of a FCC to change the design and/or operation is very expensive and typically is not justified only by environmental reasons.

Driving force for implementation
Production process.

Example plants
Carbon monoxide boiler is normally a standard practice in fluidised catalytic cracking units in the USA. Many examples also in Europe and the rest of the world.

Reference literature
[297, Italy, 2000], [316, TWG, 2000], [268, TWG, 2001]

4.5.4 Hydrotreatment of feed to the catcraker

Description
Hydrotreatment of feed to the catcracker operates at similar conditions to those used for gasoil and atmospheric residue hydrotreatment (see Sections 2.13 and 4.13).

Achieved environmental benefits
FCC feed hydrotreatment can reduce the sulphur content to <0.1 – 0.5 % w/w (depending on the feedstock). As a consequence of the hydrotreatment, emissions of SO_2 from the regenerator can be reduced by up to 90 % (flue gas concentration 200 - 600 mg/Nm^3 (3 % O_2) depending on the feedstock) and nitrogen compounds can be reduced by up to 75 – 85 % (smaller percentage for the partial combustion mode). Be aware that a percentage on reduction of nitrogen compounds does not lead to equivalent NO_x reduction. This process also reduces the metal emissions (e.g. Ni, V) to the air and prolongs the life of the catcracker catalyst. Other benefit of this technique is that hydrotreated mercaptane oxidation is not necessary. This reduces amount of used caustic and emissions into water.

Cross-media effects

Cross-media effects are the increase of energy consumption and the consequent increase in CO_2 emissions, due mainly to the hydrogen, as discussed in Section 3.14. As discussed in Section 4.13, hydrotreatment processes generate catalyst for disposal and increase the H_2S production with direct consequences for the sour water stripper and sulphur recovery units (which may need to be enlarged or replaced).

Operational data

Installation of catcracker feed hydrotreatment (or a feed hydrocracker) will reduce the sulphur content in catcracker products and improve their quality, so that they require less final processing. Hydrogen and energy are required for this process. The water used for the different catalytic sections yields 20 - 40 m^3/h of sour water. The sulphur removal efficiency achieved by hydrotreatment depends on the boiling range of the catcracker feed. The heavier the feed, the more energy is required for the same sulphur removal efficiency.

Applicability

Fully applicable. This process is more cost-effective when hydrogen, SWS and SRU capacities are available in the refinery.

Economics

Size/capacity ktonnes/yr	**Typical capital/installed cost (EUR million)** Costs include necessary interconnections to existing plant for integration purposes.	**Operating cost EUR million/yr**
1250	65	n.a.
2500	106	18
3750	150	n.a.
Note: The cost assumes that there is adequate space and existing SRU (sulphur recovery units) and sour water stripping capacity. If further hydrogen production is needed, a new hydrogen plant for a 2500 kt/yr FCCU feed hydrotreater or hydrocracker would typically cost in the range of EUR 60 - 75 millions		

Table 4.4: Catalytic feed hydrotreatment (typical feeds being atmospheric residue and vacuum gas oil)
Source: [112, Foster Wheeler Energy, 1999]

	Distillate feed desulphurisation	**Residue feed desulphurisation**	**Feedstock hydrotreating to reduce NO_x**
Capacity of process	1.5 Mt/yr	1.5 Mt/yr	1.5 Mt/yr FCCU with CO Boiler
Investment expenses (EUR million)	80 - 100 [3] 45 - 50 [1,2]	200 - 300 [2,3]	80 - 100
Operating expenses (EUR million/yr)	4 - 9	15 - 25 [3] 30 - 50 [2]	4 - 9
1 Excluding H_2 production and H_2S handling facilities **2 [45, Sema and Sofres, 1991]** **3 [115, CONCAWE, 1999]**			

Driving force for implementation

The implementation of this technique is typically product specification driven because higher conversions are achieved with hydrotreated feedstocks. The majority of the products produced by the catcracker without previous hydrotreatment need further treatment to comply with product specifications. Moreover, the flue gas from the regenerator contributes significantly to the overall refinery SO_x / NO_x emissions. Desulphurisation or mild hydrocracking of the feed is an option to reduce those emissions.

Example plants

Many examples.

Reference literature
[296, IFP, 2000], [115, CONCAWE, 1999], [112, Foster Wheeler Energy, 1999], [45, Sema and Sofres, 1991], [247, UBA Austria, 1998], [297, Italy, 2000], [268, TWG, 2001]

4.5.5 Waste heat boiler and expander applied to flue gas from the FCC regenerator

Description
Heat recovery from the regenerator flue gas is conducted in a waste heat boiler or in a CO-boiler. Heat recovery from the reactor vapour is conducted in the main fractionator by heat integration with the unsaturated gas plant as well as generation of steam with the residual heat from product rundown streams and pumparound streams. The steam produced in the CO boiler normally balances the steam consumed. Installing an expander in the flue gas stream from the regenerator can further increase the energy efficiency. Figure 4.1 gives a simplified scheme of application of a waste heat boiler.

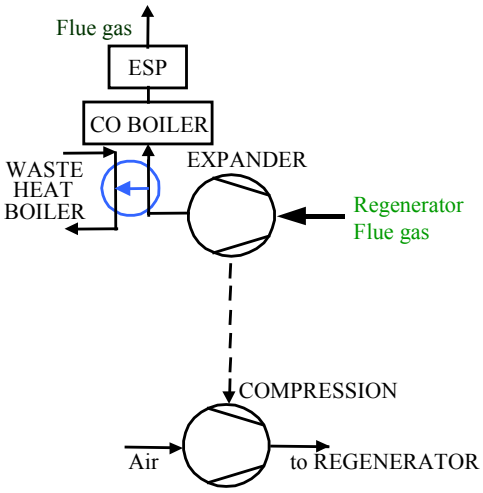


Figure 4.1: Waste heat boiler applied to a catcracker
Note: CO boiler and ESP not included in this section

Achieved environmental benefits
The waste heat boiler recovers the heat from the flue gas and the expander can recover part of the pressure to be used in the compression of the air needed in the regenerator. An example of the application of an expander saved 15MW_e for the flue gas generated by a FCC of a capacity of 5Mt/yr.

Cross-media effects
Significant quantities of catalyst fines are collected in the waste heat boiler (WHB). The newer WHBs have facilities which permanently remove the collected fines, but older WHBs are normally soot-blown once a shift. During this operation the emission of catalyst fines is especially high if the unit is not equipped with a particulate abatement technique.

Operational data
Power recovery on regeneration gas reduces CO boiler duty.

Applicability
Retrofitting of of this equipment can be very difficult because of space limitations in the refinery. On small or low pressure units, expanders are not justified economically.

Economics
Applying expander on the regenerator gas could be costly because the additional particulate systems under high temperature that they need. Turbo expanders are big cost items, and so are waste heat recovery units.

Driving force for implementation
Recovery of energy

Example plant(s)
Energy recovery by utilising an expander in the regenerator flue gas is only applied in the larger, more recently built units.

Reference literature
[136, MRI, 1997], [268, TWG, 2001]

4.5.6 Catalyst selection

Description
Techniques to consider are:
a) Use a higher quality FCC catalyst, process efficiencies can be increased while catalyst waste can be reduced and rate of replacement reduced.
b) Use of an attrition resistant catalyst to reduce the frequency of replacing catalyst and reduce emission of particulates from the regenerator.

Achieved environmental benefits
A good selection of the catalyst used in the FCC process can:
- increase the FCC efficiency by up to 20 %, coke production can be decreased and catalyst waste can be reduced
- increase the recyclability of the catalyst
- reduce the particulate content of flue gas before treatment to 300 mg/Nm^3.

Applicability
A change in the catalyst may have an adversely effect to the performance of the FCC.

Economics
Investment expenses: none.
Operating expenses: Negligible.

Driving force for implementation
Process requirements.

Reference literature
[80, March Consulting Group, 1991], [115, CONCAWE, 1999]

4.5.7 Waste water management within FCCU

Description
Some techniques to consider are:
a) Some catcracker designs contain a cascading overhead washing section designed to minimise water usage.
b) re-use waste water generated in FCCU within the refinery (e.g. desalters) or ultimately route to WWTP.

Achieved environmental benefits
Reduction of water usage and re-use of water within the refinery.

Applicability
Both techniques are fully applicable to catcrackers

Driving force for implementation
Reduction of water usage.

Example plants
Used in some catcrackers

Reference literature
[80, March Consulting Group, 1991]

4.5.8 Nitrogen oxides abatement techniques

This section includes NO_x abatement techniques that may be applied to FCCs.

4.5.8.1 Selective catalytic reduction (SCR)

Description
See Section 4.23.3.

Achieved environmental benefits
Inlet NO_x concentration to the SCR may vary from 200 - 2000 mg/Nm^3@ 3 % O_2. Inlet NO_x concentrations to the SCR vary with the type of FCC used (total or partial combustion in combination with a CO boiler) and the type of feed used (heavier feed tends to produce higher NO_x emissions). Reduction by 85 - 90 % of NO_x emissions with the outlet concentration of NO_x reduced to 30 - 250 mg/Nm^3@ 3 % O_2, depending on the inlet concentration. Those reduction efficiencies provide a reduction of 300 tonnes of NO_x per year from catcrackers of capacity of 1.65 Mt/yr. Other advantage is that some CO oxidation also occurs in the SCR process (aprox. 40%).

Cross-media effects
Use of NH_3 (storage/handling), risk of NH_3 emissions when operating outside stoichiometric proportion and depending on the age of the catalyst (<2 - 10 mg/Nm^3) and SCR catalyst regeneration and disposal. Ammonia needed for this technique may be supplied by two-stage sour water strippers (see Section 4.24.2). Another disadvantage of SCR is that a few percent of SO_2 is oxidised to SO_3 over the deNOx cat and as consequence it can potentially create plume opacity problems.

Operational data
Catalyst performance is expected to deteriorate with time, due mainly to the dust and SO_x. However, current examples have shown lifetimes well over the expected ones (6 years). Information from operators claim that not all SCR applied to FCC have operated to design loads leading that fact to increase catalyst lifetimes. Some other concerns from operators is that SCR catalyst could potentially be fouled by the particulates in the flue gas stream. More general operational data for SCRs can be found in Section 4.23.3.

Applicability
Because the temperature window is wide (300 - 400 ºC), it is very flexible for retrofit applications. However, considerable space is needed for installation. SCR applications often requires a new waste heat boiler (full burn) or CO-boiler (partial burn) if they are not present. Preferably the deNOx unit is integrated with the waste heat boiler. Because SCR operates at oxidizing conditions it cannot be installed upstream of a CO boiler (partial burn).

Economics

Table 4.5 shows some examples of the economics of the application of SCR to FCCs

Size of the FCC (Mt/yr)	Efficiency (%)	Outlet NO_x concentration (mg/Nm^3)	Installation cost (EUR million)	Operating and maintenance cost (EUR million/yr)	Specific removal cost [4] (EUR/t of NO_x removed)
1.65	90	40	3.8 [1]	0.24 (SEK 2 million) [2]	2103
1.5	85	120	6.3 - 13 [3]	0.4 - 0.8	2023
1.5	85	37.5	1.2 – 3.6 [5]	0.12 - 0.48	2042

1. Cost in original currency in brackets.
2. Including SCR reactor, ammonia storage and injection facilities and initial fill of catalyst
3. Operation and maintenance cost including ammonia, steam and replacement of catalyst
4. Including a CO boiler
5. Using the same economic analysis presented in following tables

Cost for a new installation

Table 4.5: Economics of SCR applied to FCC units

A more detail economic assessment of a SCR in a FCC unit is shown in Table 4.6.

		EUR/unit	EUR/yr
Operating hours (h/yr)	8000		
Investment costs (EUR million)	1.45		
Input factors for annual expenditure:			
Number of years	15		
Rate of interest (%)	6		
Annual repayment incl. interest (EUR/yr)	150000		
Proportional investment costs incl. interest			**150000**
Volume of catalyst (m^3)	20		
Endurance (years)	8		
Renewing of catalyst (m^3/yr)	2.5	15000 €/m^3	
Average renewing of catalyst (EUR/yr)	36300		
Catalysts			**36300**
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	29000		
Maintenance + wear and tear			**29000**
Pressure drop (mbar)	8		
Energy for reheating (MJ/h)	0	3.6 €/GJ	0
Electrical energy (kWh/h)	88	0.065 €/kWh	46000
NH_3 liquid (kg/h)	36.96	0.25 €/kg	75200
Total costs			**336269**

Notes: In a refinery with a volume of exhaust gas of 100000 Nm^3/h achieving a NO_x emission reduction of 1000 mg/Nm^3 in relation to actual oxygen content and for a clean gas concentration of <200 mg NO_x/Nm^3. Inlet concentration may vary between 200 - 2000 mg/Nm^3 @ 3 $\%O_2$. The outlet concentration of NO_x is reduced to 80 - 120 mg/Nm^3 by SCR.

Table 4.6: Main cost factors for a Selective Catalytic Reduction (SCR) installation (raw gas) after the FCC-plant

Driving force for implementation

Reduction of the NO_x emissions. A NO_x reduction of 300 tonnes annually is achieved in a FCC unit of 1.65 Mt/yr when 90 % of NO_x reduction is achieved.

Examples

At least six SCR are in operation in FCC worlwide and two in Europe (Scanraff-Sweden and Pernis-The Netherlands).

Reference literature
[107, Janson, 1999], [45, Sema and Sofres, 1991], [254, UKPIA, 2000] [247, UBA Austria, 1998], [115, CONCAWE, 1999], [316, TWG, 2000], [136, MRI, 1997], [348, Ashworth Leininger Group, 2001]

4.5.8.2 Selective non-catalytic reduction (SNCR)

Description
See Section 4.23.3.

Achieved environmental benefits
These systems reduce the NO_x emissions by 40 - 80 %. The outlet concentrations can be down to <200 - 400 mg/Nm^3@ 3 % O_2 depending on the nitrogen content of the feedstock. Instead of ammonia, urea can be also used. The use of urea has the advantage to be more soluble in water and consequently reduce the risk of handling/storage of NH_3.

Cross-media effects
Use of NH_3 (storage/handling), risk of NH_3 emissions when operating outside stoichiometric proportion. Ammonia needed for this technique may be supplied by two-stage sour water strippers (see Section 4.24.2). The use of urea generates more ammonia (from urea) slip and some N_2O formation.

Operational data
High temperatures (800 - 900 ºC) of the flue gases are needed.

Applicability
It is applicable in partial combustion FCCs with CO boiler; retrofitting in existing CO boilers is relatively simple. It is also applicable to full combustion units. Space requirements are mainly related to NH_3 storage.

Economics

Size of the FCC (Mt/yr)	Efficiency (%)	NO_x in/out concentration (mg/Nm^3 @ 3 % O_2	Investment (EUR million)	Operating cost (EUR million/yr)	Specific removal cost (4) (EUR/t of NO_x removed)
1.5	60	800 / >320	5.4 0.6 (1)	0.1 – 0.4	1300
1.5	60 - 80	200 / 40-80	0.35 - 1.5(1)	0.05 - 0.4	1700
1. Cost data not including the cost of the CO boiler					

Table 4.7: Economics of SNCR applied to FCCs

Driving force for implementation
Reduction of NO_x emissions.

Example(s)
It has been applied in Japan on an FCCU where a CO boiler provides a sufficient temperature window.

Reference literature
[115, CONCAWE, 1999], [45, Sema and Sofres, 1991], [316, TWG, 2000]

4.5.9 Particulate abatement techniques

The selection of the catalyst can be seen as a particulate abatement technique. That technique has been included in Section 4.5.6 together with other possible effects of catalyst replacement.

4.5.9.1 Additional cyclones

Description
Highly specialised cyclones are used (third-stage and multicyclones), which are designed to suit the arrangement, dimensions, contours, velocities, pressures and densities of the particles to be removed. This is the natural first choice of clean-up device for particulates: these are conventional cyclones, fitted externally to the regenerator but operating on the same principle as the internal first and second cyclones. They are high-velocity devices and recovered catalyst is returned to a dust hopper.

Achieved environmental benefits
By reducing the particulate content in the air, the metal emissions are reduced. Depending on the above factors, cyclones are generally efficient at removing particles in the range of 10 to 40 microns and above. Efficiencies can range from 30 to 90 %. An average performance figure for cyclone separation alone is in the region of 100 - 400 mg/Nm^3. (Inlet concentration from 400 - 1000 mg/Nm^3). Lower concentrations are not achievable because inlet velocities to the cyclones are in the region that causes additional attrition, which produces additional fines that pass the cyclone. The fine catalyst disposal is 300 - 400 tonnes/yr per unit. Cyclones are more effective for coarser particles and they have been designed essentially to prevent any particles greater than 10 microns from entering downstream facilities.

Cross-media effects
Catalyst fines recovered are considered as waste (300 - 400 tonnes/yr per unit). Consequently pollution is transferred from air to the soil.

Operational data
It generates a pressure drop in the flue gas. Good performance and reliability in many FCCs.

Applicability
Applicable to any FCC.

Economics

Size of the FCC (Mt/yr)	Efficiency (%)	Downstream particulate concentration (mg/Nm^3)	Investement (EUR million)	Operating cost (EUR million/yr)
1.5	30 - 40	40 - 250	1 - 2.5	0.7
1.5	30 - 90	60 - 150 *	0.5 - 1.5	0.1
1.2	75	50 - 100 #	1.5 - 2.5	
Note: Operating costs include only direct cash operating expenses i.e. do not include depreciation of investment, nor financial charges. Investment costs refer to new plant installation. Economics do not include the cost of disposal of the waste generated. * Initial concentration: 450 mg/Nm^3 (300 - 600 mg/Nm^3 range) # Initial concentration: 200 - 1000 mg/Nm^3				

Table 4.8: Economic data of third cyclone applied to FCCs

Economics of disposal of the fine catalyst is around EUR 120 - 300 per tonne, including transportation.

Driving force for implementation
To improve control of emission of particulates. Tertiary cyclones can be also used to protect downstream equipment such as heat or power recovery units (e.g. expander blades).

Example plants
Many FFC units are operating with these systems.

Reference literature
[45, Sema and Sofres, 1991], [80, March Consulting Group, 1991], [297, Italy, 2000], [115, CONCAWE, 1999]

4.5.9.2 Electrostatic precipitators

Description
A short description of an electrostatic precipitator can be found in Section 4.23.4.

Achieved environmental benefits
Typical particulate emission levels achieved with electrostatic precipitators range from 10 - <50 mg/Nm^3 of particulate matter in the flue gas of the FCC regenerator. This level is based on averaged continuous monitoring, excluding soot blowing. The range depends on the type of catalysts, the mode of FCC operation and whether other pretreatment techniques are implemented before the ESP. Particulate abatement measures in FCC with electrostatic precipitators with efficiency greater than 99.8 %. Efficiency is not dependent on particulate size or on flue gas velocity and the pressure drop is very marginal. As a consequence of the particulate reduction, the metals (Ni, Sb, V and their components) can be reduced to less than 1 mg/Nm^3 (given as Ni, Sb and V total) and, within that, Ni and its components can be reduced to less than 0.3 mg/Nm^3 (given as Ni). (Half-hourly mean values attainable in continuous operation and with soot blowing in the CO boiler). Particulate emissions from the FCC can thus be reduced to 1.1 - 2.3 kg/h.

Cross-media effects
Because these systems recover the fine particulates (mainly catalyst) coming from the FCC, the refinery may need extra facilities to manage the fine particulates recovered. ESPs also consume electricity.

Operational data
Electrostatic precipitators cause a very slight pressure drop. The extra energy consumption is relatively low, but they consume electricity. They also require high maintenance to keep the capture efficiency high. Continuous monitoring of particulates is not amongst the most reliable continuous monitoring systems. Information from a EU+ refinery shows that the use of deep-desulphurisation of the feedstock have a great impact of the electrostatic properties of the particulates (because content of sulphur and metals are smaller) reducing the availability of the ESP to catch those particulates. In those cases, they have reported that the best values achievable are 30 – 35 mg/Nm^3.

Applicability
Because the FCC outflows to be treated are large (1.5Mt/yr FCC generates 2.8 million Nm^3/day) and the flow gas speeds should be low to increase the capture of particulates, these systems require a lot of space. ESP may be difficult to apply if high electrical resistivity particulates are to be captured.

Economics

Size of the FCC (Mt/yr)	Efficiency (%)	Downstream PM concentration (mg/Nm^3)	Investement (EUR million)	Operating cost (EUR million/yr) *
1.5	90	30	4 - 6	0.25 - 0.5
1.5	85 - 95	<50	3 - 5	0.25 - 0.5
1	95	10 - 20 *	5.5	small @
1.5	90 - 95	<50 #	4 - 6	0.25 - 0.5

Note: Operating costs include only direct cash operating expenses i.e. do not include depreciation of investment, nor financial charges. Investment costs refer to new plant installation.
* Initial concentration: 250 - 300 mg/Nm^3 range
Initial concentration 4000 mg/Nm^3
@ Disposal of fines not included

Table 4.9: Economic data of ESP applied to FCCs

Driving force for implementation
Reduction of particulate emissions.

Example plants
More than 10 European refineries use ESP in their FCCs. They are also used in many refineries in the USA and Japan.

Reference literature
[45, Sema and Sofres, 1991], [297, Italy, 2000], [117, VDI, 2000], [247, UBA Austria, 1998], [222, Shell Pernis, 1999], [115, CONCAWE, 1999], [268, TWG, 2001]

4.5.9.3 Filters

Description
A further option for regenerator exhaust gases are filters (bag, ceramic or stainless steel filters).

Achieved environmental benefits
They are able to achieve higher performance figures (<1 - 10 mg/Nm^3) than cyclones and electrostatic precipitators.

Operational data
Bag filters are temperature-sensitive (<200 ºC) and hence their use is limited. They cause a high-pressure drop.

Applicability
Fabric or bag filters can be retrofitted to the underflow of third-stage cyclones. However bag filters are not favoured for use in the FCC because of the pressure drop, the potential for "blinding" of the bags, the large space required and their inability to cope with upset conditions.

Driving force for implementation
Reduction of particulate emissions.

Example plants
At least one successful application in European FCC.

Reference literature
[80, March Consulting Group, 1991]

4.5.9.4 Control and re-use of the catalyst fines

Description
Significant quantities of catalyst fines are often present around the FCCU catalyst hoppers, reactor and regeneration vessels as well as those collected by the abatement techniques mentioned above. The fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Those techniques may be considered as a housekeeping measures, included in Section 4.15. Some techniques to consider are:

- dry sweeping the catalyst fines and sending the solids to be recycled or disposed of as non-hazardous waste.
- use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse for collection.
- recycling opportunities for the fines (cement production).

Achieved environmental benefits
Reduce the emission of particulates.

Applicability
Fully applicable especially during catalyst loading/unloading processes.

Driving force for implementation
Reduction of soil contamination by particulates.

Example plants
Techniques already in use in USA refineries.

Reference literature
[80, March Consulting Group, 1991]

4.5.9.5 Removal of catalyst from slurry decant oil

Description
Two types of techniques have been applied to improve separation of catalyst from slurry decant oil from the slurry settler used in catcracker: a) One system incorporates high voltage electric fields to polarize and capture catalyst particles from decant oil. b) The amount of catalyst fines reaching the decant oil can be also be minimized by installing high-efficiency cyclones in the reactor to shift catalyst fines losses of the decant oil to the regenerator, where they can be collected by any particulate abatement technique.

Achieved environmental benefits
Decant oil sludge from the FCC can contain significant concentrations of catalyst fines. These fines often prevent the use of decant oil as a feedstock and require treatment which generates an oily catalyst sludge. Catalysts in the decant oil can be minimized by using a decant oil catalyst removal system.

Operational data
Catalyst fines suspended in the separator underflow are recycled back to the reactor.

Applicability
Hydrocyclones are applied in many FCC units.

Driving force for implementation
Reduction of consumption of catalyst and reduction of the decant oil sludge.

Example plants
Hydrocyclones, for removal of catalyst fines, are successfully applied in many FCCs.

Reference literature
[316, TWG, 2000]

4.5.10 Sulphur oxides abatement techniques

This section contains sulphur oxides abatement techniques that may be applicable to FCCs.

4.5.10.1 DeSO$_x$ catalyst additive

Description
Sulphur dioxide in the regenerator off-gas of an FCC unit can be reduced by using a catalyst (metal (e.g. Al/Mg, Ce) oxide) which transfers a significant portion of the sulphur associated with the coke on the catalyst to the reactor, where it is liberated as hydrogen sulphide. This leaves the reactor with the cracked vapour product for capture in the refinery's amine scrubbing system and hence conversion of sulphur in the SRU. DeSOx is a 3-step process: a) oxidation of SO_2 to SO_3 catalysed by cerium, b) adsorption of SO_3 produced in the regenerator to give a sulphate which, on return to the reactor, c) reverts to the oxide and releases hydrogen sulphide into the product gas stream for recovery.

Achieved environmental benefits
The amount of SO_x removed is dependent on the amount of deSO$_x$ additive added to the unit, but removal efficiency is typically 20 - 60 % in full combustion mode. This technique can remove up to 30 % of SO_x when used in the partial combustion mode. Typical downstream effluent has a SO_2 concentration of 1300 to 3000 mg/Nm^3 @ 3 % O_2 (initial concentration 4250 mg/Nm^3 @ 3 % O_2, feedstock sulphur approximately 2.5 %).

Cross-media effects
Disadvantages of the process are:
- deSOx additive is more efficient in full burn mode. However, full burn implies more SO_x and NO_x formation than partial combustion mode
- possible poorer yield of products from FCC unit
- reduced FCC unit operating flexibility
- other impacts are the increased energy consumption and the possibility of bottlenecks in the H_2S handling facilities.

Applicability
This technique is sensitive to unit design, especially regenerator conditions. It operates most effectively under full oxidising conditions, when as much as 50 % of the sulphur in the flue gases can be removed. Unit performance may, however, be affected and transfer catalyst replacement rate may be significant.

Economics
There are no major investment costs required for this option, save for the dosing equipment for introducing the additive to the catalyst system. Operating expenses are around 0.34 - 0.7 EUR/t (EUR 1 million/yr for a 1.5 Mt/yr FCC). Another reference gives a typical cost of EUR 3 million/yr (1997) for the catalyst for a gas flow of 200000 Nm^3/h (2.3 Mt/yr FCC). Cost is highly dependent on the unit, the initial SO_2 emissions and the SO_2 target.

Driving force for implementation
Reduction of sulphur oxide emissions from the FCC.

Example plant(s)
Many refineries have applied deSO$_x$ additives to the catalyst. The method is well established commercially.

Reference literature
[115, CONCAWE, 1999], [45, Sema and Sofres, 1991], [112, Foster Wheeler Energy, 1999], [297, Italy, 2000], [316, TWG, 2000]

4.5.10.2 Wet scrubbing

Description
There are several wet scrubbing processes. A brief description is included in Section 4.23.5.4.

Achieved environmental benefits
A suitably designed wet scrubbing process will normally provide an effective removal efficiency of both SO_2/SO_3 and particulates. With the inclusion of an extra treatment tower, to oxidise the NO to NO_2, NO_x can also be removed partially. Table 4.10 shows the achievable emission levels that can be expected with a wet scrubber.

	Efficiency (%)	Inlet (mg/Nm^3) @ 3 % O_2	Outlet (mg/Nm^3) @ 3 % O_2
SO_x	95 - 99.9	600 - 10000	10 - 400
Particulates	85 - 95	350 - 800	<10 - 35
NO_x	70	600	180
Hydrocarbons			50
Note: Particulates removal is very much design related and system pressure drop is big variable. Scrubbers are less effective on reducing sub micron particles.			

Table 4.10: Achievable emission levels for wet scrubbers

Technique	Reduction efficiency (%)	Inlet (mg/Nm^3) @ 3 % O_2 160 - 180 °C	Outlet SO_2 concentration (mg/Nm^3) @ 3 % O_2 120 °C
Wellmann Lord	98	2000 - 7000	100 - 700

Cross-media effects
The wet scrubbing system creates secondary problems of aqueous slurry waste disposal and increases the refinery energy consumption. The effluent water purge contains Na_2SO_4. Other drawbacks are the expensive raw material, e.g. caustic soda, if sulphur and other loadings are high, and they may need flue gas reheat to prevent plume mist. These systems are generally sensitive to other contaminants such as particulates, salts and sulphur trioxide. Other impacts are the possible debottlenecking of H_2S handling facilities (e.g. SRU, amine scrubbers), the production of a by-product as well as the raw material supply and handling.
Wellman-Lord system: Increased energy consumption, By-product, raw material supply and handling, possible bottlenecking of H_2S handling facilities.

Operational data
They are flexible and reliable. Day-to-day operating changes can be readily handled. They generate low pressure drop, operate at low temperature and do not create solid deposition problems. Some CO_2 will be removed as well by wet scrubbers, reducing the capability of the media to dissolve SO_2. More information can be found in Section 4.23.5.4

Applicability
They are compact systems and fully applicable. The system ranges from 93 to 465 m^2 for FCCs ranging from 55.2 to 276 dm^3/s feed rate (1.5 to 7.5 Mt/yr). Recent trends include forced oxidation to process the SO_2 in the SRU, reaction with lime to produce gypsum, a commercial product where there is a market. Spin-off application of power plant, equipped with Wellmann-Lord FGD. More information can be found in Section 4.23.5.4.

Economics

Objective of the process	FCC capacity (Mt/yr)	Investment expenses (EUR million)	Operating expenses (EUR million/yr)
SO_2 reduction	1.5	10	2 - 5
Particulates reduction	1.5	4 - 6 2 - 5	2 - 5
SO_2 reduction	3	15 - 20	2 - 3
SO_2 reduction (regenerative)	3	24 - 28	1.5
SO_2 reduction	5	13 *	no data
SO_2 and particulate reduction	0.5 - 4	3 - 15	no data
* Investment expenses include the water purge treatment unit.			

More information can be found in Section 4.23.5.4.

Driving force for implementation
Abatement of sulphur oxides and particulates from the flue gas.

Example plants
It exists a considerable operating experience. This technique is widely used on FCC unit plants in the USA. Wellman Lord system has been successfully applied to power plants. More information can be found in Section 4.23.5.4

Reference literature
[181, HP, 1998], [269, Confuorto, 2000], [45, Sema and Sofres, 1991], [247, UBA Austria, 1998]

4.5.10.3 Venturi scrubbing

Description
Two variants exist, the jet venturi and the high-energy venturi.

Achieved environmental benefits
Reduction of particulate emissions. Moreover, it can also remove most of the sulphur dioxide present in the flue gases. Tertiary cyclones with venturi scrubber in the FCCU regenerator have reached efficiencies of 93 % in reducing SO_2 and particulate emissions.

Cross-media effects
They produce liquid and solid waste and a wet gas plume.

Operational data
These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc.

Applicability
The high-energy venturi is the design usually favoured by recent installations. Widely applied for the treatment of small emissions flows.

Driving force for implementation
Reduction of sulphur and particulate emissions.

Example plants
Venturi scrubbing, using an alkaline liquid, has been used successfully on a less widespread scale.

Reference literature
[112, Foster Wheeler Energy, 1999].

4.5.10.4 Dry and semi-dry scrubbers

Description
Two types of techniques exist: dry and semi-dry. The key component of the semi-dry process is a spray dryer in which the hot flue gas is contacted with a spray of fine droplets of lime slurry. The SO_2 is absorbed into the droplets, forming reaction products which are dried to a fine powder by the hot flue gas. Both dry and semi-dry processes require downstream dust arrestment systems, such as an electrostatic precipitator or bag filtration. More information can be found in Section 4.23.5.4.

Achieved environmental benefits
Reduction of the SO_2 in the flue gas. Efficiency of the processes: 90 % sulphur removal with semi-dry process and about 50 % removal with dry process. Dry process efficiency of 50 % is obtained with lime at relatively high temperature (about 400 ºC) when Ca/S=1 or at 130 - 140 ºC with Ca/S=2. The Ca/S ratio has a major influence. With reactant such as $NaHCO_3$, the abatement rate would be much higher. With lime, it is also possible to have a treatement at 900 ºC in a reactor big enough to have a reasonable residence time. The abatement in this case is 80 % with CaS= 2.1 and 90 % with Ca/S=3.

Cross-media effects
Deposition of solid waste results in case that the reaction products cannot fullfill the quality needed by consumers. Other drawbacks are:

- high pressure drops across the bag filters if are used
- increased dust load in gas stream; need for dust capture
- operational difficulties in water/heat balance (spray dryers only)
- possibly significant pressure drop across bag filter dust arrestment plant, e.g. bag filters
- generation of solid waste: 1 tonne of SO_2 reduction entails about 2.5 tonnes of solid wastes being generated
- with the dry- and semidry scrubbers a mixture of $CaSO_3$, $CaSO_4$, fly-ash and lime is produced.

Operational data
These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc.

Applicability
Operate at low-temperature end of system. Waste generated can be difficult to re-use (no market for gypsum), and difficult to landfill (landfill use to be severely restricted in near future).

Economics
Dry process is a relatively low cost solution. Raw materials for those processes are cheap. Capital cost and operating costs typically less than wet scrubbing. Investment cost around EUR 15 - 20 million, and operating cost around EUR 2 - 3 million/yr (lime cost + landfill waste disposal).

Reference literature
[112, Foster Wheeler Energy, 1999], [257, Gilbert, 2000], [45, Sema and Sofres, 1991], [297, Italy, 2000]

4.5.10.5 Seawater scrubbing

Description
This scrubbing uses the natural alkalinity of the seawater to remove SO_2. More information can be found in Section 4.23.5.4.

Achieved environmental benefits
SO_2 recovery can be as high as 99 %. In order to reduce the particulate emissions to the seawater, a particulate abatement technique should be included before the flue gas is treated in the seawater scrubber. In this way, seawater scrubbing can be seen as a transfer of the remaining pollution from air to seawater.

Cross-media effects
Particulates containing metals (e.g. V, Ni, Sb) and other pollutants from the flue gas are transferred to the seawater. The sulphur content of the effluent seawater from the process itself is increased by only approximately 3 %.

Operational data
The system needs electrical power (seawater pumps, aeration fans and flue gas fan) and seawater. It is feasible to use spent cooling water, for example, when seawater is used as cooling water. The need for seawater is roughly 15000 - 20000 m^3/h per tonne of sulphur removed. Special attention should be paid to minimise corrosion and the maintenance derived from it.

Applicability
The feasibility of applying seawater scrubbing is site-dependent. The process needs access to seawater in large amounts at a competitive cost. Fully applied for fuels up to 1.5 % of sulphur. This system normally is applied after a particulate abatement technique to avoid contamination of sea environment by particulates (containing metals).

Economics
Seawater scrubber annual costs depend on size and SO_x in/out. The cost is comparable to wet scrubbers. Typical investement cost is in the order of EUR 60 /net kWe output of the power plant. The main operating cost is the electrical power for operation of the technique.

Driving force for implementation
Reduction of SO_2 emissions.

Example plants
System applied to some power plants aroung the world and one proven commercial application in FCC, Norway.

Reference literature
[278, Alstom Power, 2000]

4.5.10.6 Wet gas sulphuric acid process (WSA)

Description
See Section 4.23.5.4.

Achieved environmental benefits
99 % reduction of SO_2 and some reduction of NO_x. In combination with a SCR, simultaneous reduction of NO_x 95 %.

Reference literature
[247, UBA Austria, 1998]

4.5.11 Combined abatement techniques

Description
There are processes on the market that include an ESP, a SCR for NO_x, catalytic oxidation of SO_2 and production of sulphuric acid. More information about this technique can be found in Section 4.23.3.

Achieved environmental benefits

Pollutant	Efficiency of removal	Concentration in the outlet (mg/Nm^3)
SO_2	>94 %	
NO_x	≥90 %	
Particulates		< 10

The integrated system produces also sulphuric acid of 95 % w/w.

Cross-media effects
See each of the particular techniques included in this process.

Operational data
See each of the particular techniques included in this process.

Applicability
Process qualified for treating very high SO_2 concentrations in the flue gas.

Economics

Design capacity	1000000	Nm^3/h
Investment cost	100	EUR million

Driving force for implementation
Reduction of emissions of SO_2, NO_x and particulates.

Example plants
Applied to FCC and coking flue gas.

Reference literature
[297, Italy, 2000]

4.5.12 Waste management techniques

Description
Waste is generated during the FCC processes. The selection of catalyst used in the FCC, control of the emissions of particulates and the proper management of product and slurry tank bottoms can reduce the generation of waste. Also the implementation of benchmark performance on the waste generation may be an incentive on how and how much the total amount of waste can be reduced.

Achieved environmental benefits
Reduction of waste generation.

Operational data
Those techniques can be seen as part of the waste management programme of a refinery.

Applicability
See Section 4.5.6 for applicability restriction of selection of catalyst.

Driving force for implementation
Reduction of waste management cost and losses of catalyst.

Example plants
Applied in many refineries.

Reference literature
[268, TWG, 2001]

4.6 Catalytic reforming

The first two techniques considered are process techniques and the rest are techniques for the prevention or control of emissions from the catalytic reforming processes.

4.6.1 Continuous catalytic reformer

Description
In the continuous process, the catalyst is regenerated continuously and maintained at high activity. Catalyst is regenerated in one external reactor. More information can be found in Section 3.6.

Achieved environmental benefits
This process has a higher energy efficiency than semi-regenerative due to the heat recovery from products, from pumparounds and due to integration with topping and vacuum.

Cross-media effects
It generates more dioxins than semi-regenerative during the regeneration of the catalyst. For more information, see Section 3.6.

Operational data
It operates at lower pressures (6 - 14 bar) than and at the same temperature as semi-regenerative processes. It uses bi-metallic catalysts (Pt-Re, Pt-Sn). Hydrogen is also produced in those processes. Continuous regeneration reformer produces around 350 Nm^3 of hydrogen per tonne of feedstock. As increased coke laydown and thermodynamic equilibrium yields of reformate are both favoured by low-pressure operation, the ability to maintain high catalyst activities and selectivities by continuous catalyst regeneration is the major advantage of the continuous type of unit.

Applicability
Fully applicable.

Economics
Investment cost based in 3975 m^3/d continuous octanizing unit, battery limits, erected cost, 1998 Gulf Coast: 10000 USD per m^3/d. The erected cost based in 3180 m^3/d has been of USD 48.3 million ($15200 per m^3/d). In addition, catalyst costs add another USD 2.6 million. Costs are 4Q95 US Gulf Coast.

Driving force for implementation
Production process. The biggest disadvantage for the future is the high content of aromatics (70 - 75 %) in CCR product. A lot of refineries will have great difficulty in reaching the gasoline specifications of 35 %v/v for aromatics as from 2005 onwards.

Example plant(s)
Nowadays, only continuous catalytic reformer units are built.

Reference literature
[212, Hydrocarbon processing, 1998], [166, Meyers, 1997], [268, TWG, 2001]

4.6.2 Semiregenerative reformer

Description
A brief description can be found in Section 2.6.

Achieved environmental benefits
Heat integration is lower than in the case of continuous reformers. However, many semiregenerative units have applied better feed effluent exchange to minimise energy consumption.

Cross-media effects
In semi-regenerative reforming, the unit catalyst is regenerated at intervals of 3 to 24 months, depending upon the intensity of the process. The emission factor of dioxins per tonne of feedstock is much lower than in the case of continuous regeneration. For more information, see Section 3.6.

Operational data
The reactors operate at temperature in the range of 400 - 560º C and pressures in the range of 20 - 50 bar. This type of process produces between 130 and 200 Nm^3 of hydrogen per tonne of feedstock.

Applicability
Fully applicable.

Economics
The erected cost of a semiregenerative unit of 3180 m^3/d is 33 million USD (10400 $ per m^3/d). In addition, catalyst costs add another 3.4 million USD. Costs are 4Q95 US Gulf Coast.

Driving force for implementation
Production process.

Example plants
Many applications exist in Europe as well as in the rest of the world.

Reference literature
[261, Canales, 2000], [166, Meyers, 1997]

4.6.3 Type of catalyst promoter

Description
Ozone depleting substances (e.g. carbon tetrachloride) are sometimes used during the regeneration of the catalyst of the reformer. Emissions of such substances should be avoided or at least minimized by using less harmful substitutes or by using them in confined compartments.

Achieved environmental benefits
Optimisation and reduction of use of catalyst promoters and ozone-depleting substances.

Cross-media effects
Due to the use of chlorinated compounds, the possibility of emissions of dioxins and furanes during generation has been detected. Refer to Section 3.6.

Operational data
Promoters should be handled in enclosed systems.

Example plants
Most refiners have switched to lower ozone depleting substances such as perchloroethylene during the regeneration of the reforming catalyst.

Reference literature
[80, March Consulting Group, 1991]

4.6.4 Cleaning of the regeneration flue gas

Description
Regenerator flue gas containing HCl, H_2S, small quantities of catalyst fines, traces of Cl_2, SO_2 and dioxins can be sent to a scrubber prior to to release to atmosphere. The storage and handling of organic chlorides used during the regeneration may also lead to releases. In some reformers a further filter trap of Cl_2 ($ZnO/NaCO_3$ or NaOH over alumina) is installed.

Achieved environmental benefits
Reduction of particulates and volatile acids (HCl, H_2S). It has been reported that Cl_2 filter also traps dioxins.

Cross-media effects
The recirculated and bleed streams from the regeneration flue gas wash should be sent to the waste water treatment plant. Due to low pH of this waste water stream, neutralisation prior to biological treatment may be necessary. The use of scrubber can move some dioxins from the air to a water emission.

Applicability
Fully applicable. Cl_2 trap has been used in continuous reformers.

Driving force for implementation
Reduction of air pollutants

Reference literature
[112, Foster Wheeler Energy, 1999], [268, TWG, 2001]

4.6.5 Electrostatic precipitator in the regeneration flue gas

Description
Regenerator flue gas containing HCl, H_2S, small quantities of catalyst fines, traces of Cl_2, SO_2 and dioxins can be sent to an electrostatic precipitator prior to release to atmosphere. Other activities as venting during catalyst regeneration or replacement and plant cleaning may be sent to the ESP.

Achieved environmental benefits
Reduction of particulate content in the flue gas coming from the regenerator.

Cross-media effects
See Section 4.23.4.2

Applicability
Emissions from continuous regeneration sections require particular attention. The use of this type of systems in semiregenerative units is less extended because almost no exists mechanism for the generation of catalyst fines.

Driving force for implementation
Reduction of particulate emissions during the catalyst regeneration.

Reference literature
[112, Foster Wheeler Energy, 1999], [268, TWG, 2001]

4.6.6 Dioxins formation in catalytic reforming units

Description
Referring to Sections 3.6 and sections in 4.6 on catalytic reforming, dioxins are typically formed in the three types (continuous, cyclic and semiregenerative) of catalytic reforming during the regeneration of the catalyst.

If the regenerator flue gas is treated in a water scrubber (e.g. Section 4.6.4), the dioxins have been appeared detectable in waste water from the scrubber, but they have not been detected after the WWTP, possibly because dilution effects.

In some other cases, because the use of other techniques as fixed bed filters have result in a combine reduction of chlorine and dioxins. In some cases, activated carbon has been used to remove dioxins. Other techniques that have been used is the recirculation of regeneration vent gases. However this last one is not clear how it can reduce the emission of dioxins.

The study of dioxins emissions from reformers and how the regeneration conditions may affect those emission can be a good technique to start to understand and solve the problem.

Achieved environmental benefits
Knowledge of the problem and control of the dioxin emissions.

Cross-media effects
Some dioxins from the regenerator gases may be transferred to water via scrubbing.

Driving force for implementation
Knowledge of the formation of dioxins in regeneration of the catalyts.

Example plants
Some EU+ refineries have already applied and monitored dioxins emission from catalytic reformers. Techniques as chlorine trap and recirculation of vents have not been reported that have been applied to semiregenerative reformers.

Reference literature
[268, TWG, 2001]

4.7 Coking processes

The first four techniques considered in this section are coking processes. The information given is intended to help in assessing how well coking processes can perform from the environmental point of view. The rest of the techniques are related to the cleaning of the coke gas, the use of the coking process to destroy solid residues/sludges and, finally, those techniques related with the abatement of pollution generated by the coking processes.

4.7.1 Delayed coking

Description
A description of this process can be found in Section 2.7. The techniques that may be applied to the delayed coker to prevent emissions are the following:

1. uncondensable vapours generated in the coking processes should not pass to the flare system
2. pressure reliefs from the coke drums should pass to the quench tower
3. techniques for coke drum quench tower arrestment train to include consideration of venting the final emission to a flare header with the possible elimination of the second tower and blowdown pond
4. water use in the delayed coker is treated in Section 4.7.7
5. steam generated in this process can be used to heat up other refinery processes
6. the delayed coking process itself has a low level of heat integration. The heat to maintain the coke drums at coking temperature is supplied by heating the feed and the recycle stream in a furnace. However, the atmospheric residue and/or vacuum residue can be fed straight into the delayed coking unit without intermediate cooling, which results in a high heat-integration level between the different units and saves a considerable amount of capital on heat exchangers
7. use of coking gas. The energy efficiency of the coker can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined cycle units appears in Section 4.10.

Achieved environmental benefits
Reductions of VOC emissions, recovery of products and reduction of H_2S emissions are achieved when applying some of the above-mentioned techniques. Water re-use is also promoted by the application of those techniques.

Operational data
Some operational data of delayed cokers can be found in Section 3.7.

Applicability
Delayed coking is fully applicable. It is normally applied when the production of petroleum coke has a market or when high quality coke is required to produce anodes for the non-ferrous metal industry.

Economics
Typical investment of a full delayed coker (basis 1Mt/yr straight run vacuum residue feed, U.S. Gulf Coast 1998, fuel grade coke, includes vapour recovery): 136250 - 218000 USD per t/yr.

Driving force for implementation
Production process.

Example plants
Many delayed processes exist in Europe as well as in the rest of the world. Delayed coking is the most commonly used technology in the refinery sector.

Reference literature
[112, Foster Wheeler Energy, 1999], [19, Irish EPA, 1993], [118, VROM, 1999]

4.7.2 Fluid coking

Description
A description of this process can be found in Section 2.7. Another technique that can be used to prevent emissions or increase energy integration in the fluid cokig is to use the coking gas in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined cycle units appears in Section 4.10.

Achieved environmental benefits
Emission factors for coking (units in kg/1000 litres of fresh feed).

Process	PM	SO_x (as SO_2)	CO	HC	NO_x (as NO_2)	Aldehydes	NH_3
Fluid coking units uncontrolled	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fluid coking with ESP and CO boiler	0.0196	n.a.	Neg	Neg	n.a.	Neg	Neg
Neg: Negligible							

Operational data
This system operates under fluidised bed conditions.

Applicability
Fully applicable. Although the coke from fluid coking is of a higher grade than the coke from delayed coking, it is not suitable for some specialist applications (e.g. carbon graphite electrodes).

Economics
Investment (U.S. Gulf Coast 1996): 10000 - 13200 USD per m^3/d.

Driving force for implementation
Production process.

Example plants
Some examples exist around the world.

Reference literature
[136, MRI, 1997]

4.7.3 Calcination process

Description
A brief description of this process can be found in Section 2.7. Certain techniques can be applied to the calcination process to prevent emissions. Some of those considered to be beneficial are the following:

1. The kilns can be directly fuelled by coke gas or coke fines, driving off volatile matter and burning it within the kiln.
2. The hot stream of waste gas from the calcination of petroleum coke in *rotary kilns* contains considerable quantities of particulate, which - possibly after heat recovery from the waste gas - is separated with suitable filter devices, e.g. high efficiency multi-cyclones, bag filters and electrostatic precipitators (see also Chapter 4.7.8.2). During calcination in *multiple-hearth furnaces*, particulate abatement techniques are not usually used because of the comparatively low emissions in the waste gases.

3. The unburnt gases from the calcinator are burned in an incinerator, then passed through a waste heat boiler before being released to the atmosphere via a dust collection system.
4. The calcined coke discharges to rotary cooler where it is cooled by direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and water scrubber.
5. Collected fines from the dust abatement techniques should be conveyed to a silo with exit air filters. Collected cyclone fines may be recycled to product or may be used within the refinery or may be sold as product.

Achieved environmental benefits
Some of the techniques mentioned above increase the heat integration of the calciner, reducing the consumption of fuel in the refinery. Others just decrease the amount of particulates emitted to the atmosphere, re-using the coke fines generated during the calcination process. The emission values for petroleum coke production plants attainable in continuous operation are presented in Table 4.13. Those values can be achieved by applying the techniques mentioned above.

Emission component	Values attainable in continuous operation Emissions values as half hourly mean values mg/Nm^3 @ 3 % O_2
Particulate (dust) emissions	20 - 100
Particulate (dust) components: Ni, V and their components (given as Ni and V total)	3 - 15
NO_x (as NO_2)	450 - 875
SO_x (as SO_2)	1000 - 3000 (No SO_2 abatement technique included)
CO	100
HC (given as total carbon)	20

Table 4.11: Emission values for petroleum coke production plants (calcination of green coke)

Operational data
Some operational data of petroleum coke calciners can be found in Sections 2.7 and 3.7.

Applicability
Applied to coke produced by delayed cokers and fluid cokers.

Driving force for implementation
Production process. For certain applications, green coke produced by the delayed coker should be *calcinated* before being used or sold.

Example plants
Many examples exist in Europe and around the world. Multiple-hearth furnaces have been extensivelly applied to waste incineration. A majority of facilities that calcine coke utilise a rotary kiln. The last two calcining facilities built in the world are rotary kilns.

Reference literature
[117, VDI, 2000], [147, HMIP UK, 1995], [268, TWG, 2001], [347, Services, 2001]

4.7.4 Flexicoking

Description
A brief description of this production process can be found in Section 2.7. Some techniques that may be applied to prevent emission from the flexicoker are:

1. The flexicoking process has a high level of heat integration. The only source of heat in the Flexicoker process is the gasifier, where the coke is partially oxidised. The remainder of the heat in the coker gas is recovered by generating steam. The energy efficiency can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. See Section 4.10.
2. As coke cutting from drums is not needed, emissions and dirty effluent generation are avoided compared to delayed coking. Moreover, the sulphur components from the coke gas are easy to eliminate. Some 84 - 88 % w/w of the hydrocarbon feed is recovered as hydrocarbon product, the remainder is converted into CO, CO_2 and H_2O.
3. The coke gas from the heater is passed through a cyclone set to remove the coarser coke particles and is subsequently cooled by generation of high-pressure steam and by preheating boiler feed water. About 75 % of coke fines which pass through the two stages of heater cyclones are recovered in tertiary cyclones. Almost all the coke fines which escape the tertiary cyclones are scrubbed out in the venturi scrubber. The water slurry from the venturi scrubber is steam stripped to remove absorbed hydrogen sulphide and ammonia.

Achieved environmental benefits
1. Increases the energy efficiency of the flexicoking process.
2. Generates less waste than delayed coking.
3. Prevents particulate, hydrogen sulphide and ammonia emissions.

Operational data
Some operational data for flexicokers can be found in Sections 2.7. and 3.7.

Applicability
Fully applicable. However, because the products from flexicoking are different than other coking processes (e.g no coke is produced) the implementation of this option typically should consider the refinery product requirements.

Economics
Investment (basis U.S. Gulf Coast 1996): 15100 - 19500 US$ per m^3/d (typical).

Driving force for implementation
Production process.

Example plants
Many examples exist in Europe, USA and the rest of the world.

Reference literature
[212, Hydrocarbon processing, 1998], [271, Martinez del Pozo, 2000]

4.7.5 Use of oily sludges and/or waste as coker feedstock

Description
In refineries with a coker, oily sludges, sludges from the waste water treatment and waste can be destroyed in the coker (delayed, fluid or flexicoker). In the case that coke is produced, the coke quality produced should remains acceptable (acceptable with respect to further use as fuel within/outside refinery or as material for other purposes). Many oily sludges can be sent to a coking unit where they become part of the refinery products. In the case of delayed coker, the sludge can be injected into the coke drum with the quench water, or injected into the coker blowdown contactor used in separating the quenching products.

Achieved environmental benefits
Reduction of the amount of sludge and/or waste produced in the refinery. In principle any refinery with a coker is able to reduce its oily sludge production to ‘zero’ with the exception where high quality coke requirements that restrict its use.

Cross-media effects
Typically reduction of the quality of the coke produced.

Applicability
The quantity of sludge or waste that can be sent to the coker is restricted by coke quality specifications which may limit the amount of solids in the coke. Coking operations can be upgraded, however, to increase the amount of sludge that they can handle.

The quantity of solids injected depends on the slurry's solids content, being typically 10 to 15 %. Loading rates exceeding 82 kg of oil-free dry solids per tonne of coke have been established. Higher rates are achievable. At this loading rate, the coke is below anode-grade specifications, but within fuel-grade specifications. Cokers in general are an attractive process-integrated reprocessing outlet for oily sludges, provided the sludge-on-feed ratio is kept below 1 - 2 %, depending on the required coke quality. If that ratio is not achieved, neither the operability nor the coke quality is affected.

If sludges from the waste water treatment are included as feedstock to the coker, part of the water need to be eliminated (e.g. by vacuum evaporation or in the blowdown system) if the amount of residues would like to be maximised.

Economics
Typical applications recycle 2 to 16 t/d of oil-free dry solids at a total programme cost of EUR 0.6 - 2.5 million/yr.

Driving force for implementation
Reduction of waste generation in the refinery.

Example plants
Use of sludge as a feedstock has increased significantly in recent years and is currently carried out by most refineries.

Reference literature
[147, HMIP UK, 1995]

4.7.6 Cleaning of the coking gas

Description
After the coking gas has been cleaned to remove particulates and to recuperate part of its heat, it is heated and passed over a catalyst bed in the COS converter, where COS is converted to H_2S. The gas is then cooled and most of the water is condensed. The H_2S is recovered from the coke gas in an amine treater for ultimate recovery of sulphur (see amine treating of refinery fuel gas in Section 4.23.5.1). Clean low-sulphur coking gas can either be burned in boilers and furnaces or can be sold as low calorific-value gas. The next figure shows a scheme of that process.

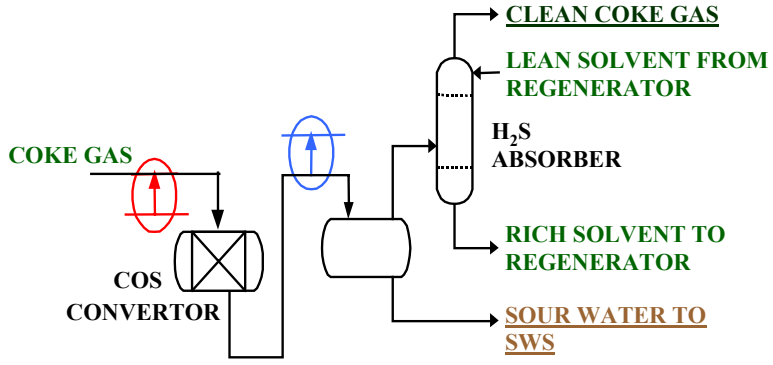


Figure 4.2: Treatment of the coking gas

Achieved environmental benefits
Reduction of the emissions of H_2S (less than 100 ppm v/v) and COS.

Cross-media effects
Increased use of the amine scrubbing system and increased energy consumption of the COS convertor.

Operational data
For amine scrubbing see Section 4.23.5.1.

Applicability
Amine scrubbing is applied to all types of cokers and COS convertor to flexicokers.

Economics
Economics of the amine absorption of H_2S can be found in Section 4.23.5.1

Driving force for implementation
Cleaning of the coke gas. Coke gas forms a main refinery gas source (after dust removal, COS conversion and amine treating for H_2S removal).

Example plants
These systems can be found in many cokers.

Reference literature
[118, VROM, 1999]

4.7.7 Water use in the cooling/cutting process

Description
The water used in the cutting/cooling operations is continuously recirculated with a bleed-off to the refinery waste water treatment. Settling and filtering over a vacuum filter enables the re-use of this water, resulting in a 'closed water loop'. For water make-up to the quenching and cutting water loop, various effluent streams can be used. For this duty treated effluent could be used. Collected water from any condenser, and for draining of wet green coke, should be re-used for coke drum quenching or drilling. This type of cooling is not used in any other process in the refinery because of environmental concern. More information about direct cooling (quenching) is found in Section 2.8.

Achieved environmental benefits
Reduce consumption of water in the refinery.

Cross-media effects
Cutting and cooling process result in vapour emissions (partially recycled in the main fractionator), significant energy losses, large water use and severe water pollution. Bleeding of cutting water to the desalter has the potential to add solids to the effluent, so it is best to keep coker waters separate.

Operational data
The amount of required make-up water depends on the evaporation losses and the bleed to other processes or to the waste water treatment plant and amounts to about 10 - 20 m^3/h for a 10^6 t/yr delayed coker unit.

Applicability
Applicable when delayed coking is used. Re-use of water is subjected to restrictions of coke quality.

Driving force for implementation
Technique typically used in the delayed coking process.

Example plants
Many examples of application exist in the world.

Reference literature
[268, TWG, 2001]

4.7.8 Handling and storage of the coke

Description
Several techniques are suitable to reduce particulate emissions that may occur during the handling of the coke (green and calcined):

1. providing the green coke is kept wet, the handling between the discharge and the calciner feed hopper is not problematic. There is the possibility of parts of the receiving pit drying out although this is limited as the coke is very wet and is covered with residual hydrocarbons which tend to make it stick together. The construction of wind-breaks around the pit might be considered. Careful design is essential, as bad design could make the situation worse. Complete enclosure of the pit and associated handling facilities is another possibility. The pits are very large and such an enclosure would be very expensive. A monitoring programme should be carried out to evaluate if this option is in fact necessary or desirable
2. cut the coke into a double-roll crusher, for example, and convey it to an intermediate storage silo. The railway waggons are then loaded from the storage silo. This approach would collect, filter, and dewater the coke prior to storage
3. spray the coke with a very fine layer of oil, which sticks the dust fines to the coke. The use of oil is limited by its acceptability in further processing. The oil option has the added advantage of reducing unloading problems
4. covered and de-pressurised conveyor belts
5. aspiration systems to extract or collect dust
6. use of an enclosed hot blowdown system
7. loading areas could be enclosed and positive/negative pressures maintained, exhausting through bag filters. As alternative dust extraction systems can be incorporated with loading equipment.
8. collected fines from the cyclones are pneumatically conveyed to a silo with exit air filters. Dust collection systems are provided for handling, storage and loading, using bag filters. Collected fines are re-cycled to storage by enclosed means.

Achieved environmental benefits
Eliminates releases to air of particulates (containing metals) from this part of the process during routine operation as well as from the storage of the coke. Achievable release level of particulate matter for solids handling is 25 mg/Nm^3 (value based on averaged continuous monitoring).

Operational data
Additionally, the storage silo provides a buffering capacity for process fluctuations and enables a controlled loading of railway waggons.

Applicability
3. Oling coke is sometimes practised in fluid and calcined coke, but is rarely applied with delayed coke.
8. That technique is mostly applicable to calciners, fluid cokers and flexicoking units.

Economics
The investment cost of about EUR 30 million for a typical coking unit with a capacity of 1.5 Mt/yr may be expected for the storage system.

Driving force for implementation
Reduction of coke spillage. If the petroleum coke is cut directly from the coking units into railway hopper waggons, it may cause overfilling of the waggons, degrading the quality of the spilled coke and increasing the amount of solids entering the waste water treatment system.
Reduction of particulate emissions from the storage system of the coker.

Example plants
Many examples available in European refineries.

Reference literature
[261, Canales, 2000], [80, March Consulting Group, 1991], [117, VDI, 2000], [268, TWG, 2001]

4.7.9 Techniques to reduce air emissions

This chapter mentiones where the abatement techniques may be used and describes the techniques used for abatement of air pollutants.

4.7.9.1 Particulate abatement in coking processes

Description
Flue gases and coke gas from coking processes normally contain coke particulates (including metals). Dust collection systems are then used in some parts of the coking processes.
1. cleaning of coke gas
2. cleaning of the gas produced during the coke cooling
3. incinerated exhaust gases from the calcinator also produce coke fines. Hot flue gases pass through a waste heat boiler and gas cleaning by a dust collection system.

In addition to the particulate abatement technique used in the FCC (Cyclones or ESP in Section 4.5.9) that may be also used here, bag filters can be used in this processes.

Achieved environmental benefits
Achievable release levels of particulate matter (values based on averaged continuous monitoring) from calciners and coolers are 10 - 100 mg/Nm^3.

Cross-media effects
See Section 4.5.9.

Operational data
See Section 4.5.9. The application of ESP for the control of particulate emission from petroleum coke calciner have shown some difficulties to achieve the lower end of the range. The main reason is that coke is a very good conductor of electricity and consequently its surface is very difficult to be electrically charged and consequently difficult to be catch by the ESP.

Applicability
See Section 4.5.9. The application of high efficiency cyclones are easier to be applied than ESP.

Economics
Bag filters can be used at a cost of about EUR 5 million EUR. Calciner boiler cyclones cost EUR 225000 (1999). Economics for other type of systems are not available. An economic study done in a EU+ refinery in 1992 shown that the cost for an ESP for a calciner was high.

Driving force for implementation
Reduce the particulate emissions from the calciner.

Example plants
Many examples are available in European refineries that have coking processes.

Reference literature
[147, HMIP UK, 1995] [60, Balik and Koraido, 1991], [297, Italy, 2000], [272, Shawcross, 2000], [117, VDI, 2000], [268, TWG, 2001]

4.7.9.2 SO_2 abatement techniques

Description
Sulphur oxides are emitted during the coking processes, especially during the calcination processes. The principal option to reduce sulphur dioxide releases from the process is the use of the lowest possible sulphur-content feedstocks. In practice, low-sulphur feeds are typically used for product quality reasons, since a substantial part of the sulphur remains fixed in the product. However, this option is not always possible and emissions of SO_2 may be significant, especially during the calcining process. To control those sulphur oxide emissions, the same abatement techniques that may be used in the FCC may be also used in this process (Section 4.5.10 and 4.23.5.4) with the exception of the $DeSO_x$ catalyst additive.

Achieved environmental benefits
SO_2 concentration of 25 - 300 mg/Nm^3 is achieved when the techniques mentioned in the Section 4.5.10 are used.

Cross-media effects
Section 4.5.10

Operational data
Section 4.5.10

Applicability
Normally applied to calciner flue gases.

Economics
Section 4.5.10

Driving force for implementation
Reduction of SO_2 emissions.

Example plants
Some examples of these techniques can be seen in some European and worldwide refineries.

Reference literature
[297, Italy, 2000] and references in Section 4.5.10

4.7.9.3 Combined abatement techniques

The same types of techniques used in the FCC can be used in the coker. More information can be found in Section 4.5.11.

4.7.10 Techniques to prevent emissions to water

This chapter analyses the ways to prevent emissions to effluents. Techniques used in the final cleaning of the waters generated in the coking processes are in Section 4.24.

4.7.10.1 Treatment of the waste water

In the coking processes, sour water is generated (steam condensate). Consequently, all water from the coking process is send to the sour water stripper (Section 4.24.2) before being sent to the waste water treatment plant.

4.7.10.2 Separation of the oil/coke fines from the coke-cutting water

Description
The proposed pollution prevention alternative was to retrofit the sump where the oil/coke fines are collected with an inclined plate separator to increase the separation efficiency.

Achieved environmental benefits
Coke fines and water generated from the coke-cutting operation enter an in-ground sump where the solids and water are separated by gravity. A refinery study indicated that over twenty-five tonnes a year of coke fines entered the sewer system from that separator.

Economics
The annual cost saving associated with the increased recovery of product (coke) and the reduction in oil/water separation solids was approximately EUR 300000 (7.5 Mt/yr refinery).

Driving force for implementation
Reduce the coke fines entering in the sewer system.

Reference literature
[60, Balik and Koraido, 1991]

4.7.11 Techniques to reduce soil contamination

4.7.11.1 Control and re-use of the coke fines

Description
Coke fines are often present around the coker unit and coke storage areas. The coke fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Collection techniques include dry sweeping the coke fines and sending the solids to be recycled or disposed of as non-hazardous waste. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse for collection.

Achieved environmental benefits
Reduced soil contamination by coke particulates (including metals). Coke fines can be recycled for fuel use or can be sold outside (e.g. cement production).

Cross-media effects
Electricity consumption by vacuum ducts/hoses.

Applicability
Fully applicable.

Driving force for implementation
Reduction of soil contamination.

Example plant(s)
Techniques already in use on USA refineries.

Reference literature
[60, Balik and Koraido, 1991]

4.8 Cooling systems

Under the IPPC process, a horizontal BREF on industrial cooling systems has been produced. The following topics of relevance to refineries are already described and analysed in that BREF:

1. Reduction of direct energy consumption
2. Reduction of water requirements
3. Reduction of entrainment
4. Reduction of emissions to water
5. Reduction of air emissions
6. Reduction of noise emissions
7. Reduction of risk of leakage
8. Reduction of biological risk

The description and analysis includes an extensive discussion of environmental benefits of systems, cross-media effects, operational data, applicability and economics. To avoid repetition, therefore, this section on cooling addresses only topics not covered by that horizontal BREF.

4.8.1 Segregation of cooling and process waters

Description
Because process waters are normally more contaminated than cooling waters, it is important to maintain the segregation of the two. Only in cases where cooling waters need treatment (recirculation systems) should they be mixed, and then only at the right point (after the primary treatment of the process waters).

Achieved environmental benefits
It reduces the contamination of cooling water by oil coming from other waters. It increases the recovery of oil by the waste water plant.

Cross-media effects
No cross-media effect has been found.

Applicability
Waste water treatment plant need to be sized to handle to the process water flow and the cooling water flow. Segregation can be very costly in some parts of existing installations.

Driving force for implementation
Avoid the contamination of cooling water by process waters, which are usually more contaminated. Some of the topics dealing with pollution of water from cooling systems have already been studied in the OSPAR and HELCOM processes (North sea and Baltic sea region).

Reference literature
[107, Janson, 1999], OSPAR, HELCOM recommendations.

4.8.2 Air cooling

Description
See Section 2.8 and BREF on cooling.

Achieved environmental benefits
The major advantage of using air coolers is that no additional medium is required.

Cross-media effects
Tend to produce more noise than water cooling. Noise production due to air cooler fan is 97 - 105 dB(A) at source.

Operational data
A major disadvantage is, that normally a large plot is required when compared to water coolers (5 – 30 m^2/MWth duty). It requires electricity but minimal maintenance cost

Applicability
Air cooling can be sufficient for the cooling needs in some parts of the refinery processes. Ambient conditions restrict the temperature levels that can be attained. Climatic conditions (hot climates or temperatures below 0 ºC) typically restrict its use. However the plant location is independent of water availability. They cannot be located near buildings because air short-circuiting may occur.

Economics
Air coolers can be expensive. Minimal maintenance cost.

Example plants
Many examples exists in EU refineries.

Reference literature
[316, TWG, 2000], [119, Bloemkolk and van der Schaaf, 1996]

4.8.3 Prevention of oil leakages into cooling water

Description
Looses of oil throught leaks can be minimised through continuous monitoring and a kind of Leack Detection and Repare system (similar as that reference for VOC in Section 4.23.6.1). At its simplest, this comprises monitoring of the cooling water separators for oil build-up. If this is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak. A further refinement is to install oil in water monitors at various point in the cooling water sytem. This allows leaks to be detercted rapidly and corrective action taken. For this procedure to be effective, sparing of critical heat exchangers will be required. More information in the cooling BREF.

Achieved environmental benefits
Reduction of oil leakages into cooling water

Driving force for implementation
Detect and correct oil leakages into cooling water.

Reference literature
[316, TWG, 2000], [119, Bloemkolk and van der Schaaf, 1996]

4.9 Desalting

4.9.1 Good desalting practices

Description
A short description of desalters can be found in Section 2.9. Several good desalting designs have been included in this section:
1. multistage desalters and the combined use of AC and DC fields provide high desalting efficiencies as well as energy savings
2. recycling, in multistage desalters, part of the brine effluent water of second desalters to the previous one minimises the wash water quantity
3. use a low shear mixing device to mix desalter wash water and crude
4. avoid turbulence in desalter vessels by using lower water pressure.

Achieved environmental benefits
Increased efficiency of desalters may reduce wash water usage. Other environmental benefits would be limited to energy savings, if any, related to a more efficient electric field.

Operational data
Two-stage processes achieve 99 % or better efficiency (more than 99 % of the salts/solids are removed from the crude oil). This high efficiency provides process benefits because it allows less corrosion in the topping units.

Applicability
Two-stage or even three-stage desalting is used either if the crude oil salt content is higher than 0.02 %w/w, or if heavy residue is further catalytically processed.

Driving force for implementation
Increase the efficiency of the desalting process.

Reference literature
[113, Noyes, 1993], [297, Italy, 2000], [268, TWG, 2001]

4.9.2 Enhance the oil/water separation before discharge to the waste water treatment plant

Description
Techniques that may be applied are:
1. transfer the water effluent from desalting units to a settling drum where a further separation between oil and water can be achieved. The oil can be directly recovered in the slop system
2. choice of optimum interface level controllers. As a function of specific gravity and range of crudes processed, it is possible to consider the most accurate level sensors among displacers, capacitance probes or radio wave detectors. The accuracy of interface level control is fundamental for the good operation of a desalter.
3. a good improvement in water-oil separation can be achieved using “wetting”agents, whose aim is to de-oil the solid contaminants that are usually responsible for a significant entrainment of oil in the water
4. use of non-toxic, biodegradable, safe to use, non-flamable specific demulsifying chemicals to promote coalescense of the water droplets.

Achieved environmental benefits
Systems described above enhance the oil/water separation, reducing the charge of oil to the waste water treatment and recycling it to the process as well as reductions in the oily sludge generation (see Section 4.9.3). With the application of the first technique mentioned above some

10 - 20 % less oil is sent to the API separators. The second one can separate off some 5 - 10 % oil from the water phase.

Cross-media effects
Some of the techniques proposed need the application of chemicals.

Applicability
Fully applicable.

Driving force for implementation
Enhance the oil/water separation

Reference literature
[297, Italy, 2000]

4.9.3 Enhance the solid/water-oil separation

Description
Solids entering the crude distillation unit are likely eventually to attract more oil and produce additional emulsions and sludges. The amount of solids removed from the desalting unit should, therefore, be maximized. Then the objective is to minimize solids leaving the desalter with the crude oil. A number of techniques can be used such as:

1. use low-shear mixing devices to mix desalter wash water and crude oil
2. use low-pressure water in the desalter to avoid turbulence
3. replace the water jets with mud rakes. They cause less turbulence when removing settled solids
4. the water phase (suspension) can be separated in a pressurised plate separator. Alternatively a combination of a hydrocyclone desalter and a hydrocyclone de-oiler can be used
5. evaluate the effectiveness of a sludge wash system. The sludge washing is a batch operation meant to stir the water phase in the desalter to suspend and remove the solids accumulated on the vessel bottom. This cleaning operation increases the efficiency of desalters during normal run, particularly for long cycle runs.

Achieved environmental benefits
With the application of the techniques mentioned above, the content of oil in the generated sludges can be decreased and the separation of the sludges from the water phase can be enhanced.

Cross-media effects
The application of these techniques increases the sludge generation within the refinery. At a bottom sediment content of the crude of 0.015 % w/w, theoretically 1500 t/yr sludge can be collected in a 10 Mt/yr refinery.

Applicability
Where bottoms, sediments and water are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids.

Driving force for implementation
Enhance the separation of solids from the oil and water phase.

Example plant(s)
Desalters with desludging facilities are scarce. Atmospheric residue desalters are also few, but the number is increasing with the increasing complexity of refineries with respect to residue conversion. In a few refineries, desalters have been equipped with a bottom flushing system (See design in Figure 2.10).

Reference literature
[297, Italy, 2000]

4.9.4 Re-use of water for the desalter

Description
The desalting process plays an important role in the waste water management in a refinery (see Section 4.15.7). The water used in other processes can be re-used in the desalter. For instance, if stripped sour water is used as desalter wash water, the ammonia, sulphides and phenols that it contains can be reabsorbed by the crude to some extent.

The following process water streams can be suitable for use as desalter wash water:
1. the accumulated water in the crude distillation unit overhead drum, usually 1 - 2 % w/w on crude feed from steam injection
2. the (unstripped) steam condensates from the light and heavy gasoil dryers and the vacuum distiller overhead (about 3.5 % w/w on feed)
3. stripped sour water and also other solid-free process water streams. Scrubber or quench water is dirty and requires oil and solids separation prior to biotreatment and/or re-use as desalter wash water. The sour water is routed to and stripped in a sour water stripper prior to re-use and/or final purification in effluent water treatment facilities
4. slowdowns from cooling water and boilers.

Achieved environmental benefits
By using the water in this way, the refinery could reduce the hydraulic loading to the waste water treatment units and reduce consumption of water.

Cross-media effects
Recycling of water streams that may form emulsions need to be avoided, because it results in deterioration of the oil/water phase separation in the desalter, which in turn leads to excessive oil carry-over to water.

Operational data
The scrubber water would be hard-piped to the desalter water storage tank without being stripped first, in most cases.

Applicability
Examples of effluents that may form emulsions in the desalter are: bitumen blowing units, hydrocrackers, cokers (fines stabilise emulsions), other deep conversion facilities (insoluble metal sulphides that can stabilise emulsions) and HF-Alkylation units (corrosive fluoride deposits). This option is fully applicable to new refineries and more difficult to apply in existing refineries. This option is also limited in use when the salinity of the waste water may reach values that would negatively impinge on the Biox unit.

Economics
The costs of collecting, treating, pumping and piping these waters need to be considered.

Driving force for implementation
The refinery could reduce the hydraulic loading to the waste water treatment units and reduce consumption of water.

Reference literature
[79, API, 1993], [268, TWG, 2001]

4.9.5 Stripping of the desalter brine

Description
Strip desalter brine for hydrocarbons, sour components and ammonia removal before sending brine to waste water treatment. Recovered hydrocarbons can be blended with several refinery streams. Acid injection can also be employed to enhance the stripping of oil from emulsions.

Achieved environmental benefits
Reduction of the hydrocarbon, sulphur and ammonia content of the waste water generated within the desalter. For example, phenol emissions can be reduced by 90 % and benzene emissions by 95 %.

Applicability
Pretreatment of desalter brine is normally applied when processing a very heavy crude. In one refinery: 8.7 Mt/yr refinery produces a waste water flow in the crude unit of 1.3 m^3 per minute containing 90 kg/day of phenols. The water discharge from the desalters contains a maximum of 20 ppm benzene, and the quantity of desalter wash water is equivalent to 4 - 8 %v/v of the crude charge. The discharge from the stripper bottoms, with benzene levels in the 20 ppb range, is then routed to the waste water treatment system. A brine de-oling vessel is installed ahead of the stripping column to decant any free oil undercarry from the desalter. For the above-mentioned refinery, with this system the phenols can be reduced to an annual emission of 3.29 kg/yr.

Reference literature
[113, Noyes, 1993], [79, API, 1993]

4.10 Energy system

As mentioned under "Scope", this document does not analyse energy production techniques that use conventional fuels. In other words, emission, consumption, cross-media effects etc., related to commercial fuels (natural gas, fuel oil, etc) can be found the BREF on Large Combustion Plants (>50MWth).

The energy system is an important activity from the environmental perspective. Although heat-producing plants are an essential and integral part of most refining processes, the systems tend to be very similar and they are therefore dealt with in this horizontal section. This section therefore includes a detailed analysis of the energy systems that are specific to refineries, i.e. only energy technologies that run (partially or totally) on refinery fuels. When a refinery uses a commercial fuel that can be found on the open market (e.g. natural gas, fuel oil) the emission levels that can be achieved by a certain energy technique (e.g. gas turbines, boilers) are found in the BREF on Large Combustion Plants. Techniques to reduce the energy consumption of a process or activity are addressed in each of the other sections of this document because the reduction of energy consumption is considered an environmental benefit. However, issues such as how the energy system can be integrated within a refinery and how the different processes/activities may share energy are addressed in this section.

Combustion improvement campaigns, installation of alternative concepts (gas turbines, CHP, expanders, improved heat integration) and a switch to cleaner burning fuels are some examples of techniques to consider in the determination of BAT. For example, a switch from liquid refinery fuel to natural gas as refinery fuel will reduce not only SO_2 emissions, but also particulates (including metals) and NO_x. All measures to reduce energy consumption will result in a reduction of all emissions to air including CO_2. This section has therefore been structured in four blocks of techniques. The first one includes the energy management systems, including general techniques to reduce energy consumption.The second one includes techniques to consider in the selection and cleaning of fuels that can be used in the refinery. The third block contains the technologies for energy production that can provide a good environmental performance using the different type of fuels as well as the utilities needed to run those techniques. The last block includes the abatement techniques to control air emissions that are applicable to the energy systems.

Table 4.12 summarises and shows how the main pollutants may be affected by the techniques that have been considered in this section.

Section	Techniques to consider in the energy system	CO_2	NO_x	PM	SO_2	Waste water	Residues	Energy
1	Energy management	↓	↓	↓	↓			↓
2	Refinery fuels: types and cleaning		↓	↓	↓		↓	↑
3	Energy production techniques	↓						↓
4	Nitrogen oxide abatement techniques		↓					↑
5	Particulate abatement techniques			↓		↑		↑
6	Sulphur oxides abatement techniques				↓	↑	↑	↑
	↓Reduction ↑Increase							

Table 4.12: Possible effect on the main pollutants of the techniques to consider for the determination of BAT in the energy system

4.10.1 Energy management

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal aim is to match continuously the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This section should be seen as an integration of all techniques proposed below, since an increase in the energy efficiency of a refinery can be achieved through energy conservation technique and heat integration/recovery techniques.

4.10.1.1 Increasing energy efficiency

Description
Some techniques to improve and calculate the energy efficiency within the refinery are mentioned below.

a) The continuous matching of consumption at lowest cost is to be performed at all organisational levels and to be assured at the highest management level. By the adoption of a proper management system, this can be done in a similar way to practise in a number of other fields, notably in the field of safety. In principle the ISO 14000 system series or EMAS [285, Demuynck, 1999] provide an adequate framework to develop an adequate Energy Management System. In order to ensure continuous improvement, formal reporting of energy consumption data to the authorities can be instigated. Energy audits are part of such a system and it is further recommended that, in the pursuit of continuous improvement, refineries learn from best practice by participating in ranking/benchmarking activities. An annual investment plan on energy consumption reduction is also to be included as a technique to consider in the determination of BAT.

b) Another way to match production and consumption is to try to improve the energy efficiency within the refinery. More efficient refineries make better use of the energy produced within the refinery. To evaluate that, several methodologies exist, including the Solomon energy efficiency index (the most detailed one), specific energy consumption and (less accurate and more simple) the index relating the energy consumption to the amount of feedstock processed (Methods described briefly in Section 3.10.1). Solomon data is also available in that section. Solomon data are available in a form, that only makes sense in its context, and one needs to understand certain underlaying (benchmarking) concepts that are proprietary to Solomon.

Techniques to increase the energy efficiency are available in next sections of this chapter.

Achieved environmental benefits
An increase in the energy efficiency of a refinery has a direct impact reducing the air emissions and indirectly the generation of waste water and waste. Less consumption of fuels or more energy conservation, increasing the likelyhood that the refinery gas supply will be sufficient for the whole refinery.

Cross-media effects
Some difficulties have been identified in the collection of Solomon energy efficiency data from refineries. The main reason is that the figure is considered as confidential by both refineries and the provider of the market study (Solomon Associates). Futhermore, Solomon Associates has not provided to the TWG data on the methodology used to calculate the figures. Moreover, it was identified that not all refineries participate in this benchmarking exercise because different reasons (e.g. cost, confidence in their figures was not high). Also not all refineries participate every year.

Applicability
Fully applicable. The wide range of energy consumption in refineries means that in certain refineries a considerable reduction in energy consumption can be realised. A concerted and well managed effort based on an integrated approach in reducing energy use, improved operations, good housekeeping, adequate management and selective investment are good practices that are worth highlighting in this context.

Economics
Energy consumption may account for some 50 % of the total operating cost of refineries. As consequence a reduction in the energy consumption, or an increase in the refinery efficiency, reduce the total operating cost.

Driving force for implementation
Increase the energy performance of the refinery is typically done in refineries because reduce their operating cost.

Example plants
Many refineries have installed an energy management system, they issue annual reports on energy consumption performance and participate in benchmarking of energy consumption. Worldwide market studies of the wide variety of refineries (configurations/capacities) on the basis of Equivalent Distillation Capacities has proved useful in helping refineries to compare their performance.

Reference literature
[118, VROM, 1999], [316, TWG, 2000]

4.10.1.2 Energy conservation techniques

Description
A concerted and well managed effort based on an integrated approach to reduce energy use, improved operations, good housekeeping, good management and selective investments are the best practices worth highlighting here. There follows a list of techniques that are considered for the determination of BAT in the refinery sector. As can be seen, some of them are related to each other in some way.

Description of the technique	Performance and remarks
To have a management focus on energy	To ensure decisions are made on a process-integrated basis
To instigate an energy consumption reporting system	To measure progress and ensure targets are met
To instigate an incentive scheme for energy savings	To promote identification of improvement areas
To carry out energy audits on a regular basis	To ensure activities are in conformance with instructions
To have a formal energy consumption reduction plan	To set targets and strategy for improvements
To carry out combustion improvement campaigns	To identify areas of improvement (e.g. air/fuel ratio, stack temperature, burner configuration, furnace design)
To participate in ranking/benchmarking activities in energy consumption	Verification by an independent body
To review the integration between and within units and systems	Heat integration between units in the refinery can be sub-optimal. “Pinch” studies

Achieved environmental benefits
All measures to reduce energy consumption will result in a reduction of all emissions to air including CO_2. Any energy conservation action has an impact on pollution due to the marginal fuel consumption.

Applicability
Especially applicable to those refineries with very high specific energy consumption. The wide range of specific energy consumptions in refineries (by a factor of 4, see Section 3.10) means that in certain refineries a considerable reduction in energy consumption can be realised.

Reference literature
[297, Italy, 2000], [118, VROM, 1999]

4.10.1.3 Heat integration/recovery

Description
Actions that can be taken to improve integration and recovery of heat within a refinery to increase efficiency can be (list do not try to be comprehensive):

- general measures to reduce refinery CO_2 emissions, such as optimised heat integration and improved furnace efficiency combined with computer controlled combustion. This will lead to lower fuel consumption per tonne of crude processed
- installation of waste heat boiler in heaters
- installation of expanders/power recovery
- expanded heat exchanger areas in heat exchangers where cold streams are preheated by warm product streams directly from processes
- direct feed of "semiproducts" to processes without cooling and storage. It is always useful, from an energy conservation point of view, to recover the waste heat of hot products of the crude distillation unit, for instance, by later feeding them directly to the downstream units, rather than cooling them for storage and later feeding the downstream units from tankage
- balancing of vapour and refinery fuel gas systems
- use of high-efficiency pumps and compressors
- use of heat pumps
- decreased film temperature and increased turbulence on heat transfer surfaces
- waste heat delivery to adjacent buildings. The identification and use or opportunities for synergy outside the refinery fence (e.g. district/industrial heating, power generation) may reduce the cooling needs within the refinery and will reduce the consumption of fuel somewhere else.
- application of advanced process control to optimise energy utilisation
- insulation of buildings and process units (Minimisation of heat losses by thermal radiation)
- optimisation of energy production (within 4.10.3).
- optimise recycle gas rates, operating temperatures and pressures and steam pressure levels
- minimising or even avoiding slops production and their necessary reprocessing
- keeping heat exchanging surfaces clean or cleaning them regularly (good housekeeping)
- repairing leaks and leaking steam traps
- increase of heat exchanger surface areas of new sections of existing plants (so-called "add-ons"). In the case more add-ons have been added to an existing plants: re-routing of intermediate process streams and re-definition of the number of steam pressure levels and steam duties

Achieved environmental benefits
Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled. In a refinery, it is important to maximise heat integration in a plant to minimise heating and cooling duty. This way, substantial amounts of products can be sold instead of

being burnt. Heat integration/recovery techniques directly result on lower emissions of CO_2, NO_x, particulates and SO_2 (see Section 3.10.3 for air emissions from energy system).

Cross-media effects
The interchange of heat between processes implies the transference of disturbances from one process to another. This can affect safety, so stability control systems may be required.

Applicability
Waste heat is abundant at refineries, and so is low/medium-pressure, low-temperature steam. Any effort to recover waste heat as low-pressure/low-temperature steam is pointless if there is no additional use for the extra steam produced. Options for using that heat need to be carefully quantified and qualified. Heat exchangers require space. The identification and use or opportunities for synergy outside the refinery fence is some times difficult and need the compromise not only by the refinery but also for the other part.

Economics
It makes economic sense to maximise heat integration in a plant, and as a result minimise heating requirements and the cooling system burden. Heat integration/recovery offers an opportunity for energy cost savings (50 % of total operating cost of refineries), but the cost of heat exchangers and piping need to be considered when heat integration is analysed.

Driving force for implementation
Economics because they reduce the fuel consumption.

Example plants
Techniques widely applied in refineries.

Reference literature
[107, Janson, 1999], [118, VROM, 1999], [268, TWG, 2001]

4.10.1.4 Steam management

Description
Several techniques have been considered:

- steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. Steam used for mechanical and/or electrical energy generation and heating is usually recovered as condensate in the HP-, MP-, and LP-condensate systems and collected in the condensate storage tank. Reducing the amount of steam stripping is an option to reduce the generation of waste water. Stripping steam is normally used to meet flash point specification and to improve front end fractionation and yields distribution. In order to reduce the sour water loads to SWS strippers and reduce chemical treatments in the overhead systems, an option would be to strip sidedraw products, particularly the lighter cuts, using reboiled sidestrippers instead of steamed strippers. However, the majority of steam is used to strip the column bottom, which could not be reboiled by any other means, so the reduction of condensed steam would be limited anyway; besides, the stripping is far better under vapour stream than under reboiling conditions, because the more volatile fraction distillates off
- where inert gas as N_2 is available at an economic price, it can be an alternative to steam for stripping operations, especially for the lighter ends
- optimising steam production by waste heat recovery in waste heat boilers (WHB or CHP) from hot flue gases (e.g. stacks) and hot product streams (related to the techniques shown in Section 4.10.1.3).

Achieved environmental benefits
Reducing steam stripping reduces waste water generation. Reduction of energy use in steam production will lead to a reduced energy requirement and therefore to lower emissions to air.

Driving force for implementation
Environmental driving force

Example plants
Applications are found in some refineries

Reference literature
[297, Italy, 2000]

4.10.2 Refinery fuels: types and cleaning

As mentioned above, this document offers a detailed analysis only of refinery fuels produced in the refinery. Whist the use of marketable fuels such as LPG, commercial fuel oil and gasoil in refineries is a technique to consider that may be included in this chapter of the BREF, such use is extensively analysed in the LCP BREF [317, EIPPCB, 2002], which also gives achievable emissions levels using those fuels.

4.10.2.1 Increase the use of gas

Description
An alternative to reduce SO_2, NO_x, CO_2 and metals emissions from a refinery would be to replace or to decrease the use of liquid refinery fuel with LPG – often produce on site -, refinery fuel gas (produced by some conversion techniques) or natural gas. This increase of the use of gas is typically accompanied with a balance and control of the RFG system between suitable pressure limits to give the system flexibility, with make-up available from clean fuels such as LPG or imported gas. In those cases, an state-of-the-art controls to optimise the performance of the RFG is necessary.

Achieved environmental benefits
A full switch to a 100% gas-fired refinery would reduce SO_2 emissions by up to 99 %, CO_2 by 30 - 38 % and NO_x by 30 - >50 %. Releases of heavy metals would also be slashed. Furthermore, the use of gas generates very little dust and very low SO_2 emissions, as the refinery gases are usually cleaned in amine scrubbers (see next section). Sulphur emissions are significantly lower when clean refinery fuel gas is used instead of a distillate such as automotive gasoil, i.e. 10 - 20 times better than low-sulphur (1 %) conventional fuel oil. Because of the low SO_2 concentrations in the flue gases of gas fired boilers, the emission temperatures at the stack can be lowered to 150 °C (dew point corrosion is less of or no longer a constraint). The lower flue gas temperature represents a difference in energy efficiency and inherent CO_2 emission reduction. Gaseous fuels typically release less NO_x per unit of energy compared to liquid fuels, especially liquid refinery fuels. For gaseous fuels usually only thermal NO_x is relevant. Oil burning normally leads to higher levels of NO_x releases for several reasons, especially the problem of fuel NO_x arising from the nitrogen content, the need to balance NO_x and particulate releases and the frequent design requirement for firing in combination with gas. More detailed information for achievable emission values can be found in Table 4.15 to Table 4.21.

As a matter of summary the benefits for a switch to 100% gas-fired refinery are:

- SO_2 emissions will be reduced to nil for the single unit and for the refinery bubble will be given by the emissions from other sources (very small from refinery gas, from the SRU, from the FCCU, the flare etc)
- particulate emissions including heavy metals will be reduced
- NO_x will be reduced to the levels typical for natural gas firing for energy production techniques, and consequently other sources as catcrackers will become predominant emitters in the refinery

- CO_2 emission reduction is achieved mainly because of the lower carbon content of gas, its higher calorific value and in addition because of a higher attainable efficiency (Stack gases can be cooled further).

Cross-media effects
It is acknowledged that the residual fuel replaced by gas results in a further surplus of residue, which has to be considered in any integrated solution for the fuel system of a refinery. It can be the case that those residual fuels can be burned unproperly outside, so emissions produced by that can be seen as an emission shift to outside the refinery. Furthermore, the conversion of heavy fractions into light products and the targets for lower sulphur specifications of fuels require considerable extra energy. This will lead to an inevitable increase in CO_2 emissions. As a first approximation, NO_x emissions can be magnified by the use of hydrogen and residual fuels containing fuel bound nitrogen. High-hydrogen fuels result in higher flame temperatures, which typically lead to higher NO_x levels. Although not all the fuel nitrogen ends up as NO_x emissions, the fuel NO_x contributions can range from non-existent, as in the case of natural gas fuelled equipment, to several times the thermal NO_x contribution of the equipment for refinery fuels. Refinery fuel gas may contain amines (nitrogen compounds) and other compounds. Further information on conversion techniques of heavy fractions to refinery fuel gas can be found in Section 4.10.3.5, coking sections and hycroconversion processes.

Operational data
The move from liquid to gas fuel would require process upgrades and gas grid connections.

Applicability
Some gases are used locally, i.e. in the process of origin or an adjacent process, but most refineries operate a common RFG main into which most RFG is fed and transferred to the gas users. In a modern refinery the RFG main is carefully "balanced" with respect to supply and demand; necessary flexibility is obtained by control of production (i.e. reformer throughput, LPG evaporation). The relationship to the refinery flare system is important and RFG will normally include gas received from flare gas recovery. It may also release excess gas to flare if the upper limit pressure is exceeded. The application of energy conservation concepts (see Section 4.10.1) can help refineries to meet all their needs with refinery gas produced in-house.

Economics
The cost of switching to gas can be up to EUR 30 million per year for a 10Mt/yr refinery.
Use of LPG in lieu of fuel oil: Approximate capital cost is small (some reburnering) and the approximate operating cost per year is 120EUR per tonne of fuel (cost differential between LPG and fuel oil). However, operating costs can vary significantly, depending on the season of the year and on the price of LPG in the market.
Use of natural gas in lieu of fuel oil: Approximate capital cost of installation is around GBP 4 million. The approximate operating cost per year may vary from below 50 EUR per tonne to above 100 EUR per tonne (cost differential between natural gas and fuel oil). Again, operating cost can vary significantly, depending on the season of the year and on the market.

Driving force for implementation
Reduction of CO_2, NO_x, SO_2 and particulate emissions (including metals)

Example plants
The amount of refinery gas plus natural gas combusted by European refineries typically account from 60 to 100 % (in terms of megawatts fired). However data from some single European refineries shows that the amount of heavy fuel oil fired can approach to 60 %.

Reference literature
[118, VROM, 1999], [292, HMIP UK, 2000], [317, EIPPCB, 2002], [249, BMUJF, 1999], [268, TWG, 2001]

4.10.2.2 Cleaning of refinery fuel gas

Description
Some refinery fuel gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking and all hydrodesulphurising processes). In the latter case the gas streams are normally treated by amine scrubbing to remove H_2S before being released to the refinery fuel gas system. More information about amine scrubbers can be found in Section 4.23.5.1.

Achieved environmental benefits
Amine treated refinery fuel gases can be controlled to levels of 20 – 200 mg H_2S/Nm^3, which will achieve the release level of between 5 - 25 mg/Nm^3 SO_2 @ 3 % O_2 in flue gases.

Cross-media effects
Possibility of bottlenecking the amine scrubbing system. More information in Section 4.23.5.1.

Operational data
See Section 4.23.5.1.

Applicability
Fully applicable.

Economics
See Section 4.23.5.1.

Driving force for implementation
Reduce the sulphur content of the refinery flue gas.

Example plants
The treatment of refinery fuel gas in amine scrubbers are commonly used in all refineries.

Reference literature
[297, Italy, 2000]

4.10.2.3 Hydrotreatment of liquid refinery fuels

Description
The nitrogen, sulphur, particulates and metals content of the fuel used in refineries are determined by the crude that is used at the refinery and by the process units it has passed through. Liquid refinery fuel streams originate from various processes such as crude distillation units, vacuum distillation, thermal cracking, catcracking and hydrocracking of residues. Except for the latter one, the sulphur content of these residues can only be controlled by feedstock choice. In general, the liquid refinery fuel may comprise one or more of the above-mentioned fractions and the sulphur content can vary greatly. Table 4.13 shows the sulphur content of different fractions suitable to be used as liquid refinery fuel.

Fraction suitable to be used as liquid refinery fuel	Crude oil origin	S (%)	N (%)	Metal content (%)
Atmospheric residue	North sea	0.6 - 1.1	0.03 - 0.32	0.03 - 0.06
Atmospheric residue	Middle East	2.3 - 4.4		0.04 - 0.06
Vacuum residue	North sea	1.1 - 1.8	0.18 - 0.58	
Vacuum residue	Middle East	3.6 - 6.1		0.07 - 0.13
Cracked residue	Middle East	3.5 - 6.5		

Table 4.13: Sulphur, nitrogen and metal content of fractions suitable to be used as liquid refinery fuels

Hydrotreatment of fuels can reduce the sulphur, nitrogen and metal content of the refinery fractions. Hydrotreatment of liquid fuels can reduce the sulphur content to 0.03 – 1 %. For more information on hydrotreatments see Section 2.13. This technique is a pre-combustion operational change, treating the feed before it is used.

Achieved environmental benefits
Feed hydrotreating of fuels reduce the feed nitrogen, sulphur and metals content, which in turn reduces the SO_2, NO_x and particulate emissions. It has been calculated that, by switching to fuel oil with a sulphur content of 1 % or less, UK refineries can reduce SO_2 emissions by 19 - 64 %. Another advantage of switching to low sulphur fuel is that it reduces heat loss to the flue gas stack (investment in extra heat exchangers or heat exchanger surface to be made) because dew point corrosion is minimised or is no longer a constraint.

Cross-media effects
The hydrotreatment of fuels is a very energy intensive process. Moreover, effluent water and waste (used catalyst) are generated (see Section 3.13).

Operational data
Information on performance and consumption of hydrotreatments can be found in Section 2.13 and 3.13.

Applicability
Fully applicable

Economics
A severe hydrotreatment is very expensive, increasing the cost of the liquid refinery fuel. Table 4.14 shows an example of cost of liquid refinery fuel desulphurisation process.

Capacity of the refinery	5 Mt/yr
Fuels used in the refinery	120000 t/yr liquid refinery fuels 180000 t/yr refinery fuel gas
Volume of flue gas emitted	1.68×10^9 Nm^3/yr
Sulphur emission	5000 mg/Nm^3 (for liquid refinery fuels with 3 % S) representing 8400 t/yr 750 mg/Nm^3 with hydrotreatment
Desulphurisation efficiency	Up to 85 %
Investment cost (EUR)	100 - 300 million
Operating costs (EUR/yr)	20 - 50 million

Table 4.14: Economics of a liquid refinery fuel desulphurisation

Driving force for implementation
Reduction of sulphur and nitrogen oxide emissions.

Example plants
The amount of refinery gas combusted by refineries compared to liquid fuel, in terms of megawatts fired, is typically 60 % refinery gas to 40 % liquid refnery fuel. However data from the public register for 1996 in the UK, shows that, in some refineries, the amount of fuel oil fired can approach 60 %.

Reference literature
[45, Sema and Sofres, 1991], [292, HMIP UK, 2000], [118, VROM, 1999], [248, Ademe, 2001]

4.10.3 Energy production techniques

All types of energy production techniques found in refineries are included here. However, the emission levels associated with each technique are different from those included in Chapter 3 of this document, because in only good performance levels are included in this section. Techniques to prevent emissions from those energy production techniques are also included.

4.10.3.1 Furnaces and boilers

Description

Primary measures considered in this section for furnaces and boilers are (see also LCP BREF):

- installation of combustion air preheaters, which would increase the furnace efficiency significantly (more than 5 %)
- optimise furnace operation, and hence combustion efficiency, by an advanced control of the operations variables (Air/fuel ratio for the fuel mix, avoid sensible heat losses by optimising excess air)
- high thermal efficiency heater/boiler designs with good control systems (e.g. oxygen trim)
- minimisation of heat losses via radiation or exhaust gas (e.g. minimisation of heat losses via unburnt gases (H_2, CO) or unburnt residues (ignition loss))
- continuous monitoring of temperature and O_2 concentration of flue gas for combustion optimisation. Monitoring of CO may be also considered
- high boiler pressure
- preheating of fuel charged to the boilers
- preheating of boiler feed water with steam (See also 4.10.3.2)
- prevention of the condensation of exhaust gas on surfaces
- minimisation of own requirements by high efficient pumps, vents, and other equipment
- optimisation of combustion conditions (from 4.15.2)
- Techniques to control CO emissions are:
  - Good operation and control
  - Constant delivery of liquid fuel in the secondary heating
  - Good mixing of the exhaust gases
  - Catalytic afterburning.

Achieved environmental benefits

Fired boilers and furnaces generate substantial CO_2, SO_2, NO_x and particulate emissions, particularly when heavy fuel oil is used. Gas-fired boilers generate hardly any dust and low SO_2 emissions, when the refinery gases are cleaned in amine scrubbers. NO_x emissions are also much lower than those of oil-fired boilers. Because of the low SO_2 concentrations in the flue gases of gas fired boilers the emission temperatures at the stack can be lowered to 150 °C. The lower flue gas temperature represents a difference in energy efficiency and inherent CO_2 emission reduction.

Table 4.15 to Table 4.20 provide the achievable emission levels when primary measures are implemented in furnaces and boilers for each air pollutant. Other measures, such as low- NO_x, flue gas desulphurisation and others are reviewed later in this chapter. Values in the tables are in mg/Nm^3 attainable in continuous operation (half-hourly mean values) and based on a 3 % oxygen volume in the waste gas, except where specified. Gas: The lower values in the ranges given below relate to natural gas firing. Liquid refinery fuel: Thermal cracked residue, vacuum residue, etc.

	Gas	Liquid refinery fuel
Process furnaces	5 - 80	20 - 100
Boilers	5 - 80	20 - 100
Engines	10 - 150	

Table 4.15: Expected CO emissions from furnaces and boilers with optimal burner and design

	Gas	Liquid refinery fuel
Process furnaces	2.75 - 3	3.2 - 3.3
Boilers	2.75 - 3	3.2 - 3.3
Values in kg CO_2 per kg of fuel See Table 3.47.		

Table 4.16: Expected CO_2 emissions from furnaces and boilers with optimal burner and design

	Gas	Liquid refinery fuel	
		0.3 %N	0.8 %N
Process furnaces	70 - 150	280 - 450	280 - 450
Boilers	100 - 300	300 - 450	350 - 600
Engines	250 - 400		

Table 4.17: Expected NO_x emissions from furnaces and boilers with optimal burner and design

	Gas	Liquid refinery fuel
Process furnaces	<5	20 - 250
Boilers	<5	20 - 250

Table 4.18: Expected particulate emissions from furnaces and boilers with optimal burner and design

Metals (As, Pb, Cd, Cr, Co, Ni, V and their components) (given as the sum of the elements)	Gas	Liquid refinery fuel
Process furnaces	0	5 - 10
Boilers	0	5 - 10

Table 4.19: Expected metal emissions from furnaces and boilers with optimal burner and design

	Gas	Liquid refinery fuel		
		0.2 %S	1 % S	3 % S
Process furnaces	5 - 100	350	1700	5000
Boilers	5 - 100	350	1700	5000

Table 4.20: Expected SO_x emissions from furnaces and boilers

Cross-media effects
Air preheaters typically increase the production of NO_x.

Operational data
Direct gas-fired heaters and boilers normally achieve thermal efficiencies of over 85 %. If air preheat is applied and the combustion products (flue gas) are cooled close to their dew point, the thermal efficiency can be as high as 90 - 93 %.

Applicability
Fully applicable

Driving force for implementation
Process requirements of heat or steam

Example plants
Each refinery contains many furnaces and boilers of different sizes.

Reference literature
[117, VDI, 2000]], [195, The world refining association, 1999], [45, Sema and Sofres, 1991], [317, EIPPCB, 2002], [249, BMUJF, 1999], [297, Italy, 2000], [118, VROM, 1999], [268, TWG, 2001]

4.10.3.2 Boiler feed water (BFW) production and re-use

Description
Techniques to consider for the BFW production and re-use are:
1) the condensate tank is generally equipped with an oil detection system and an oil skimming device
2) to avoid corrosion in the steam and condensate systems, oxygen and carbon dioxide are removed in de-aerators, and oxygen scavengers and corrosion inhibitors are added. For further conditioning of BFW, dispersing, alkaline and sometimes anti-foaming agents are dosed
3) minimisation of heat losses via flue gas (unburnt gases, such as H_2, CO), via residues (ignition loss), via ashes and slags, via thermal radiation
4) preheating of boiler feed water (to de-areator) by waste heat
5) reduction of own energy requirement in the BFW production
6) production of boiler feed water: common techniques are ion-exchange, microfiltration and reversed osmosis. Unlike ion-exchange techniques, membrane processes do not generate waste water containing high loads of salts. Technologies should be preferred which generate recyclable residues (e.g. iron-containing sludges). Preferred use of non-toxic chemicals for water preparation, which are easily degraded by micro-organisms. Use of mineral oil-free flocculation agents. Use of chemicals with no or only low content of chloroorganic compounds. Rejection of the following compounds: EDTA (and homologous compounds) and its salts; aminopolycarbonic acids and their salts; metal-organic compounds; chromates, nitrites, organic polyeletrolytes with a monomer content >0.1 % w/w. Treatment of waste water from boiler feed water preparation in a well designed WWTP, especially in case of regenerates that contain high amounts of NH_3 derived from condensate recovery applying ion exchange. [317, EIPPCB, 2002]
7) conditioning of boiler feed water: Good operation is the combined operation with oxygen dosage: By addition of ammonia the pH is adjusted to an alkaline milieu and a small amount of oxygen is added. With this measure, addition of hydracine (which is considered cancinogenic substance) can be avoided and the demand for ammonia is decreased. Furthermore a protective layer of magnetite and haematite is formed on the inner surface of the pipes, which is less rough thereby decreasing the pressure drop within the pipes and decreasing the energy demand of the pumps. Waste water from water conditioning need to be neutralised and treated in a well designed WWTP [317, EIPPCB, 2002].
8) repeated reheating of steam

Achieved environmental benefits
The BFW condensate has a very low pollutant content. The reduction in water actual use because of re-use is the most significant environmental benefit.

Cross-media effects
Biotreatment may be required if anti-foaming inhibitors are used. Corrosion inhibitors are not biodegradable in the waste water treatment plant.

Operational data
BFW should not be recycled or routed to the desalter.

Applicability
When the re-use of condensate water as deareator feed water or preheating the BFW is applied, in some instances, where the condensate and the deareator are located far apart, their integration is not always possible because economical reasons.

Economics
Site-specific availability and economics determine the choice of the BFW source.

Driving force for implementation
The production of BFW is necessary for the production of steam in boilers.

Example plants
BFW production occurs in all refineries, in some measure.

Reference literature
[327, Broughson,], [317, EIPPCB, 2002], [316, TWG, 2000], [268, TWG, 2001]

4.10.3.3 Gas turbines

Description
A description of gas turbines can be found in the LCP BREF [317, EIPPCB, 2002]. A brief description can also be found in Section 2.10. Some techniques that can be applied to gas turbines in order to reduce air emissions are listed below:

- steam injection
- gas turbines with exhaust gas as combustion air
- optimised transformation of steam into electrical energy (highest possible pressure difference in the steam turbine, generation of steam with high temperature and pressure, multiple reheating of the steam)
- other primary techniques as dry low NO_x burners included in the following sections (4.10.4 to 4.10.6).
- use high-efficiency turbines by, for example, optimisation of the design of the turbines, reduce as low technically feasible the outlet steam pressure in the back-pressure turbine

Achieved environmental benefits
Table 4.21 sumaries the emission levels that can be achieved with the application of the above techniques to gas turbines.

Pollutant	**Gas[1] in g/GJ (mg/Nm^3)**	**Liquid refinery fuel[2] (mg/Nm^3)**
CO	(< 30)	< 50
CO_2	n.a.	n.a.
NO_x (as NO_2) @ 15 % O_2	15 – 130[3] (30 - 200) 240 – 700[3] without primary measures	250 – 450 200 with water injection
Particulates (@ 15 % O_2)	(<2)	<10 - 100 without abatement <5 - 30 with abatement
SO_x (as SO_2)	n.a.	n.a.
1 The lower range relates to natural gas firing 2 Gas oil/jet oil. 3 Range depends on the gas turbine type		

Table 4.21: Expected air emissions from gas turbines with optimal design

Cross-media effects
Steam injection typically produces higher emissions of CO and hydrocarbons. Steam should be produced if it is not available in the refinery.

Applicability
Fully applicable.

Economics
Steam injection applied to a 85MW_e output turbine. Uncontrolled NO_x emissions of 500 mg/Nm^3 @ 15 % O_2. Down to 50 - 80 mg/Nm^3 @ 15 % O_2. Investment cost (1998) EUR million 3.4 (including cost of steam production) Operating Cost: 0.8 EUR million (excludes capital charge).

Driving force for implementation
Process technique used for the production of electricity.

Example plants
Many examples exist in refineries. A number of refineries have, or are currently installing, combined cycle gas turbine (CCGT), designed to produce steam and power for the refinery. This is usually done to replace in whole or part old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators.

Reference literature
[45, Sema and Sofres, 1991], [118, VROM, 1999], [115, CONCAWE, 1999].

4.10.3.4 Cogeneration plants (CHP)

Description
A brief description can be found in Section 2.10.

Achieved environmental benefits
For the combination Refinery/Other Power Generators (OPG), the energy consumption and CO_2 emissions will be reduced by the application of the CHP concept. At the OPG, fuel consumption and all related emissions will be reduced but, at the refinery, fuel consumption and emissions may increase. A refinery that generates its own steam and electricity (no import from the OPG) can benefit from (enhanced) co-generation. In these cases the environmental effect in reduced fuel use and its related emissions accrue completely to the refinery.

Cross-media effects
No cross-media effects have been detected.

Operational data
Most turbines require a particularly stable mix of fuel in order to be sure of flame stability and are basically designed to burn natural gas. Refinery fuel gas components can vary considerably, especially when surplus hydrogen is produced, such as when a hydrotreatment unit is temporarily shut down, resulting in excess hydrogen being sent to the fuel gas system. However, these problems can usually be overcome, up to a limit of about 70 % hydrogen in the fuel.

Applicability
Generally applicable. The steam and power cogeneration concept can be also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high-pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Driving force for implementation
Production of steam and power to be used within or outside the refinery.

Example plants
A number of refineries have, or are currently installing, combined cycle gas turbine (CCGT) or Combined Heat and Power (CHP) plant, designed to produce steam and power for the refinery. This is usually done to replace in whole or part old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators.

Reference literature
[118, VROM, 1999]

4.10.3.5 Gasification of heavy oils or coke (IGCC)

Description
Integrated gasification combined cycle (IGCC) is another technique and its purpose is to produce steam, hydrogen (optional) (see Section 2.14) and electric power from a variety of low grade fuel types with the highest conversion efficiency possible. More information can be found in Section 2.10.

Achieved environmental benefits
Syngas produced in this process has a sulphur content of 0.01 - 0.05 % and could be used, as refinery fuel gas for hydrogen, fuel or chemical production. Water containing the soot particulates is filtered and the filter cake is subjected to a controlled burning process. The process is in principle autothermic, the heat of combustion being sufficient to evaporate the moisture content of the filter cake.

The IGCC is a highly integrated and efficient process which can supply power, hydrogen and steam. Furthermore, it offers in principle an acceptable outlet for heavy residues and feedstocks or even refinery sludges, provided the latter are less than 1 % of feed. Hot gas clean-up systems have the potential to increase system efficiency and lower system costs. The achieved emissions to the atmosphere from that system are: SO_2 50 mg/Nm^3, NO_x 65 mg/Nm^3 @ 3 % O_2, particulate 5 mg/Nm^3 and carbon monoxide 10 - 30 mg/Nm^3.

The emissions from the IGCC show a significant decrease compared with conventional power/steam plants. The SO_2 concentration in the refinery exhaust is reduced by 80 % but CO_2 emissions increase.

The use of by-product and residual streams to meet the fuel requirement of refineries cannot only be cost-effective, but also is environmentally beneficial in that it makes use of what would otherwise be a waste refinery stream that would be flared without recovering the energy content.

Cross-media effects
In some cases, some difficulties may occur in burning low calorific value gas produced. Water effluent is normally sent to the existing waste water treatment plant of the refinery. It may contain significant amounts of metals as V, Cr or Ni and PAHs.

Operational data
Utility requirements for the gasification processes are 1800 - 4900 kWh/t of power and 1140 kg/t of steam consumption. The soot product is about 50 - 75 % w/w V_2O_5 residue, which can be sold to metal reclaimers. The IGCC complex is also equipped with all the necessary auxiliary systems, including cooling water (mixed system with an open seawater circuit for large users and a closed clean water circuit for the other users), demi-water, air, nitrogen, water and fuel gas networks, fire fighting, flare, storage, electrical distribution, buildings, etc.

IGCC is a technology with high flexibility in start-up, shutdown and part-load operation, depending on the level of integration between the different sections. Typically, systems that use heat exchange equipment are more efficient than those using quench cooling; however, the capital cost of the system with heat exchange is higher and there is a risk of fouling. Handling of the soot and filter cake should be done with care to avoid dust (even at 80 % moisture) due to the toxic properties of the residue.

Applicability
This technique can be seen as an alternative approach to removing sulphur using feed hydrotreatment (see Section 4.10.2.3). During normal refinery operation the gasifiers of the

IGCC plant are able to convert almost any refinery residue (atmospheric residues, vacuum residues, visbroken or thermal tars, etc.) to heat and power. These feedstocks can have a high sulphur content.

Economics
Table 4.22 gives the economics of two examples of IGCC applied in European refineries.

Refinery capacity	5	Mt/yr
Some characteristics of the refinery are: Fuel used in the refinery	 120000 liquid 180000 gaseous	 t/yr
Volume of flue gas generated in the refinery	1.68×10^9	Nm^3/yr
SO_x emissions (as SO_2) before application of IGCC	5000 (for liquid refinery fuels with 3 % S)	mg/Nm^3
SO_x emission load	8400	t/yr
Efficiency of the process measured as sulphur content of the gaseous fuel	0.01	%
Investment cost	200 - 400	EUR million
Operating costs	20 - 40	EUR million/yr

Size of the IGCC	280	MW
Net cogeneration efficiency	47.2	%
Investment cost	648	EUR million
Characteristics of the feedstock used	density: 1.05 - 1.1	kg/dm^3
	viscosity: 100 - 3500	cts @ 150 ºC
	sulphur: 3.5 - 7	%
	metals: 300 - 800	ppm
	heating value: 8800 - 9200	kcal/kg

Table 4.22: Economics of two IGCC plants of European refineries

Example plant(s)
The IGCC concept as such is quite a recent technological application for power stations. The main sections of an IGCC plant, i.e. Gasification, Air Separation, Gas Cleaning and Combined Cycle are well known technologies that have previously been used separately for different applications and with different feedstocks. Integration (the "I" in IGCC), though, is a more recent idea. Oil gasification is a process that has been applied for many years. Gasification of heavy residues, according to the principles of IGCC, is rather new. At least 4 IGCC plants are already in operation within European refineries and some others are in the design/construction phase. Coal gasification, also applying the IGCC concept, is new as well and a few plants are in operation.

Reference literature
[45, Sema and Sofres, 1991], [297, Italy, 2000], [320, Italy, 1996]

4.10.3.6 Fluidised bed boiler

Description
An alternative method for disposal of heavy residual oils or petroleum coke is combustion in a fluidised boiler with limestone injection for sulphur capture.

Achieved environmental benefits
About 90 % of the sulphur content of the fuel is captured and about 50 % of the calcium in the limestone is used in sulphur absorption.

Cross-media effects
The resulting calcium sulphate and unconverted calcium oxide together with the nickel and vanadium in the fuel are discharged from the boiler as a solid residue which can be used as road aggregate or disposed of to landfill.

However, such schemes have a lower sulphur capture performance than gasification and they do not provide the option of producing hydrogen. There could also be environmental objections to the mining and transport of limestone and disposal of the residue. For these reasons, gasification may be generally more attractive in the long-term.

Applicability
A combination of fluidised bed boilers with upstream solvent deasphalting or delayed coking can be a cost effective solution for refineries with existing FCCU capacity and steam/power deficiencies.

Economics
Typically cheaper than gasification.

Driving force for implementation
Reduction of solid waste generation.

Reference literature
[118, VROM, 1999]

4.10.4 Nitrogen oxide control and abatement techniques

Techniques to reduce NO_x emissions fall into two broad categories. Primary techniques include NO_x control techniques, such as pre-combustion operational changes and combustion modifications. Secondary techniques include the post-combustion flue gas treatments or NO_x abatement techniques. More information about NO_x abatement techniques can be found in Section 4.23.3. Primary and secondary techniques are considered in this section. The types of NO_x control and abatement techniques to be considered in the energy systems are summarised in Table 4.23.

Type of techniques	Fired Heaters	Boilers	Gas Turbines
Primary measures (control techniques)	Low-NO_x Burners Ultra-low-NO_x Burners Reburning	Flue Gas Recirculation Ultra-Low-NO_x Burners Low-NO_x Burners Reburning	Dry Low-NO_x combustors Steam Injection Water injection Low-NO_x Combustors
Secondary measures (abatement techniques)	SCR SNCR	SCR SNCR	SCR

Table 4.23: NO_x control and abatement techniques considered to be applied into energy systems

4.10.4.1 Low-NO_x burners

Description
Low- NO_x burners, either air staged or fuel staged, have the aim of reducing peak temperature, reducing oxygen concentration in the primary combustion zone and reducing the residence time at high temperature, thereby decreasing thermally formed NO_x Staging of fuel addition is also thought to provide a reburning effect, further reducing the NO_x Ultra-low-NO_x burners add internal recirculation of flue gases to the features of the low-NO_x burner, enabling further NO_x reductions.

Achieved environmental benefits

Low-NO_x burners achieve NO_x reduction performances of 40 - 60 % for gaseous fuels and 30 - 50 % for liquid fuels. Ultra-low-NO_x burners applied to process heaters and boilers can achieve a 60 - 75 % reduction of NO_x emissions. Table 4.24 shows a summary of the achievable emission levels that can be found when the different types of fuel are fired in different types of combustion techniques and when low-NO_x burners are applied.

Type of fuel	Natural and forced draft heaters	Boilers	Gas Turbines
Refinery fuel gas	30 - 150 (15 - 50)	30 - 150 (15 - 50)	n.a.
Liquid refinery fuel (0.3 % N)	100 - 250 (25 – 70)	100 - 250 (25 - 70)	n.a.
Liquid refinery fuel (heavy)	150 – 400	150 - 400	n.a.
Note: Units in mg/Nm^3 at 3 %O_2 (within brackets in mg/MJ)			

Table 4.24: NO_x emissions achieved with low and ultra-low-NO_x burners for different type of equipment

Cross-media effects

For oil firing there is a direct link between NO_x and particulates i.e. reduction in NO_x as the flame temperature falls will lead to an increase in particulates. For low-NO_x fuel oil burners, as with conventional fuel oil burners, a further reduction of thermal NO_x results in an increase in carbon particulates. CO emissions are also increased.

Operational data

Refinery gas firing with ultra-low-NO_x burners in both forced or natural draft conditions may show signs of instability at some points, particularly at low turndown and low excess air. Care needs to be taken during the installation of these burners. Burner testing to explore the limits of combustion prior to site installation is highly recommended for reliable operation and to evaluate that this technique is applicable in specific case.

Applicability

Application is straightforward for new installations of both fired heaters and boilers. Some liquid fuels are not suitable for the latest generation of low-NO_x burners and some older fired heaters are fitted with large high intensity burners which cannot be retrofitted with new low-NO_x burners. Retrofitting of low-NO_x burners depends on the furnace design and may be simple, difficult or, because of the increased flame volume, impossible without changing the furnace. For instance the increased length of low-NO_x burners may restrict applicability in furnaces built low above-ground. NO_x abatement on older furnaces and boilers may also be less effective due mainly to the need to avoid flame impingement on the furnace tubes.

Economics

The following tables show the economics of several applications of low- and ultra-low-NO_x burners in different refineries.

	NO_x Control for Fired Heaters and Boilers Firing Refinery Blend Gas in Ultra-Low-NO_x Burners	**Boilers Firing Residual Fuel Oil in Low-NO_x Burners**	**Heaters Firing Residual Fuel Oil in Low-NO_x Burners**
Down to ppm @ 3 % O_2	30	150	150
Investment cost (1998) (EUR million)	0.2 - 0.6	0.3 - 0.9	0.3 - 0.9
Operating costs per year (excludes capital charge) (EUR million)	Nil	Nil - 0.02	Nil - 0.02

Capacity of the refinery	5	Mt/yr
Fuel consumption	120000 (liquid refinery fuels) 180000 (refinery fuel gas)	t/yr
Volume of flue gas	$3x10^9$	Nm^3/yr
Efficiency of the low-NO_x burners	10 - 50	%
NO_x emissions (as NO_2)	100 - 250	mg/Nm^3
Investment cost	0.5 - 1.0	EUR million

Applied to	Investment cost	More information
Reburnering a typical crude oil furnace consisting of 40 forced-draught burners	EUR 3.3 million (GBP 2 million)	Including the general upgrading of the furnace air, fuel and control systems likely to be carried out at the same time by a refiner
Replacement of conventional burners with low-NO_x burners	EUR 0.3 to 0.9 million for each burner	
Replacement of burners in the two crude oil heaters	EUR 4.2 million (SEK 35 million (1998))	
Retrofitting		Normally requires major changes to the furnace floor structure and controls that add greatly to the capital cost

Driving force for implementation
Reduction of NO_x emissions.

Example plants
There are many examples of applications in refineries.

Reference literature
[115, CONCAWE, 1999], [45, Sema and Sofres, 1991], [112, Foster Wheeler Energy, 1999], [107, Janson, 1999], [348, Ashworth Leininger Group, 2001]

4.10.4.2 Dry low-NO_x combustors

Description
More information can be found in the LCP BREF.

Achieved environmental benefits
90 % reduction in NO_x emissions in natural gas-fired gas turbine applications.

Type of fuel	Fired Heaters	Boilers	Gas Turbines
Refinery fuel gas	n/a	n/a	50 - 100 (40 - 60)
Light fuel oil	n/a	n/a	n.a.
Heavy fuel oil	n/a	n/a	n.a.
Note: Data in mg/Nm^3 @ 15 % O_2 (g/GJ). n/a: not applicable			

Table 4.25: NO_x emissions achieved with dry low-NO_x combustors for different types of equipment.

Applicability
Applicable to gas turbines. Dry low-NO_x combustors are not available for gas turbines fired with refinery blend gas that contains more than 5 to 10 % v/v of hydrogen.

Economics
The investment cost is EUR 2.2 million (1998) and the operating cost is nil for an 85MWe output turbine.

Driving force for implementation
Reduction of NO_x emissions.

Reference literature
[115, CONCAWE, 1999], [316, TWG, 2000]

4.10.4.3 Flue gas recirculation

Description
External flue gas recirculation (FGR) is applied to boilers and heaters to increase the diluent effect, hence to reduce combustion temperature. Typically 20 % of the available flue gas from the boiler stack is ducted to mix with fresh combustion air.

Achieved environmental benefits
Using recirculated flue gas as part of the combustion air can further reduce NO_x formation.

Type of fuel	Fired heaters	Boilers	Gas Turbines
Refinery fuel gas	n.a.	n.a.	n/a
Light fuel oil (LCP)	n.a.	n.a.	n/a
Heavy fuel oil	n.a.	n.a.	n/a

Table 4.26: NO_x emissions achieved with flue gas recirculation for different types of equipment

Operational data
The process is difficult to control especially during turndown.

Applicability
It is applied to boilers and fired heaters. In a boiler retrofit, FGR increases hydraulic loads, and shifts the heat load towards the convective section(s) and may not be practical.

Economics
Higher cost than other primary measures.

Driving force for implementation
Reduce the NO_x emissions from boilers and heaters.

Reference literature
[115, CONCAWE, 1999], [316, TWG, 2000]

4.10.4.4 Diluent injection

Description
Inert diluents, such as flue gas, steam, water and nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NO_x in the flue gases.

Achieved environmental benefits
Control of NO_x in gas turbine combustors may be carried out by using steam/water injection, which can achieve reduction performances of 80 - 90 %.

Type of fuel	Fired Heaters	Boilers	Gas Turbines
Refinery fuel gas	n.a.	n.a.	50 - 80
Light fuel oil	n.a.	n.a.	n.a.
Heavy fuel oil	n.a.	n.a.	n.a.
Note: Data in mg/Nm^3 @15 % O_2			

Table 4.27: NO_x emissions achieved with diluent injection for different types of equipment

Cross-media effects
Energy to produce steam, higher emissions of CO and hydrocarbons.

Operational data
The use of steam generates more corrosion in the system than the use of nitrogen.

Applicability
Steam and water injection is widely applied to gas turbines both in new installations and retrofits and is also applicable to fired heaters and boilers (see also Section 4.10.5.2). There are technical difficulties in applying water injection in boilers and furnaces. Nitrogen dilution is only applied when nitrogen is already available in the refinery.

Economics
Capital cost of the steam and water injection is less than that of SCR, making the technology a good first choice for substantial levels of NO_x reductions, with SCR often added on if higher NO_x reduction is needed. Substantial recurring operating costs are, however, encountered for producing high purity steam, and maintenance costs for re-blading may be high.

Cost relates to a 85 MW output turbine	NO_x control for gas turbines firing refinery blend gas
Investment cost (1998) (EUR million)	3.4
Operating costs per year (excludes capital charge) (EUR million)	0.8
Cost / effectiveness EUR per tonne NO_x removed (incl. capital charge @ 15%)	1500

Other sources give that operating costs in a gas turbine using 80 t/h steam injection would cost EUR 0.9 million per year.

Driving force for implementation
Reduction of NO_x emissions.

Example plants
By-product nitrogen from the air separation plant in refinery residue gasification projects has recently been commercially demonstrated as a diluent for gas turbine NO_x reduction. Within the refining industry, steam injection predominates.

Reference literature
[112, Foster Wheeler Energy, 1999], [115, CONCAWE, 1999], [268, TWG, 2001]

4.10.4.5 Reburning

Description
Fuel staging, also called reburning, is based on the creation of different zones in the furnace by staged injection of fuel and air. The aim is to reduce NO_x emissions, which have already been formed back to nitrogen. This technique adds to the flame cooling a reaction by which organic radicals assist in the breakdown of NO_x.

Achieved environmental benefits
Achievable levels are < 100 ppm.

Applicability
It is applied at the burner level.

Driving force for implementation
Reduction of NO_x emissions.

Reference literature
[112, Foster Wheeler Energy, 1999]

4.10.4.6 Selective Non-Catalytic reduction (SNCR)

Description
This technique also called THERMAL deNOx reduces the NO_x that has been formed in the combustion process. This process is a non-catalytic process which utilises ammonia or urea to reduce NO_x to nitrogen and water. More information can be found in Section 4.23.3.

Achieved environmental benefits
Reductions of NO_x of between 40 % and 70 % have been demonstrated in full-size combustion plant.

Type of fuel	Fired Heaters	Boilers	Gas Turbines
Refinery fuel gas	150 – 200	150 - 200	n/a
Light fuel oil (0.3 % N)	150 – 300	150 - 300	n/a
Heavy fuel oil (0.8 % N)	200 – 400	200 - 400	n/a
Note: Data in mg/Nm^3 @3 % O_2			

Table 4.28: NO_x emissions achieved with SNCR for different types of equipment

Cross-media effects
Risk of NH_3 or urea emissions (storage and non-reacted). Turndown is a problem. The emissions of N_2O may be increased by this technique. A side reaction of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphates give rise to the fouling and corrosion of downstream equipment. Storage of gaseous ammonia has a great hazardous potential. Therefore a liquid solution of ammonia (25 %) is preferred. The use of urea causes higher emissions of CO and N_2O and can cause high-temperature corrossion.

Operational data
More information can be found in 4.23.3.2.

Applicability
SNCR requires temperatures above 650 ºC. Application is complicated when flue gases to treat come from the combustion of heavy fuel oil. Space requirements are mainly restricted to ammonia storage.

Economics

Table 4.29 shows the economics of application of SNCR for the treatment of flue gases coming from the combustion processes from different sources.

Values corresponding to a 100 GJ/h installation – Retrofit of existing installation.	**Fired Heaters and Boilers Firing Refinery Blend Gas**	**Boilers Firing Residual Fuel Oil**
Down to ppm @ 3 % O_2	50	100
Investment cost (1998) (EUR million)	0.4 - 0.5	0.4 - 0.9
Operating costs per year (excludes capital charge) (EUR million)	0.025	0.05 - 0.07

Capacity of the refinery	5	Mt/yr
Fuel consumption	120000 (liquid refinery fuels) 180000 (refinery fuel gas)	t/yr
Volume of the flue gas	$3x10^9$	Nm^3/yr
Efficiency of the SNCR	60 - 80	%
NO_x emissions (as NO_2)	200	mg/Nm^3
Investment cost	3 – 5	EUR million
Operating costs	0.2 - 1	EUR million/yr

		EUR/unit	**EUR/yr**
Operating hours (h/yr)	8000		
Investment costs (EUR)	1090093		
Input factors for annual expenditure: Number of years Rate of interest (%)	 15 6		
Annual repayment incl. Interest (EUR/yr)	112239		
Proportional investment costs incl. Interest			**112239**
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	21802		
Maintenance + wear and tear			**21802**
Electrical energy (kWh/h)	40	0.07 EUR/kWh	**20930**
Air (Nm^3/h)	1200	0.01 EUR/Nm^3	**118602**
NH_3 liquid (kg/h)	83.15	0.25 EUR/kg	**169201**
Total cost			**442774**
Note: installation on a volume of exhaust gas of 250000 Nm^3/h after a power plant in a refinery achieving a NO_x emission reduction of 500 mg/Nm^3 in relation to actual oxygen content and for a clean gas concentration of <200 mg NO_x/Nm^3			

Table 4.29: Examples and main cost factors for a Selective Non Catalytic Reduction (SNCR)

Investment cost for a SNCR applied to an existing boiler was EUR 0.56 million including equipment for storage of urea. Storage of gaseous ammonia is even more expensive than urea storage.

Driving force for implementation
Reduction of NO_x emissions.

Example plants
This process has been applied in heaters and boilers of refinery plants. The experience of application of SNCR on oil-fired heaters is more limited. An USA study reports that SNCR is

less used than SCR for control of NO_x and that only 12 of the 150 boilers/heater installations of 8 refineries use this type of technique.

Reference literature
[107, Janson, 1999], [115, CONCAWE, 1999], [45, Sema and Sofres, 1991], [250, Winter, 2000], [348, Ashworth Leininger Group, 2001]

4.10.4.7 Selective Catalytic reduction (SCR)

Description
Another secondary technique is known as catalytic deNO_x. As in THERMAL deNOx, ammonia is used to reduce the NO_x to nitrogen and water vapour. The ammonia vapour is mixed with the flue gas and the mixture passed through a catalyst to complete the reaction. More information can be found in Section 4.23.3.

Achieved environmental benefits
SCR is capable of reducing NO_x by 90 - 94 % in boilers and heater applications. In a refinery in Sweden a SCR unit has been installed at a boiler. The unit was put into operation in October 1998. Fuel oil is used and NO_x emissions are 16 mg/MJ (55 mg/Nm^3, 3 % O_2). The NO_x reduction is about 94 % and the ammonia slip well below 5 ppm. (68 MW). At the STEAG power station (Mider refinery in Germany), the three oil-fired heaters (each producing 160 t/h steam (100 bars, 505 ºC) and consuming 12 t/h of heavy fuel oil (3.7 % S)) are equipped with a SCR-plant (high-dust); they have to reach NO_x emissions below 150 mg/m³. Data concerning the power plant in the Mider refinery are:

	Raw gas	Clean gas
Flue gas volume, wet (m^3/h, 7 % O_2)	171690	188249
Temperature (°C)	180 - 200	bis 72
Dust (mg/m^3, 3 % O_2)	220	<10
NO_x as NO_2 (mg/m^3, 3 %O_2)	800	<150
SO_2 (mg/m^3, 3 % O_2)	6500	
SO_3 (mg/m^3, 3 % O_2)	650	<10
SO_x as SO_2 (mg/m^3, 3 % O_2)		<400

Table 4.30: Power plant of the Mider refinery in Germany, raw gas and clean gas concentration

Cross-media effects
Risk of NH_3 emissions when operating outside stoichiometric conditions and catalyst disposal. The risk of ammonia emissions during storage of gaseous ammonia can be minimised if ammonia is stored and used as an aqueous solution (25 %). It may increase the emissions of N_2O. Operational slip of NH_3 is around 5 ppm, a value that normally increases during the catalyst's lifetime. A side reaction of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphates give rise to deactivation of the catalyst and to fouling and corrosion of downstream equipment.

Operational data
More information can be found in 4.23.3.2.

Applicability
The application of this technology to existing process furnaces can be limited by problems of space, pressure and temperature. However SCR is considered in California technologically feasible in boilers and heaters. Oil fly ash contains metal oxides, soot and coke. Unabated fly-ash concentrations for oil firing are in the range of 100 - 600 mg/Nm^3 (with highest values for vacuum residues). SCR applied under these conditions may suffer from clogging by fly ash and sulphates (with coal firing, the sandblasting effect of the fly ash keeps the catalyst clean). The

potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 - 4 %).

Economics

Costs of SCR vary over a range, depending on the fuels, exhaust volume and required reduction. The range may be EUR 25 - 110/kW for new power generation installations. Maintenance costs are minimal, the bulk of which are from NH_3 consumption. Some examples of the application of SCR in refinery power plants are shown in Table 4.31 and Table 4.32. The use of a SCR-unit after the power plant has been estimated in raw-gas and clean-gas operation mode. The two cost-tables are given below.

		EUR/unit	**EUR/yr**
Operating hours (h/yr)	8000		
Investment costs (EUR)	3270278		
Input factors for annual expenditure: Number of years Rate of interest (%)	 15 6		
Annual repayment incl. Interest (EUR/yr)	336717		
Proportional investment costs incl. interest			**336717**
Volume of catalyst (m^3)	20		
Endurance (years)	15		
Renewing of catalyst (m^3/yr)	1.33	14535 EUR/m^3	
Average renewing of catalyst (EUR/yr)	19379		
Catalysts			**19379**
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	65406		
Maintenance + wear and tear			**65406**
Pressure drop (mbar)	35		
Energy for reheating (MJ/h)	11806.67	3.63 EUR/GJ	**343210**
Electrical energy (kWh/h)	610	0.07 EUR/kWh	**319187**
NH_3 liquid (kg/h)	46.20	0.25 EUR/kg	**94001**
Total costs			**1177900**
Note: Installation on a volume of exhaust gas of 250000 Nm^3/h in the dedusted off-gas after a power plant in a refinery achieving a NO_x mission reduction of 500 mg/Nm^3 in relation to actual oxygen content and for a clean gas concentration of <100 mg NO_x/Nm^3			

Table 4.31: Main cost factors for a Selective Catalytic Reduction (SCR)

		EUR/unit	EUR/yr
Operating hours (h/yr)	8000		
Investment costs (EUR)	2180185		
Input factors for annual expenditure: Number of years Rate of interest (%)	 15 6		
Annual repayment incl. interest (EUR/yr)	224478		
Proportional investment costs incl. Interest			**224478**
Volume of catalyst (m^3)	35		
Endurance (years)	8		
Renewing of catalyst (m^3/yr)	4.38	14535 EUR/m^3	
Average renewing of catalyst (EUR/yr)	63589		
Catalysts			**63589**
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	43604		
Maintenance + wear and tear			**43604**
Pressure drop (mbar)	8		
Energy for reheating (MJ/h)	0	3.63 EUR/GJ	**0**
Electrical energy (kWh/h)	160.07	0.07 EUR/kWh	**83753**
NH_3 liquid (kg/h)	46.20	0.25 EUR/kg	**94001**
Total costs			**509425**
Note: Installation (raw gas) on a volume of exhaust gas of 250000 Nm^3/h after a power plant in a refinery achieving a NO_x emission reduction of 500 mg/Nm^3 in relation to actual oxygen content and for a clean gas concentration of <100 mg NO_x/Nm^3			

Table 4.32: Main cost factors for a Selective Catalytic Reduction (SCR)

	Fired Heaters and Boilers Firing Refinery Blend Gas	Boilers Firing Residual Fuel Oil	Gas Turbines Firing Natural or Refinery Blend Gas
Reduction Performance NO_x reduction %	90	75	90
Down to mg/Nm^3 @ 3 % O_2 (15% O_2 for gas turbines)	30	130	50
Investment cost (1998) (EUR million)	2.8 - 3.2	2.4 - 3.4	4.9 - 5.4
Operating costs per year (excludes capital charge) (EUR million)	0.15	0.1 - 0.2	1.3

Capacity	68 MW	(Reformer furnace of Swedish Preem refinery)	Nm^3/h
Efficiency	94	91	%
Down to @ 3 % O_2	55 (14 - 15)	55	mg/Nm^3 (mg/MJ)
Investment cost (1998)	0.9	3.2	EUR million (1998)

Capacity of the refinery	5	Mt/yr
Fuel consumption	120000 (liquid refinery fuels) 180000 (refinery fuel gas)	t/yr
Volume of the flue gas	$3x10^9$	Nm^3/yr
Efficiency of the SCR	85	%
NO_x emissions (as NO_2)	150	mg/Nm^3
Investment cost	15 - 20	EUR million
Operating costs	2	EUR million/yr

Driving force for implementation
Reduction of NO_x emissions.

Example plant(s)
They have been applied to FCC off-gases, gas turbines, process boilers, process heaters such as naphtha reformers, steam reformers, crude and vacuum distillation units, thermal cracking and hydroprocessing units. SCR has been also successfully applied to gas streams with high particulate content in high sulphur coal-fired utility industry and FCC units combined with upstream particulate removal. A report on USA refineries show that the 20.7 % (or 31 boilers/heaters) of 150 boiler/heater installations at 8 refineries employs SCR as a control technology. The same study shows that 3 SCR installations have been applied to the 4 turbines found in the 8 refineries analysed.

Reference literature
[181, HP, 1998], [107, Janson, 1999], [45, Sema and Sofres, 1991], [250, Winter, 2000], [115, CONCAWE, 1999], [348, Ashworth Leininger Group, 2001]

4.10.4.8 DeNO$_x$ scrubbing

Description
A separate spray tower is usually required prior to the main SO_2 absorption spray tower. An additive applied in this extra tower oxidises the NO to NO_2, which is then absorbed with the SO_2. The reaction for the absorption of NO_2 is $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$.

Achieved environmental benefits
Reduction of NO_x emissions

Cross-media effects
If using wet gas scrubbing, slurry can be expected as a solid waste from this process. Nitrates generated should be treated in the WWTP.Because the gas effluent from this process generates NO, it may need further reduction of NO_x emissions.

Economics
Wet deNO$_x$ scrubbing has advantages including lower capital cost, if installed in conjunction with SO_2 wet gas scrubbing.

Driving force for implementation
Reduction of nitrogen oxides emissions.

Examples
It is normally used in nitric acid production.

Reference literature
[108, USAEPA, 1995]

4.10.4.9 Catalytic reduction of CO and NO_x

Description
The technology uses a single catalyst that operates in two cycles: oxidation/absorption and regeneration. The catalyst works by simultaneously oxidising CO to CO_2, NO to NO_2, and then absorbing NO_2 onto its surface through the use of a potassium carbonate absorber coating. The regeneration of the catalyst is accomplished by passing a controlled mixture of regeneration gases across the surface of the catalyst in the absence of oxygen. The regeneration gases are steam, hydrogen and carbon dioxide. Consequently the nitrates are reduced to nitrogen. An additional catalyst layer is required to reduce SO_2 emissions and preserve the CO- and NO_x -reducing catalyst when sulphur is present in the fuel.

Because the regeneration cycle should take place in an oxygen-free environment, a section of catalyst undergoing regeneration must be isolated from exhaust gases. This is accomplished using a set of louvres, one upstream of the section being regenerated and one downstream. During the regeneration cycle, these louvres close and a valve opens, allowing regeneration gas into the section.

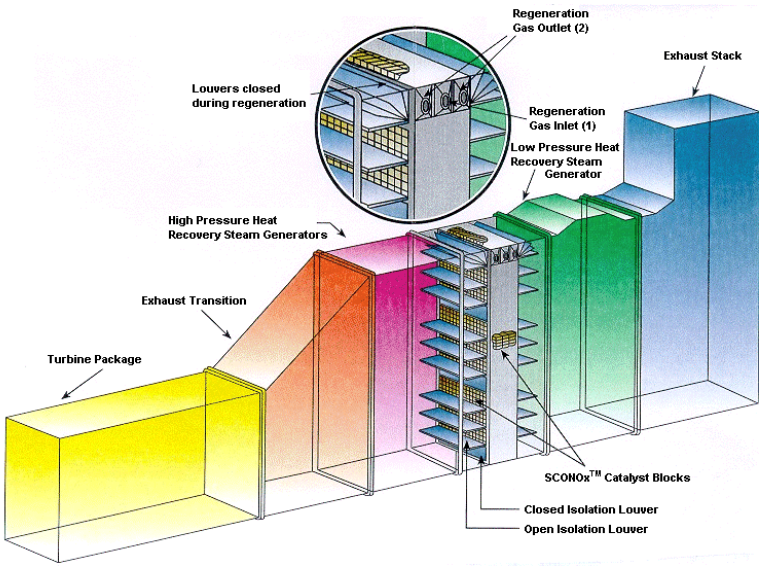


Figure 4.3: Schematic presentation of the catalyst system

Achieved environmental benefits
By using this technology, combined cycle gas turbines can be operated with very low-NO_x emissions levels. At the same time, the system reduces emissions of CO and non-methane volatile organic compounds. It uses no ammonia. In conjunction with a sulphur removal catalyst technology this system can also be used for reducing sulphur compounds from exhaust gas if required. Achievable levels are the following:

- NO_x emissions below 2 ppm (4 mg/Nm^3 as NO_2 at standard conditions 0 ºC; 1013 mbar)
- conversion rate of CO into CO_2 is 90 %
- destruction of non-methane volatile organic compounds (NMVOC) is greater than 90 % at 315 °C
- destruction of formaldehyde and acetaldehyde has been measured at 97 % and 94 % respectively at 150 °C.

Cross-media effects
The system emits CO_2, H_2O, N_2 and trace levels of SO_2 to the stack. Due to masking and poisoning of the catalyst, annual catalyst cleaning is required with de-ionised water and a potassium carbonate solution (K_2CO_3). The spent cleaning fluids can be neutralised and disposed of through the sewerage system and are harmless to the water and soil. Precious metals on the spent catalyst have residual value and can be reclaimed. There is no waste disposal issue caused by spent catalyst.

Operational data
This system requires electricity for control systems, valves and actuators, natural gas for regeneration gas production and steam both for regeneration gas production and as a dilution carrier. The typical pressure drop is between 8.5 mbar and 15 mbar. The system can operate effectively at temperatures ranging from 150 °C to 370 °C. The utility requirements for a 25 MW gas turbine are steam (333 to 389 ºC): 1590 kg/h and natural gas: 14 kg/h.

Applicability
Applicable to both new and retrofit applications, the system can operate effectively at temperatures ranging from 150 °C to 370 °C and does not limit gas turbine performance. Such unit can be installed at the back of the boiler or in the Heat Recovery Steam Generator within the same envelope reserved for a conventional SCR system.

Economics
The estimated cost numbers presented refer to a typical 400 MW size combined-cycle gas-fired power plant. The cost estimate numbers below are based on 8000 h/yr of operation and a NO_x reduction from 25 ppm to 5 ppm (50 to 10 mg/Nm^3 as NO_2 at standard conditions 0 ºC; 1013 mbar), which equals approx. 666 tonnes annually of NO_x removed. Included in the numbers are investment cost, operation & maintenance cost and indirect annual costs.

Cost	EUR million	Including
Investment cost	19.2	Delivery, erection and commissioning/start-up
Operation & Maintenance cost	1.6	General maintenance Steam and natural gas consumption in the regeneration cycle Pressure drop across the unit (approx. 10 mbars) (converted to power consumption) Average cost/year for catalyst replacement (7 year catalyst life for leading row) Catalyst disposal/refund

Additional indirect annual costs to the contractor are not included.

A reduction of NO_x from 25 ppm to 2 ppm (50 to 4 mg/Nm^3 as NO_2 at standard conditions 0 ºC; 1013 mbar) will contribute to an increase in the investment cost due to the need for additional catalyst. It will also somewhat increase the operation & maintenance cost-due to increased consumption of natural gas and steam and increased pressure drop.

A second example gives an installation cost of EUR 6.2 million for the application of this technique to a gas turbine of 25 MW. The operating costs are estimated to be approximately EUR 0.42 million/yr, including maintenance, steam and natural gas, pressure drop through the system, and the cost of catalyst replacement.

Driving force for implementation
Demands for very low NO_x emissions and limitations of air pollution control equipment utilising ammonia, especially for plants situated in densely populated areas.

Example plants
There are example applications in USA in small gas power plants.

Reference literature
[276, Alstom Power, 2000], [268, TWG, 2001]

4.10.4.10 Combinations of NO_x control and abatement techniques

The next table provides some examples of combination of NO_x control and abatement techniques that may be applicable to refineries.

ENERGY PRODUCTION TECHNOLOGY	Fired Heaters and Boilers firing Refinery Blend Gas		Gas Turbines firing Refinery Blend Gas	Gas Turbines firing Natural Gas
$DeNO_x$ technology	Flue Gas Recirculation plus Low-NO_x Burner	Ultra-Low-NO_x Burner plus SCR	Steam Injection plus SCR	Dry Low-NO_x Combustors plus SCR
NO_x reduction performance (%)	70	90+	98 - 99	98
Down to ppm @ 3 % O_2	45	10	3 - 6	5
Investment cost (1998) (EUR million)	0.9	2.1 - 3.5	8.3	7.2
Operating costs per year (excludes capital charge) (EUR million)	0.08	0.15 - 0.26	2.1	1.2
Cost effectiveness EUR/tonne NO_x removed (incl. capital charge @ 15%)	2000 – 4300	9100-10500 9000		9100 – 10500 9000
Other impacts	Add energy for fans	Risk of NH_3 emissions, catalyst disposal/ regeneration, potentially reduces heat duty	Risk of NH_3 emissions, catalyst disposal/ regeneration	Energy to produce steam, risk of NH_3 and higher CO emissions, catalyst disposal/ regeneration

Reference literature
[115, CONCAWE, 1999], [268, TWG, 2001]

4.10.5 Particulate abatement techniques

Particulate loads (containing metals) from refinery combustion plant are normally fairly low unless heavy residues are burnt. Those particulates may be abated using a number of methods including electrostatic precipitators (ESP), bag filters and wet scrubbing, as already described in Section 4.23.4.

4.10.5.1 Switching to low ash content fuels

Description
Refinery fuel gas and hydrotreated liquid refinery fuels contain less particulate loads than heavy liquid refinery fuels. Switching to those fuels has a positive impact in the reduction of particulates emissions. The achieved emission particulate levels as well as cross-media effects, operational data, applicability and economics have already been described in Section 4.10.2

4.10.5.2 Steam injection

Description
Steam injection together with the liquid refinery fuel to lower the particulate concentration.

Achieved environmental benefits
In the flue gas of older furnaces firing liquid refinery fuel, PM content may range from 500 - 1000 mg/Nm^3. For new optimal burner design with steam atomisation this can be well below 200 mg/Nm^3. For boilers, all these figures are on average lower. The range of 150 - 500 mg/Nm^3 represents the current typical range with liquid fuels employed (ash contents) and burners installed (low NO_x with steam atomisation).

Applicability
Steam injection in fired furnaces/boilers is widely practised with liquid fuel.

Driving force for implementation
Reduction of particulate emissions.

Reference literature
[118, VROM, 1999]

4.10.5.3 Filters

Description
See Section 4.23.4.

Achieved environmental benefits
See Section 4.23.4. PM values of less than 5 mg/Nm^3 can be achieved.

Cross-media effects
Pressure drop. Filter material life is limited and may add to disposal problem.

Operational data
Limited utilities (e.g. compressed air) are needed. For more information see Section 4.23.4.

Applicability
Bag blinding can arise from "sticky" soot particles from boilers when burning fuel oil. Filters are normally used for cleaning flue gases with flows below 50000 Nm^3/h.

Economics
Investment cost details depend on installation. Operating costs are low, but the filters normally need to be changed every 1 - 2 years.

Example plants
There are many power plants in Europe operating with bag filters.

Reference literature
[250, Winter, 2000], [118, VROM, 1999]

4.10.5.4 Electrostatic precipitator (ESP)

Description
For more information see Section 4.23.4.

Achieved environmental benefits
They can achieve dust emissions of 5 - 50 mg/Nm^3 with up to 95 % of reduction. Sootblowing is an operation that is carried out at regular intervals to remove soot that is accumulating on the furnace equipment and hampers proper functioning. During this operation the PM content of the exhaust gas can reach values of 2000 mg/Nm^3. ESPs and similar dust removal techniques installed for normal operations will be effective to reduce the PM emissions to the accepted level. Thus, ESPs working on process furnaces normally yield higher average concentrations due to that fact of sootblowing.

Cross-media effects
Electricity consumption. More information in Section 4.23.4

Operational data
ESPs consume electricity. More information in Section 4.23.4

Applicability
ESPs are widely applied in FCCs, in thermal power plants and incinerators. They can be installed both in new and existing plants. They require space for their application.

Economics
Typical installed capital costs for ESPs are from 1 - 3.8 EUR million.

Driving force for implementation
Reduce particulates and metal emissions.

Examples
Wet ESPs are the most common type used for the abatement of particulates in heavy fuel oil combustion processes.

Reference literature
[247, UBA Austria, 1998], [45, Sema and Sofres, 1991]

4.10.6 Sulphur oxides abatement techniques

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Techniques to reduce sulphur oxide emissions are fuel optimisation (described in the 4.10.1), fuel desulphurisation (hydrotreatments described in Section 4.10.2.3) or flue gas desulphurisation. The lower the sulphur content of the fuel, the lower the emission of sulphur dioxide. In this section, techniques for the capture of SO_2 from the flue gas after combustion or flue gas desulphurisation techniques and the use of additives are included. More generic information on those techniques is given in Section 4.23.5.4.

4.10.6.1 Additives to fuels

Description
Use of lime or limestone as additive to fuels to capture the sulphur oxides.

Achieved environmental benefits
This technique would abate the SO_2 release by about 90 %. Limestone 100 % in excess of the stoichiometric quantity would be required.

Cross-media effects
Limestone/ gypsum mixture has to be disposed of.

Applicability
For conventional refinery boiler and furnaces, the injection of lime or limestone into the furnace for sulphur capture cannot be applied. If the heaters and boilers are fluidised bed or circulating fluid boilers to burn petroleum coke or heavy bitumens resulting from solvent deasphalting, then lime/limestone injected into the furnace as abatement would be practical.

Driving force for implementation
Reduce the sulphur oxide emissions.

Reference literature
[45, Sema and Sofres, 1991]

4.10.6.2 Flue gas desulphurisation processes

Description
The techniques that may be considered for application to the flue gas desulphurisation are: Wet limestone scrubber, Walther process, Wellman Lord process, SD-process, AI-process, SNOx process and seawater scrubbing. More information about those processes can be found in Section 4.23.5.4

Achieved environmental benefits

Name of technology	**Flue gas desulphurisation**	**Regenerative catalytic flue gas desulphurisation**
Efficiency	90 % (500 mg/Nm^3)	95 - 98 % (250 - 100 mg/Nm^3)
Example: Capacity of the process: 5Mt/yr, 120000t/yr liquid refinery fuels, 180000 t/yr refinery fuel gas. Volume of the flue gas 1.68x10^9 Nm^3/yr Pollutant: Initial concentration: 5000 mg/Nm^3 (for liquid refinery fuels with 3 % S). Total quantity 8400 t/yr		

Caustic soda scrubbers can reduce emissions of NO_x, SO_2 and particulates significantly, as well as removing CO_2 as carbonate. A report suggests that SO_2 could be cut by up to 67 % and NO_x by up to 47 %.

SNO_x process

Particulate removal rate	less than 10 mg/Nm^3 at ESP outlet
NO_x removal rate	90 - 94.7 %
SO_2 removal rate	94 - >96 % with 5 %v/v O_2 and a temperature of 410°C inlet the SO_2 converter.

Cross-media effects

Name of technology	**Flue gas desulphurisation**	**Regenerative flue gas desulphurisation**
Other impacts	Increased energy consumption, by-product, raw material handling	Increased energy consumption, possible bottlenecking of H_2S handling facilities

Operational data
More information can be found in Section 4.23.5.4.

Applicability
More information can be found in Section 4.23.5.4. It can be applied to both new and existing installations.

Economics
Annual costs for a caustic soda scrubber would range from GBP 1.1 million to nearly GBP 7 million per refinery.

Name technology	Flue gas desulphurisation	Regenerative catalytic flue gas desulphurisation
Efficiency	90 % (500 mg/Nm^3)	95 - 98 % (250 - 100 mg/Nm^3)
Investment cost (EUR million)	30 - 50 (2 - 4 stacks)	50 - 80 (2 - 4 stacks)
Operating costs (EUR million/yr)	5	3
Example: Capacity of the process: 5Mt/yr, 120000t/yr liquid refinery fuels, 180000 t/yr refinery fuel gas. Volume of the flue gas 1.68x10^9 Nm^3/yr Pollutant: Initial concentration: 5000 mg/Nm^3 (for liquid refinery fuels with 3 % S). Total quantity 8400 t/yr		

The SNO_x plant is designed for a flue gas load of 1.0 million Nm^3/h at the exit of the existing induced draught fans. Investment cost EUR 100 million

Driving force for implementation
Reduce the sulphur emissions

Example plants
Wellman Lord system after three oil fired heaters of the power plant is used in Austria. The Gela Refinery SNO_x plant was designed for cleaning the flue gas produced in the boilers at a power plant burning a mixture of high-sulphur Fuel Oil and high-sulphur Petroleum Coke. The Mider refinery in Germany uses a wet desulphurisation process with lime after the three oil fired heaters of the power plant. The fuels used in this plant are vacuum residues, visbreaker residues and FCC slurry.

Reference literature
[112, Foster Wheeler Energy, 1999], [45, Sema and Sofres, 1991], [292, HMIP UK, 2000], [258, Manduzio, 2000], [297, Italy, 2000]

4.10.6.3 Seawater scrubbing

This scrubbing uses the natural alkalinity of the seawater to remove SO_2. Information about these techniques is already included in Section 4.23.5.4.

4.11 Etherification

4.11.1 Catalytic distillation

Description
More information in Section 2.11.

Achieved environmental benefits
Increased conversion process eficiency decreases the energy consumption within the system per tonne of product manufactured.

Operational data
The advantages of the process that include the reaction catalyst within the distillation column include essentially complete isoolefin conversions. It can be applied for MTBE, ETBE or TAME production. Conversions of 98 % of isobutylene are typical for refinery feedstocks. Conversion is slightly less for ETBE than for MTBE. For TAME, isoamylene conversions of 95 %+ are achievable. It requires an additional reactor.

Typical utility requirements, per m^3 of product	Range depending on the technology licensor	Units
Electricity	1.3 - 3.1	kWh
Steam (10.3 barg)	600 - 1150	kg
Steam (3.4 barg)	100 - 1150	kg
Water cooling (ΔT=17 ºC)	1.5 - 4	m^3

Catalyst handling in elevated places during installation and catalysts change may cause safety risks.

Economics
Investment, EUR 25000 per m^3/d of MTBE product.

Reference literature
[212, Hydrocarbon processing, 1998]

4.11.2 Prevent upsets in the waste water biotreater

Description
Water effluents from MTBE and TAME production contain releases of methanol, formic acid and ethers. Those compounds or degradation products of them can be toxic for the fauna of the biotreater. So high concentrations of those components need to be prevented from entering. This can be easily controlled by the use of a storage tank or by planning of production in order to dosify the right flow to the waste water treatment.

Achieved environmental benefits
The methanol, formic acid and ethers content of the waste water generated in the etherification processes need to be controlled to prevent upsets in the waste water biotreater.

Applicability
Fully applicable.

Economics
The implementation of this technique is not expensive.

Driving force for implementation
Avoid upsets of the biotreater.

Reference literature
[272, Shawcross, 2000]

4.11.3 Prevent leaking of water soluble compounds

Description
Ethers produced in the etherification processes are very soluble in water. If they leak may contaminate the soil, raining water and ground water. It can be seen as a part of a programme for prevention, detection and control of the soil and groundwater (See Section 4.25.1)

Achieved environmental benefits
Reduce the risk of contamination of water by ethers and alcohols used in these processes.

Driving force for implementation
Avoid contamination of ground water and surface water by ethers.

Reference literature
[349, Finnish Environmental Institute, 2001]

4.12 Gas separation processes

4.12.1 Increase the heat integration with upstream plants

Description
The gas plant is a relatively simple process and the temperature levels are not high enough to create the opportunity for steam generation. No great efficiency improvements are to be expected within a gas plant, but heat integration with upstream plants will normally make use of e.g. reboiling heat available from upstream plant streams, saving direct heating capacity in the gas separation plant.

Achieved environmental benefits
Reduced energy consumption in the gas plant and therefore in the refinery as a whole.

Cross-media effects
No cross-media effects.

Driving force for implementation
Reduced energy consumption within the refinery.

Example plants
Technique widely applied.

Reference literature
[282, Conoco, 2000]

4.12.2 Improve the condensate knock-out system

Description
Re-sizing/improving condensate knock-out system on gas streams & on-site recycling.

Achieved environmental benefits
Appreciable waste minimisation.

Applicability
Relatively minor modifications.

Driving force for implementation
Reduction of waste generation.

Reference literature
[115, CONCAWE, 1999]

4.12.3 Fugitive emissions minimisation

Description
Gas plants process light compounds and are consequently more likely to produce fugitive emissions. The use of double mechanical seals on pumps, compressors and agitators can reduce VOC emissions. Use of low-leaking valves also can contribute to reduce VOC emissions. This topic is described as an integrated measure within Section 4.23.6.1 because fugitives occur in all refinery processes, but it is mentioned here explicitly because the light compounds used lead to a relatively high level of fugitive emissions.

Achieved environmental benefits
Applying those techniques, fugitive emissions such as VOC, H_2S and other sulphur compounds can be reduced considerably.

Cross-media effects
Section 4.23.6.1.

Operational data
Section 4.23.6.1.

Applicability
Section 4.23.6.1.

Economics
Section 4.23.6.1.

Driving force for implementation
Reduction of product loss.

Example plants
Programmes of minimisation of VOC emissions can be found in many European and non-European refineries.

Reference literature
Section 4.23.6.1.

4.12.4 Re-use of the fuel gas used in LPG production

Description
Molecular sieve dryers used in LPG production are regenerated using hot fuel gas.

Achieved environmental benefits
The fuel gas can be vented to fuel gas drums to be re-used instead of being flared.

Applicability
Easily applicable.

Driving force for implementation
Reduced flaring.

Example plants
Many examples exist.

Reference literature
[18, Irish EPA, 1992]

4.12.5 Prevention of emissions of LPG odorant

Storage and handling of odorants used in the LPG production is going to be covered in the horizontal BREF on Storage. However the dosing of odorant to the LPG product need to be handled in a proper way to prevent emissions to the environment. This technique is included in the Section 4.21.21.

4.13 Hydrogen-consuming processes

4.13.1 Hydrotreating

Description
See Section 2.13. Another technique that can be used is the use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting down liquid) to increase the heat integration.

Achieved environmental benefits
Reduction of sulphur, nitrogen, aromatics and particulate emissions. Hydrotreatment, in addition to removing sulphur compounds, will remove nitrogen compounds by about 15 - 40 % (Very severe hydrotreating might achieve higher percentage removals).

Cross-media effects
See next technique in this chapter.

Operational data
See Section 2.13.

Applicability
Fully applicable.

Economics
The investment associated with the installation of a hydrotreating unit depends on the feed characteristics and the product specifications. Generally speaking, as the feed gets heavier or the individual product specifications are reduced, the processing requirements are increased. These more severe processing conditions can result in more pieces of equipment, larger equipment, and higher operating pressure, all of which increase the cost of the unit. The required capital investment for a hydrotreating unit can vary from EUR12 to EUR48 per tonne per year of capacity.

Type of hydrotreater	Capacity (Mt/yr)	Typical capital/installed cost 1997 million EUR	Typical operating cost million EUR per year
Naphtha hydrotreatment	1.3	50	
	1.7	58	
	2.2	68	
Catalytic feed hydrotreatment (typical feeds being atmospheric residue and vacuum gas oil)	1.1	70	
	2.2	113	20
	3.2	160	
Vacuum residue	1.1	90	16
	2.2	150	

Driving force for implementation
Reduction of sulphur and aromatic content of the feedstock.

Example plants
Many examples exist in refineries.

Reference literature
[166, Meyers, 1997], [112, Foster Wheeler Energy, 1999], [212, Hydrocarbon processing, 1998]

4.13.2 Hydrodesulphurisation processes

Description
See Section 2.13. Another technique that can be used is the use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting down liquid) to increase the heat integration.

Achieved environmental benefits
Reduction of sulphur content of the different fractions. Modern techniques can reduce the sulphur content of distillates to less than 10 ppm. For example, the application of one-step hydration by means of a Co/Mo catalyst (30 - 40 bar) to middle distillates reduces the sulphur content by more than 90 % (down to some 100 ppm) depending on the product, the S-content of the feed and the reaction conditions. If demand for diesel fuel increases, additional compounds (e.g. LCO from the FCC) have to be used in its production. However these feedstocks contain a variety of aromatic compounds, which have to be hydrated under severe conditions (high temperature, high pressure, highly active catalysts, two step processes).

New diesel specifications can be met in conventional single-stage hydrotreating units by lowering Liquid Hourly Space Velocity (LHSV) from 3.7 in conventional units to 0.8 - 1.1 by implementing a reactor in series to the existing ones and applying the latest catalyst generation available for gasoil hydrotreating units. Processing Russian export blend with 1.3 % w/w S and an intermediate sulphur content ahead of the final desulphurisation unit of 0.12 % S, a final sulphur content of 8 ppm S in the raffinate can be achieved during normal operation.

Cross-media effects
Energy consumption, waste generation, effluent water and air emissions.

Operational data
Gasoil hydrotreating units need the additional measure of a high-pressure amine washer in the hydrogen recycle stream to avoid recombination of H_2S from the recycle hydrogen stream with hydrocarbons from fresh feed. The unit will operate at 45 bar, utilizing 40 Nm^3 Hydrogen/t of gasoil feed and anticipating a run length of 30 months.

Applicability
Applicable to distillates from naphtha to heavy residues.

Economics
The estimated erected cost for a reduced-crude desulphurisation process (basis 132 m^3/h unit) unit is EUR 47 millions. Another estimated investment summary for residue desulphurisation system hydrotreater to prepare residue fluid catalytic cracking feed is shown below.

Feed Rate, Mt/yr	3.8
Run length, days	335
Operating factor	0.92
On-plot investment, million EUR	272
Total off-plot cost(30 % of on-plot), million EUR	82
Catalyst cost per charge, million EUR	10
Basis: second quarter 1995 US Gulf Coast	

Driving force for implementation
Reduce sulphur content of the feedstock. Deep desulphurisation is an important technique applied for compliance with Auto-Oil Programme II. Costly two-stage hydrotreating units applying a noble metal catalyst in the second stage of hydrodesulphurisation are not needed to meet Auto-Oil Programme II or German diesel specifications. But, depending on the final specification on cetane of diesel issued by the European parliament, two-stage units may become mandatory for refiners being short in cetane index in their diesel pool. Normally those

refiners do not operate a hydrocracker unit. Two-stage units are also mandatory for refiners who need to lower the aromatics content and/or the CFPP in their gasoil pool.

Example plants
Many desulphurisation processes exist in refineries.

Reference literature
[166, Meyers, 1997].

4.13.3 Catalytic distillation

Description
Catalytic distillation for desulphurisation of gasoline in a two stage process.

Achieved environmental benefits
Reduction of 95 % of sulphur content in FCC-gasoline containing 1800 ppm of sulphur have been achieved. This type of technique consumes less energy than traditional desulphurisation processes.

Cross-media effects
Energy consumption, waste generation, effluent water and air emissions.

Applicability
Fully applicable. This technique may also be used for the reduction of benzene in the reformate.

Economics
A two-stage process is designed to treat 7950 m^3/d of FCC-gasoline containing 1800 ppm of sulphur. Its efficiency has been of 95 % and its investment costs are approximately EUR 20 millions.

Driving force for implementation
Since the sulphur content of gasoline will be reduced to 50 ppm by law, techniques for the reduction of sulphur content will become more used.

Example plants
At least one catalytic distillation plant for desulphurisation of 7950 m^3/d of FCC-gasoline is available in Europe.

Reference literature
[247, UBA Austria, 1998]

4.13.4 On-stream catalyst replacement technology for processing high-metal feeds

Description
While the main objective of this process is to extend catalyst life in a down-stream fixed-bed reactor by maintaining high hydrodemetallisation performance, the catalyst also achieves high hydrodesulphurisation/hydrodemetallisation and hydrodesulphurisation Conradson carbon removal/hydrodemetallisation activity ratios.

Achieved environmental benefits
On-stream catalyst replacement technology improves the residual desulphurisation in the refinery, thereby decreasing the waste generation.

Operational data
Reactor typically operates at 390 ºC and 2000 psia.

Applicability
Fully applicable.

Driving force for implementation
Extend the catalyst life of the hydrotreatment processes.

Example plants
Till 1997, there were 15 on-stream worldwide.

Reference literature
[166, Meyers, 1997]

4.13.5 Hydrogenation of light dienes

Description
The hydrogenation of light dienes serves the purpose of producing a more stable refinery stream reducing upstream, gum formation. The process converts dienes to useful olefins. More information in Section 2.13.

Achieved environmental benefits
The process helps reduce acid losses in downstream processes (e.g. alkylation). Typical product diene levels from the selective hydrogenation process unit may range from 25 to 1 ppm.

Cross-media effects
Low energy consumption.

Operational data
Low temperature, liquid-phase operation means that no utilities are required in most cases if the feed and hydrogen are both available at suitable conditions. Heating or cooling duties are limited to cases with relatively high diene concentrations in the feed. Commercial operation for a period of more than two years without the need to regenerate or replace the catalyst is typical.

Applicability
The design of the units is simple. Most of the units are designed for diene reduction to less than 5 ppm in the product.

Economics
The design of the units is simple and requires low capital and nominal operating costs. The cost of the catalyst is low compared with the installation cost. The capital investment, including catalyst, for the unit is small, usually within the range of EUR 0.6 - 1.2 million. The investment base on recent projects is of some EUR 3 millions for a plant of 100000 t/yr capacity.

Driving force for implementation
Reduce gum formation in downstream operations. The flexibility and minimal cost of this technology make the unit a valuable processing tool.

Reference literature
[166, Meyers, 1997], [261, Canales, 2000]

4.13.6 Hydrocracker

Description
Hydrocracking is an exothermic process and heat integration techniques can be applied. For more information on hydrocrackers see Section 2.13. Some techniques to consider are:

a) The heat generated in the reactors can be partially recovered in a feed/product heat exchanger. A furnace heats the feed to its required temperature. The reactor temperature is controlled via the injection of cold hydrogen between the catalyst beds.
b) A significant amount of heat is required in the fractionation section. Heat integration is applied to minimise heat consumption.
c) The energy efficiency can further be increased by applying a four-stage separator system. The feed to the fractionation section is in that case rendered significantly hotter, and consequently less heat is required in the fractionation section.
d) The use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting down liquid)

Achieved environmental benefits
Reduced hydrocracker energy consumption.

Cross-media effects
No cross-media effects known.

Operational data
Control system need to be enhanced.

Applicability
In some cases, the heat integration can be difficult to apply. Replacement of existing hydrocrackers by new and highly heat integrated hydrocrakers is in many cases not justified environmentally and economically.

Economics
The cost of a hydrocracker with heat integration varies from 36 - 84 EUR/(t/yr). Annual operating cost varies between 0.6 and 1 % of the investment cost. In many cases the economics of the process do not justify the replacement of an existing hydrocracker, because payback period can be very long.

Driving force for implementation
Reduction of energy consumption.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [112, Foster Wheeler Energy, 1999], [268, TWG, 2001]

4.13.7 Residue hydroprocessing

Description
See Section 2.13. Another technique that can be used is the use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting down liquid) to increase the heat integration.

Achieved environmental benefits
Upgrading of fuel oil in lighter products, and reduction of sulphur, nitrogen and metal contents in the fuel oil and other products.

Cross-media effects
Cross-media effects are increased energy consumption and a consequent increase in CO_2 emissions, due mainly to the hydrogen. As discussed in Section 3.14, the production of hydrogen is very energy-intensive, generating large quantities of CO_2. As discussed in Section 4.13, hydrotreatment processes generate catalyst for disposal and increase H_2S production with direct consequences (enlargement or new) for the sour water stripper and sulphur recovery units. Other cross-media effects are the increase of waste generation (catalysts) and effluent waste water (containing H_2S).

Operational data
Hydroconversion is an exothermic reaction, the heat generated in the reactor system being partially recovered in the feed product exchanger. Normally a high level of heat integration and heat recovery is applied in the fractionation section. The amount of hydrogen required depends on feed (heavier feeds tend to increase hydrogen consumption) and process objectives (lower sulphur, nitrogen, aromatics content in the products, higher hydrogen consumption). In most cases extra energy is required.

Applicability
Commercial experiences range from low-sulphur atmospheric residues to high-metal, high-sulphur vacuum residues with over 300 ppm metals.

Economics
Investment costs for the various options depend strongly on the feed properties and process objectives of the residue hydroprocessing unit. Investment costs for a typical new single string 5000 t/day unit will range from 200 - 300 million US$, the higher figure including an integrated hydrocracker.

Driving force for implementation
Residue hydroprocessing is used for the upgrading of fuel oil into lighter products.

Example plant(s)
Many different concepts of residue hydroconversion processes are licensed. The selection of the type of process depends on feedstock quality (metal content and Concarbon number) and the required conversion and product quality.

Reference literature
[115, CONCAWE, 1999], [212, Hydrocarbon processing, 1998]

4.14 Hydrogen production

As mentioned in Section 2.14, the production of hydrogen it is not exclusive to the refinery sector. Therefore this chapter should also be seen as applicable to other industrial sectors where hydrogen production is necessary (e.g. ammonia production, chemical industry etc).

4.14.1 Gas Heated Steam Reformer Technology

Description

- Gas Heated Steam reforming replaces the reformer furnace: the reforming heatload is provided by cooling the exit gas from a secondary reformer which uses oxygen. The feed consists of natural gas or light naphtha.
- The steam reformer has to supply a large amount of heat at high temperature for the steam reforming reaction by burning fuel, with the result that a large amount of heat is lost in the flue gas. In order to minimise the amount of heat lost in the stack, a large heat recovery system is used. A large proportion of the recovered heat is by raising and superheating steam. Some heat integration is possible around the solvent absorber and the methanator.

Achieved environmental benefits

- Gas heated steam reforming reduces the energy consumption of the reforming process.
- Recovery of heat from flue gas can be used elsewhere in the refinery, reducing consumption elsewhere.

Cross-media effects

The environmental regulations with the most impact on plant design are typically NO_x limitations. Other impacts, such as SO_x or water emissions, are minimal, because low-sulphur fuel is typically used and there are few emissions other than flue gas. The choice of heat recovery system can have a major effect on NO_x production, since both the amount of fuel fired and the flame temperature will be affected. Preheating combustion air will reduce firing, but since NO_x formation is strongly influenced by flame temperature, there will be an overall increase in NO_x formation. Other methods of reducing firing, such as pre-reforming or heat exchange reforming, do not affect the flame temperature and will therefore reduce NO_x production. The production of CO_2 is also important. Each tonne of H_2 produced also produces a minimum of 12 tonnes of CO_2 (7.5 tonnes if related to the steam generation).

Operational data

The combination of high temperature and pressure imposes severe demands on the steam reformer tubes, which must have thick walls to withstand the stresses and must be fabricated from expensive alloys. The furnace box must be large to obtain the high rates of heat transfer from the fluegas to the tubes. These combined factors make the steam reformer the largest and most expensive single item of equipment in a hydrogen plant. The large size of the unit means that it takes a long time to heat up and cool down, and this makes it the most time-consuming part of the start-up and shutdown procedure. The large thermal inertia makes it liable to damage during plant upsets.

Applicability

Fully applicable.

Economics

Relative hydrogen production costs of the two processes are primarily a function of feedstock cost. A new hydrogen plant for a 7950 m^3/day FCCU feed hydrotreater or hydrocraker would typically cost in range of EUR 60 - 75 millions (1997).

Driving force for implementation

Production process. Hydrogen is needed for the hydrotreatments in the refinery.

Example plants
A new alternative, already proved commercially for ammonia and methanol production, is the Gas Heated Steam Reformer Technology.

Reference literature
[112, Foster Wheeler Energy, 1999]

4.14.2 Coke and heavy oils gasification

Description
The IGCC plant can also function as a hydrogen supplier, in which case hydrogen is removed from the syngas (after the sulphur removal). For more information see Section 2.14, 2.10 and 4.10.3.5.

Achieved environmental benefits
Coke gasification
A fixed-bed desulphurisation system using regenerable zinc ferrite as the sorbent has been tested as a continuation of the gasification exhaust gases treatment. Sulphur levels of 10 - 20 ppm in the treated gas were achieved in this system. The product gas also contains traces of ammonia (less than 5 %) and hydrogen cyanide (HCN), derivatives of the nitrogen in the feed. Using limestone in the gasifier tends to reduce the level of these components. Ammonia is not removed by zinc ferrite in the external desulphurisation process. If there is any alkali in the feed, some of it may vaporise in the gasifier and may have to be removed by an alkali sorbent or by cooling the gas going to the filter. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm.
Heavy oil gasification
Another environmental benefit of gasification is that it reduces heavy oils that, used in another way may pollute the environment much more. See also 4.10.3.5.

Cross-media effects
Partial oxidation requires an oxygen plant (95 - 99 % purity), which increases costs.

Operational data
Normally, an IGCC plant includes a water purification section with the following units:
- soot recovery either by washing with naphtha and recycle of naphtha/soot mixture to gasification section and/or by filtration.
- water pretreatment to remove solids (carbon, metals, salts) by filtration before final treatment in biological plant (GTW)

The grey water treatment (GWT) is designed to treat water blowdown from a carbon extraction unit with syngas condensate and possibly the amine regeneration overhead system; water from grey water treatment is finally sent to biological treatment. The GWT may employ physical and chemical treatment for cyanides destruction and removal of heavy metals followed by a sour water stripper, which removes sulphides, ammonia, and carbon dioxide from the water.

The gaseous streams are totally washed to remove any contaminant and the process normally includes the following ancillary units for gas purification:
- washing with water and sometimes oil to remove soot and particulate
- reactor for COS or cyanides by hydrolysis
- sour gas absorbing with amine or equivalent system and production of elemental sulphur from H_2S in Claus unit.

Applicability
Relative hydrogen production costs are primarily a function of feedstock cost. The main problem with investment in gasification plant is its capital and operating cost. To be attractive commercially it usually needs to be undertaken on a large scale. Typical requirement for

chemicals production are the generation of more than 200 MWe of electrical power through IGCC or the use of hydrogen, carbon monoxide and steam on a large scale.

Economics
Generally accepted investment costs for an oil gasification based combined cycle plant in the 200+ MWe range are 1300 - 1700EUR per kW installed, with a thermal efficiency of around 40 % and close to 99 % sulphur emission abatement. As average electrical demand in a refinery is usually less than 80 MWe, the investment in IGCC often depends on the opportunity to export the surplus of electrical power generated. However high pressure steam can also be a valuable gasification product and there are examples of much smaller gasification units that fit in well with a refinery.

Relative hydrogen production costs of the process are primarily a function of feedstock cost. Steam reforming of methane usually produces hydrogen at lower costs than partial oxidation of fuel oil, if the cost of methane is less than about 65 % of fuel oil cost on an energy basis.

Driving force for implementation
Production of hydrogen, reduction of the production of heavy oils, power export and production of synthesis gas as feed for petrochemistry.

Example plants
At least five gasification processes are currently running in European refineries.

Reference literature
[166, Meyers, 1997], [297, Italy, 2000]

4.14.3 Purification of hydrogen

Description
Information about the processes can be found in Section 2.14. Some techniques that may be applied to the hydrogen purification units to achieve better environmental performance are:

- several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is normally accumulated in a vessel and used as fuel at a convenient location
- one technique to reduce air emissions is to use PSA systems only for purification of hydrogen
- use the PSA purge gas as refinery fuel gas in the reforming furnace instead of higher C/H ratio fuels.

Achieved environmental benefits
Re-use of waste fuel gas as fuel within the process.

Cross-media effects
Because of loss of hydrogen to the PSA tail gas, the reformer and front end of a PSA plant are larger than in a wet scrubbing plant. However, a PSA plant uses less process steam and does not require heat for the reboiler. PSA is a high energy consumer due to the high vacuum/pressure systems that it uses.

Operational data
The PSA system is completely automatic and offers a higher purity product. The PSA unit is simpler to operate than a wet scrubbing system, since it has no rotating equipment or circulating solutions. The conventional process produces a hydrogen product of maximum 97 - 98 % v/v purity, while the pressure swing adsorption process produces a very pure hydrogen product between 99.9 % v/v and 99.999 % v/v. The residual constituents of the product gas are mainly methane and less than 10 ppm CO. Some data on the utility consumption of the PSA system are:

3700 Nm^3/h with a H_2 content of at least 85 % and a pressure between 37 and 47 bar. Product-stream: 2400 Nm^3/h purified H_2 with a concentration of at least 99.5 %, Temperature: 45°C, Pressure: 35 bar; waste gas: 1300 Nm^3/h, P: 3 bar, T: 30°C, contains 60 % H_2, 1.4 %H_2S and 40 % C_1 - C_6 compounds with higher boiling points.

Driving force for implementation
Production process to purify the hydrogen. The choice between the PSA system and the scrubbing system depends on product purity required, reliability and process economics. The extra investment for the PSA system for large plant capacities can normally be offset by the lower operating cost. Also a PSA system will yield a higher H_2 purity.

Example plants
Many examples exist.

Reference literature
[166, Meyers, 1997], [297, Italy, 2000], [211, Ecker, 1999]

4.15 Integrated refinery management

This section structured in the same way as Chapter 2 and 3, contains those integrated refinery management activities that are not included in other sections. The first techniques to consider are environmental management activities and other utility management techniques.

4.15.1 Environmental management tools

Description

An environmental management system (EMS) can contain the following elements:

- the implementation and adherence to international accepted system such as those from the ISO 14000 series or to EMAS. Those systems ensure the continuous improvements, complaints handling training, performance reporting, process control and improvement planning etc.
- proof can be enhance by e.g. internal and/or external auditing, certification.
- EMS does not stand in isolation from the other systems (safety, maintenance, finance etc.) but is to be integrated with the other systems where relevant and beneficial. More specifically the management systems for Energy and Environment can be combined, which is in line with the fact that a reduction in energy consumption goes hand in hand with improvement of environmental performance.
- the preparation and publication of an annual environmental performance report, to be externally verified. Such a report will also enable the dissemination of improvements to others, and will be a vehicle for information exchange (to neighbouring environments, to authorities etc).
- The delivery to stakeholders on an annual basis of an environmental performance improvement plan. Continuous improvement is assured by such a plan.
- It is common practice in the quest for continuous improvement to compare own performance with that of others in the field, and to identify the current "best practices". Taking these "best practices" from others to heart and applying them will lead to environmental performance improvements. Systems are available for comparing own performance with others for energy, for efficiency, for maintenance, in which performances of refineries with different capacities and complexity are normalized. (e.g quivalent Distilling Capacity). This technique of performance measurement, comparisons with others and identification of "best practices" and the adoption in one's own workplace is also called "benchmarking". This technique has scope for application in a number of areas of environmental performance improvements as well.
- practise of such benchmarking on a continuous basis, including energy efficiency and energy conservation activities, emissions to air (SO_2, NO_x, VOC, and particulates), discharges to water and generation of waste. Benchmarking for energy efficiency typically involve an internal system of energy efficiency improvements, or intra- and inter-company energy efficiency benchmarking exercises, aiming for continuous improvements and learning lessons.
- perform an Environmental Impact Assessment (EIA) for major new activities.
- mass balance data on sulphur input and output via emissions and products (including low-grade and off-spec products and further use and fate), to be reported on an annual basis.

Achieved environmental benefits

Those systems typically ensure the continuous improvements, complaints handling training, performance reporting, process control and improvement planning.

Applicability

Those techniques can be typically applied to all refineries

Example plants

Many of those techniques are applied in many refineries

Reference literature
[118, VROM, 1999], [285, Demuynck, 1999]

4.15.2 The bubble concept

Description
The bubble concept usually refers to air emissions of SO_2, but can also be applied to NO_x, dust, CO and metals (Ni, V). The bubble concept is a regulatory tool applied in several EU countries. As represented in the picture below, the bubble approach for emissions to air reflects a "virtual single stack" for the whole refinery. The treatment of process water in the refinery is typically done in a single waste water treatment plant (for technical and economical reasons) and conceptually can be regarded as a similar approach to the "bubble concept"[4] for air.

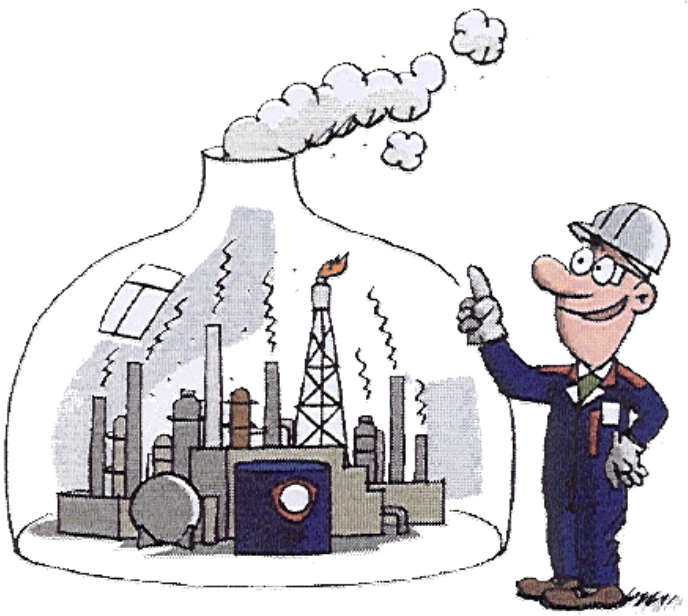


Figure 4.4: The bubble concept

Why is it applied to refineries?
The bubble concept is used for refineries because it is recognised that they meet some or all of their energy needs with a variety of gaseous and liquid fuels that are by-products of the various processes. In this respect, refineries differ from other industries that generally buy all their specified fuels from outside.

The technical justification of the bubble concept in refineries is the complexity of the installation. Aspects of this complexity include the number of emission points and the technical and economic interrelationships in a modern refinery between feedstock, types of processes and the variations in different operating conditions in relation to product slate and product quality requirements.

The economic justification is that the refinery should be allowed to use, at different plants and at different times, the various fuels it produces in-house. At the same time, it enables the operator to:

[4] The requirements on a refinery to reduce its discharges to water can be also conceived as a bubble approach. Water from various process units is collected into one water treatment system. The load in g/tonne crude oil processed in the refinery can be defined in terms of a "bubble", aimed at the minimisation of water consumption, re-use of water in different processes and BAT at the waste water treatment unit in an integrated way and for all processes together with the objective to reach as low a load as is technically and economically feasible for the whole refinery.

- choose the most cost-effective place to reduce emissions
- respond to opportunities in the crude oil market and the supply & demand situation for oil products
- operate effectively in a competitive environment.

The environmental justification is that the authority should be allowed to define emission conditions in line with its environmental targets while allowing the refinery operator flexibility in the operation of its processing units and in the selection of the various technical and economic options to fulfil the energy requirements of the refinery in competitive market conditions. Moreover, it allows easy comparison of the emission performance of a refinery and between refineries.

Definition and applicability

For the application of the bubble concept, the associated emission levels need to be given in a transparent way. This includes:

1. the pollutants involved
2. the approach used to define the bubble (concentration bubble and load bubble). (See below)
3. a comprehensive list of installations included in the bubble concept (see below)
4. the corresponding flue gas volumes and their measurement conditions (e.g. under standard conditions, dry)
5. reference data (oxygen content and averaging time (daily, monthly, yearly, 3-yearly)) (see below)

Follows explanations of the above points:

1. Self-explanatory (See Description in this Section)

2. Different approaches (point 2 above) can be used to define the bubble, i.e:
   - in a concentration units of the flue gas emitted by the refinery, whereby the complexity of the refinery is reflected in the energy consumption of the refinery, or
   - in a annual load per tonne of crude oil processed which can be combined with the complexity factor (Nelson index) of the refinery

   The load bubble includes energy efficiency of a refinery and the concentration approach does not. This is the major advantage of the load bubble. There are simplified factors (See Table 3.2) for switching between the two approaches. It should be notised that such a factor calculated on an average European energy consumption value could, however, be misleading because energy efficiencies in European refineries vary greatly (See Section 3.10.1). The conversion between the two approaches in each specific refinery is more accurate.

   Other methods may be used. It is more a question of convenience and custom than of principle how and in which units of measurement the bubble is defined, as long as it is clear which approach is used, which methodology is used to define the unit of measurement and which units are included.

3. There are different interpretations in various countries of the units to be considered (e.g. combustion only, including or excluding FCC and/or SRU and/or flares). As an example, a Member State has reported that for an existing EU+ refinery the bubble concentration increases by 20% when flares are included in the bubble. Another example was given by Concawe were the calculated average of the SO_2 fuel bubble was 1000 whereas the average was 1600 if all installations are included within the bubble.

4. Self-explanatory

5. When the short averaging time is defined (e.g. daily, monthly), additional flexibility for outages, changes of feedstock and other technical problems may be granted by allowing the

high values in the current period to be corrected by lower values in the next period, when the technical problems have been sorted out. The mass bubble limit (g/tonne crude oil processed) is typically defined over a long period (e.g. one year). In one EU+ refinery, a period of three years is applied. Also, it has been recognised by the TWG that the averaging time may depend on the pollutant. (e.g. environmental and health effects of NO_x and SO_x are different). The averaging period is also related to the stringency of the bubble emission level (the more stringent the levels, the longer the averaging period, to allow flexibility).

The above paragraphs imply that a large amount of data is needed to continuously calculate the bubble value. For example, for SO_2:

- RFG sulphur contents need to be continually measured (e.g. by mass spectrometer) and hourly values produced; SO_2 is then calculated by recording hourly fuel flows to furnaces and boilers.
- Fuel oil S content is measured daily.
- FCCU figures are estimated based on a percentage of the S feed to the unit (the daily flow of feed to the unit; the S content is measured after any change of crude slate). This needs months of data collection to establish a relationship.
- SRUs, calciners etc all have different algorithms to estimate releases continously based on data collection.
- Data are also needed to continuously estimate moisture and O_2 content in the flue gases to correct to the reference conditions.

The last paragraph indicates the scope for considerable variability in the way refiners calculate the bubble and thus in the accuracy and reliability of the data when comparing bubble values. However when a good sample schedule is establish together with an approved calculation method, the follow up of the emissions become very easy.

Environmental concerns

As in some situations refineries are physically or logistically connected to a nearby chemical plant, there may be a temptation to extend the bubble to the “non-refinery” processes which then may create misuse of the bubble concept because of dilution effects. These dilution effects can occur due to the high volumes of flue gases generated by some non-refinery processes that typically contain low levels of SO_2 and NO_x. An example of such dilution was submitted by a Member State where a refinery bubble profits from a large chemical plant and the bubble concentration is reduced by 50% (included in the LVOC BREF). Dilution effects do not affect the load approach.

A second concern may be that the concentration bubble is defined as a relative standard, directly related to the fuel use in the refinery, and therefore not enhancing efficient use of energy in the refinery. This can be addressed by defining the bubble according to a load per tonne of crude oil processed or by defining an absolute ceiling (in tonnes/year), in addition to emission values in mg/Nm^3 flue gas in the bubble. However, there is a possible trade-off between the stringency of the environmental requirements and the need for flexibility in the operation of a refinery. Special care should be taken not to introduce additional complexity into the regulatory system, thereby losing part of the attractiveness of the bubble concept. For example, in a MS a 3-year average is chosen for the SO_2 bubble (load) for the refinery. In the case of NO_x, however, the differences in long-term environmental and health effects of SO_2 and NO_x need to be borne in mind.

Another possible environmental concern with this concept, is the possibility of high emissions at the lower stacks (e.g. SRU). This can easily be redressed by requiring that the flue gases of the cleaner fuels be discharged at the lower stacks and the high stacks are used to avoid high concentrations of pollutants at ground level, affecting workers and the neighbourhood. Of course, the regulator should be aware that traditional measures used to ensure that ground level concentrations of hazardous pollutants are within Air Quality Standards are still required when using the bubble concept. This comment can be extended to all legislation, because the use of

the bubble concept as a regulatory tool does not prevent other existing/new limit values for specific units/facilities within the refinery for being applied.

Establishing associated emission values in the bubble concept

If the bubble concept is to be used as an instrument to enforce the application of BAT in the refinery, then the emission values defined in the refinery bubble should be such that they indeed reflect BAT performance for the refinery as a whole. The most important notion is then to:

- identify the total fuel use of the refinery;
- assess the contribution of each of the fuels to the total fuel consumption of the refinery;
- quantify the emissions from process units implicated in such emissions (e.g. FCC, SRU);
- review the applicability of BAT to each of these fuels and/or the process units
- combine this information with the technical and economical constraints in using these techniques.

This may imply different emission values associated with the use of BAT, depending on the type of fuels used and their contribution to the total refinery fuel use, together with emissions of process units such as the FCC and the SRU and their contribution to the total refinery emissions.

Associated emission values in the case of a gas-fired refinery will be inherently lower than the emissions in a situation where a major part of the fuel use of the refinery is provided by liquid fuels. In this latter case BAT may be defined by assessing the emissions associated with the gaseous fuels used in combination with the emissions associated with using liquid residual fuels and flue gas treatment, or using clean liquid fuels, i.e. gas oil with limited S-content. If deemed necessary, these emission values for a bubble based on concentrations can easily be translated into a yearly or monthly load bubble, i.e. tonne of SO_2 and/or NO_x per million tonnes of crude oil processed.

In Annex V, several examples show how, emission values for the bubble concept can be defined which reflect the SO_2 and NO_x performance that is technically feasible for the refinery as a whole. The assessment of BAT-associated emission values involves however also an economic and an environmental assessment of these values. The investment decision to convert an existing refinery into a full conversion, gas-fired refinery involves much more technical, economic and environmental considerations than only the SO_2 and NO_x emissions from the refinery itself. Similarly, the decision to invest in flue gas desulphurisation and/or NO_x abatement via SCR may also involve the concentration of liquid fuel firing of the refinery in one or two larger combustion plants, which will have major implications on the way the refinery will be able to respond to commercial pressures. The same holds true for the other technical options that a refinery will be faced with. However, maximum flexibility will be high on the agenda in assessing the various technical considerations open to the refinery. By defining emission values in the bubble that respect this need for operational flexibility, the permitting authority can support the proper environmental outcome of the investment decision process by the refinery

The bubble concept is an environmental regulatory instrument that may be used to enforce the application of BAT in the refinery without becoming entangled in the complex technical-economic interrelationships in the refinery. As mentioned before, there is a link to the BAT concept provided that the bubble is set at a level that reflects BAT performance of the refinery as a whole.

Examples

TWG has provided some reference numbers when bubble concept is applied to refineries. Data has been divided in two groups. One group represents actual performance of refineries and the second one represents proposals provided by different TWG member(s).

Data from	SO_2 emission level (mg/Nm^3 @ 3% O_2 unless written)	NO_x emission level (mg/Nm^3 @ 3% O_2 unless written)	Particulates (mg/Nm^3 @ 3% O_2)
Actual bubble calculation in refineries			
European refinery survey (76 refineries). Annual averages. Upper quartile	200 – 1000 (average 311)	35 - 250	
European yearly weighted average	1600 (including all installations)		
Tables 3.3 and 3.6 within Section 3.1.2. Upper quartile of 40 EU+ refineries	50 – 210 t SO_2 / Mt of crude processed 80 – 350 (annual average)	20 – 150 t NO_x / Mt of crude processed 35 – 250 (annual average)	
Range found in a EU+ country	470 – 1250 daily average	100 – 350 daily average	
Natural gas plant	30		
Refinery in EU+	1000 – 1400 monthly average (Value dependent on the amount of liquid oil that they fire.	250 – 300 (little variations from daily to monthly averages)	
Refinery in EU+ (Not oil fired)	600 monthly average 1000 daily average	300 – 350 (little variations from daily to monthly averages)	
EU+ refinery	680 (half hourly averages per year)		
Refinery outside EU+ (100 % gas)[2]		20 - 30	
Refinery outside EU+ (10% liquid fuel)[3]		60	
One EU+ refinery	53 t SO_2 / Mt of crude processed	78 t NO_x / Mt crude	
One EU+ country	60 – 120 t SO_2 / Mt of crude processed	20 – 100 t NO_x / Mt crude	
TWG proposals (benchmarks)			
TWG member supported by a refinery (Not including flaring)	60 – 200 50 – 230 t/Mt	70 – 150 80 – 170 t/Mt	
TWG member supported by calculations in Annex V	100 - 600 (monthly average)	100 – 200 (monthly average)	
TWG member	600 monthly average 850 daily average	150 monthly average 200 daily average	
Two TWG members[1] based on current practices	800 - 1200 monthly average	250 - 450 monthly average	30 – 50 monthly average
TWG member based on European current practices	1000 - 1400 annual average	300 – 500 annual average[4]	15 – 50 annual average

[1] In the revision of the Large Combustion Plants Directive the SO_2 emission limit values for new and existing refineries are respectively 600 and 1000 mg/Nm^3. Having considered that the bubble emission levels in the BREF are referred to all plants, these emission limit values are slightly increased to include the SO_2 emission also from Claus, catalytic cracking plants and flare. The emission limit values for NOx, in the revision of the Large Combustion Plants Directive are defined in the same range we proposed for refinery bubble and this seems enough to justify our proposal.

[2] Achieved on a long-term period using gaseous fuels and secondary measures on gas fired units and converting heavy residues with cokers.

[3] Achieved on a long-term period hydrotreating liquid fuels (0.03% S) and implementing SCR on 73 % of the gas flow (15 SCR reactors on the main emitters of 25 furnaces, 7 boilers, 1FCC).

[4] For a new refinery (gas fired) possibly 200 can be reached.

Data on legislation applying bubble concept in some countries are provided in Annex I.

Reference literature
Austria, Belgium, Concawe, France, Greece, Italy, Netherlands, Norway, Spain, Sweden, UK, [248, Ademe, 2001]

4.15.3 Good housekeeping

Description
This section includes good practices applied to maintenance, cleaning and other horizontal issues within refineries. What was considered "good housekeeping" in the past may nowadays seem self-evident, as it is embedded in day-to-day refinery practice. New measures, based on experience gained, are however included over time. "Good housekeeping" is often used in the broader context of good management and conduct of the business. Quite a number of business performance parameters, such as safety, maintenance, efficiency (of energy and manpower), product quality, information, unit/equipment reliability, human resources and finance require approaches that start with a concept of "good housekeeping". For refineries, safety provides numerous examples of this approach, often grouped under the heading Safety Management. Similarly, Product Quality Management stands for a well-developed approach to assure customer satisfaction and Maintenance Management for improved unit reliability/on-stream time and maintenance effectiveness. There are also systems for the other business parameters. All these systems are in place to assure that the correct practices are adopted, and that the "lessons learned" are reflected in these systems (e.g. ISO 9000 series).

The more traditional aspects of good housekeeping are included in this section. These systems can also be regarded as the tools to ensure that the right procedures are adhered to in order to safeguard the proper functioning of the refinery hardware. The following techniques are considered to be good environmental practices within the industrial sectors.

- Planning and carrying-out of *maintenance* by:
  - all plant and equipment should be subject to regular preventive maintenance programmes, in line with operational requirements, to ensure continued optimum performance.
  - prompt clean-up of minor spillages with adsorbents.

- Regular *cleaning* of equipment and refinery premises. Cleaning, by its nature, generates waste. By choosing the right procedure and technique this waste may be minimised or its nature altered so as to make it more easily disposable:
  - drain equipment to the maximum
  - recycle "spent" rinse water
  - use high pressure water cleaning rather than detergents or chemicals
  - use on-site pretreatment whenever possible, e.g. wash/steam filter material (e.g. filter clays) prior to dumping
  - minimise tank sludge prior to cleaning (solvent & mixers)
  - during cleaning, vents and vessel steaming to be directed to flare. This technique may raise serious safety issues if oxygen is present. In addition when Hg is present – particularly when steaming overhead coolers- mercury emissions may occur.
  - in many refineries, using high-pressure water to clean heat exchanger bundles generates and releases water and entrained solids to the refinery waste water treatment system. Exchanger solids may then attract oil as they move through the sewer system and may produce finer solids and stabilized emulsions that are more difficult to remove. Solids can be removed at the heat exchanger cleaning pad by installing concrete overflow weirs around the surface drains or by covering drains with a screen. Other ways to reduce solids generation are by using anti-foulants on the heat exchanger bundles to prevent scaling and by cleaning with reusable cleaning chemicals that also allow for the easy removal of oil

  - cleaning at designated places in order to have control over run-off material and contaminted water
  - prompt clean-up of minor spillages with adsorbents.
  - install weirs at cleaning places, in order to hold back solids, which otherwise might attract oil in CPI separators
  - minimise and re-use cleaning chemicals.

- Use techniques in *common industrial equipment (pumps, compressors, etc.)* that can reduce the environmental impact as for example:
  - implementation of operational improvements in new designs
  - equipment reliability improvement
  - use lubrication technique based on the lubrication by an oil mist. The technique consists of a vortex generator, which generates, with the help of dry pressurised air, a mixture of air and lubricant oil, This mixture is called oil mist, and lubricates the dynamic equipment. Once lubricated the air is recirculated to the vortex.

Some techniques that may be considered as good housekeeping techniques are already included in other sections. Those include for example:

- application of advanced process control (see Section 4.15.5) that can include the on-line continuous (equipment and process) performance measurement, the measurement of performance and comparison with targets
- prevention of soil contamination (see Section 4.25.1)
- leak detection and repair (LDAR) (see Section 4.23.6)
- minimisation and prevention of spillage of hydrocarbons (see Section 4.23.6)
- minimisation of waste generation (included in each of the process sections).

Achieved environmental benefits
The lubricant technique can reduce the use and subsequent waste of lubricant oil up to 75% and reduce the electrical consumption within the electrical motors.

Operational data
These systems are dynamic; they are kept alive by the incorporation of continuous improvement opportunities.

Applicability
The lubricant technique can be applied to lubrication of dynamic equipment with lubricated bearings, e.g. centrifuge pumps, electrical engines, gears assemblies, intermediate supports.

Economics
Less than two years pay-off is claimed by the technology provider in the lubricant technique.

Example plants
The lubricant technique has been already used by the main petrochemical companies

Reference literature
[118, VROM, 1999], [285, Demuynck, 1999], [19, Irish EPA, 1993], [316, TWG, 2000], [324, Sicelub, 2001]

4.15.4 Training

Staff training plays an important role in the prevention of contamination within the refinery. Some important aspects are:

- include environmental concern and environmental issues in the training of the refinery staff
- train staff to reduce solids in sewers. A facility training programme which emphasizes the importance of keeping solids out of the sewerage systems will help reduce that portion of waste water treatment plant sludge arising from the everyday activities of refinery staff
- train staff to prevent soil contamination. Contaminated soil can be reduced by educating staff on how to avoid leaks and spills.

Reference literature
[118, VROM, 1999], [256, Lameranta, 2000]

4.15.5 Production planning and control

Description
Some techniques to consider in this respect are:
- pollution control equipment should, in general, be kept running during start-up and shutdown, for as long as is necessary to ensure compliance of authorisations, provided no other safety or operating considerations prevent it
- reduce the start-ups and shutdowns to a minimum. Proper production planning can reduce the frequency and duration of process shutdown
- implemention of advanced process control for the planning and control of production
- advanced process control to optimise energy use within the refinery (related to 4.10.1.2).

Reference literature
[118, VROM, 1999]

4.15.6 Safety management

Safety is an important cross effect of environmental measures. Any direct relation of influence exists. Measures may affect safety in a:
- positive way. Closed loop sampling minimizes accidental releases of material
- no way. The process water recycle to desalters has no relevant impact on safety
- negative way. Gas recovery systems often have to deal with explosive atmospheres, where the untreated offgases are outside the explosibility limits. Negative impacts on plant safety can reach such an extend, that the additional dangers exceed what a plant is willing to handle. Even by others reasons promising techniques may lose applicability by that criterion – at least, until significant improvements of the safety properties of such techniques are developed.

Some techniques to consider are the following:
- prepare a safety report and practise risk management
- use of results obtained from risk analyses
  - identified risks are assessed with reference to the acceptance criteria for risk in the activities in order to identify the dimension of accidental events
  - dimensioning accidental events form the basis for a systematic selection of the technical, operational and/or organizational risk-reducing measures to be implemented. Risk-reducing measures consist of probability-reducing and consequence-reducing measures, including contingency measures
  - the effect of the risk reducing measures to be implemented is documented, assessed both individually and in a wider perspective
  - implementation of the risk reducing measures and of the basic assumptions made in the risk analysis is systematically followed up in order to ensure that safety in the activities is maintained within the defined acceptance criteria for risk
  - results from of risk analyses are communicated to the employees and shall be used actively in preventive safety efforts.

Reference literature
[118, VROM, 1999], [285, Demuynck, 1999], [302, UBA Germany, 2000], [260, Sandgrind, 2000]

4.15.7 Water management

4.15.7.1 Water stream integration

Studies for the optimisation of water, effluent and drainage are often relevant. Similar to the identification of energy saving opportunities, water pinch studies can be carried out to identify process water integration options and water reduction and re-use opportunities. In most refineries some internal water streams are already used as desalter wash water, such as condensate water and steam-stripped sour water. There is scope for increased water reduction and re-use in refineries, which will lead to reduced size and costs of both water make up and end-of-pipe treatment facilities.

Purpose and principle
The purpose of *water stream integration* (WSI) is the reduction of process water produced for final treatment prior to discharge in order to save operation costs. It saves high quality potable and demineralised water, which can be expensive at some locations; it reduces the size, investment costs and running costs of water supply and effluent treatment facilities. Moreover, it reduces the size and the environmental impact of effluent discharges.

The principle of WSI is maximising prevention, reduction, recycling and re-use of process water, rainwater, cooling water and sometimes contaminated ground water with the aim of minimising the amount of process water for end-of-pipe treatment. WSI need to be carried out as part of a Water Masterplan for the refinery. This plan aims at optimisation of the use and re-use of all water streams in the refinery. For greenfield refineries and in existing refineries, when new treatment installations are installed, a win-win situation is created when the amount of imported water, the size of effluent treatment facilities and the discharge are all minimised. Ideally it may become feasible to use treated effluent as a source for make-up of process water, cooling water and/or boiler feed water. Every refinery has its specific optimum WSI scheme.

Reduction of fresh water use is a goal for most refineries for two main reasons. Firstly, fresh water, particularly high quality water, is a valuable resource which in many parts of Europe is becoming increasingly scarce. Where water of lower quality is used, treatment to acceptable standards also requires the use of energy and chemicals. Secondly, water used has to be discharged. Minimising the volume of water discharged reduces the size of effluent treatment plant required, the amount of energy and chemicals used, and the quantity of pollutants discharged to the environment. Data on actual fresh water usage is included in Section 3.15. As a general guide, approximately 0.1 - 5 m^3 of waste water (process waste water, cooling water and sanitary waste water) per tonne of crude is generated when cooling water is recycled. The process water generated in a refinery is of the magnitude of 0.1 to 0.2 m^3 per tonne of crude oil input. Some techniques to consider for the minimisation of fresh water consumption, can be the following:

- by substitution of wet cooling processes by dry processes
- recirculation of cooling water
- use of treated process water as cooling water
- use of condensates as process water
- use of rainwater as process water
- other measures are: Use of production techniques which allow recovery and re-use of rawmaterials, process- and product aids (e.g. use of regenerable extraction agents, desulphurisation by hydrotreatment). Use of process- and product aids with low hazardous potential and substitution of hazardous chemicals by less hazardous ones.

Concept Description

The concept or methodology to design an effluent/water integration system for a refinery is to inventorise water demand and effluent production of each refinery unit operation and to assess the water losses. This inventory provides the water balance across the refinery. It is recommended to visualise the water balance by a block scheme as presented as an example in Figure 4.5. The next step is to identify all possibilities to reduce the amount of water required and to re-use as much as possible by matching (quantity and quality) effluents by means of a water optimisation scheme. This "water-pinch" methodology includes giving consideration to the re-use of treated effluent. The WSI concept aims at "closing the water loop".

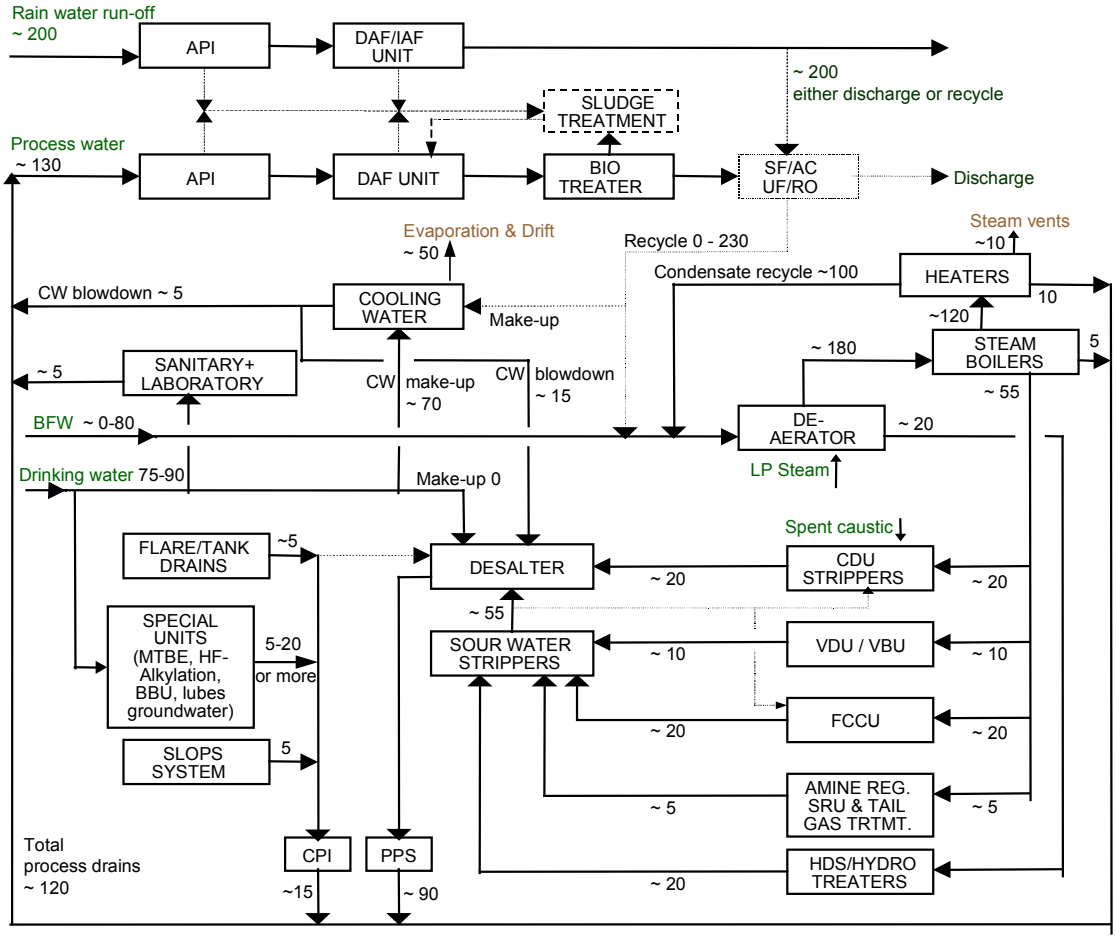


Figure 4.5: Example of a process water integration scheme for a catcracker refinery configuration (10 Mt/yr)
Notes: dotted lines only to indicate the hypothetical "closed loop". Figures within the graph are water flows in tonnes per hour.

WSI is dependent on the refinery configuration, the crude quality and the level of desalting required, the cost of potable water, the availability of rainwater and the quality of cooling water. Within a refinery a number of standard process-integrated effluent/water treatment provisions are available as well as a number of standard possibilities for water reduction and re-use. In most refineries a number of these options have already been implemented to some extent, either in the original design or by retrofit:

(1) in a refinery a number of clean condensate streams are generated from condensed steam that has not been in contact with product. These condensate streams are suitable for direct re-use as boiler feed water (BFW), leading to cost savings

(2) the standard provisions for process water treatment are the sour water stripper (SWS, to treat the sour water produced in various process units) and the desalter, which is a major water consuming unit whereas the water quality requirement in the desalter does not constrain the use of SWS effluents. Sour water is produced if wash water and/or steam comes into contact with hydrocarbon products which contain H_2S and NH_3. In the SWS the H_2S and NH_3 are largely eliminated. This renders a treated effluent into a suitable quality wash water for the desalter

(3) the re-use of stripped sour water as wash water for crude desalting is a first step in any WSI. A crude desalter uses 5 - 10 % water on crude, dependent on the crude quality and the level of desalting required

(4) process units that produce significant quantities of waste water are the Crude Distillation Unit (CDU) and the Fluid Catalytic Cracker (FCC). In the CDU overhead, 2 - 3 % waste water on crude intake is produced as steam condensate. This water does not require SWS treatment but can be directly routed as wash water in the desalter. An FCC-unit, if present in the refinery, also produces significant quantities of waste water in the range of 5 - 10 % on feed. This amount can be reduced to 2 - 4 % if cascading of wash water is accomplished. Stripped sour water can in principle be used as wash water and, on the other hand, the FCC wash water can either be recycled to the SWS or used as desalter wash water. Depending on the quantities of effluent generated, optimisation of water integration is possible

(5) boiler blowdowns, cooling water blow downs and treated rainwater run-off are water streams that may be suitable for desalter wash water as well, dependent on the salt concentration

(6) a site-specific Water Masterplan can be designed, applying the concept of WSI. It will be dependent on and will take account of the location and site-specific elements such as climate/rainfall, river/sea, existing segregation, availability of two desalters/SWS, specific refinery units, fresh water costs, groundwater situation, etc

(7) use of phenolic spent caustic for stripped water neutralisation and subsequent desalter wash to allow phenols resorption into the crude

(8) if the stream generated in the boiler feed water production is not recycled to the desalter, biotreatment is required because of anti-foaming agents and corrosion inhibitors

(9) refinery waste water need to be properly segregated to ensure the most effective treatment or re-use. A typical segregation scheme for a petroleum refinery would provide a “clean” water sewer, an oily water sewer, and a highly-contaminated water sewer

(10) water pinch or water optimisation studies

(11) water coolers/condensors may be replaced by air coolers (closed cooling water systems) (reference to cooling section)

(12) air cooling, reduced cooling water blowdown, using hydrocracking and hydrotreating processes that produce less waste water than older processes; and using improved drying, sweetening and finishing procedures to minimise the generation of spent caustics and acids, water washes and filter solids; recycling and re-using waste water elsewhere in the refinery

(13) treated waste water that can be re-used in make-up to process and pump cooling systems, washdown water and water from fire control systems

(14) use of vacuum liquid ring compression instead of steam ejectors to minimize water consumption; use waste water free vacuum technique (recirculation of water) if otherwise harmful substances are transfered to the environment

Energy and process materials utilisation

The steam boilers and steam system require corrosion inhibitors and oxygen scavengers and the de-aerator uses LP steam. The DAF unit and the sludge work-up require poly-electrolytes. The biotreater requires nutrients (phosphor) if no sanitary waste water or cooling water blow down (which could contain phosphates as corrosion inhibitor) is co-treated. A comprehensive WSI will result in minimisation of these expensive chemicals and in minimum pollution and discharge levies.

Environmental aspects
The environmental implications of the conceptual approach of a process water integration scheme are favourable. Enclosed systems and closed water loops limit the hydrocarbon emissions to air and discharges to surface water, and also lead to reduced generation of waste in the form of sludges.

Quantification of the reductions of the water used (and products lost) vary from location to location but can be substantial (>50 %). A newly built refinery in Thailand generates only 40 t/h process water at a crude throughput of 8 Mt/yr due to such an approach. Values of 0.5 m^3 per tonne of crude oil have been also achieved within Europe.

Reference literature
[118, VROM, 1999], [113, Noyes, 1993], [268, TWG, 2001], [117, VDI, 2000]

4.15.7.2 Water and drainage system

Purpose and principle
The ideal for a water and drainage system is to create the flexibility to cope with changing circumstances such as sudden rainfall, process upsets, process changes, additional plants, capacity extensions and new legislation. It would also provide a basis for integrated water management, including spill prevention and potential re-use of water streams without or after treatment. The principle is based on a thorough qualitative and quantitative analysis of the various water and effluent streams, the assessment for re-use potential with maximum reliability and environmental protection. A flexible water and drainage design allows for water integration and allows for short-term and long-term changes at optimised cost. Enclosed sewerage systems for transfer of contaminated water from tanks and processes to separation facilities is also a technique to consider.

System description
A modern and optimised water and drainage system of an industrial site is a result of a conceptual design of many unit operations lined up in such a way that water management can be optimised. The basis of the concept is segregation of the different water streams into oil-free water streams, accidentally oil-contaminated (AOC) streams and continuously oil-contaminated (COC) streams. The latter need to be subdivided into low and high BOD streams with the possibility for biotreatment, effluent polishing and re-use.

The application of a segregation concept takes a certain level of housekeeping and operational discipline into account. The decision to choose a different route for a certain type of effluent would be based on monitoring of water qualities, both internal streams and the collective discharge. The environmental performance and the effluent management of the refinery requires a constant level of alertness and dedication, sufficient training and motivating instructions and an extensive monitoring (sampling and analysis) scheme. The first flush principle entails the collection, separation and treatment of the first charge of rainwater from the potentially contaminated refinery surface. After the first flush the rest of the rainwater is collected, analysed and discharged without treatment, if acceptable.

Energy and process materials utilisation
Energy requirements are mainly for pumping the waste waters and are system and site-dependent.

Application
A number of elements of the current design philosophy for a new water and drainage system can be considered for implementation in existing refineries, and more particularly in cases where the old effluent and drainage system has become obsolete.

Environmental aspects

A new problem in most refineries is the management of contaminated groundwater. Possibilities exist to manage and re-use this stream either inside the refinery (after iron removal) or to accommodate and route this stream directly to the WWT facilities. Source reduction and spill prevention by good housekeeping are also essential elements for VOC and odour emission reduction at CPI, API, DAF units and biotreaters. Some refineries employ an H_2S oxidation tank to prevent toxic and odorous emissions from process water prior to DAF and biotreatment.

Status

Not many refineries have segregated process water and rainwater run-off. If they have, these streams are routed to separate and dedicated treatment systems. The extent of segregation varies from refinery to refinery (by design or retrofit). Most refineries use sour water and some condensate streams as desalter wash water (see Section 4.9). Other effluent streams are also candidates for desalter wash water such as cooling water and boiler blowdowns. Re-use of treated effluent (biotreatment, sand filtration followed by reversed osmosis) as a source for boiler feed water is technically feasible. Re-use of treated effluent as cooling water make-up is done at several locations. First flush principles are followed in several refineries. Figure 4.6 shows a block diagram of an example of an optimised Water/Effluent Routing for a refinery.

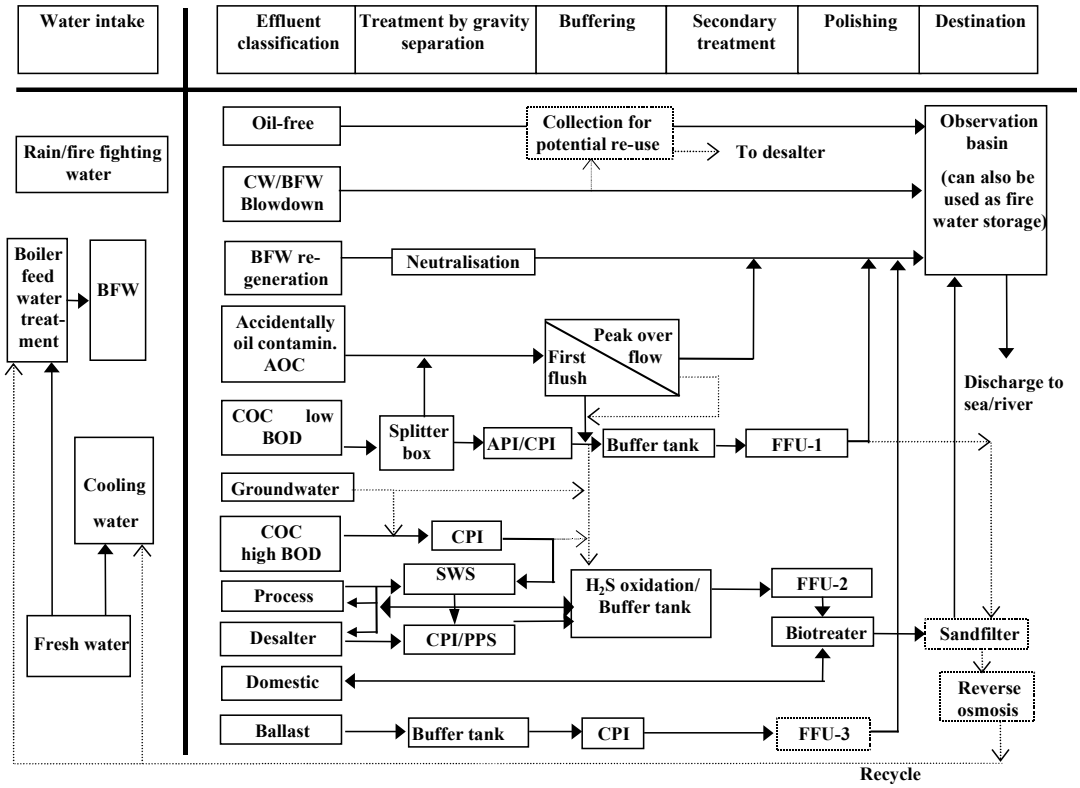


Figure 4.6: Block diagram of an example of an optimised water/effluent routing for a refinery Dashed lines indicate hypothetical " closed loop".

Reference literature

[308, Bakker and Bloemkolk, 1994], [118, VROM, 1999], [19, Irish EPA, 1993]

4.15.7.3 Rainwater

Some techniques that may be applied to rainwater are:

- surface water run-off or rainwater can be segregated into accidentally oil-contaminated and continuously oil-contaminated effluents. Those effluents may require treatment. Rainwater on contaminated surfaces may lead to effluent to be treated in a CPI/API

- in specific situations rainwater may be a useful source of rawwater for the preparation of process water make-up, boiler feed water and cooling water
- some refineries have segregated effluent and drainage systems. In modern refineries the water and drainage system includes a segregation of process water, condensate blowdowns, rainwater and cooling water in order to minimise the environmental impact of effluent discharges at minimum cost. Moreover, adequate process water integration and water management measures will include a review of all options to recycle water streams with the aim of achieving a significant reduction of end-of-pipe treatment. Segregation of the process water discharges, surface water run-off, cooling water and boiler feed water blowdowns and other effluents may be considered. Separation of storm water and other effluents of different origin in order to permit appropriate treatment options. In some cases, retroffiting cost can be very high.

Reference literature
[118, VROM, 1999], [113, Noyes, 1993]

4.15.7.4 Use of sanitary waste water

Sanitary waste water effluent is collected in a septic tank. As this stream is small compared to the total waste water of a refinery, and contains sufficient nutrients (micronutrients and phosphorus) required for an industrial biotreater, this effluent can be usefully combined with the process water to a dissolved air flotation-unit preceding a biotreater.

4.15.7.5 Ballast water

Ballast water is typically discharged at a very high rate provoking generation of high volume waste water peaks. That waste water contains high salt concentrations (seawater), and are heavily polluted with oil. It can easily lead to an upset of existing effluent treatment systems. Therefore the use of ballast water tanks is an important equalisation tool for feeding the water in a controlled way to either the process water system or the COC system, if the COD is lower than 100 ppm. Because of this, (and because jetties are often remote from the rest of the refinery) ballast water is often treated in a separate dedicated plant. As more and more crude tankers are equipped with double hulls, the ballast water problem is slowly phasing out.

4.15.7.6 Fire-fighting water

Some techniques to consider are:
- The fire-fighting water system can sometimes be a water re-use sink within the refinery.
- Provision should be made to collect fire fighting water in a lagoon. Serious pollution has been caused by the release of firefighting water in an emergency. Design of Containment Systems for the Prevention of Water Pollution from Industrial Accidents can be found in Construction Industry Research and Information Association Report 164 1996.

4.15.7.7 Blowdown systems

The blowdown liquid system is typically composed of mixtures of water and hydrocarbons containing sulphides, ammonia, and other contaminants, which are sent to the waste water treatment plant.

4.15.8 Emissions integrated management

Some of the air emissions issues are by its nature refer to many processes or activities then they should be considered as a refinery as a whole issue. Under those issues, we can include sulphur emissions and VOC emissions. The application of a good environmental performance should take the refinery as a whole as well as in the case of the sulphur the amount of sulphur contained in the products. A good environmental planning for reduction of those emissions should consider those aspects. In order to clarify those aspects, the next table shows were in this document, topics that may have integrated related issues are tackle.

Integrated environmental issue	**Section in Chapter 4 where it is analysed**
Sulphur emissions from refineries	4.23.5
VOC and fugitive emissions	4.23.6.1
Protection of contamination of soil and groundwater	4.25
Waste generation	4.25
Energy	4.10
Utilities related to energy (e.g. steam)	4.10
Odour and noise	4.23.9 and 10

Reference literature
[316, TWG, 2000]

4.16 Isomerisation

4.16.1 Active chloride promoted catalyst isomerisation process

Description
More information in Section 2.16.

Achieved environmental benefits
Higher process efficiencies compared with the zeolitic catalsyts and lower reaction temperatures (less energy consumed).

Cross-media effects
The chloride promoted, chlorinated alumina catalyst (containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activities. This is converted to hydrogen chloride in the reactor. The chloride promoted catalyst cannot be regenerated.

Operational data
The highly active chloride promoted catalyst, chlorinated alumina catalyst (containing platinum), operates at a relatively low temperature (190 - 210 °C and 20 barg) and gives the highest octane improvement. In such a reactor, the feed must be free of oxygen sources, including water to avoid deactivation and corrosion problems. The desorption process consumes utilities and energy.

Applicability
This catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to 0.5 ppm is required.

Economics
Investment estimated (basis ISBL, USA Gulf Coast 1998) 4150 - 10400 EUR per m^3/d.
Investment erected cost (basis: 2Q98 USA Gulf Coast) were evaluated for 1590 m^3/d of fresh feed capacity EUR 8.8 millions (±50 %).

Driving force for implementation
Production process.

Reference literature
[212, Hydrocarbon processing, 1998], [316, TWG, 2000]

4.16.2 Zeolitic isomerisation process

Description
More information in Section 2.16. Some refiners need more octane from the light straight run naphtha fraction than is possible from the O-T zeolitic isomerisation process. Adsorption technology can then be used to remove the unconverted normal paraffins. The utilities needs for that process are quite low.

Achieved environmental benefits
No chloride compounds are used in this type of processes. The zeolite and sulphated zirconia catalyst can be regenerated several times before sending the catalyst to a reclaimer to recover the platinum.

Cross-media effects
Higher temperature of the process, requiring more heating.

Operational data
The zeolite catalyst operates at significantly higher temperatures (250 - 275°C and 28 barg) and is much more tolerant to contaminants, though the resulting octane improvement is lower.

Applicability
The zeolite catalyst is mainly used for non hydrotreated feedstreams. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures.

Refiners with idle hydroprocessing equipment, such as old catalytic reformers or hydrodesulphurisation units, can consider converting this equipment to the once-through zeolitic isomerisation process. With isomerisation, a 10 to 12 octane-number increase for the C_5 - 71 ºC light naphtha can be achieved.

Economics
Estimated cost of the reaction process is EUR 4654 per m^3/d. For the absoprtion process, the investment is EUR 18900 - 25160 per m^3/d. The catalyst and adsorbent cost is around EUR 1700 per m^3/d.

Driving force for implementation
Production process. Selection of a once-through or recycle scheme depends on factors such as quantity of light naphtha to be blended in the gasoline pool, the required octane number of the gasoline pool and the availability of other high octane gasoline blend components. If the isomerate product has an octane number exceeding 87, a recycle scheme is the only option. Selection of a fractionation-based scheme or an absorption based scheme is dependent on feed composition and to a certain extent on the product requirements. In general it can be said that the fractionation based scheme is lower in investment cost but significantly higher in operating cost as a result of high energy requirements.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [316, TWG, 2000]

4.16.3 Increase of the cyclic hexanes in the isomerisation feedstream

Description
As the benzene content in the gasoline pool is being reduced by new specifications, the practice will be to fully dehexanise the reformer feed, leaving in the cyclic hexanes to pass to the isomerisation unit (preventing their conversion to benzene in the reformer).

Achieved environmental benefits
Reduced benzene content in the gasoline out of the reformer.

Reference literature
[247, UBA Austria, 1998]

4.17 Natural gas plants

As mentioned in the Scope section and in Section 2.17, the processes treated in this section are those used in the refining of natural gas. As with mineral oil refineries, the processes used on production platforms are not included in this BREF.

4.17.1 Amine sweetening of natural gas

Description
The reaction occouring in the process is given below and the process is illustrated in Figure 4.10 of Section 4.23.5.1

$2\ R\text{-}NH_2 + H_2S \rightarrow (R\text{-}NH_3)_2S$ R = mono, di, or tri-ethanol

If the recovered H_2S gas stream is not to be used as a feedstock for commercial applications, the gas is usually passed to a tail gas incinerator in which the H_2S is oxidized to SO_2 and is then passed to the atmosphere via a stack. More information can be found in Section 4.23.5.1.

Achieved environmental benefits
Reduction of H_2S concentration in natural gas.

Cross-media effects
Section 4.23.5.1.

Operational data
The recovered hydrogen sulphide gas stream may be: (1) vented, (2) flared in waste gas flares or modern smokeless flares, (3) incinerated, or (4) used for the production of elemental sulphur or sulphuric acid.

Applicability
Fully applicable.

Economics
Section 4.23.5.1.

Driving force for implementation
Comply with sulphur specifications of natural gas.

Example plants
At present, the amine process (also known as the Girdler process) is the most widely used method for H_2S removal.

Reference literature
[136, MRI, 1997], [144, HMIP UK, 1997]

4.17.2 Sulphur recovery unit

Extensive information can be found in Section 4.23.5.2.

4.17.3 Re-use of carbon dioxide

Description
Acid gas streams containing carbon dioxide free from sulphur and hydrocarbon compounds may be vented directly to air, although this may require heating of the stream to air dispersion. However, carbon dioxide can be used for other purposes. If the CO_2 stream has a significant hydrocarbon content, it can be used within combustion processes, e.g. mixed into site fuel gas or used in a utility designed to burn gas of low flame stability.

Reference literature
[144, HMIP UK, 1997]

4.17.4 Techniques to reduce VOC emissions

During routine operation of natural gas terminals and other processes, the aim need to be to prevent releases to air of natural gas. Techniques to consider to reduce those emissions include:

- minimise frequency of pig/sphere use by operating sea-lines at high velocity, ie use "mist flow"conditions
- minimise recovery of spheres by use of receivers holding several devices
- vent receivers of high-pressure gas to a low-pressure part of the process for gas recovery by recompression, before opening for access to pig/spheres
- the occasional shutdown and venting of process plant is necessary, e.g. for maintenance, upset and changeover purposes. This need to be minimised by appropriate plant selection and design
- avoid the use of refrigerants for gas dew point control that are of significant environmental concern (CFCs)
- overheads and any gas vented from storage and glycol and methanol regeneration units should be condensed and incinerated
- leak detection and repair programme. More information can be found in Section 4.23.6.1.
- VOC emissions, including fugitives, can be maintained within a range of 200 to 250 kg/h (300 - 350 kg/MNm^3)

Reference literature
[144, HMIP UK, 1997], [268, TWG, 2001]

4.17.5 Techniques to reduce NO_x emissions

NO_x emissions come from the combustion processes applied in the natural gas plant. The techniques that can be applied for control and abatement of NO_x are the same as those applied to refinery fuel gas. See Section 4.10.4 and 4.23.3 for a detailed explanation.

4.17.6 Techniques to reduce water emissions

Description
Prevention techniques that may be applied to reduce the releases to water can be:

- if possible, the quantity and contamination level of waste water to be treated on-shore need to be minimised and controlled "at source", i.e. wste water coming from off-shore activities
- a three-phase separator can be used on the liquids from the slug cutcher to control and minimise hydrocarbon content of the aqueous phase
- sour water can be treated in a sour water stripper unit. See Section 4.24.2
- process effluent from glycol or methanol regeneration plants and any other high BOD/COD effluents should be kept separate from other streams, e.g. surface water, and treated before discharge to the site effluent system
- water management techniques. See Section 4.15.7.

The techniques that may be used in the waste water treatment are the ones described in Section 4.24.

Achieved environmental benefits
The achievable emission levels that may be achieved with a well-performing waste water treatment within a natural gas plant are shown below: (Values in this table are daily average)

Water paramenter/compound	Concentration (ppm)	Load (kg/MNm^3 feedstock)
Waste water		160 m^3/MNm^3
Total oil content	0.9 - 5	0.4 - 0.6
TOC	60 - 100	3.5 - 12
COD	400	
Suspended solids	25	
Phenol	0.1 - 0.5	

Reference literature
[144, HMIP UK, 1997], [268, TWG, 2001]

4.17.7 Techniques to reduce waste generation

Description
Techniques that may be appplied to reduce waste generation are:

- catalysts, absorbents, adsorbents, etc can be returned to the manufacturers for recycling
- where desalination of glycol purge stream is practised this will give rise to solids for disposal and any residual glycol in these should first be reduced to a low level.
- Some of the gas fields contain mercury vapour in very low concentrations. This mercury is removed from the gas in a 'cold trap' (e.g. by gas expansion) and recovered as a mercury containing sludge. A specialised company processes this sludge by treatment in a vacuum distillation unit.

Reference literature
[144, HMIP UK, 1997], [268, TWG, 2001]

4.18 Polymerisation

4.18.1 Process

Description
More information in Section 2.18.

Achieved environmental benefits
Reduction of the process emissions and reduction of acid consumption and consequently waste. Good polymerisation units can reduce the phosphoric acid consumption to levels of 0.1 - 0.2 gr/t of polymer produced. Another source relates that the typical catalyst consumption (H_3PO_4 + support) is around 1.18 kg catalyst per tonne of polymer produced.

Cross-media effects
No cross-media effects.

Operational data

Utilities	
Electric power (kW/tonne of C_5+ product)	20 - 28
Steam (t/ tonne of C_5+ product)	0.7 - 1.1
Cooling (m^3/tonne of C_5+ product)	4.4 - 6.0

Applicability
Production process

Economics
The catalytic condensation process is relatively simple to operate and requires a minimum of labour. Its simplicity is reflected in the operating requirements summarised in the following table.

Catalyst and chemical cost (EUR/tonne of C_5+ product)	5.00 - 8.20
Labour and operating cost workforce	1 operator-helper
Typical operating cost (EUR/t C_5+ product)	20 - 30
Investment (EUR1995/(t/yr) of C_5+ product)	50 - 95

Only one operator is required. Overall, the cost of operating a catalytic condensation unit ranges from EUR16 – EUR22.6 per m^3 of C_5+ polymer gasoline. This cost includes utilities, labour, catalyst, chemicals, and an allowance for process royalty, but does not include any direct or indirect capital-related costs.

Driving force for implementation
Production process.

Example plants
Some polymerisation processes are running in European refineries. Nowadays alkylation units are more predominant than polymerisation units, even though polymerisation units are cheaper.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [268, TWG, 2001]

4.18.2 Management and re-use of the catalyst

Description
Two techniques can be applied to minimise the impact of catalyst disposal:

- the catalyst to be disposed of from the process is potentially pyrophoric and requires special treatment. However, removal by steam/water avoids any risk of fire. The catalyst solidifies in situ, and removal is achieved manually under nitrogen purge, or more recently by 'explosive' steam decompression with steam suppression to a catchment system. The catalyst may then be sent for either off-site disposal as special waste or on-site treatment. On-site treatment involves neutralisation and fixing with cement. The material may then not be classified as special waste
- the spent catalyst can be re-used as fertiliser or as phosphorous feed to the biotreater.

Achieved environmental benefits
Reduction of risk of fire due to the pyrophoric characteristics of the catalysts and reduction of waste generation.

Cross-media effects
No cross-media effects.

Operational data
Disposal frequencies of up to 12 times per year may be expected.

Applicability
Fully applicable.

Driving force for implementation
Treatment of catalyst and re-use of phosphorous compounds within the refinery.

Reference literature
[34, Italy, 1999]

4.19 Primary distillation units

As mentioned in Section 3.19, the atmospheric and vacuum distillation units are large consumers of heat. The techniques to consider for application to the crude oil furnaces are those described in the section dealing with the energy system 4.10.

4.19.1 Progressive distillation unit

Description
A progressive distillation unit with integrated CDU/HVU, which saves up to 30 % on total energy consumption for these units. The technology includes atmospheric distillation (topping), vacuum distillation, gasoline fractionation, naphtha stabilizer if required and gas plant.

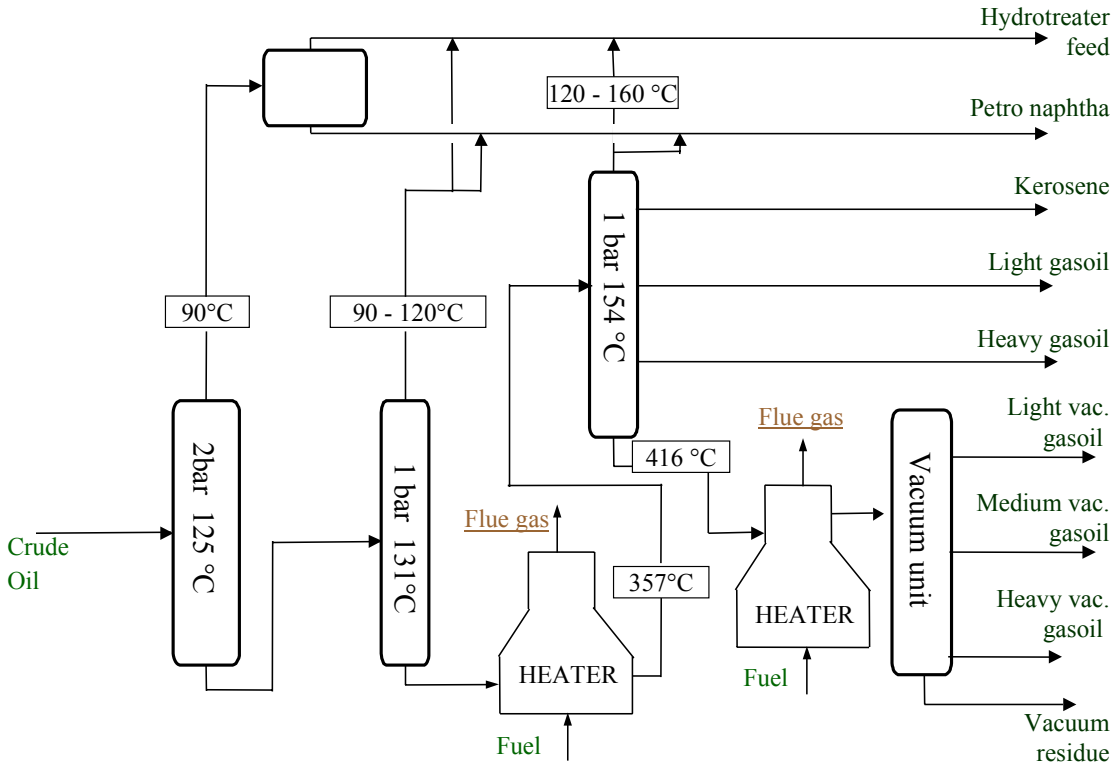


Figure 4.7: Process flow diagram of a progressive distillation unit

Achieved environmental benefits
The heater process duty (MW/100 tonnes of crude) of a distillation capacity of 10 million tonnes per year is around 17.3 for an Arabian light crude. Using progressive crude distillation it is reduced to 10.1. The specific energy consumption (overall energy consumption in tonnes of fuel equivalent per 100 tonnes of crude) for a distillation capacity of 10 million tonnes per year is 1.7 - 2.0 for an Arabian light crude, whereas using the progressive distillation unit only consumes 1.15. The energy savings for a 9700000 tonnes/year refinery is in the range of 50000 tonnes heavy fuel compared to conventional technology.

Total primary energy consumption
For Arabian light or Russian export blend: 1.25 tonnes of fuel per 100 tonnes of crude
For Arabian heavy: 1.15 tonnes of fuel per 100 tonnes of crude.

Progressive distillation is the extreme of heat integration between atmospheric and vacuum distillation. It also avoids superheating of light cuts to temperatures higher than strictly necessary for their separation and it avoids degrading the thermal levels associated with the drawing-off of heavy cuts.

Cross-media effects
No cross-media effects identified.

Operational data

	Heavy Arabian (887 kg/m^3) 6.5 Mt/yr			EKOFISK (810 kg/m^3) 5 Mt/yr		
	Consumption	TOE/h	TOE/100 t	Consumption	TOE/h	TOE/100 t
Fuel (MWh/h)	67.5	5.81	0.75	67.5	5.81	1.04
Steam (tonnes/h)	15.95	0.8	0.11	21.0	1.05	0.19
Electricity (MWh/h)	6.4	1.41	0.18	6.4	1.41	0.25
TOTAL		8.02	1.04		0.27	1.48
Note: The energy consumption is defined according to the following hypothesis: 1 TOE (tonne of oil equivalent) = 11.6 MWh 1 kg of low-pressure steam = 0.581 kWh Yield of the electrical power plant = 39 % Products are sent to storage (cold temperature)						

Table 4.33: Energy consumption of the progressive crude distillation when the same plant is used to process two types of crude oil

Utility requirements, typical per tonne of crude feed		Units
Fuel fired	1100 - 1400	kWh
Power	6.6 - 8.8	kWh
Steam, 4.5 barg	0 - 17	kg
Water cooling (ΔT = 15 ºC)	1.4 – 2.8	m^3

Applicability
The process is applicable to all or part of these units when being constructed and can also be used in revamps for debottlenecking.

Economics
Reduce fuel consumption and thus reduce operating cost of the distillation units.
Investment (basis 11.45 Mt/yr including atmospheric and vacuum distillation, gas plant and rectification tower): EUR 41000-55000 per t/yr (US Gulf Coast 1998).

Driving force for implementation
Reduction of fuel consumption in refineries.

Example plant(s)
Some European refineries employ a progressive distillation unit with integrated CDU/HVU.

Reference literature
[195, The world refining association, 1999], [212, Hydrocarbon processing, 1998], [247, UBA Austria, 1998]

4.19.2 Heat integration of crude distillation units

Description
As stated in Section 4.10.1, there is a tendency towards improved heat integration with crude and other units. The high energy consumption of the CDU makes heat integration very relevant. To optimise heat recovery from the atmospheric distillation column, two or three reflux streams are normally kept in continuous circulation at several points per top and middle pumparounds.

In modern designs, integration with the high vacuum unit and sometimes the thermal cracker is achieved. Some techniques applied are:

- optimise the heat recovery, studying and implementing the optimal energy integration. In this context, major progress has been made in recent years in understanding the design of efficient heat recovery networks. "Pinch Analysis" has emerged as a tool for the evaluation of total systems designs, helping to balance investments against energy savings. See also Section 4.10.1
- apply pinch analysis to the crude preheat train heat integration. Increase crude preheat temperature and minimise heat losses to air and cooling water
- increase crude distillation column pumparounds from two to four. Reboil sidestrippers with a heat transfer oil rather than by steam stripping
- heat transfer in the crude preheating can be improved using specific antifoulant treatments in crude heat exchanger train. Antifoulants are available from many chemical companies and, in many applications, are efficient in increasing the run cycle length of the exchangers ; antifoulant can help prevent plugging of tube exchangers, improving heat recovery and preventing hydraulic losses, depending on the nature of fouling. Service factors of the various units/trains, as well as heat recovery (energy efficiency) increase at the same time.
- application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits
Reduce the fuel consumption in distillation columns.

Cross-media effects
Control of plants is impaired because disturbances are transferred between them, influencing plant safety.

Applicability
Integration in retrofitting application may will normally depend on plot space available. Except in a very few cases this technique is commonly applicable.

Driving force for implementation
Reduce energy consumption within the refinery.

Example plants
Heat integration procedures are extensively applied in crude units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature
[147, HMIP UK, 1995], [79, API, 1993], [297, Italy, 2000]

4.19.3 Heat integration of the vacuum distillation units

Description
The number of side-streams in a high vacuum unit is chosen to maximise heat integration of producing streams at different temperatures, rather than to match the number of products required, with the exception of the luboil vacuum distillation units. Heat integration with the crude units can be achieved. The atmospheric residue is then taken directly from the crude distillation unit to the vacuum furnace, and the product streams and circulating refluxes of the high-vacuum unit are cooled against crude oil.

The main feed stream to the high-vacuum unit is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue, which is either supplied directly hot or (relatively) cold from storage tanks. The latest option requires higher energy consumption.

The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits
Reduce fuel consumption in the refinery.

Cross-media effects
Control of plants is impaired because disturbances are transferred between them, influencing plant safety.

Applicability
Integration in retrofitting application may will normally depend on plot space available. Except in a very few cases this technique is commonly applicable.

Driving force for implementation
Reduce fuel consumption in the refinery.

Example plants
Heat integration procedures are extensively applied in vacuum units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature
[147, HMIP UK, 1995], [79, API, 1993], [297, Italy, 2000]

4.19.4 Use of vacuum pumps and surface condensers

Description
Vacuum liquid ring compressors instead of steam ejectors.

Achieved environmental benefits
Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily waste water stream. Replacing the steam ejectors by vacuum pumps will reduce the sour water flow from 10 to 2 m^3/h. The vacuum may be generated by a combination of vacuum pumps and ejectors to optimise energy efficiency. Other benefits are cross linked with cross-media effects.

Cross-media effects
Replacement of the steam ejectors by vacuum pumps will increase the electricity consumption for vacuum generation, but will reduce the heat consumption, the cooling water consumption, the electricity consumed for cooling pumps and the consumption of agents used for conditioning of cooling water. Within the refinery there are many processes where surplus steam can recovered and be used for the production of vacuum. However, an energy management analysis will help to decide, whether use of surplus steam for steam ejection instead of applying vacuum pumps is more efficient than using surplus steam for other purposes.

Operational data
The use of vacuum pumps consumes electricity.

Applicability
Fully applicable.

Driving force for implementation
Reduction of production of waste water.

Example plants
At present, vacuum pumps are used more often than ejector sets.

Reference literature
[79, API, 1993], [268, TWG, 2001]

4.19.5 Reduction of the vacuum pressure in the vacuum distillation unit

Description
Lowering the vacuum pressure, e.g. down to 20 - 25 mm Hg, will allow a reduction in the furnace outlet temperature, while maintaining the same target cut point of the vacuum residue.

Achieved environmental benefits
This technique would provide some benefits, both in terms of energy conservation and of pollution. The environmental benefits are:

- a lowered potential for cracking or coking at furnace tubes
- a reduced cracking of feed to lighter products
- a lowered furnace fired duty and hence lowered fuel consumption.

Cross-media effects
Energy (electricity or steam) is necessary to generate the vacuum.

Applicability
It is limited usually by tower capacity, condensing fluid temperature or material restrictions.

Driving force for implementation
Reduce the heat duty of the vacuum distillation process.

Reference literature
[297, Italy, 2000], [79, API, 1993]

4.19.6 Treatment of non-condensables from vacuum ejector set condensor

Description
Techniques for controlling releases from vacuum units include scrubbing, compression into refinery fuel gas and burning in adjacent process furnaces, or combinations thereof. The gases from some units may contain significant amounts of air and such gases are normally best combusted locally. Amine scrubbing techniques may need to be applied carefully as hydrocarbon contamination may cause foaming problems in amine regeneration units.

Incondensables from overhead condensers can be passed to light ends treatment or recovery systems or refinery fuel gas systems; sour incondensable gases vented from sealed barometric pumps of vacuum distillation units should be extracted and dealt with in a manner appropriate to the nature of the sour gas.

A control technique applicable to the non-condensable emissions vented from the vacuum ejectors or pumps consisting of venting into blowdown systems or refinery fuel gas systems, and incineration in furnaces or waste heat boilers.

Achieved environmental benefits
Vacuum distillation column condensers may emit 0.14 kg/m^3 of vacuum feed and can be reduced to negligible levels if they are vented to heater or incinerator. Pollution reduction is achieved if vacuum gaseous streams (vent gas) are routed to an appropriate amine scrubbing unit instead of being directly burned in the process heater. Vacuum vent gas routing to scrubbing requires significant investment due to compressor costs.
The efficiency of incineration control techniques is generally greater than 99 % as regards NMVOC emissions.

Cross-media effects
In the incineration technique, the combustion products have to be accounted for.

Applicability
Fully applicable.

Driving force for implementation
Reduce the emissions of pollutants.

Example plants
Applied in some European refineries.

Reference literature
[136, MRI, 1997], [127, UN/ECE, 1998]

4.19.7 Waste water treatment and re-use

Description
This topic is also treated in Section 4.15.7. Two techniques are considered in this section:

- the overhead reflux drum generates some waste water. That water can be re-used as a desalter wash water
- sour water from atmospheric and vacuum unit condensates should pass to a sour water stripper in enclosed systems
- optimise water re-use by application of side-stream softening to blowdown streams.

Achieved environmental benefits
Reduce water consumption and reabsorb pollutants.

Applicability
Fully applicable.

Driving force for implementation
Reduce the water consumption.

Reference literature
[79, API, 1993]

4.19.8 Other techniques to consider in the atmospheric units

Description
Some other techniques to consider are the following:

(1) where applied, ammonia injection should be handled in enclosed systems. Alternative neutralising techniques are available and can reduce the ammonia/ammonium load on sour water and sulphur recovery systems
(2) de-coking vents need to be provided with suitable knock-out and dust suppression facilities;suitable methods of preventing emissions during clean-out procedures need to be used
(3) many oily sludges can be sent the crude distillation (or in alternative to the coking unit. See 4.7.5) where they become part of the refinery products. This technique typically imply to send the light slops to floating roof tanks (double sealed), and the heavy slops typically to fix roof tank. Typically the heavy slop after setting is blend with liquid fuel. The blended light slops after enough setting may be also blent to liquid fuel or sent to the crude distillation at a mixing rate to avoid fouling.
(4) Pressure relief valves on column overheads; relief from overhead accumulator should be piped to flare as well as the vent points.
(5) Use of spent caustic instead of fresh caustic for corrosion control on distillation unit. (More information in Section 4.20.2

Operational data

The process of oily sludges in the crude distillation may generate problems in the desalter or may foul up the heat exchangers of the distillation column.

Reference literature

[79, API, 1993], [268, TWG, 2001]

4.20 Product treatments

A brief explanation on which kind of processes are included within this section is given in Section 2.20 and within the Section on Scope.

4.20.1 Cascading of caustic solutions

Description
An overall reduction in the caustic consumption of wet treating units can be obtained if semi-spent caustic from one treating unit can be re-used in another one. A typical example of this procedure is the use of the bleed of regenerated caustic (e.g. in mercaptan treaters for catcracked gasoline or for removal of H_2S or thiophenols) in a pre-wash step of the non-catalysed catcracked gasoline sweetening processes. An example of a caustic integration scheme is given in Figure 2.28.

Achieved environmental benefits
Reduce the use of caustic solutions.

Operational data
Systems handling spent caustic require particular care regarding sulphur compounds.

Economics

Product	Types of gasoline sweetening process	Estimate capital cost, million EUR	Est. operating cost, EUR/m^3
LPG	Extraction*	2.2	0.05
Light naphtha	Minalk	1.1	0.04
	Caustic-free	1.1	0.15
Heavy naphtha and kerosene	Conventional fixed-bed	2.6	0.18
	Caustic free	2.6	0.40

- * Include pretreating and post-treating facilities.
- Sample economics of the MEROX process on the basis of 1590 m^3 per stream day capacity for various applications. The capital costs are for modular design, fabrication and erection of MEROX plants. The estimated modular cost is inside battery limits, U.S. Gulf coast, FOB point of manufacturer. The estimated operating costs include catalysts, chemicals, utilities and labor.

Sweetening treatment is much cheaper than hydrotreating, both in terms of capital investment and in operation costs. The caustic is normally almost fully regenerated and only a small bleed results.

Reference literature
[115, CONCAWE, 1999], [166, Meyers, 1997], [83, CONCAWE, 1990]

4.20.2 Management of the spent caustic

Description
Caustics are used to absorb and remove hydrogen sulphide and phenol contaminants from intermediate and final product streams can often be recycled. Spent caustic solutions from some sweetening units are odorous and need to be handled in enclosed systems and treated as necessary before release at a controlled rate to the effluent system. Several techniques exist to maximise the use of caustics within a refinery. They include recycling within the refinery or outside the refinery or destruction within incinerators. Techniques considered are:

- Treatment of caustic may include neutralisation and stripping
- Because of the very high concentration of organic compounds in spent caustic solutions (COD>>> 50 g/l), incineration can be an appropriate alternative to waste water treatment.

- Spent catalyst/caustic need to be handled and disposed of in a manner that avoids dust generation. They should not be disposed of to the land.
- Some techniques are available to re-use spent caustic within the refinery:
  (1) corrosion control on crude distillation units using spent caustic rather than fresh caustic. Ustable chloridic (magnesium) salts that are not extracted from the crude oil in the desalter will decompose upon heating to the crude distiller and cause chloridic corrosion. To prevent corrosion of the exposed equipment, small quantities of caustic (sodium) are injected in the crude oil feed by which the chloridic components are neutralised due to the formation of stable sodium chloride. For this purpose of neutralisation of chloridic decomposition products often spent caustic can be used, which is recommended as well to minimize waste generation.
  (2) recycle to crude desalter or sour water strippers
  (3) addition to biotreaters for pH control.
  (4) Caustics containing phenols can also be recycled on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation. The caustic can then be treated in the refinery waste water system.
- Re-use spent caustic outside refinery:
  (1) in paper mills (sulphidic caustic only)
  (2) as raw material for Na_2SO_3, cresylics and Na_2CO_3 (may require segregation of sulphidic, cresylic and naphthenic caustics).
  (3) Spent caustics may be saleable to chemical recovery companies if concentrations of phenol or hydrogen sulphide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical.
- Measures to regenerate or oxidise spent caustic are:
  (1) Hydrogen peroxide
  (2) Fixed bed catalyst
  (3) Pressurised air: 120 - 320°C; 1.4 - 20.4 MPa
  (4) Biological system

Achieved environmental benefits
Reduce odour emissions and caustic use.

Cross-media effects
The cross-media effects found in the different techniques mentioned above are:
(2) the addition of caustic within the desalter or within the crude unit may enhance the coke formation within later units.
(3) it adds phenols and BTX to waste water treatment. As a consequence, the degradation efficiency of the biotreater can be adversely affected or the emissions from the waste water treatment plant for these components can increase.

Operational data
Systems handling spent caustic require particular care regarding sulphur compounds.

Driving force for implementation
Reduce caustic use.

Example plants
Most refineries are able to regenerate their spent caustic, but sometimes they have to dispose of some excess quantities, mainly from caustic pre-wash activities. Usually these quantities are small and can be managed within their effluent treatment system or, if this is not the case, they are disposed of via contractors for use as a bleaching agent in the paper and pulp industry. Some refineries sell their concentrated phenolic caustic for the recovery of cresylic acids. Some refineries work up the phenolic caustics themselves. From the extraction process the disulphide recovered can be sold as product, or be recycles to a hydrometer or incinerator.

Reference literature
[115, CONCAWE, 1999], [259, Dekkers, 2000], [268, TWG, 2001]

4.20.3 Incineration of foul air vented from sweetening

Description
Four air vented from sweetening process contain sulphur compounds that typically have strong odour. The range of quantity of sulphur in the foul air vented from sweetening processes is around 0.7 – 7 kg/day (disulphide concentration can be as high as 400 ppm) for a 10000 t/d crude unit and the percentage contribution it makes to the stack gases where it is incinerated has been estimated to 0.16 – 2.48 %. For this reason, the abatement previous an incineration is not justified and the foul air vented from sweetening processes is incinerated in local furnaces.

Reference literature
[268, TWG, 2001]

4.20.4 Replace clay filtration with hydrotreating

Description
Where a need to remove colour bodies and olefins exists, hydrotreating is replacing clay filtration as the method of choice. Hydrotreating does a better job of improving colour and increasing stability against oxidation, and has no yield loss (the oil measured in the spent filter clay represents a loss of some of the most valuable products produced in a refinery). It also eliminates the problem of spent clay disposal.

Achieved environmental benefits
Reduction of waste generation.

Cross-media effects
Need for hydrogen and energy consumption. See Section 4.13.1.

Operational data
See Section 4.13.1.

Economics
See Section 4.13.1.

Driving force for implementation
Product requirements.

Reference literature
[113, Noyes, 1993]

4.20.5 Treating

Description
Treating gas, LPGs, butanes, gasolines, kerosenes and diesels with caustic, amines, water and acid to remove amines, caustic contaminants, H_2S, COS and mercaptans. Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide may also be used to reach specification (LPG) and prevent odour problems. (See also.4.23.9)

Reference literature
[212, Hydrocarbon processing, 1998]

4.20.6 Catalytic dewaxing

Description
Catalytic dewaxing process typically produces a lower-pour product than solvent dewaxing. This system produce fuel components instead of waxes. A short description of the technique can be found in Section 2.20.

Achieved environmental benefits
Aromatics and sulphur content of the products produced with this technique are lower than with solvent dewaxing. The products generated by the cracking of the wax remain as part of the product.

Cross-media effects
Hydrogen consumption.

Applicability
Fully applicable for new units. It is unlikely to be retrofit on another type of dewaxing process because it is a completely different process. Catalytic dewaxing has a pour point advantage, but has a viscosity index disadvantage compared to solvent dewaxing.

Economics
The following table compares the relative cost of debottlenecking a 300 kt/yr solvent extraction complex to 500 kt/yr with the cost involved in the construction of a a new 200 kt/yr solvent extraction complex and hybrid debottlenecking with a catalytic dewaxing.

Investment (basis: 795 m^3/day of lube base oils excluding fuels hydrocracker, 1998 USA Gulf Coast) $80 million.		
	Solvent extraction (200 kt/yr grass-roots) (% of the total cost)	Hybrid desbottlenecking (from 300 to 500 kt/yr) (% of the solvent extraction cost)
Capital change	36	24 - 36
Fixed costs	20	7 - 9
Variable costs	8	8
Hydrocarbon cost	35	11
Total	100	50 - 64

Driving force for implementation
Produce distillate with low wax content.

Example plants
It has been identifed one EU+ refinery that have this process to produce distillates with low wax content.

Reference literature
[212, Hydrocarbon processing, 1998], [247, UBA Austria, 1998], [268, TWG, 2001]

4.21 Storage and handling of materials

As has been mentioned more information can be found in the Horizontal BREF on Storage [264, EIPPCB, 2001].

4.21.1 Underground caverns

Description
More information in Section 2.21.

Achieved environmental benefits
- VOC emissions from underground storage caverns are very low or non-existent. The main reasons are: the temperature of the cavern is low and stable, the product is under pressure, the breathing gases from the cavern are not led to atmosphere but to an other cavern
- the land above caverns is free for other purposes
- improve safety.

Cross-media effects
Ground water leaking into the cavern must be removed and treated with other oily waters.

Applicability
The geology of the site should be adequate to install a cavern: non porous rock.

Economics
The construction costs of storage caverns are markedly smaller than for above-ground tank farms. In Finland, profitability begins at 50000 m^3 under favourable conditions (depends highly on the rock type). Maintenance costs have been calculated to be one-sixth those of above-ground tanks.

Driving force for implementation
Avoidance of visual intrusion, the reduction of energy consumption, saving of land surface and economic for large storage systems.

Example plants
Used in some European countries.

Reference literature
[256, Lameranta, 2000]

4.21.2 Internal floating roof tanks

Description
Internal floating roof tank (IFRT)s. Emissions primarily occur during standing storage, with an additional contribution from withdrawal emissions. In addition to the rim seal area and roof fitting penetrations, sources of standing loss from internal floating roof tanks include bolted seams in the floating roof. More information in Section 2.21. Some techniques that might be applied to IFRT are:
- the replacement of primary/secondary seals with tighter seals, which can also reduce the VOC emissions
- drain design on floating roof tanks to avoid hydrocarbon contamination of rainwater.

Achieved environmental benefits
Reduction of VOC emissions. Conversion of fixed roof tanks to internal floating roof and seals to minimise evaporation of the product being stored. The control efficiency of this method

ranges from 60 to 99 % depending on the type of roof and seals installed and the true vapour pressure of the liquid stored.

Cross-media effects
The net storage capacity of a fixed roof tank is reduced by aprox. 10 %.

Operational data
Performance data on emissions and other useful information about IFRT are available in [323, API, 1997].

Applicability
An acceptable alternative to an EFRT is to retrofit a fixed roof tank with an internal floating cover (IFRT).

Economics
The costs of retrofits are given in Table 4.34 below. Costs are dependent on the tank diameter.

Emission Source	Refinery Storage		
Control Technology	Internal Floating Roofs in fixed roof tanks	Secondary/Double Seals on Floating Roof Tanks	Other Roof Fitting Emission Controls (roof legs, still wells) and options (tank paint)
Efficiency	90 – 95 %	95 %	Over 95 % when together with secondary seals
Investment Costs EUR million	0.20 - > 0.40 for 20 - 60 metres diameter tanks(1)	0.05 - 0.10 for 20 - 50 metres diameter tanks(2)	0.006 for 50 metre diameter tanks(1)
Operating Costs	Minor	Replacement every 10 years	Minor
Other Impacts Comments	Requires tank to be taken out of commission Reduces the net storage by 5 – 10 %	Can reduce maximum storage capacity of tank	Not suitable for high sulphur crude oils due to pyrophoric scale possibility
References: (Installed and Retrofitted) (1) UN-ECE/IFARE, and Industry Propriety Information (2) UN-ECE/IFARE and Industry Propriety Information (UN-ECE EC AIR/WG6/1998/5)			

Table 4.34: VOC controls in storage

Driving force for implementation
European Directive 94/63/EC (Stage 1) prescribes either fixed roof gasoline storage tanks are fitted with internal floating roofs (with a primary seal in existing tanks and with secondary seals in new tanks) or are connected to a vapour recovery unit. Vapour destruction is also a technically viable option which may be applied, provided energy recovery is included.

Reference literature
[45, Sema and Sofres, 1991], [127, UN/ECE, 1998], [323, API, 1997], [268, TWG, 2001]

4.21.3 Fixed-roof tanks

Description
The *fixed-roof tank* can give rise to emissions in the following ways:

- filling losses; during tank filling the existing tank vapour space, which is more or less saturated with vapour, is expelled to the atmosphere, while when a tank is emptied the incoming air is slowly saturated with vapours, which are then expelled by subsequent filling and/or breathing. Generally those emissions are greater than standing emissions. A technique to reduce VOC from those tanks is to increase the storage pressure by blanketing.

- breathing losses; during storage of the liquid there will be vapour emissions from tank breathing caused by the difference in night and day temperatures and by changes in atmospheric pressure. To a certain extent, pressure controllers and insulation can prevent breathing losses
- vapours released during water draining.

The techniques that are considered to reduce emissions from fixed roof tanks are:
- a technique to reduce VOC from those tanks is to blanket them
- installation of an internal floating roof.

Achieved environmental benefits
The installation of an internal floating roof in fixed-roof tanks can reduce VOC emissions up to 90 %.

Cross-media effects
The installation of an internal floating roof in a fixed roof tank requires the tank to be taken out of commission and reduces the net storage by 5 - 10 %.

Operational data
Performance data on emissions and other useful information about EFRT are available in [323, API, 1997]

Applicability
Fixed roof tanks are typically used for low or non volatile products e.g. kerosene, heating oil, with TVP less than 14 kPa. These tanks can be retrofitted to internal floating roof tanks. But are not suitable for all products, e.g. bitumen tank with an internal floating roof will not work due to bitumen solidifying in the flaw between wall and internal floating roof.

Economics
The investment cost of installing internal floating roofs in fixed roof tanks can be 0.2 - 0.4 EUR million for tanks 20 - 60 meters in diameter.

Driving force for implementation
Reduction of VOC emissions.

Reference literature
[107, Janson, 1999], [115, CONCAWE, 1999], [323, API, 1997], [268, TWG, 2001]

4.21.4 External floating roofs

Description
External Floating roof tanks (EFRT). Filling and breathing losses are greatly diminished in comparison with fixed roof tanks, but the following vapour losses are inherent to this type of tank:
- standing storage emissions from floating roof tanks include rim seal and roof-fitting emissions, which result from stock vapour pressure changes due to temperature, and pressure variations but more importantly wind effects as well as openings in the roof. The influence of wind effects is not a factor on internal floating roof tanks. Standing emissions on external floating roof tanks are generally much more significant than withdrawal emissions
- wetting losses; by evaporation of liquid from the wet wall, when the level of the liquid is lowered by discharge
- vapours released during water draining
- in many cases, for an external floating roof tank, the emissions through fittings can exceed the rim seal losses especially on tanks with secondary seals. In terms of fitting losses, the major source is from the slotted stillwell (sample well or dipping well).

External floating roof tanks are used to store crudes, light products and intermediate stocks having a vapour pressure of more than 14kPa but less than 86 kPa at normal storage temperature. More information can be found in Section 2.21. Techniques to minimise emissions there include:

- installing wipers at the floating deck
- sleeves around the pipe, incorporating still well wipers
- floats with wipers inside the slotted pipe
- land as infrequently as possible the floating roof tanks to avoid unnecesary vapour releases.

Achieved environmental benefits
For the same substance, e.g. gasoline, EFRTs have the advantage over fixed roof tanks of significantly lower emissions to the atmosphere of VOCs. An EFRT can avoid 95 % of the losses from a fixed roof. Product savings give operating benefits.

Cross-media effects
They have potentially more emissions to water than fixed roof tanks, since it is possible for rainwater to enter the tank past the roof seal. Any such water needs to be drained before despatch of the product to a customer since the quality of the product can be seriously jeopardised.

Operational data
Performance data on emissions and other useful information about EFRT are available in [323, API, 1997].

Applicability
In retrofit situations where a change in the service of the tank is desired, an acceptable alternative to an EFRT is to retrofit a fixed roof tank with an internal floating cover.

Economics
Investment cost for the retrofitting of a fixed rood tank to a EFRT is EUR 0.26 million per tank diameter 20 m. Operator is necessary for tank draining, giving rise to some operating cost.

Driving force for implementation
The Directive 94/63/EC (Annex 1) defines an appropriate floating roof tank as one having at least a VOC release efficiency of 95 % as compared with a fixed roof one.

Reference literature
[45, Sema and Sofres, 1991], [252, CONCAWE, 2000], [258, Manduzio, 2000], [323, API, 1997], [268, TWG, 2001]

4.21.5 Pressurised vessels

Pressurised vessels such as bullets and spheres are often fitted with pressure relief valves, which vent to atmosphere or flare. VOC emissions can occur if these valves or by-pass block valves have internal leaks.

4.21.6 Double and secondary seals

Description
Two seals at the floating roof rim provide a double barrier to control VOC emissions from storage tanks. Fitting secondary roof rim seals is an accepted technology for emission reduction. Rim-mounted seals (as opposed to shoe-mounted seals) are favoured, since the former offer emission control if the primary seal fails.

Achieved environmental benefits
VOC emissions can be significantly reduced by installing secondary seals on storage tanks. The Amoco/USAEPA joint study estimated that VOC losses from storage tanks could be reduced by 75 to 95 %. When they are applied in EFRT, secondary seals also reduce the likelihood of rainwater ingress into the tank. Secondary seals for gasoline storage can reduce VOC emissions by up to 95 %.

Cross-media effects
Retrofitting seals usually results a loss of operating capacity of about 5 %.

Operational data
Performance data on emissions and other useful informations about rim seals are available in [323, API, 1997].

Applicability
They can be readily installed in new units (named double seals) and generally retrofitted (secondary seals).

Economics
Equipping an average tank with a secondary seal system was estimated to cost about $20000 (1991). Investment costs: EUR 0.05 - 0.10 million for tanks 20 - 50 metre diameter.
Operating costs: Replacement likely every 10 years.

Driving force for implementation
European Directive 94/63/EC (Stage 1) prescribes secondary seals for external floating roof tanks and for new internal floating roof tanks for gasoline storage in refineries and terminals.

Example plants
In common use world-wide.

Reference literature
[45, Sema and Sofres, 1991], [252, CONCAWE, 2000], [323, API, 1997], [268, TWG, 2001]

4.21.7 Storage strategy

Description
The need for certain tanks can often be eliminated through improved production planning and more continuous operations. This technique is closely related to Section 4.15.5. An example is the implementation of an in-line blending system. See Section 4.21.14.

Achieved environmental benefits
Since storage tanks are one of the largest sources of VOC emissions, a reduction in their number contributes to a reduction of VOC emissions. By minimizing the number of storage tanks, tank bottom solids and decanted waste water may also be reduced.

Applicability
The reduction of number of tanks typically requires a full change in the management of product and intermediates. As consequence this technique is easier to be applied to new units.

Driving force for implementation
Space usage can be improved by reducing the number of storage tanks in operation.

Reference literature
[268, TWG, 2001]

4.21.8 Prevention of leakage through tank bottoms

It follows techniques to consider in the determination of BAT for prevention of leakage through tank bottoms. This topic is well documented in EEMUA pub 183 "Guide for the Prevention of Bottom Leakage from Vertical, Cylindrical, Steel Storage Tanks".

4.21.8.1 Double tank bottoms

Description
Double bottoms can either be retrofitted in existing tanks or incorporated into the design of new tanks. If retrofitted, the existing tank bottom is normally used as the secondary flooring, and sand, gravel or concrete can be installed between the new primary and the secondary floors. In this case, it is general practice to keep the interstitial space to a minimum and therefore the secondary bottom should slope the same way as the primary bottom. The slopes to the base of tanks can be either straight, cone-up (sloping from the centre down to the tank perimeter) or cone-down (sloping downward from the tank perimeter). Nearly all tank floors are made of carbon steel. If a double bottom is to be installed (either retrofit or new build), there are choices in material selection for the new floor. A second carbon steel floor can be utilised or a more corrosion-resistant stainless steel floor can be installed. A third choice is to use a glass fibre-reinforced epoxy coating over the steel.

The use of double bottom tanks allows a vacuum system to be installed, and in this case the space between the lower and upper floor is not filled, but retained as an air space using steel spacers (which can typically be a steel reinforcement mesh). In this more recent system, the space between the floors is kept under a vacuum that is continuously monitored. Any leak in the primary or secondary floor will dissipate the vacuum and trigger an alarm. A further test of the extracted air will indicate an upper floor failure if product or vapours are present, or a lower floor failure if neither product nor vapour is present (subject to any previous underfloor contamination).

Achieved environmental benefits
Installing a second impervious bottom to a tank provides a measure of protection against non-catastrophic releases due to corrosion, faulty weld joints, or flaws in the bottom material or the construction details. In addition to containment, the secondary bottom provides a means of allowing detection of a bottom leak which is not obviously visible to an operator, as a similar shell defect would be.

Cross-media effects
In the case of retrofitting, the application of this technique may prolong the outage time of tanks during installation of the double bottom. Its application can reduce the capacity of the tank.

Operational data
By installing double bottoms, the time between inside inspections and the the number of the annual tank cleaning procedures are decreased.

Applicability
Either retrofit or new-build tanks.

Economics
Typical retrofit costs for double bottoms, as quoted from German or Swiss suppliers, are as follows and include provision of a vacuum leak detection system:

- carbon steel: 110 EUR/m^2
- stainless steel: 190 EUR/m^2
- glass fibre-reinforced epoxy: 175 EUR/m^2

An UK refinery reported that the actual cost of installing a double bottom on a 10340 m^3 tank was 600000 EUR.

Driving force for implementation
Prevention of leaks from storage tanks.

Reference literature
[253, MWV, 2000], [112, Foster Wheeler Energy, 1999]

4.21.8.2 Impervious membrane liners

Description
The impervious membrane liner is a continuous leak barrier under the entire bottom surface of the tanks. It can be an alternative to a double bottom or it can be added as an extra measure of safety below the double bottom. Like the double bottom, it is primarily intended to arrest the small but persistent leak rather than address a catastrophic failure of the entire tank. The key to an effective liner is that the seams need to be liquid-tight against either the steel shell of the tank or the concrete wall that supports and surrounds the tank. The minimum thickness of the flexible membrane is 1 mm, although 1.5 to 2 mm thick sheets are commonly used. The membrane need to be chemically resistant to the product stored in the tank.

Achieved environmental benefits
Prevention of leak from storage tanks.

Cross-media effects
Prolonged tank outage if liner has to be retrofitted to existing tank.

Applicability
They can be installed either in a new-build design or as a retrofit and they generally include a leak detection system.

Economics
The cost of retrofitting a liner is slightly higher than installing a double bottom as it involves jacking-up the existing tank to install the membrane and leak detection system. An indicative cost is of the order of 200 EUR/m^2. As new-build construction, an impervious liner may be cheaper than a double bottom, but it may have a higher life cycle cost. This is because any future failures of the liner would require re-lifting the tank or reverting to a new double bottom solution.

The following are costs per unit for placing the following materials on the ground:
- concrete: 30 EUR/m^2
- asphalt: 24 EUR/m^2
- HD polyethylene: 23 EUR/m^2
- bentonite: 18 EUR/m^2
- clay: 11-17 EUR/m^2

This costs exclude the cost of lifting the tank for installation. However, costs of placing such materials in the floors of bunds would be of this order. An additional cost arises from moving any pipework in the bunds.

For comparison of the installed costs of such a liner, one refinery reported that since 1994, it had installed a clay bottom liner under each lifted tank during maintenance. A leak detection system was installed at the same time. The cost of this was about 20000 to 30000 EUR per tank with the cost of the clay liner being 11 to 17 EUR/m^2. The total cost for 14 tanks amounted to 350000 EUR. A similar cost (35000 EUR) was quoted in another installation of an impervious liner (plus leak detection) for a 12000 m^3 concrete tank.

Driving force for implementation
Preventing soil contamination.

Example plant(s)
Impervious membrane liners are used in lieu of double bottoms in a number of non-European countries.

Reference literature
[45, Sema and Sofres, 1991], [268, TWG, 2001]

4.21.8.3 Leak detection

Description
As with sewers, one way to protect against soil and groundwater contamination is by detecting leaks at an early stage. Leaks through a tank bottom can be detected by a leak detection system. Conventional systems include inspection ports, inventory control and inspection wells. More advanced systems include electronic sensing probes or energy pulse cables whereby product that comes into contact with the probe or cable will alter its impedance and trip an alarm. In addition, it is common practice to use a variety of inspection procedures on tanks at intervals to prove their integrity. See also Section 4.23.6.1 LDAR programme. Some techniques to consider are:

- Equipping storage tanks with overflow alarms and automatic pump shut-offs.
- Installing double bottoms with integrated leak detection systems on tanks where practicable.

Relief valves on pressurised storage should undergo periodic checks for internal leaks. This can be carried out using portable acoustic monitors or, if venting to atmosphere with an accessible open end, tested with a hydrocarbon analyser as part of an LDAR programme.

Achieved environmental benefits
Avoid soil and groundwater contamination.

Applicability
Probes and cables have to be packed pretty densely if the leak to be detected is small. Consequently, inspection, where possible, may in some cases be more reliable than probes.

Economics
One refinery reported that the installation of a leak detection system on a group of four 12 m diameter tanks cost a total of 55000 EUR with an operating cost of 4000 EUR per year. The routine inspection of tanks at another refinery was quoted as 2000 EUR/tank/year.

Driving force for implementation
Avoid soil and groundwater contamination.

Reference literature
[253, MWV, 2000]

4.21.8.4 Cathodic protection

Description
To avoid corrosion on the underside of the tank bottom, tanks can be equipped with cathodic corrosion protection.

Achieved environmental benefits
Avoid soil and groundwater contamination and air emissions due to the prevention of corrosion.

Cross-media effects
Electricity is needed.

Driving force for implementation
Avoid corrosion of tanks and pipes, reducing the maintenance cost.

Reference literature
[253, MWV, 2000]

4.21.9 Tank farm bund containment

Description
Whereas double bottoms or impervious liners protect against the small but incessant leak, an impermeable tank farm bund is designed to contain large spills (for safety as well as environmental reasons), such as caused by a shell rupture or a large spill from overfilling. The bund consists of a wall or dike around the outside of the tank to contain all or part of the tank contents in the event of a spill, and (in some cases) an impermeable ground barrier between the tank and the dike to prevent infiltration of the product into the ground. The dike is typically constructed of well-compacted earth or reinforced concrete. The height is normally sized to accommodate the maximum contents of the largest tank within the volume enclosed by the dike. However this philosophy of total capture is flawed if the ground between the tank and dike is permeable. Oil can permeate downward and under the dike in these situations. Asphalt, concrete surface or high density polyethylene (HDPE) liner are some of the possibilities.

Achieved environmental benefits
Containment of large spills from liquid storage tanks.

Cross-media effects
This technique might call for the soil to be compacted, which may be seen as negative impact. A study in the United States has concluded that the effectiveness of liners in protecting the environment is limited because of their unreliability and the difficulty in inspecting or testing their integrity. Also, there are few releases that would be contained by such liners, and moreover, they are expensive to install. Because of this, it was concluded that other preventative measures are more effective in protecting the environment and are more cost-effective in the long run.

Applicability
In some cases, retrofitting may not be possible.

Economics
Some refineries have quoted the total cost for installing concrete paving under 6 big tanks at EUR 1.3 millions (0.22 per tank), the cost of sealing bund dike walls with asphalt (around 10 tanks) at EUR 0.8 million, and the cost of concrete paving bunds at 70 - 140 EUR/m^2. One refinery quoted the cost of installing 200m of impermeable HDPE barrier along the site boundary at 150000 EUR (750 EUR/m).

Driving force for implementation
Containment of large spills that may occur from liquid storage tanks is normally regulated by national laws. In Italy, current legislation foresees for some liquids a volume of the bund less than 100 % of the tank volume.

Reference literature
[147, HMIP UK, 1995]

4.21.10 Reduce the generation of tank bottoms

Description
Minimization of tank bottoms can be carried out through careful separation of the oil and water remaining in the tank bottom. Filters and centrifuges can also be used to recover the oil for recycling. Other techniques to consider are the installation of side entry or jet mixers on tanks or the use of chemicals. This means that basic sediment and water is passed on to the receiving refineries.

Achieved environmental benefits
Tank bottoms from crude oil storage tanks constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem due to the presence of heavy metals. Tank bottoms are comprised of heavy hydrocarbons, solids, water, rust and scale.

Cross-media effects
Passing the sediments and water from the crude oil tanks to the refinery means that they will most probably show up in the desalter.

Reference literature
[147, HMIP UK, 1995]

4.21.11 Tank cleaning procedures

Description
For routine internal tank inspections and for the purpose of repair, crude oil and product tanks have to be emptied, cleaned and rendered gas-free. A technique to clean tank bottoms include to dissolve the majority of the tank bottoms (>90%) with hot diesel fraction at temperatures of around 50 ºC where it disolve most of the tank bottoms and they can be blended after filtration to the crude tanks.

Achieved environmental benefits
Emissions during the cleaning of tanks arise during natural or mechanical ventilation. A variety of cleaning methods has been developed for the cleaning of crude oil tanks. Knowledge of the technology for cleaning crude oil tanks has improved, so that with primary measures emissions of VOC less than 0.5 kg/m^2 tank bottom area can be achieved. With secondary measures, e.g. installation of mobile flares, which are currently under development for cleaning crude oil and product tanks, further emission reductions of VOC of up to 90 % can be expected.

Cross-media effects
If the refinery operates its own sludge incineration plant, cleaning residues can supplied to it.

Operational data
The emission arising during the cleaning of crude oil tanks and the reduction of these emissions are exhaustively described in [302, UBA Germany, 2000]. The use of hot diesel to clean up the tank bottoms require heating.

Applicability
Fully applicable.

Driving force for implementation
Reduce VOC emissions and tank bottoms.

Example plants
Examples exist of applications in many EU+ refineries and tank farms.

Reference literature
[117, VDI, 2000], [316, TWG, 2000], [302, UBA Germany, 2000], [122, REPSOL, 2001]

4.21.12 Colour of tanks

Description
It is preferable to paint tanks containing volatile materials in a light colour to prevent a) increasing the evaporation because of increased product temperature and b) increasing the breathing rate of fixed roof tanks.

Achieved environmental benefits
Reduction of VOC emissions.

Cross-media effects
Painting in light colours can result in tanks being more "visible" which can have negative visual effect.

Applicability
Painting of the roof and the upper part of the shell of a tank in the middle of a tank farm can be as effective as painting the entire tank.

Driving force for implementation
Also a requirement of 94/63/EC for gasoline tanks, except there are derogations for visually sensitive areas.

Reference literature
[262, Jansson, 2000], [268, TWG, 2001], [302, UBA Germany, 2000]

4.21.13 Other good storage practices

Description
Proper material handling and storage minimises the possibility of spills, leaks and other losses which result in waste, air emissions and emissions to water. Some good storage practices are:

- use larger containers instead of drums. Larger containers are reusable when equipped for top and bottom discharge, whereas drums have to be recycled or disposed of as waste. Bulk storage can minimize the chances of leaks and spills as compared to drums. Applicability: Safe disposal of un-refillable large containers can be a problem.
- reduce generation of empty oil drums. Bulk purchasing (via tank truck) of frequently used oils and filling tote bins as intermediate storage. Personnel could then transfer the oils from the tote bin to reusable drums, buckets, or other containers. This would reduce the generation of empty drums and their associated handling costs
- storage of drums off the floor to prevent corrosion through spills or concrete 'sweating'
- keeping containers closed except when removing material
- practise corrosion monitoring, prevention and control in underground piping and tank bottoms (Related with 4.21.8 and 4.21.22)
- tanks for storage of ballast water may cause large VOC emissions. They can be therefore equipped with a floating roof. Those tanks are also relevant as equalizing tanks for the waste water treatment system
- vents from sulphur storage tanks to pass to sour gas or other arrestment systems
- vent collection and ducting from tank farms to central abatement sytems.
- install self-sealing hose connections or implement line draining procedures
- install barriers and/or interlock systems to prevent damage to equipment from the accidental movement or driving away of vehicles (road or rail tank cars) during loading operations

- implement procedures to ensure that arms are not operated until inserted fully into the container to avoid splashing where top loading arms are used
- apply instrumentation or procedures to prevent overfilling of tanks
- install level alarms independent of normal tank gauging system

Achieved environmental benefits and Economics

	Emission factor for NMVOC (g/Mg throughput)	Abatement efficiency (%)	Size (diameter, m)	Cost (EUR)
Fixed roof storage tanks FRT	7 - 80			
EFRT	7 - 80			
IFRT	2 - 90			
External paint finish in a lighter shade		1 - 3 FRT	12	3900
			40	25400
Installation of an internal floating roof in existing fixed-roof tank		97 - 99 FRT	12	32500
			40	195000
Replacement of a vapour-mounted primary seal with a liquid-mounted primary seal		30 - 70EFRT 43-45 IFRT	12	4600
			40	15100
Retrofitting secondary seals on an existing tank		90 - 94EFRT 38 - 41 IFRT	12	3400
			40	11300
Improvement of primary seal, plus secondary seal and roof fitting control (pontoon&double deck)		98 EFRT 48 - 51 IFRT	12	200
			40	200
Installation of a fixed roof on an existing external floating-roof tank		96EFRT	12	18000
			40	200000
Note: Colums for abatement efficiency, Size and Cost are related to the tehcniques and not to each other. Costs are average cost for the two diameters and abatement efficiencies are ranges for the technique applied to different types of tanks.				

Reference literature
[127, UN/ECE, 1998], [268, TWG, 2001], [252, CONCAWE, 2000], [19, Irish EPA, 1993], [262, Jansson, 2000]

4.21.14 In-line blending

Description
Figure 4.8 shows a scheme of a in-line blending system for gasoils.

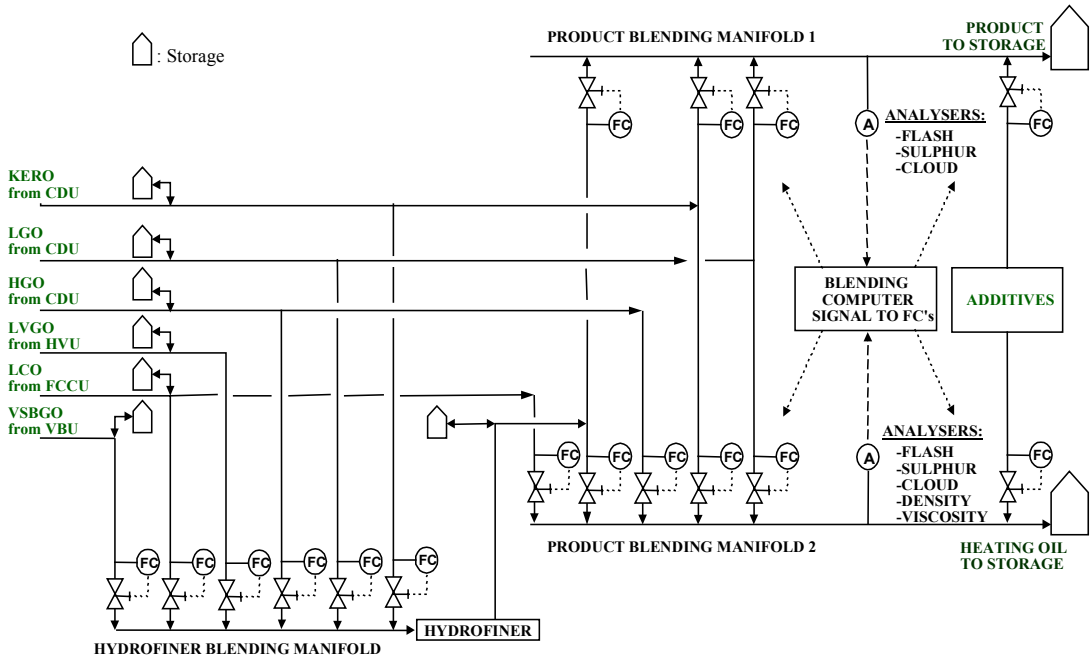


Figure 4.8: Simplified scheme of an in-line blending system for gasoils (automotive diesel and heating oil)

Achieved environmental benefits

The energy saving realised by in-line blending compared to batch blending can be substantial, especially in electric power consumption. Using in-line blending reduces the total number of handling operations with respect to feed and product streams -less filling and emptying of tanks- and thus reduces the total emission to atmosphere. The numerous valves and pumps can be provided with double mechanical seals and regularly maintained in order to minimise fugitive VOC emissions. In-line blending generally creates more flexibility towards product specifications and product quantities, and represents a large saving by avoiding intermediate storage.

Cross-media effects

In-line blending systems contain many flange connections and valves, which could be sources of leakage, particularly during maintenance.

Operational data

Extreme care has to be paid to on-line quality analysers to assure quality of the blended product.

Applicability

Optimising the blend ratios to meet all critical specifications is to a certain extent a trial-and-error procedure which is most economically accomplished with the use of a computer. The large number of variables usually permits a number of comparable solutions that give roughly equivalent total overall cost or profit. Optimisation programmes allow the computer to provide the optimum blend to minimise cost and maximise profit.

Example plants

In-line blending systems are normally applied for high volume feed and/or product streams.

Reference literature

[118, VROM, 1999]

4.21.15 Batch blending

Description
See Section 2.21

Applicability
The reasons for batch blending are the minimum storage requirements for strategic reasons, fiscal and tax control, operating flexibility and tank dimensions.

Example plants
For a variety of reasons given under applicability, batch blending of feed and product is still done to a certain extent.

4.21.16 Vapour recovery

Vapour recovery/destruction systems and vapour return during loading applied to storage are included in Section 4.23.6.2.

Description
Vapour recovery systems, used for the reduction of hydrocarbon emissions from storage and loading facilities of gasoline and other highly volatile products. Displaced vapour containing air/gas from loading of volatile products (such as gasoline or products of similar vapour pressure) into vessels and barges should ideally be recycled or routed through a vapour recovery unit. The pressure swing adsorption technique is one of a number of techniques to recover chemical compounds from vapour streams. Examples of these vapour streams are process vents, refinery fuel gas, flare or incinerator feed streams. The units can recover organic compounds from gaseous streams. More information in Section 4.23.6.

Achieved environmental benefits
It has been estimated that VOC emissions from barge loading can be reduced by 98 % by installing a marine vapour loss control system. A vapour recovery unit used in fixed tanks can reduce VOC emissions by 93 - 99 % (down to 10 g/Nm^3). Table 4.35 provides some data on the efficiency and environmental performance of vapour recovery units

VOC recovery technique	Emission reduction (%)	down to (g/Nm^3)
Single stage	93 - 99	10
Lean oil absorption	90 - 95	
Activated carbon as adsorbent	95 - 99	
Condensation with liquid nitrogen	90	
Membrane	99	
Double stage	near 100 %	0.10 - 0.15

Plant type	Recovery rates (%)	Half-hourly mean values attainable in continuous operation. Total hydrocarbons	
		NMVOC[1] (g/Nm^3)	Benzene (mg/Nm^3)
Single-stage condensation plant	80 - 95	50	1
Single-stage absorption, adsorption and membrane separation plants	90 - 99.5	5 [2]	1
Single-stage adsorption plants with supplementary blower [2]	99.98	0.15	1
Two stage plants	99.98	0.15	1
The sum of hydrocarbons and methane ranges from 100 to 2500 mg/Nm^3 or higher. The methane content is only insignificantly reduced by absorptive or adsorptive processes. If single-stage plants are used as a preliminary stage for gas engines, a concentration of approx. 60 g/m^3 is necessary for operation of the gas engine. (The HC concentration in the uncleaned gas is approx. 1000 g/Nm^3)			

Table 4.35: Emissions values for vapour recovery plants during the loading of motor gasolines

Cross-media effects

Where explosive mixtures can occur, it is important that safeguards are implemented to limit the risk of ignitions and ignition propagation. Need to implement safeguards for the handling of explosive mixtures, especially from mixed chemical vapour streams. Two stage units are high energy consumers. The energy consumption of these plants is about twice as high as that of plant with a residual emissions of 5 g/m^3, which correlates with higher CO_2 emissions.

Operational data

Energy consumption (for cooling, pumping, heating, vacuum), waste (adsorbent / membrane replacement), water effluent (i.e. condensates from steam regeneration of adsorbent, defrost water from condensation units).

Applicability

It can be applied to crude loading (with the exception of adsorption if a pretreatment as sulphur stripper is not used, because of adsorbent fouling) having smaller effectiveness than those mentioned above because methane and ethane are collected in the vapour stream, despatch product stations and ship loading of products. These systems are not applicable in unloading processes when the receiving tank is equipped with an external floating roof. Vapour recovery units are not considered applicable when recovery of small quantity of chemicals is under discussion.

VOC recovery technique	Restriction in the applicability of the technique
Activated carbon as adsorbent	Handling of non-compatible compounds present in the vapour stream may either poison or destroy active carbon
Condensation with liquid nitrogen	Might require double heat exchanger set to enable unit defrosting during continuous operation requirement. SO_2 might result in deposition of elemental sulphur.
Membrane	Up to 5000 ppm. Technology applicable up to full saturation of HC in vapour stream.

Economics

Next table shows some examples of the cost of vapour recovery units

Equipment	Installation cost (EUR million)	Operating cost (EUR million/yr)[1]
Vapour recovery unit for 4 fixed tanks of 20 m diameter (loading volatile products to roal, rail or barge not including equipment for trucks and wagons)	1	0.05
Vapour recovery systems for loading of volatile products to roal, rail or barge (not including equipment for trucks and wagons). Cost referred to 4 tanks of 20 m of diameter	Single stage 1.3 Double stage 1.8	0.05 0.12
Vacuum recovery systems. Design flow rate of 14 – 142 m^3/h. System will provide overall recovery up to 99.9 % of feedstream with a hydrocarbon concentration of 40 % and a moisture content of 8.7 %v/v (dew point = 38 ºC).	0.28 - 1.7	
[1] not considering the value of products recovered		

Driving force for implementation
European Council Directive 94/63/EC (Stage 1) prescribes the installation of vapour balancing lines and vapour recovery units (VRUs) or vapour recovery systems (VRS) during gasoline loading/unloading activities at refineries and terminals.

Example plants
Many examples are found in European refineries. Gothenburg oil harbour is going to install a VRU for ship loading.

Reference literature
[107, Janson, 1999], [181, HP, 1998], [211, Ecker, 1999], [45, Sema and Sofres, 1991], [117, VDI, 2000], [316, TWG, 2000], [247, UBA Austria, 1998], [268, TWG, 2001]

4.21.17 Vapour destruction/ use

Description
Vapour destruction is also a technically viable option, which may include energy recovery. It also includes the destruction of vented products in process heaters, special incinerators or flares.

Achieved environmental benefits
Efficiency up to 99.2 %. Catalytic combustions can achieve higher efficiencies of 99.9 %. Efficiency of the flameless thermal oxidation can achieve removal efficiencies of 99.99 % or greater. In the absence of a high-temperature, thermal NO_x is typically less than 2 ppm v/v.

The heat generated in the combustion can be used to produce low-pressure steam or to heat water or air.

Cross-media effects
CO_2 is produced in the combustion process. CO and NO_x may be also produced. Additional fuel is consumed in the combustion of streams with low concentrations and for preheating of catalysts. Experience with existing units shows 19 - 82 kg/h of gasoil. Continuous ignition source within vapour system is a major safety concern that requires implementation of systems to prevent ignition propagation.

Applicability
Applicable to reactor and process vents, tank vents, loading facilities, ovens and dryers, remediation systems and other manufacturing operations. Applicability limited to very light hydrocarbons, methane, ethane and propylene.

Economics
Investment Costs (EUR million) 2 - 25 and 3.2 - 16 for marine loading (0.1 - 0.22 EUR million /ship for conversion).
Operating Costs: 0.02 - 1.1 EUR million
Retrofit costs are very site-specific.

Driving force for implementation
Reduce VOC emissions.

Example plants
Catalytic combution processes have been applied in the chemical industry.

Reference literature
[181, HP, 1998], [118, VROM, 1999], [268, TWG, 2001]

4.21.18 Vapour balancing during loading processes

Description
In order to prevent emissions to atmosphere from loading operations, several options are available. Where loading takes place from fixed roof tanks, a balance line can be used. The expelled mixture is then returned to the liquid supply tank and so replaces the pumped-out volume. Vapours expelled during loading operations may be returned to the loading tank, if it is of the fixed roof type, where it can be stored prior to vapour recovery or destruction. This system can also be used for vessels and barges.

Achieved environmental benefits
This reduces greatly the vapour volumes expelled to atmosphere. It can reduce emissions by up to 80 % of the VOC emitted.

Cross-media effects
Due to evaporation in the receiving vessel during transfer (vapour evolution by splashing), there is usually a surplus volume of vapours compared to the displaced liquid volume. The balancing line is not considered an efficient means of VOC-abatement for the most volatile liquids.

Operational data
Where explosive mixtures can occur, it is important that safeguards are implemented to limit the risk of ignitions and ignition propagation. Tanks should remain closed to prevent emissions, so they may operate under a low pressure and ullaging and sampling should not be undertaken through open dipatches. Detonation arresters require regular cleaning when vapours contain particulates (e.g. soot from badly operated cargo tank inerting systems).

Applicability
Not all vapours can be collected. May affect loading rates and operational flexibility. Tanks which may contain incompatible vapours cannot be linked.

Economics
Investment costs are 0.08 EUR million per tank and the operating costs are low.

Driving force for implementation
Reduce the VOC emissions.

Example plant(s)
LPG loading. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the refinery fuel gas system.

Reference literature
[115, CONCAWE, 1999], [268, TWG, 2001]

4.21.19 Bottom loading measures

Description
The loading/unloading pipe is flange-connected to a nozzle situated at the lowest point of the tank. A vent pipe on the tank can be connected to a gas balancing line, VRU or to a vent. In the last case VOC emissions can occur. The flange connection in the filling line has a special design ("dry connection") which enables it to be disconnected with minimum spillage/emissions.

Achieved environmental benefits
It reduces VOC emissions

Driving force for implementation
European Directive 94/63/EC (Stage 1) prescribes for gasoline loading for road tankers.

Reference literature
[80, March Consulting Group, 1991], [268, TWG, 2001]

4.21.20 Tightly-sealed floors

Description
Handling of materials used in the refinery may result in spills that contaminate soil or rainwater. This technique paves and kerbs the area where materials are handled, for the collection of the possible spilled material.

Achieved environmental benefits
Avoid soil pollution and direct any spillage of product to slops.
This would minimise the volume of waste generated and allow for the collection and reclamation of the material.

Driving force for implementation
Avoid soil and rainwater contamination.

Example plants
Many examples can be found in European refineries.

Reference literature
[80, March Consulting Group, 1991]

4.21.21 LPG odorant plant

Description
The design and operation of odorising facilities should be to a very high standard which minimises the risk of odorant leaks or spillages. To an extent, the operational aspects of this are facilitated by the ease of detection of even the smallest odorant release, but this need to be used as an aid to vigilance, not as a reason for lax control.

Odorising plants should be designed to minimise the potential for leaks, e.g. by having the minimum number of pumps/valves/filters/tank connections, etc, by using welded, not flanged, connections wherever possible and by protecting the plant from possible impact damage. All such items used need to be designed to a very high standard of sealing efficiency. Devices such as automatic self-sealing couplings for loading lines are preferred.

Plants should be designed to deal with the high vapour pressure of odorants and should use inert or pressure controlled natural gas blanketing of the vapour spaces above stored odorant. During deliveries into tanks any displaced vapour need to be returned to the delivery vehicle, adsorbed on activated carbon or incinerated. The use of demountable semi-bulk containers avoids the generation of displaced vapours and is preferred where appropriate.

Achieved environmental benefits
In view of the nature and power of the odorants used there should be no normal release of odorant to any environmental medium.

Reference literature
[18, Irish EPA, 1992]

4.21.22 Overground pipelines and transfer lines

Description
In overground pipelines is easier to detect leakings

Achieved environmental benefits
Decrease the soil contamination

Applicability
Its implementation is easier in new installations.

Economics
The replacement of existing underground pipelines is typically very expensive.

Reference literature
[19, Irish EPA, 1993]

4.22 Visbreaking

4.22.1 Deep thermal conversion

Description
Deep thermal conversion bridges the gap between visbreaking and coking. It maximizes yields of stable distillates and produces a stable residue, called liquid coke.

Achieved environmental benefits
Increase the performance of visbreaking.

Cross-media effects
Increased energy consumption.

Economics
The investment amounts to 9120 to 11300 EUR/m^3 installed, excluding treatment facilities and depending on the capacity and configuration (basis: 1998)

Reference literature
[212, Hydrocarbon processing, 1998], [316, TWG, 2000]

4.22.2 Hydrovisbreaking

Achieved environmental benefits
A modern technology, which increases the conversion rate of the feed by addition of H-donators and water without reducing the stability of the process.

Economics
Investment (basis: 750 kt/yr of topped heavy Canadian crude; battery limits including desalting, topping and engineering; 1994 USA$ Gulf Coast)

Process alternative	Normal visbreaker	Hydro visbreaker
EUR per t/yr	85000	115000
Utilities, typical per m^3		
Fuel oil fired (80 % effic.) kg	15.1	15.1
Electricity, kWh	1.9	12.0
Steam consumed (produced), kg	(15.1)	30.2
Water, process, m^3	nil	nil
Hydrogen consumption, Nm^3	-	30.2

Example plants
This technology was tested in a 2 Mt/yr visbreaker in a refinery in Curaçao.

Reference literature
[212, Hydrocarbon processing, 1998], [250, Winter, 2000]

4.22.3 Soaker visbreakers

Description
In this process, a soaker drum is added after the furnace. So the cracking takes place at lower furnace outlet temperatures, and longer residence time.

Achieved environmental benefits
The product yields and properties are similar but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption (30 – 35 %) and longer run

times before shutting down to remove coke from the furnace tubes (run times of 6 - 18 months versus 3 - 6 months in coil cracking).

Cross-media effects
The above apparent advantage to reduce the number of clean-ups for soaker visbreakers is at least partially balanced by the greater difficulty in cleaning the soaking drum.

Operational data
Run times of 3 - 6 months are common for furnace visbreakers and 6 - 18 months for soaker visbreakers. Fuel consumption is around 11 kg FOE/t. Power and steam consumption is similar to the coil one. Operating temperature is 400 - 420 ºC.

Example plants
Some soaker visbreakers exists in European refineries.

Reference literature
[297, Italy, 2000], [268, TWG, 2001]

4.22.4 Sour gas and waste water management

Description
The gas generated in the visbreaking may be sour and contain sulphur compounds, in which case a gas sweetening operation, typically amine scrubbing, should be applied before the gas is recovered into products or used as refinery fuel gas. Visbreaking gas, apart from being amine scrubbed to remove H_2S, is further treated to remove approximately 400 to 600 mg/Nm^3 of mercaptan sulphur (depending on feed) in order to meet the refinery fuel gas sulphur-content specification.
The aqueous condensate is usually sour, and should pass to the sour water stripper in an enclosed system.

Achieved environmental benefits
Reduce sulphur content of products.

Cross-media effects
Need for chemicals and utilities to run the processes.

Driving force for implementation
Sulphur specifications of the products.

Example plants
Those techniques are applied in many refineries.

Reference literature
[316, TWG, 2000]

4.22.5 Reduction of coke formation in visbreakers

Description
During the thermal cracking some coke formation is produced and deposits in the furnace tubes. The coke should be cleaned when necessary. It exist in the market additives to control the sodium content within the feedstock. Also the control of the addition of caustics to the feedstock upstream can be also used.

Achieved environmental benefits
Reduction of the coke formation and as consequence reduction of cleaning waste.

Driving force for implementation
This technique is typically applied to prevent cleaning.

Reference literature
[268, TWG, 2001]

4.23 Waste gas treatments

This section together with the following two sections (namely Sections 4.24 and 4.25) are dealing with the end-of-pipe processes that appear in a refinery. Deeper information about the techniques included in this section and next one can be found in the Common waste water and wastegas treatments BREF. The reason why those techniques are appearing here is to give an overall description of the techniques and to avoid repetition. Description of end-of-pipe techniques does not appear in the previous sections. In this Sections (23 and 24), general information on environmental benefits, cross-media effects, operational data, applicability is described here. However, the application of those techniques to a certain activity refinery may vary its operational data, its cost, its performance etc. Consequently the data included in these sections is broader and more general than the one appearing within the activities. Complementing those techniques that may appear within the production activities, this section and the next one also contains end-of-pipe processes applied and that are techniques to consider in the determination of BAT for refineries. Under this category folds the sulphur recovery units, flares, amine treatment or the waste water treatments. Those techniques are only discussed here.

4.23.1 CO abatement techniques

Description
CO boilers and catalyst reduction of CO (and NO_x). Good primary measures for the CO reduction are:

- good operation control
- constant delivery of liquid fuel in the secondary heating
- good mixing of the exhaust gases
- catalytic afterburning
- catalysts with oxidation promoters.

Achieved environmental benefits
Reduction of CO emissions. Emissions after the CO boiler: < 100 mg/Nm^3. In the case of conventional firings a CO concentration below 50 mg/Nm^3 is achievable at temperatures above 800 °C, at sufficient air delivery and sufficient retention time.

Applicability
FCC and in heavy residues fired. (Section 4.10.4.9 and 4.5.5)

Reference literature
[316, TWG, 2000]

4.23.2 CO_2 emission control options

Description
Unlike SO_2, NO_x or particulates treatment of flue gases, as a feasible abatement technology for CO_2 is not available. CO_2 separation techniques are available but the problem is the storage and the recycling of the CO_2. Options for the refiner to reduce CO_2 emissions are:

I. effective energy management (topic discussed in Section 4.10.1) including:
   - improving heat exchange between refinery streams
   - integration of refinery processes to avoid intermediate cooling of components (e.g. 4.19.1 Progressive distillation unit)
   - recovery of waste gases and their use as fuels (e.g. flare gas recovery)
   - use of the heat content of flue gases.

II. use of fuels with high hydrogen contents (topic discussed in Section 4.10.2)

III. effective energy production techniques (see Section 4.10.3). It means the highest possible recovery of energy from fuel combustion.

Achieved environmental benefits
Reduction of CO_2 emissions

Cross-media effects
Use of fuels with high hydrogen contents reduce CO_2 emissions from the refineries but overall will not reduce CO_2 as these fuels will not then be available for other uses.

Operational data
Rational energy use needs good operation to maximise heat recovery and process control (e.g.: O_2 excess, heat balances between reflux, product temperature to storage, equipment survey and cleaning). To get optimum results repeated operator training and clear instructions are necessary.

Reference literature
[252, CONCAWE, 2000], [268, TWG, 2001]

4.23.3 NO_x abatement techniques

The NO_x emission level of an oil refinery or a natural gas plant is influenced by the refining scheme, the type of fuels used and the abatement techniques implemented. As the number of emission sources and their contribution to the overall emission level may vary greatly, one of the first techniques to consider is the precise quantification and characterisation of the emission sources in each specific case. For more information see Section 3.26.

4.23.3.1 Low-temperature NO_x oxidation

Description
The low-temperature oxidation process injects ozone into a flue gas stream at optimal temperatures below 200 ºC, to oxidise insoluble NO and NO_2 to highly soluble N_2O_5. The N_2O_5 is removed in a wet scrubber by forming a dilute nitric acid waste water that can be used in plant processes or neutralised for release. General information about this technique can be found in Waste water and wastegas BREF [312, EIPPCB, 2001]

Achieved environmental benefits
It can achieve 90 - 95 % removal of NO_x, with consistent NO_x levels as low as 5 ppm. Additional benefits are the heat-recovery fuel savings. The entire process is controlled to produce no secondary gaseous emissions. Because ozone is used as oxidant agent, emissions of CO, VOC and ammonia are also reduced.

Cross-media effects
Ozone should be produced on site, on demand, from stored O_2. Risk of ozone slip. The system can increase nitrate concentration in the waste water.

Operational data
The use of ozone and the low optimal temperatures of the process provide stable treatment conditions. Energy consumption for the production of ozone range from 7 - 10 MJ/kg (2 – 2.8 kWh/kg) of ozone produced with a concentration of 1-3 % w/w with dry oxygen feed. Temperature should be below 160 ºC to minimise ozone decomposition. Heavy particulate laden fuels may require additional equipment.

Applicability
It can be used as a stand-alone treatment system or can follow other combustion modifications and post-combustion treatment systems, such as low-NO_x burners, SCR or SO_x removal, as a final polish step. The process can be used either as a “stand alone”treatment system or as a

retrofit to existing plant. It can also be used as a polishing system to other NO_x removal technologies and for the treatment of ammonia slips.

Economics
It requires low maintenance and low operator interface. The relative capital cost and operating costs given by technology providers claim that are equal to, or less than SCR-type systems.

Example plants
The process is in use on USA commercial installation for sectors as acid pickling, steam boilers and coal fired boilers. A demonstration is currently planned on a refinery FCCU.

Driving force for implementation
Reduce the NO_x emissions.

Reference literature
[181, HP, 1998], [344, Crowther, 2001], [268, TWG, 2001]

4.23.3.2 Selective Non-Catalytic Reduction (SNCR)

Description
SNCR is a non-catalytic process for removing oxides of nitrogen from the flue gas by gas phase reaction of ammonia or urea at high temperature. General information about this technique can be found in Waste water and wastegas BREF [312, EIPPCB, 2001]

Achieved environmental benefits
Reductions of 40 - 70 % can be achieved giving values of less than 200 mg/Nm^3 by the use of this technique. Higher reduction figures (up to 80 %) can only be achieved under optimal conditions.

Cross-media effects
Ammonia injection produces significantly less N_2O and CO emissions than other reagents. When the temperature lower it is needed to reheat-up the flue gas with the consequent use of energy. The systems also need the equipment necessary for the storage of ammonia or urea. Disadvantages are also NH_3 slip (5 - 40 mg/Nm^3) and possible side reactions (N_2O). The U.S. EPA identified ammonia as the single largest precursor of fine particulate (2.5 microns in size and smaller) air pollution in the country.

Operational data
SNCR process needs to achieve temperatures of 800 ºC to 1200 ºC for efficient conversion. With the injection of hydrogen along with the NH_3 and carrier, optimum temperatures can be shifted to as low as 700 ºC. To achieve good mixing, the small amount of reactant is injected along with a carrier gas, usually air or steam. The ammonia produced in the sour water stripping (see Section 4.24.2) can be used as denox agent. The effectiveness of this process is very temperature dependent.

Applicability
It is typically applied to flue gases from heaters and boilers. No or very small space requirements. Space requirements are mainly restricted to NH_3 storage.

Economics
Cost considerations include the initial capital costs for modifying the furnace or boiler, piping to inject the reactant, the reactant supply system and a recurring cost for ammonia or urea to react with the NO_x. Cost estimates for the use of an SNCR after a power plant are reported in the Section 4.10.4.6. The following table gives cost effectiveness of the use of SNCR under different conditions

SNCR on	Cost effectiveness EUR/tonne NO_x removed (includes capital charge 15%)
Fired heaters and boilers firing refinery blend gas	2000-2500 1800-4300
Boilers firing Residual fuel oil	1500-2800 1500-4300
Fluid catalytic cracking units	1900
Details on the conditions are given in Annex IV	

Driving force for implementation
Reduction of nitrogen oxide emissions

Example plants
Applied to FCCs and boilers

Reference literature
[211, Ecker, 1999], [302, UBA Germany, 2000], [115, CONCAWE, 1999], [181, HP, 1998], [247, UBA Austria, 1998], [268, TWG, 2001]

4.23.3.3 Selective catalytic reduction (SCR)

Description
A further $deNO_x$ technique is known as catalytic $deNO_x$. The ammonia vapour is mixed with the flue gas through an injection grid before being passed through a catalyst to complete the reaction. Various catalyst formulations are available for different temperature ranges: zeolites for 300 - 500 °C, traditional base metals employed between 200 - 400 °C, for low temperature applications 150 - 300 °C metals and activated carbon are used. More information about this technique can be found in the Waste gas BREF [312, EIPPCB, 2001]

Achieved environmental benefits
It is especially suitable for situations where emission standards are strict. With SCR removal efficiencies of 80 to 95 % can be obtained. Residual NO_x stack levels of 10 - 20 mg/Nm^3 can be obtained by application of SCR in gas fired boilers and furnaces. When firing heavy residues emissions of < 100 mg/Nm^3 (3% O_2, half hourly mean value, efficiencies up to 90 %) can be achieved.

Cross-media effects
SCR has some cross-media effects as NH_3 slip of less than <2 – 20 mg/Nm^3 depending on the application and requirements or sulphate aerosols are controllable to very low levels. SCR operation at the end of its catalyst life may also entail bigger slip of NH_3. This means a constraint in conversion efficiency. The U.S. EPA identified ammonia as the single largest precursor of fine particulate (2.5 microns in size and smaller) air pollution in the country. N_2O generation can occur with some catalysts. At the end of its life, some components of the catalyst can be recycled and the other are dispose.

Operational data
The ammonia produced in the sour water stripping (see Section 4.24.2) can be used as denox agent. The catalytic $deNO_x$, process operates at low temperatures (250 ºC to 450 ºC). Operator and maintenance requirements are low for clean gas applications. More attention is required for applications where fouling substances like SO_3 and soot or dust are present in the off-gas. The presence of SO_3 will lead to formation of ammonium sulphates, which have a detrimental effect on the activity of the catalyst and lead to fouling of downstream heat exchangers. However sulphate deactivation can be avoided with a relevant temperature control. Reactivation of the catalyst can be executed by heating at 400°C, to counteract fouling a water washing step is generally applied. Soot has to be removed by blowing of the catalyst with steam or inert gas

(e.g. nitrogen), while a 'dummy' layer can optionally be applied for extra protection of the catalyst. If the flue gas contain particulates containing metals, metal deactivation may occur.
The NH_3 consumption is directly related to the NO_x concentration in the flue gas and amounts to about 0.4 tonne NH_3 per tonne of NO_x removed. The amount of ammonia is normally dosify in a 10 % more than the stoquiometric needs. The catalyst has a lifetime of 4 to 7 years for oil firing, for gas firing 7 to 10 years. The pressure drop of the catalyst bed will lead to a minor amount of additional power consumption from fans in the system or loss of efficiency in case of a gasturbine application (equivalent to 0.5 - 1 % of the heat-input). Additional fuel in the event of reheating the flue gas is necessary, corresponding to a loss of energy efficiency of 1 - 2 %. Common safety precautions need to be taken when using pure NH_3. To avoid elaborate safety measures (required for larger volumes of NH_3) the trend is towards using aqueous NH_3 or urea. The NH_3 storage also varies in size allowing 1 - 3 week operational hold-up.

When a so-called tail-end configuration is preferred (e.g. where the SCR is projected behind a wet scrubber, or at the end of a gasfired unit where the flue gas has reached a temperature of less than 150°C), it may be necessary to reheat the flue gases to have an adequate temperature for the reduction reaction. For these applications in-line burners are required. If the required temperature rise is larger than 70 - 100°C heat recuperation by means of a gas-to-gas heat exchanger could be cost-effective.

Applicability
Selective catalytic reduction (SCR) has been applied to combustion flue gases or process off-gases (e.g. FCC). The introduction of an SCR-system into an existing installation is a challenge due to space, pressure and temperature problems. Creative solutions can often be found to reduce the retrofit costs. Higher operating temperatures reduce the catalyst size and costs but introduce retrofit complexity. Lower operating temperatures increase the required catalyst volume and costs but often allow a simple retrofit.

Sofar, predominantly operating temperatures between 200 and 450°C prevail. These temperatures are normally available before the economiser section or the air preheater of a boiler. Gas fired refinery furnaces generally have a stack temperature of 150 - 300°C. Dependent on the flue gas sulphur content a medium (MT) or low temperature (LT) catalysts can be applied in tail-end configuration. Zeolite type catalysts have reached the market place. In the USA a number of gas turbines have been fitted with these catalysts, some other applications also exist (the DESONOX process, a combined technique for SO_2 and NO_x removal, has such catalyst). As for oil firing, only MT catalysts can be applied, because of the presence of sulphur and particulates. MT catalysts have been widely applied in coal fired power plants predominantly at conditions where the flue gas still contain all the fly-ash and SO_2 from the boiler. Two other configurations are low dust / high SO_2 level and low dust / low SO_2 level (tail-end configuration). There is little experience with the use of SCR for units applying vacuum residue as fuel. However, the power plant of the refinery Mider in Germany uses vacuum residue, visbreaker residue and FCC-slurry as fuel in its three oil-fired heaters. A SCR-plant in high dust configuration is installed after the heaters, cleaning the gas of NO_x to concentration less than 150 mg/Nm^3. The particular difference oil firing represent, lies in the nature of its fly ash. In contrast to coal, the fly ash is extremely fine (> 90 % fall in the category of $PM_{2.5}$), though the quantity is much less. The composition is also quite different. Coal fly ash predominantly consists of silica compounds, with a minimum of unburnt HCs. Oil fly ash contains metal oxides, soot and coke. Unabated fly-ash concentrations for oil firing are in the range of 100 - 600 mg/Nm^3 (with highest values for vacuum residues). SCR applied under these conditions may suffer from clogging by fly ash and sulphates (at coal firing the fly ash by its sandblasting effect keeps the catalyst clean). The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 - 4 %).

Pressure drop can be an important consideration as to whether SCR can be applied to a flue gas system. For this reason natural draft furnaces could probably not be fitted with it.

See Section 4.23.8 for combined flue gas desulphurisation and deNOxing.

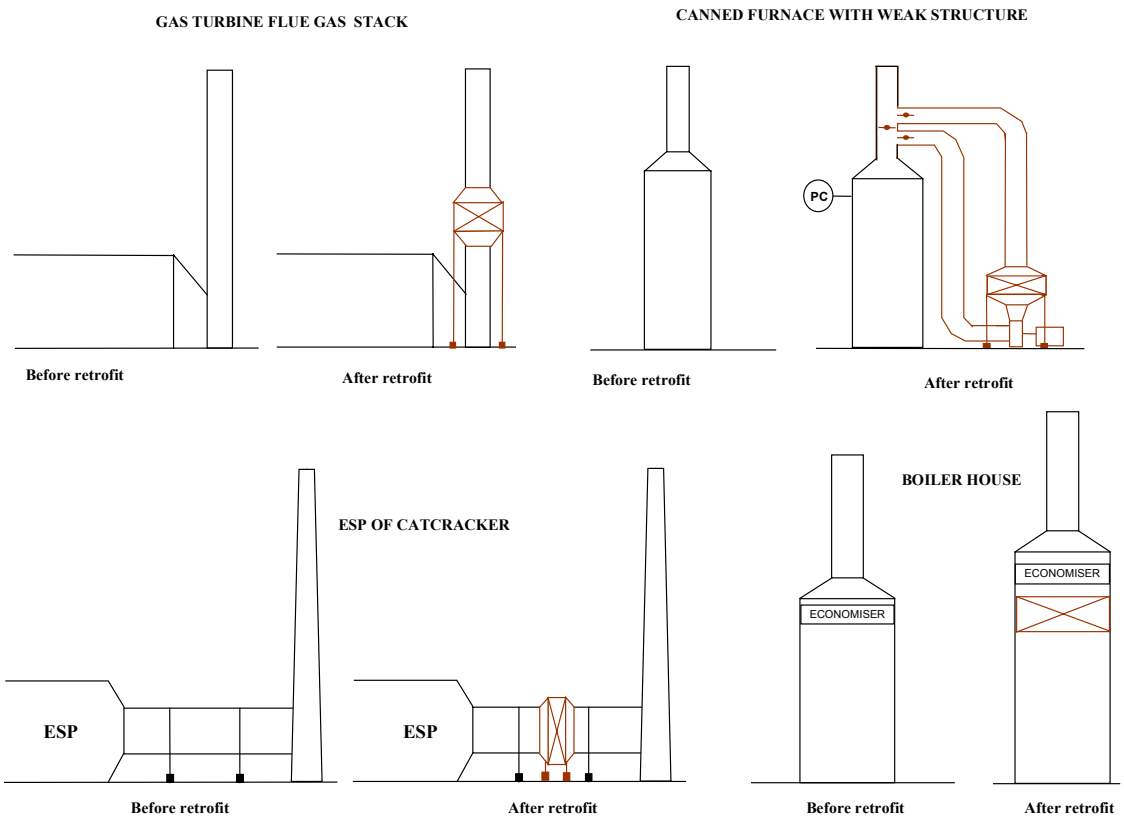


Figure 4.9: Some examples of SCR retrofit situations in refineries (clean gas situations)

Economics

See applications in each Section (Energy, catcracker and coker). The investment costs of new SCR-system depend largely on the flue gas volume, its sulphur and dust content and the retrofit complexity. The total erection costs for an SCR system (including all material costs - i.e. reactor system + first catalyst charge, NH_3 dosage & storage, piping & instrumentation -, engineering and construction costs) for a flue gas flow of 100000 Nm^3 are EUR 1 - 3 million for gas firing and between EUR 3 - 6 million for liquid fuel firing. For existing installations the possible location of the catalyst bed is often constrained by space limitations, which will lead to additional retrofit costs.

Operation costs comprise costs of energy, NH_3 and catalyst replacement. Specific costs for NH_3 and the catalyst charge are of the order of EUR 250 per tonne NH_3 respectively EUR 1 per Nm^3 of flue gas when firing gas and EUR 1.5 per Nm^3 of flue gas when firing oil.

Abatement	Plant size range	Approximate capital cost (EUR million installed)	Approximate operating cost per year (EUR million)
SCR	Flue gas flows 150000 Nm^3/h 650000 Nm^3/h	 5 - 8 13 - 23	0.87(costs are mainly for ammonia)
They are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, construction and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.			

The following table gives cost effectiveness of the use of SCR under different conditions

SCR	Cost effectiveness EUR/tonne NO_x removed (includes capital charge 15%)
Fired heaters and boilers firing refinery blend gas	8300-9800 12000 4200-9000
Boilers firing Residual fuel oil	5000-8000 4500-10200
Gas Turbines firing Natural or refinery blend gas	1700-8000
Fluid catalytic cracking units	2800-3300
Details on the conditions are given in Annex IV	

Driving force for implementation
Reduction of NO_x emissions

Example plants
It has been applied to FCC off-gases, gas turbines, process boilers, process heaters. SCR has been applied successfully on a large variety of applications: coal and oil fired power plants, waste incineration plants, diesel and gas engines, gas turbine plants, steam boilers and refinery furnaces (such us naphtha reformers, steam reformers, crude and vacuum distillations units, thermal cracking and hydroprocessing units) and FCC plants. Some examples are shown in Figure 4.9. Less experience is available with flue gas from firing high-sulphur residual oil.

SCR is used extensively on power plant in Japan, Germany, Austria and on gas turbine plant in Netherlands, California in the USA- SCR are also widely used in waste incineration plants. To date, SCR has been sucessfully applied worldwide in refinery processes as power plants and the FCCs. For example, at refineries in Japan, SCR applications are common. In European refineries, more than 6 applications have been found (Austria, the Netherlands and Sweden).

Reference literature
[302, UBA Germany, 2000], [211, Ecker, 1999], [118, VROM, 1999], [257, Gilbert, 2000], [175, Constructors, 1998], [181, HP, 1998], [115, CONCAWE, 1999], [268, TWG, 2001]

4.23.4 Particulates

PM emissions from refinery units entail particles present in the flue gas from furnaces, particularly soot, catalyst fines emitted from FCC regeneration units and other catalyst based processes, the handling of coke and coke fines and ash generated during incineration of sludges. Particulates generated in the refinery contain metals. Then, a reduction in the particules content reduces the metal emissions from the refinery. The particles may range in size from large molecules, measuring a few tenths of a nanometer, to the coarse dusts arising from the attrition of catalyst. Distinction is usually made between aerosols, < 1 - 3 µm and larger dust particles. The avoidance of fine particulates < 10 µm (PM_{10}) is particularly important for health reasons.

The available dust removal techniques can be subdivided into dry and wet techniques or a combination of the two. The usually at refineries applied techniques for dust emission reduction are briefly discussed below. Dry techniques are cyclones, electrofilters and filtration and wet techniques are wet scrubbers and washers. More information can be found in the waste gas BREF [312, EIPPCB, 2001].

4.23.4.1 Cyclones

Description
The principle of cyclone separation is based on centrifugal force, whereby the particle is separated from the carrier gas. More information can be found in the waste gas BREF [312, EIPPCB, 2001].

Achieved environmental benefits
Cyclones are used to reduce dust concentrations to the 100 - 500 mg/Nm^3 range. A novel cyclone design, called the rotating particulate separator (RPS), is able to effectively remove particles > 1 µm, this design, however, has a limited capacity compared to the conventional cyclone. Third cyclone achieve 90 % reduction of particulate emissions (100 - 400 mg/Nm^3). Modern multicyclones used as third stage cyclones achieves 80 % reduction of particulate emissions to about 50 mg/m^3. Particulate concentrations below 50 mg/Nm^3 are only achievable in combination with specific catalysts.

Cross-media effects
A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem.

Operational data
Cyclones can be designed for high temperature and pressure operation. Dust collection equipment is normally simple to operate and fully automated. For the dry separation no utilities are needed. For dust removal normally no additives are used. Sometimes the collected dust needs rewetting to avoid spreading of dust during handling.

Applicability
Multi-cyclones as employed in FCC-units, cokers are not able to remove fine particulate matter (PM_{10} = dust <10 µm) and therefore they are mainly used as pre-separation step.

Driving force for implementation
Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal containing cat fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
In refineries multi-cyclones and ESPs are employed in FCC-, heavy oil and residue cracker units.

Reference literature
[250, Winter, 2000], [118, VROM, 1999]

4.23.4.2 Electrofilters (ESP)

Description
The basic principle of operation of electrofilters (Electro-Static Precipitator, ESP) is simple. The gas is ionised in passing between a high-voltage electrode and an earthed (grounded) electrode; the dust particles become charged and are attracted to the earthed electrode. The precipitated dust is removed from the electrodes mechanically, usually by vibration, or by washing in so called wet electrofilters.

Achieved environmental benefits
ESP are capable of collecting bulk quantities of dust including very fine particles, <2 µm, at high efficiencies. ESP can achieve values of 5 - 50 mg/Nm^3 (95 % reduction or higher with higher inlet concentration only)

Cross-media effects
High voltage in an ESP introduces a new safety risk in refineries. A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem.

Operational data
An ESP uses some electricity. For dust removal normally no additives are used. Sometimes the collected dust needs rewetting to avoid spreading of dust during handling.

Applicability
Application of ESPs can be found in FCC-units, FGD processes, power plants and incinerators. It may not be applicable for some particulates with high electric resistance. They typically can be installed in new and existing plants.

Economics

Abatement	Plant size range	Approximate capital cost (EUR million installed)	Approximate operating cost per year (EUR million)
Electrostatic precipitator	Flue gas flows 150000 Nm^3/h 650000 Nm^3/h	 1.9 4.4	0.16
They are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, contruction and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.			

Operating costs are in the order of EUR0.5 to 10 per 1000 Nm^3 treated flue gas. Inclusion of fines disposal costs gives figures 2.5 - 3 times higher than the ones specified in the above table and 10 times higher the operating cost.

Driving force for implementation
Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal containing cat fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
In refineries multi-cyclones and ESPs are employed in FCC-, heavy oil and residue cracker units.

Reference literature
[250, Winter, 2000], [118, VROM, 1999]

4.23.4.3 Filtration

Description
Fabric filters

Achieved environmental benefits
Fabric filters can achieve values less than 5 mg/Nm^3

Cross-media effects
A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem. Filter material life is limited (1 - 2 years) and may add a disposal problem.

Operational data
Dust collection equipment is normally simple to operate and fully automated. For the dry separation only limited utilities are needed.

Applicability
Fabric filters are effective, except in applications with sticky dust or at of temperatures over 240 ºC. Filters are typically used for cleaning of flue gases with a volume < 50000 Nm^3/h.

Driving force for implementation
Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal containing cat fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Reference literature
[250, Winter, 2000], [118, VROM, 1999]

4.23.4.4 Wet Scrubbers

Description
In wet scrubbing the dust is removed by counter-current washing with a liquid, usually water, and the solids are removed as slurry. Venturi and orifice scrubbers are simple forms of wet scrubbers. The Electro-dynamic venturi washer (EDV), is a recent development which reduces the dust emission to 5 mg/Nm^3. The technique combines venturi with electrostatic dust separation. EDV is sometimes used in the flue gas treatment of combustion installations and incinerators.

Achieved environmental benefits
Particles sizes down to 0.5 µm can be removed in well designed scrubbers. Wet scrubbers reduce between 85 - 95 % of the particulates and can achieve values of particulate concentration < 30 - 50 mg/Nm^3. In addition to solids removal, wet scrubbers can be used to simultaneously cool the gas and neutralise any corrosive constituents. The collecting efficiency can be improved by the use of plates or packings at the expense of a higher-pressure drop.

Cross-media effects
A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem. Scrubbers for dust removal, may also be effective for SO_2 reduction.

Operational data
Dust collection equipment is normally simple to operate and fully automated. Wet scrubbing requires pumping energy as well as water and alkali.

Applicability
Spray towers have a low pressure drop but are not suitable for removing particles below 10 µm. Venturi and packed bed washers have been installed for sludge incinerators.

Economics
Operating costs are in the order of EUR0.5 to 10 per 1000 Nm^3 treated flue gas.

Driving force for implementation
Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal containing cat fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
Some FCC-units are equipped with scrubbers.

Reference literature
[250, Winter, 2000], [118, VROM, 1999]

4.23.4.5 Washers

Description
Ventury washers.
Centrifugal washers combine the cyclone principle and an intensive contact with water, like the venturi washer.

Achieved environmental benefits
Dust emissions can be reduced to 50 mg/Nm^3 and below if very large quantities of water are used such as in an absorber used in a two stage scrubbing system.
Dependent on the operating pressure and the construction, dust emissions can be reduced below 10 mg/Nm^3 with centrifugal washers or ventury washers.

Operational data
Dust collection equipment is normally simple to operate and fully automated.
Venturi washers, need to be operated at sufficient pressure and at full water saturation of the gas phase to reduce the dust emission.

Applicability
Wash columns, or absorbers with packing are applied in various processes.

Driving force for implementation
Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal containing cat fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
Ventury washers: they are mostly applied for removal of a combination of dust, acidic components (HCl and HF) at for example cokers and incinerators. For SO_2 removal scrubbing at pH ± 6 with caustic or lime is necessary.

Reference literature
[118, VROM, 1999]

4.23.4.6 Combination of particulate abatement techniques

Often a combination of techniques is applied, such as cyclone/ESP, ESP/venturi/wash column or a cyclone/venturi/absorber leading to >99 % dust elimination.

4.23.5 Sulphur management system

Sulphur is an inherent component of crude oil. Part of this sulphur leaves the refinery in its products, part of it is emitted to the atmosphere (already described in all the processes) and part of it is recovered by some processes located in the refinery for this purpose (more information about the sulphur split in a refinery in Section 1.4.1). Sulphur is an environmental issue that cannot be addressed in an integrated manner if sulphur coming out with the products is not considered. In other words, decreasing emissions from a refinery may result in the production of fuels (products) that may later be burned in a way that is not environmentally efficient, thereby jeopardising the environmental effort made in refineries.

Because it is such an integrated issue, proper sulphur management (See Annex VI) should also consider other topics that are not within the objectives of this document. For example, a global environmental impact assessment of sulphur dioxide emissions should contain:

1. Atmospheric emissions from processes generating SO_x (furnaces, boilers, FCC, etc.). Those issues are in fact included in this document in each of the process sections.

2. Atmospheric emissions from sulphur recovery units or of gases containing sulphur in an H_2S form before incineration. This category of sulphur is normally recovered, as shown in Section 4.23.5.2.

3. Atmospheric emissions generated by sulphur contained in products for which more stringent specifications already exist, such as gasolines, gasoils, etc. Those emissions cannot be considered here because they do not fall within the scope of IPPC legislation, but they should be considered as part of an integrated approach.

4. Atmospheric emissions generated by products with less stringent specifications (bunkers, coke, heavy fuel oil). Typically, those products (heavy residues) contain high quantities of sulphur. If they are not used in a proper way from the environmental point of view, the emissions can jeopardise the integrated approach to reducing sulphur emissions from the refinery sector. Another threat to this integrated approach is the exporting of those products to countries with less environmental control.

5. Sulphur contained in non-fuel products such as bitumen or lubricants is typically not identified as a problem.

In principle refiners have the following options and combinations thereof to reduce the SO_2 emissions of the refinery:

- increase the use of non sulphur containing gas (LPG, natural gas, etc.) discussed in Section 4.10 Energy system
- to lower the sulphur content of the fuels used (reduce the H_2S content in the refinery fuel gas with amine treating Section 4.23.5.1, gasification of heavy fuels Section 4.10, hydrotreatment of fuels in Section 4.13.2)
- to use low sulphur crudes discussed in Sections 4.10 Energy system
- increase the efficiency of the SRU discussed in Section 4.23.5.2 Sulphur recovery units (SRU)
- to apply end-of-pipe techniques to capture the SO_2 from the fumes (namely flue gas desulphurisation(FGD)) (those techniques are the ones discussed in Section 4.23.5.4and have been considered in Sections 4.5 Catalytic cracking and 4.10 Energy system).
- reduce SO_2 emission from typically small contributors whey they become significant part of the total emission. For example in the case of gas refineries, the overall picture of the sulphur emissions change because small contributors in liquid-fired refineries become significant.

In this section, only those processes dealing with the recovery of sulphur is going to be considered. Between 17 to 53 % (average 36 %) of the sulphur is recovered in European

refineries. H_2S formed at various processes such as hydrotreating, cracking, and coking in a refinery, finally ends up as contaminant in refinery fuel gas and treat gas streams. In addition to H_2S these gases also contain NH_3 and to a lesser extent CO_2 and traces of COS/CS_2. H_2S removal from these gases is achieved by extraction with an amine solvent. After regeneration of the solvent the H_2S is released and sent to a Sulphur Recovery Unit (SRU).

4.23.5.1 Amine treating

Description

Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulphide. This is typically accomplished by dissolving the hydrogen sulphide in a chemical solvent (absorption). Solvents most commonly used are amines. Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide may also be used. In the amine solvent processes, amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulphide is dissolved in the solution. The fuel gases are removed for use as fuel in process furnaces in other refinery operations. The amine-hydrogen sulphide solution is then heated and steam stripped to remove the hydrogen sulphide gas. In Figure 4.10 a simplified process flow diagram of an amine treating unit is shown.

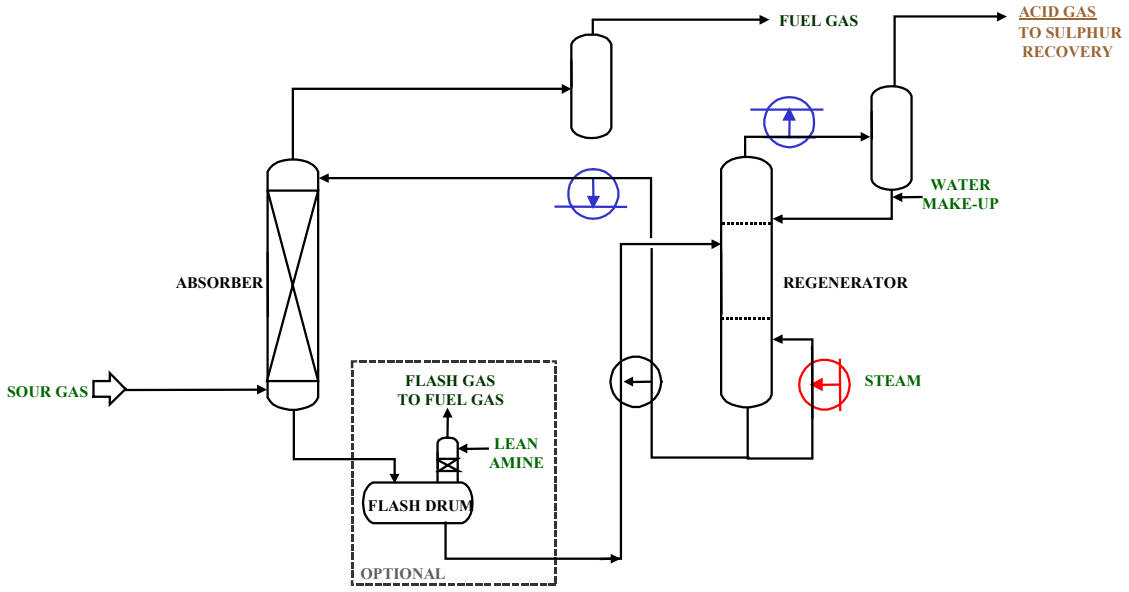


Figure 4.10: Simplified process flow diagram of an amine treating unit

The main solvents used are MEA (Mono ethanol amine), DEA (diethanol amine), DGA (diglycol amine), DIPA (Di-isopropanol amine), MDEA (Methyl diethanol amine) and a number of proprietary formulations comprising mixtures of amines with various additives. One important issue concerning the selection of the type of amine is the selectivity concerning H_2S and CO_2.

1. **MEA** has had a wide spread use, as it is inexpensive and highly reactive. However, it is irreversibly degraded by impurities such as COS, CS_2 and O_2, and therefore is not recommended to use when gases from cracking units are present.
2. **DEA** is more expensive than MEA but is resistant to degradation by COS and CS_2 and has obtained a wide spread use.
3. **DGA** is also resistant to degradation by COS and CS_2 but is more expensive than DEA and has the disadvantage to absorb also hydrocarbons.

4. **DIPA**, which is used in the ADIP process, licensed by Shell. It can be used for selective H_2S removal in the presence of CO_2 and is also effective in removing COS and CS_2.
5. **MDEA** is nowadays most widely used, MDEA has a similar characteristic as DIPA, i.e. it has a high selectivity to H_2S, but not to CO_2. As MDEA is used as a 40 - 50 % solution (activated MDEA) in water, this has also potential energy savings. Because of the low selectivity for CO_2 absorption DIPA and MDEA are very suitable for use in Claus Tailgas amine absorbers, as these do not tend to recycle CO_2 over the Claus unit. MDEA is applied as a single solvent or as in proprietary formulation comprising mixtures.

Achieved environmental benefits

Sulphur is removed from a number of refinery process off-gas streams (sour gas or acid gas) in order to meet the SO_x emissions limits of the applicable regulation and to recover saleable elemental sulphur. The amine treating unit produces two streams for further use/processing in downstream units:

- The treated gas stream usually can contain between 20 and 200 mg/Nm^3 H_2S (H_2S content depends on absorber operating pressure; at only 3.5 bar H_2S level is 80 – 140. At higher pressures as 20 bars the H_2S level is around 20).
- The concentrated H_2S/acid gas stream is routed to the SRU for sulphur recovery (discussed in next Section 4.23.5.2).

Cross-media effects

	Source	Flow	Composition	Comments
Effluent: amine blow down	Amine regenerator	10 - 50 t/yr for a 5 Mt/yr refinery	Decomposed amine up to 50 % in water	In order not to disturb the biotreater operation and to meet effluent discharge specifications on N-Kj an storage tank or production planning can be used to control very small flow to the WWTP
Waste 1:	Amine filter cleaning residue	plant specific	FeS and salt deposits	Removed by skid mounted unit operated by a specialised contractor (usually the filter supplier)
Waste 2:	Saturated activated carbon from skid mounted unit	plant specific	Decomposition products, heavy ends and amine emulsions	The saturated activated carbon filling has to be replaced occasionally for disposal or regeneration

Operational data

The use of selective amines should be considered, e.g. for a stream containing carbon dioxide. Measures should be taken to minimise hydrocarbons entering the sulphur recovery system; operation of regenerator feed drums should be controlled to prevent hydrocarbon accumulation in, and sudden release from, the amine regenerator as this is likely to lead to an emergency shut-down of the SRU.

Utility consumption per tonne of H_2S removed in an amine treating unit is approximately:

Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m^3/t, ΔT =10°C)
70 – 80	1500 - 3000	25 - 35

Usually a fresh solvent make up rate of 10 - 50 t/yr is required to maintain solvent strength for a 5 Mt/yr refinery.

Amine solutions should be re-used wherever possible and where necessary, suitably treated before disposal which should not be to land. Recycling of monoethanoleamine-solutions:

Corrosive salts, which concentrate during recycling, can be removed via ion exchange techniques. Some proprietary solutions may be biodegradable under suitable conditions.

It is important also that the amine processes have sufficient capacity to allow maintenance activities and upsets. This sufficient capacity can be achieved by having redundancy equipment, apply load shedding, emergency amine scrubbers or multiple scrubber systems.

Applicability
Process off-gas streams from the coker, catalytic cracking unit, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulphide mixed with light refinery fuel gases. Emergency H_2S scrubbers are also important.

Economics
The cost of upgrade the refinery amine treatment system (2 %) to meet 0.01 to 0.02 % v/v of H_2S in fuel gas is around 3.75 to 4.5 million EUR. This cost is battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.

Driving force for implementation
Reduce the sulphur content of flue gases.

Example plant(s)
Common technology used all over the world

Reference literature
[118, VROM, 1999], [211, Ecker, 1999], [19, Irish EPA, 1993], [268, TWG, 2001]

4.23.5.2 Sulphur recovery units (SRU)

H_2S-rich gas streams from Amine Treating Units (see above section) and Sour Water Strippers (see Section 4.24.2) are treated in a Sulphur Recovery Unit (SRU) normally a Claus process for bulk sulphur removal and subsequently in a Tail Gas Clean-up Unit (TGCU, see later in this section) for trace H_2S removal. Other components entering the SRU include NH_3, CO_2 and to a minor extent various hydrocarbons.

4.23.5.2.1 Claus Process

Description
The *Claus process* consists of partial combustion of the hydrogen sulphide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulphur dioxide and unburned hydrogen sulphide in the presence of a activated alumina catalyst to produce elemental sulphur.

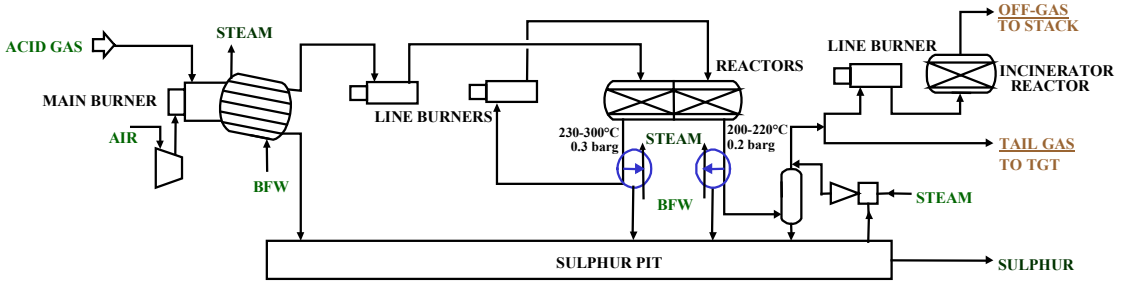


Figure 4.11: Simplified process flow diagram of a sulphur recovery unit (CLAUS) unit

The capacity of the Claus plants can be increased with the use of oxygen instead of air (*OxyClaus* process) however this has not any beneficial effect in the efficiency of the Claus plant. Use of this process increase capacity up to 200 % in existing Claus sulphur recovery units, or for a more economical design of Claus sulphur units.

Achieved environmental benefits

Number of Claus reactors	Efficiency (%H_2S converted)
1	90
2	94 - 96
3	97 - 98

Table 4.36: Efficiencies of the Claus process

Cross-media effects

Emissions based on 20000 t/yr SRU

	Source	Flow	Composition min/max	Comments
Emissions: CO_2, SO_2, NO_x	Incinerator off-gas	0.2 % of total H_2S-load to the SRU	SO_2 1500 mg/Nm^3 Through presence of NH_3 non-catalytic deNOxing takes place	Amount of SO_2 released depends on total sulphur production and overall sulphur recovery
Effluent:	Knock-out drum for water in SWS off-gas	0.02 m^3/h	H_2S: 50 mg/l; Phenol: 100 mg/l; NH_3: 2000 mg/l	To be treated in the SWS
Waste	Spent SRU catalyst	plant specific	Mainly Al_2O_3	

The reduction of SO_2 leads to an increase of the CO_2 emission. For example for a 100 t/d sulphur claus plant, the application of three reactors would lead to an emission of 4.8 tonnes of sulphur per day at a cost of 8.5 tonnes of CO_2 per day.

Operational data

- Feed/air ratio control, temperature control of the furnace, reactors and condensers and good demisting of liquid sulphur, especially from the final condenser exit gas stream are important parameters in obtaining maximum sulphur recovery. Good control and availability is crucial as a technique, to deliver any design targets. In this line, the use of state-of-the-art control and monitoring systems can be seen as an important technique. Use of a tail gas analyser linked to the process control system (feedback control) will aid optimum conversion during all plant operating conditions, including changes to sulphur throughput
- To have a SRU configuration with sufficient capacity for the H_2S feed to the unit including the sourest crude oil to be used is important. The duplication of the SRU capacity is important to consider to obtain low sulphur emissions. This enough capacity also should consider to allow the scheduled maintenance activity to proceed every two years, without a significant increase of sulphur emissions.
- To have utilisation factors close to 100% increase how efficient the units are used. Those capacity factors should plan also major turnaround maintenance.
- use a good furnace burning-zone design and effective furnace temperature and oxygen control systems where sour water stripper off-gases are a feed stream, because the process must also be designed and operated to complete the destruction of ammonia. Ammonia breakthrough may lead to deposition and blockages of catalyst beds by ammonium salts (eg carbonate/sulphate) and these SRUs need to be monitored for evidence of this.

The utilities necessary in the SRU are summarised in next table

Fuel (MJ/t)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m^3/t, ΔT=10 °C)
1000 – 1600	60 - 75	1500 - 2000	0 - 20

In some cases, the SRU need a pilot flame when the H_2S concentration is so low that a stable flame cannot be achieved.

Applicability
Fully applicable

Economics

Abatement	Plant size range	Approximate capital cost (EUR million installed)	Approximate operating cost per year (EUR million)
Upgrade SRU with O_2 enrichment to increase throughput from100 t/d to 170 t/d.	100 t/d	2.1 - 5.3	1.6 (costs are for oxygen)
They are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.			

Another example of the upgrade of SRU with oxygen enrichment (Oxyclaus)
Economics: For a reference 200 tpd sulphur recovery unit (Claus and tail gas unit) requiring 99.9 % overall sulphur recovery, capital cost savings of $2 - 3 million are achievable with oxygen enrichment as compared to an air only design. Based on typical pipeline oxygen costs of $35 per tonne, even if oxygen enrichment were used 100 % of the time, it would take over 8 years for oxygen costs to equal the increamental capital saving.

Example of the economics of the installation of a third Claus reactor.
Capacity of process: 30000 t/yr sulphur production (sulphur recovery efficiency 94 - 96 % for a two stage unit); Volume of gas: 60 million m^3/yr; Pollutant initial concentration: 34000 mg SO_2/m^3 (1.2 % molar or 2.3 % weight, rest considered as air) The investment cost to build a new third reactors is between EUR 2 and 3 millions and the operating cost around EUR 0.1 million per year.

Driving force for implementation
Reduction of sulphur emissions

Example plants
In the market, it exists more than 5 licensors of this process. The Claus process is public domain and virtually applied at any refinery. Two stages Claus process is the most common in Europe. More than 30 Oxyclaus systems are in operation in the world.

Reference literature
[250, Winter, 2000], [258, Manduzio, 2000], [115, CONCAWE, 1999], [45, Sema and Sofres, 1991], [181, HP, 1998], [114, Ademe, 1999]

4.23.5.2.2 Tail Gas Treatment Unit (TGTU)

Description
Current methods for removing sulphur from the hydrogen sulphide gas streams are typically a combination of two processes: the Claus process (See section above) followed by a tail gas clean-up or treatment unit. Since the Claus process by itself removes about 96 % (2 stages) of the hydrogen sulphide in the gas stream, the TGTU processes are often used to further recover sulphur.

More than 20 processes for TGTU have been developed in order to enhance the recovery of Sulphur compounds from natural gas and/or refinery sources. TGTU processes can be broadly divided according to the principles applied:

- *Dry bed processes*, where the main process step is achieved on a solid catalyst. Two paths have been followed within this group: a) Extend Claus reaction on a solid bed, b)Oxidise sulphur compounds to SO_2 prior to absorption, or reaction.

- *Liquid Phase Sub-DewPoint processes*, consisting of extending the Claus reaction under sub-dewpoint conditions in liquid phase.

- *Liquid scrubbing processes*. There are two main categories, H_2S scrubbing processes and SO_2 scrubbing processes. In the most commonly applied configurations, H_2S or SO_2 are recycled to the upstream Claus Unit.

- *Liquid Redox process*. Liquid phase oxidation processes to absorb H_2S.

The first and third categories can further be divided in sub-categories depending on the sulphur recovery method used. It should be noted that a strict distinction between dry beds and liquid scrubbing processes may become uneasy as some arrangement combine the capabilities of both types of processes. Some processes belonging to the four groups above-mentioned are further explained below; this list is not intended to be exhaustive:

The ***H_2S Scrubbing*** process is by far the most widely applied. The concept underlying H_2S scrubbing processes are:
- Hydrogenation and hydrolysis of all sulphur compounds to H_2S passing it through a cobalt-molybdenum catalyst with the addition of a reducing gas
- Absorption of H_2S by an amine solution (generic amine or specialty amine)
- Regeneration of the amine solution and recycle of the H_2S to the upfront Claus reaction furnace.

Several Licensor currently propose variations on the H_2S scrubbing process, using solvents available on the market place, or in some instances proprietary solvents.

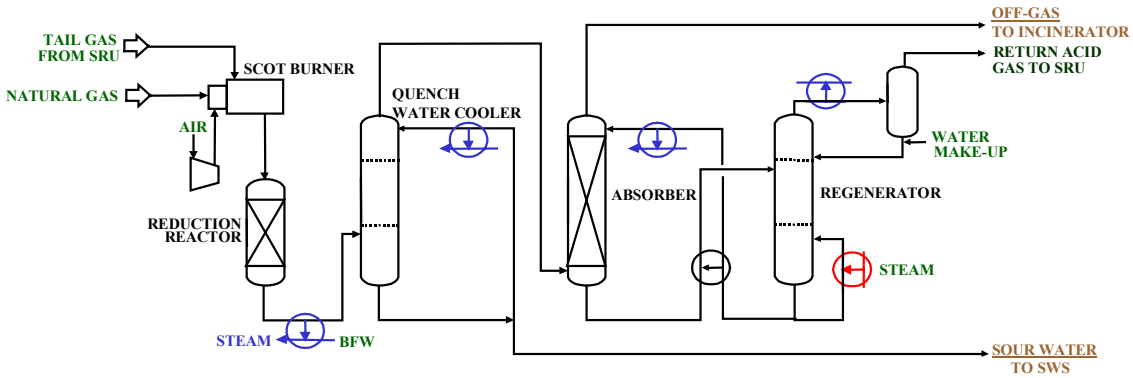


Figure 4.12: Simplified process flow diagram of a tail gas Claus unit (SCOT) unit

The ***Sulfreen*** process is a dry-bed, sub-dew point absorption process based on the extension of the Claus reaction, i.e. catalytic oxidation of H_2S to S. Basically consists of two (occasionally three for large capacities) Sulfreen reactors in series with the Claus reactors. Activated Alumina is used as a catalyst. Regeneration is needed since the sulphur accumulates on the catalyst decreasing its activity. Sulphur from the hot regeneration stream is condensed in a dedicated condenser. Two variations are used: Hydrosulfreen and DoxoSulfreen.

The *HydroSulfreen* adds a conversion step upstream of the first Sulfreen reactor, to perform the hydrolysis of COS and CS_2 to H_2S with the help of a activated Titanium oxide Claus catalyst.

The Claus reaction takes place in the HydroSulfreen reactor and produced sulphur is condensed in a dedicated condenser

The *DoxoSulfreen* concept is based on two ideas: the upstream units are operated to get a slight excess of H_2S, compared to the quantity necessary to maintain the Claus ratio, therefore a nearly total SO_2 conversion takes place on the conventional Sulfreen catalyst; then the remaining H_2S is directly oxidised to elemental Sulphur

In the **Beaven process**, the hydrogen sulphide in the relatively low concentration gas stream from the Claus process can be almost completely removed by absorption in a quinone solution. The dissolved hydrogen sulphide is oxidized to form a mixture of elemental sulphur and hydro-quinone. The solution is injected with air or oxygen to oxidize the hydro-quinone back to quinone. The solution is then filtered or centrifuged to remove the sulphur and the quinone is then re-used. The Beaven process is also effective in removing small amounts of sulphur dioxide, carbonyl sulphide, and carbon disulphide that are not affected by the Claus process. These compounds are first converted to hydrogen sulphide at elevated temperatures in a cobalt molybdate catalyst prior to being fed to the Beaven unit.

The **CBA** (cold bed absorption), process is very similar to the Sulfreen process except in the fact that the CBA process uses a hot process stream indigenous to the Claus process to accomplish regeneration of the sulphur loaded catalyst bed. The hot process stream is part of the effluent of the first Claus reactor. Several configurations are available depending on the number of Claus converters.

The **Clauspol** is a process where the tail gas is put in contact with a solvent (polyethylene glycol) and the reaction of H_2S and SO_2 is catalysed by a dissolved catalysts. (sodium salt of an inorganic acid) which is a solvent for H_2S and SO_2, but not for liquid sulphur.The Claus reaction can therefore proceed at low temperature (120 °C) and is shifted further to the right as the produced sulphur is removed from the reaction medium, as it is not soluble and separates.

The ***Superclaus*** process is based on two principles:
- Operating the Claus plant with excess H_2S to minimise the SO_2 content in the Claus tail gas. This feature simplifies and makes more flexible the air ratio control.
- Selective oxidation of the remaining H_2S in the Claus tail gas by means of specific catalyst which efficiently convert the remaining H_2S in the presence of water vapour and excess oxygen to elemental sulphur only.

This reaction takes place in a specific converter (oxidation reactor), downstream of a two or three reactors traditional Claus unit. The catalyst used is an alumina based catalyst coated with iron oxide and chromium oxide layers.

The ***LO-CAT*** process. Absorption and regeneration are performed in a single vessel divided in two sections: the centerwell and the outer space where aeration with air is performed. The purpose of the Centerwell is to separate the sulphite ions from air in order to minimize by-product formation (e.g. thiosulphate). The difference in aeration (and therefore of density) between the centerwell and the outer space give sufficient driving force for solution circulation between the absorption and the regeneration zones without the need of a specific pump. The last type of processing scheme is called the “aerobic unit” and is used to treat air contaminated with H_2S. All reactions take place in the same vessel, at the expense of increased by-product formation, but with the advantage of a reduced capital cost.

The *SO_2 abatement* from the Claus plant is a process that uses a physical scrubbing mechanism to remove SO_2 from the incinerated tail gas of a Claus plant. The recovered SO_2 is recycled to the inlet of the Claus plant unit.

Achieved environmental benefits

Tail gas treatment units increase the overall recovery of H_2S decreasing the sulphur emissions from the refinery. For example, if a refinery has a 100 t/d SRU, with a two stage Claus reactor

emits around 5 t/d of sulphur. If a tail gas clean-up process is included in such a refinery the emissions of sulphur may be reduced to 0.5 t/d, representing that a reduction of 90 % of the sulphur emissions from the sulphur recovery units. Next table shows the expected overall sulphur recovery yield, the resulting additional recovered sulphur and the dry basis sulphur emission (in the form of SO_2 specie) after incineration, of the tail gas treatments considered in this Section.

	Expected sulphur recovery yield	Expected additional sulphur recovered	Expected SO_2 emissions (Dry Basis)
Process	**(%)**	**t / d**	**mg / Nm^3**
Claus	96.01	-	13652
Superclaus	98.66	2.77	4631
Sulfreen	99.42	3.56	2010
Beavon	99-99.9	-	-
CBA	99 - 99.50	3.65	1726
Clauspol	99.5 – 99.9		
Clauspol II	99.60	3.75	1382
SO_2 abatement	99.9		
HydroSulfreen (1)	99.67	3.82	1066
DoxoSulfreen (2)	99.88	4.04	414
RAR	99.94	4.10	242
LO-CAT II (3)	99.99	4.16	18
SCOT	99.5-99.99		

(1) Sulfreen reactors and hydrolysis section
(2) Sulfreen reactors, hydrolysis section and DoxoSulfreen reactors
(3) As LO-CAT II tail gas cannot be incinerated, sulphur is in the form of H_2S specie.

Table 4.37: Expected overall sulphur recovery yield, the resulting additional recovered sulphur and the SO_2 emissions (dry basis) after incineration

Cross-media effects

The reduction of SO_2 leads to an increase of the CO_2 emission. For instance the application of a tailing gas treatment would lead to a SO_2 reduction of 96 % (if compared with the three reactor option), however at an increase for CO_2 of 110 %. For example for a 100 t/d sulphur claus plant with three reactors, the application of a TGTU would reduce the emissions of SO_2 to 0.1 t/d but at a price of increasing the CO_2 emissions to 18 t/d.

Emissions based on 20000 t/yr SRU/TGCU.				
	Source	**Flow**	**Composition min/max**	**Comments**
Effluents	Sour water from quench column for SRU off-gas	1m^3 / tonne S produced (2 m^3/h)	H_2S: 50 mg/l; Phenol: 100 mg/l; NH_3: 2000 mg/l	To be treated in the SWS
Waste: SCOT	Spent TGCU catalyst	Regeneration and disposal 20 - 100 t/yr	2 - 8 % Ni/Mo on Al_2O_3, S: 5 - 15 %; Coke: 10 - 30 %	Spent Claus catalyst is pyrophoric and needs purging with N_2

Table 4.38: Cross-media effects associated to some of the TGTU

Operational data

Good control and availability is crucial as a technique, to deliver any design targets. The estimate of operating costs, including sulphur produced, utilities and chemicals as well as additional manpower expense are given in the following table:

	OPERATING COST ESTIMATE						
	Utilities Consumption	Utilities Production	Catalyst Consumption	Chemical Consumption	Operation Cost	Recovered Sulphur	TOTAL
Process	**k$ / y**	**k$ / y**	**k$ / y**	**k$ / y**	**k$ / y**	**k$ / y**	**k$ / y**
Sulfreen	52	-6	37	n/a	20	-24	**79**
HydroSulfreen	82	-22	74	n/a	20	-26	**128**
DoxoSulfreen	125	-29	264	n/a	30	-27	**363**
CBA	36	n/a	13	n/a	10	-25	**34**
Superclaus	106	-32	44	n/a	10	-19	**109**
Clauspol II	52	n/a	26	26	20	-25	**99**
RAR	133	n/a	16	10	30	-28	**161**
LO-CAT II	138	n/a	15	148	30	-28	**303**

Table 4.39: Operating costs of some TGTU units

Applicability

Applicable to both new and existing plants. Capacities range from 2 to more than 2000 tonnes of sulphur per day from the combined Claus/tail gas treatment units.

Economics

The cost of the SRU depends strongly on the type of tail gas treatment. Following several tables show some examples of economics of the TGTUs.

Abatement	Plant size range	Approximate capital cost (EUR million installed)	Approximate operating cost per year
SRU including Tailgas treatment unit (TGTU) to give>99 % S recovery	50 t/d 100 t/d 250 t/d	12 19 35	New SRU operating cost approximately equal to existing costs.
Tailgas treatment unit to improve SRU recovery to 99 %	50 t/d 100 t/d 250 t/d	1.6 2.1 2.9	Operating cost relatively low
Tailgas treatment unit to improve SRU recovery to 99.8 %	50 t/d 100 t/d 250 t/d	3.5 4.4 6.3	Operating cost relatively low
They are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.			

Usual practice is to relate the capital cost of the TGCU to the one of the up front Claus unit. The following table gives estimate of such ratio, for a 100 t/d Claus unit (including catalyst) in a refinery environment.

Process	Without Licence, Catalysts and Chemicals (%)	Licence, Catalyst and Chemicals included (%)
Sulfreen	29.2	30.9
HydroSulfreen (1)	44.7	47.6
DoxoSulfreen (2)	67.0	76.0
CBA	35.4	36.1
Superclaus	12.3	15.3
Clauspol II	33.7	37.3
RAR	67.2	67.5
LO-CAT II	46.8	49.0
(1) Sulfreen reactors and hydrolysis section (2) Sulfreen reactors, hydrolysis section and DoxoSulfreen reactors		

The reference to the upstream sulphur unit is indicative and corresponds to the way this kind of comparison is usually presented in the literature. This comparison should be taken with care when comparing with other studies, as the capital cost of a sulphur unit may vary greatly.

A particular example of the cost of a three stages Claus plant plus TGTU superclaus process is shown in the following table:

3rd Stage Claus plus super-Claus (1997)		
DESCRIPTION	k EUR	%
INDIRECT COSTS		
Detailed Engineering	8.0	27
Field Supervision	1.6	5
Owner	2.4	8
Subtotal	12.0	40
DIRECT COSTS – EQUIPMENT		
Materials	7.3	25
Catalysts and Chemicals	0.6	2
Subtotal	7.9	27
DIRECT COSTS - NON EQUIPMENT		
Subcontracts	8.6	29
Temporary Construction & Consumables	0.4	1
Subtotal	9.0	30
Total Capital	28.9	97
EXPENSE		
Licensing Fee	0.5	2
Subtotal	0.5	2
Final Total	29.4	99

Table 4.40: Economics of tail gas treatment units of the sulphur recovery units

Another example of the cost of a TGTU unit reports that for a Clauspol unit treating a typical Claus unit tail gas, combined production of 100 tonnes of sulphur per day (ISBL 1998 Gulf Coast location), the investment (excluding engineering and license fees) came up to 3 million US$.

The following table shows specific costs data for SO_2 abatement under the assumptions outlined in Annex IV.

Name of the technique	EUR/tonne SO_2 abated (1)	EUR/tonne SO_2 abated (2)
3rd reactor		32
Stand Alone Scot	321-538	32
Cascade Scot Common regenerator		32
Super Claus	155-228	32-161
Super Claus + Claus Stage		32-160
Clauspol	198-330	32
Sulfreen	174-288	32-160
Hydro-sulfreen	253-417	32-160
CBA/AMOCO cold real absorption	169-300	-
(1) [346, France, 2001]. Bases for calculation in Annex IV (2) [115, CONCAWE, 1999] Bases for calculation in Annex IV		

Driving force for implementation
Reduction of sulphur emissions and recovery of sulphur.

Example plants

Technique	Number of installations all over the world
Beavon	More than 150 installations
Clauspol	More than 50 units
Sulfreen/Hydrosulfreen	More than 150 units in operation
Superclaus	More than 70 commercial plants

Table 4.41: Approximate number of commercial installations in the world

Reference literature
[195, The world refining association, 1999], [112, Foster Wheeler Energy, 1999], [309, Kerkhof, 2000], [257, Gilbert, 2000], [115, CONCAWE, 1999], [107, Janson, 1999], [181, HP, 1998], [114, Ademe, 1999], [45, Sema and Sofres, 1991], [346, France, 2001]

4.23.5.2.3 Sulphur storage

Description
In order to reduce the emissions of H_2S from the storage and transport of liquid sulphur, the amount of H_2S and polysulphides in the sulphur can be reduced to <10 ppm by oxidation or treatment with a suitable additive.

Reference literature
[268, TWG, 2001]

4.23.5.3 Hydrogen sulphide and light mercaptan removal

Description
The system works with a fixed-bed or batch-type granular reactant.

Achieved environmental benefits
Processes for odour and low emission control features.

Applicability
Applications to waste water sytems, land oil tanker vent, oil storage and transportation, and bitumen plants.

Driving force for implementation
Processes for odour and emission control features.

Example plants
More than 1000 applications worldwide.

Reference literature
[181, HP, 1998]

4.23.5.4 Sulphur dioxide abatement techniques

Flue gas desulphurisation is a technique by which SO_2 is removed from flue gases or other waste gases. The process often involves an alkaline sorbent which captures SO_2 and transforms it to a solid product. SO_2 in refinery waste gases may have unabated concentration levels of 1500 - 7500 mg/m^3. Various FGD methods exist with varying SO_2 removal efficiencies. The FGD market is dominated by the so-called wet lime/limestone process followed by spray dry scrubbers, and the application of sorbent injection and regenerable processes. More information can be found in the Waste gas waste water BREF [312, EIPPCB, 2001].

Systems either of the regenerable or the non-regenerable type, do exist for SO_x removal only, but also for simultaneous removal of dust and NO_x. Most of these combined processes are still in the development phase, but some are commercially available already. They are or may become competitive with systems consisting of separate units for SO_2 elimination (i.e. wet scrubbers) and NO_x removal (i.e. SCR).

Description
Additive injection (AI) and *Spray Dry Absorber* (SD) are scrubbing processes that remove SO_2 according to the same principle as WS (reacting with a Ca-based sorbent) however, without the complicating requirements for producing a high-grade gypsum by-product (i.e. prescrubbing and oxidising). The by-product is a mixture of sulphites, sulphates and fly-ash for which there are few or no useful applications.

The *AI-process* provides moderate SO_2 removal at relative low sulphur loads. A dry sorbent is injected in the furnace. The sorbent used is limestone or hydrated lime (for small boilers, more active sodium bicarbonate ($NaHCO_3$) is injected in the flue gas duct).

The *SNOX* process combines high removal of SO_2, NO_x and particulates. More information see Section 4.23.8

The s*eawater scrubbing* process uses the natural alkaline - bicarbonates - of seawater to remove SO_2. This implies a potential for high removal efficiencies. The discharge will contain sulphate and chlorine ions - which are a natural constituent of seawater.

In the *Walther* (WA)-process, SO_2 is absorbed by spray injection of aqueous ammonia, yielding ammonium sulphite. The sulphite is subsequently oxidised to sulphate. The ammonium salt solution from the scrubbing section is concentrated in an evaporation unit and granulated. The end-product is a marketable fertiliser.

The *Wellman Lord* (WL)-process is the most widely used regenerable process. The process is based on sodium sulphite/bisulphite equilibrium.

Present-day *Wet Limestone Scrubber* (WS)-systems are very much improved and less complex than the earlier systems. Generally a limestone/water slurry is used as the sorbent. Gypsum is produced by oxidation (aeration) in the sump of the absorber.

Achieved environmental benefits

Desulphurisation technique	SO_2 reduction (%)	Other benefits
Additive injection (AI) and Spray Dry Absorber (SD)	> 92	Like with WS the SD-system combines good removal of SO_2, SO_3, chlorine and fluorine (> 90 % on sulphur compounds, 70 - 90 % on the halides).
AI-process	50 - 70	
Seawater scrubbing	99	The acidic effluent from the absorber flows by gravity to a water treatment plant. Here, air is blown into the water to convert the absorbed SO_2 into dissolved sulphate and to saturate the seawater with oxygen (COD treating). The pH is adjusted back to neutral partly by added seawater and partly by aeration. The effluent from the treatment plant is discharged directly back to the sea.
SNOX	99.9	Up to 95 % for nitrogen oxides. Particulates are essentially completely removed.
Walther	> 88	Product that can be sell as fertiliser. This product has to meet certain criterias (especially heavy metal content)
Wellman Lord	98 (100 mg/Nm^3).	Sulfur is recovered as a product. For the removal of SO_3, ammonia is injected, which leads to the formation of ammoniumsulphate. Ammonium sulphate may be used as a fertiliser under certain circumstances (especially heavy metal content).
Wet Limestone Scrubber	90 - 98	If the chlorine content is low, this system produces no waste water.

Table 4.42: Achieved environmental benefits of the desulphurisation processes

Cross-media effects

Desulphurisation technique	Cross-media effects
Additive injection (AI) and Spray Dry Absorber (SD)	As the by-product generated by these techniques contains unreacted lime, it requires conditioning before disposal.
AI-process	The disposal of the by-product requires similar care as for SD.
Seawater scrubbing	Some fly ash with associated heavy metals and organic substances is transferred to the seawater.
SNOX	
Walther	The process does not generate solid by-products or liquid waste. If particulates with possible content of metals are present in the flue gas they appear together with the product.
Wellman Lord	Dust: NH_3 is injected to prevent the formation of SO_3. Therefore up to 80 % of the ash consists of $(NH_4)_2SO_4$, which can be used as a fertiliser or as a basic material for NH_3 production. Waste water from the pre-scrubber has a sour water quality with a pH of around 2 and must be neutralised and stripped. The purified water may still contain up to 100 mg/l ammonia, but most often, values are in the range of 10 to 50 mg/l.
Wet Limestone Scrubber	Waste water generated by the gypsum dewatering process contains suspended solids and trace elements (metals, chlorides) and is to be treated by sedimentation, flocculation and filter pressing. The filter cake is disposed of by landfill and the purified water is drained to sewer.
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Those techniques generally produce a lot of waste.

Table 4.43: Cross-media effects of the desulphurisation processes

Operational data

Desulphurisation technique	Operation data
Additive injection (AI) and Spray Dry Absorber (SD)	Being a dry process, corrosion conditions are less severe than is the case with WS. Hence, the scrubber is usually made of (uncoated) carbon steel. Calcium chlorides may yet prompt acid corrosion as they precipitate on the absorber walls and attract moisture. Recycling by-product with wet flue gas to the sorbent make-up tank may suffer from plugging; regular cleaning is required.
AI-process	The system is less effective as regards the removal of HCl, hence the fuel should not have a higher Cl content than approximately 0.3 % for corrosion prevention.
Seawater scrubbing	The process offers simplicity, thus high availability,
Walther	Chloride aerosols and a visible waste gas plume may occur when fuels are used with a high chlorine content. Aerosol formation can be mitigated by increased liquid to gas ratio in the absorber and the use of multiple tube filters. Deposits of sulphates can be removed by blowing with hot flue gas or by water washing. NO_x has no influence on the FGD process as it does not react with ammonia.
Wellman Lord	Operational aspects include problems with respect to fouling, corrosion and erosion. In the pre-scrubber deposits of ammonium sulphate can occur. The evaporator is susceptible to wear by the abrasive salt slurry, corrosion during shutdowns and mechanical strains related to the high speed centrifuge.
Wet Limestone Scrubber	Through good engineering practice (liberal sizing of spray systems and mixers, applying washing on demisters etc.) deposits and plugging of the various components can largely be avoided. For high-grade gypsum production, forced oxidation and good pH control is required. Furthermore, good quality limestone (> 93 % purity in $CaCO_3$) must be used and dust and trace elements, in particular chlorine, should be removed by prescrubbing of the raw gas and dewatering and optional washing of the product. Organic buffers (such as adipates and dibasic acid) can be used for pH control, thereby substantially enhancing the SO_2 removal efficiency – by typically 4 %. Early corrosion problems have been overcome; often rubber lining is used in the absorber, requiring some care in view of abrasion damage.

Table 4.44: Operational data of the desulphurisation processes

Applicability

Desulphurisation technique	Applicability
Seawater scrubbing	Because particulates (may be containing heavy metals) are tranferred to the seawater, a particulate abatement technique is necessary previous the seawater scrubbing.
SNOX	The three main treatment areas in refineries of applications of this sytem are H_2S gases, onsite regeneration of H_2SO_4 used in the alkylation unit and FCCU regenerator off-gases.
Walther	The system is not suitable for fuels with elevated sulphur content, as these results in increased ammonia slip due to the formation of ammonia sulphates. The sulphates are objectionable because of corrosion and aerosol emissions.
Wellman Lord	Despite of its excellent emission profile, the process complexity has been an obstruction to wide-spread application.
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Those techniques are typically used when the ammount of SO_2 to recover are small because they produce waste. For example in small specialised refineries or small natural gas plants.

Economics

Desulphurisation technique	Economics
AI-process	35 - 55 EUR/kWth (unit size: 75 - 300 MWth). annual operating cost roughly equals capital cost.
Seawater scrubbing	Low capital costs and low operating costs (no bulk chemicals required, although sometimes magnesium hydroxide is used to enhance the alkalinity).
Wellman Lord	The investment cost is estimated to be $50 million for a unit to handle a flue-gas flow rate of 500000 Nm^3/h and a SO_2 concentration of 0.8 %. The cost includes licensing fees, engineering, equipment delivery, construction, commissioning and startup services.
Wet Limestone Scrubber	75 - 180 EUR/kWth (unit size: 75 - 300 MWth). Anual operating cost roughly equals capital cost. Capital cost: EUR 10 - 20 million. Operating cost EUR 1.6 - 4 million/yr (costs are mainly for caustic soda). Flue gas flows 200000 to 650000 Nm^3/h They are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, construction and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	They are tipically very cheap compared with other FGD techniques

Driving force for implementation

Desulphurisation technique	Driving force for implementation
Wellman Lord	The process characteristics can suit the needs of particular industrial sites using high-sulphur fuels (in the US, Japan and Austria the process has been used in refineries).
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Abatement of small quantities of SO_2

Example plants

Desulphurisation technique	Example plants
Seawater scrubbing	The process has been applied to some extent (in 1994: 2500 MWe / 47 units), also used for smelters, refineries and oil-firing (at 3 % S).
SNOX	More than 25 units have been successfully installed worldwide. Applied in Italy in a big oil refinery which produces and burns high sulphur petcoke
Wellman Lord	More than 40 systems have been applied over the world.
Wet Limestone Scrubber	Operational experience with WS is highly satisfactory, demonstrated by high availability. This system is widely applied in power plants.
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Applied in some small refineries and natural gas plants

Reference literature

[250, Winter, 2000], [257, Gilbert, 2000], [181, HP, 1998], [258, Manduzio, 2000]

4.23.6 VOC abatement techniques

When transferring liquids to vessels at atmospheric pressure, the existing mixture of vapour and gas (often air, but also inerts) in the receiving vessel is often emitted to atmosphere. Such loading operation is recognised as having an impact on the environment due to the presence of VOC, a precursor of ozone. EU Stage 1 Directive 94/63/EC requires that Member States prescribe the specific emission reduction measures is laid down in the annexes of the Directive. Also the application of VRUs to prevent escape of these vapours to the atmosphere is specified in the directive. VRUs aim for recovery of hydrocarbons for re-use. In some cases recovery is not economic, and preference will be given to vapour destruction units (VDU). A more general term covering both options is Vapour Handling Systems (VHS).

4.23.6.1 Establishment of a programme for prevention, detection and control of fugitive emissions

Description
Control of fugitive emissions involves minimising leaks and spills through equipment changes, procedure changes, and improved monitoring, good housekeeping and maintenance practices. The aim in all refinery processes should be to prevent or minimise the release of VOCS. Because of the size, scope and nature of hydrocarbon processing on refineries, this presents a major challenge, which requires an overall strategy that also devolves down into individual action at a process unit and plant item level. Most VOCs are released through fugitive losses from sources including valves, flanges, pump seals and equipment vents. Even a small simple refinery may have over 10000 potential sources and the problem is magnified proportionally on the complete complex refineries.

In the case of process component fugitive releases the only real option, is the implementation of a permanent on-going Leak Detection and Repair (LDAR) programme. This should be developed and tailored to suit the situation concerned, using appropriate techniques, frequencies and priorities. It should provide estimates of fugitive VOC releases for monitoring returns and enable action to be taken to minimise releases. A LDAR contains the following elements:

- type of measurement (e.g. detection limit of 500 ppm for valves and flanges, against the interface of the flange)
- frequency (e.g. twice a year)
- type of components to be checked (e.g. pumps, control valves, heat exchangers, connectors, flanges)
- type of compound lines (e.g. exclude lines that contain liquids with a vapour pressure above 13 kPa)
- what leaks should be repaired and how fast the action should be taken

The principal areas of fugitive loss are well known and their minimising has been the subject of much investigation and action on refineries world-wide, mainly led by operators subject to extremely tight regulation. Some techniques to consider can be:

- an essential first step of any programme is to establish a fugitive release inventory for the refinery. This normally involves a combination of sampling, measurements, environmental monitoring, dispersion modeling and estimates based on emission factors
- identify all potential sources of VOC releases, by establishing population counts of equipment components in line with up-to-date P & I drawings for processes. This survey should cover gas, vapour and light liquid duties
- quantifying of the VOC releases, initially as "baseline" estimates, and subsequently to more refined levels. Suitable protocols for this include the “1995 Protocol for Equipment leak Emission Estimates” (USAEPA-453/R-95-017) for process component losses and API methods(9) for tankage losses. Some major companies have developed their own techniques and protocols. USAEPA method defines an emission estimate of 10000 ppm and is more correct for a plant that until today, has not implemented LDAR programme. A recent report shown that from 1000 valves analysed by type found that the average leakage measured on

regulating control valves was over 70000 ppm. Some TWG members question that high emission leakage limit and propose to set the limit to 500 - 1000 ppm and specially with small chemicals are handled.

- using appropriate dispersion modeling techniques, predict atmospheric mass flux and concentrations
- employing environmental monitoring techniques, compare the predicted situation with the measured one
- identification of the processes that have higher fugitive releases
- VOC releases need also to be minimised from refinery utility and ancillary systems and during plant maintenance and cleaning operations. Hydrocarbons should be minimised in cooling water and adequate separation facilities provided to deal with incidents of contamination. After depressurising off-line process vessels to RFG/flare, they need normally to be steamed out to flare and residual liquids returned to oil slops plants, not run to drain before venting to air, when personnel entry is required
- vapour recovery/incineration/use
- a strategy to reduce VOC emissions may include a complete inventory and quantification by a DIAL LIDAR technique (differential absorption light detection and ranging) (see Section 3.26 for more information).
- emissions that occur through relief valves are to be routed to flare or dedicated incineration systems, and in exceptional cases vented to a safe location
- fugitive VOC emissions (sometimes containing H_2S) can be minimised through double mechanical seals on pumps, compressors or agitators. For example dual pressurized sealing systems on pumps virtually eliminate leakage of the process fluid into the environment and typically have emissions approaching zero, usually described as 'not measurable with existing instrument technology'
- use of low emission valve stem packing (500 ppm) on critical valves, e.g. rising stem gate type control valves in continuous operation, particularly on gas/light liquid high pressure/temperature duties. Valves is the type of equipment that causes most of the leaks (40 - 65 %) Valves with rising stems and in particular control valves are an important source of leaks and may account for as much as 64% of the leaking losses in a plant. It is therefore recommended that a high integrity low emission packing be installed on these valves that can provide emissions performance below 500 ppm and at the same time is fire safe. To ensure low term leakage performance valve live loading spring assemblies mounted on the gland bolts will ensure that the low emission packing is constantly loaded even as the material relaxes over time. Control Valve solutions with valve live loading exist as Maximum Achievable Control Technology (MACT) and emissions performance of 3-5 years is achievable at below 500 ppm. Low emission packing should be specified, and should be certified by an independent test by a reputable testing house. Packing also be fire safe. Rising Stem control valves even with low emission packings can leak excessively after the packing has relaxed in the stuffing box. Studies carried out by a French research institute have shown average leakage concentrations on control valves to be as much as 70000 ppm. (Power Point Slide Enclosed) In the chemical, petrochemical and refinery industry the use of packed valves incorporating live loading spring assemblies mounted on the gland bolts compensates for normal packing relaxation or the effects of thermal cycling and vibration. Valve Live Loading systems offer considerable improvements in long-term sealability on rising stem gate valves, globe valves and regulating control valves. On frequently operated rising stem valves (most problematic) Live Loading offers a considerable improvement in long-term emissions performance (< 500 ppm for 3-5 years). Valves have been identified as the greatest source of fugitive emissions in refineries and rising stem valves particularly frequently operated valves represent the greatest sources of fugitive emissions.
- use of alternative proven types of low-release valves where gate valves are not essential, e.g. quarter turn and sleeved plug valves, both of which have two independent seals
- use of balanced bellows type relief valves to minimise valve leakage outside the design lift range and piping of reliefs to RFG or flare gas, normally via phase separation, without header back pressure

- minimising the number of flanged connections on pipelines and the use of high specification jointing materials. Flanges should be minimized and high integrity sealing materials should be used and should be fire safe materials. In some critical services, particularly where thermal cycling or possible vibration may exist, flange disc springs can be mounted under the flange bolts to compensate for the effects of thermal cycling and gasket relaxation. Such solutions combined with high performance sealing materials can provide emissions performance of <500 ppm for periods of 3-5 years. Often heat exchangers are not given a separate consideration in the discussion of fugitive emissions. On a typical refinery there can be several hundred heat exchangers. Due to the size of these flanged connections, the large no. of bolts involved, the non uniform temperature on the flange and the thermal cycling conditions under which many operate, it is recommended that flange disc springs are fitted under the nuts of the bolts to maintain a constant gland load on the sealing material. Heat exchangers have a far greater tendency to leak than normal pipe flanges due to their dimensions and particularly in thermal cycling conditions. High integrity sealing materials are recommended and not the standard typical metal jacketed gaskets as indicated in the design codes.
- use of canned pumps or double seals on conventional pumps. Study the use of non-leaking pumps as diaphragm pumps, bellow pumps, canned rotor pumps, or pumps with magnetic clutches. Magnetic pumps cannot be used for clean liquids at low temperature. Emissions from centrifugal pumps can be reduced to 33 % by replacing packed seals by mechanical seals. Turbo-compressors can be sealed with labyrinth glands, with rotating rings or floating rings in liquid seals. An escape of the transported medium through the seals should be prevented e.g. by inert gas or liquid sealing medium at elevated pressure. Furthermore, magnetic drive pumps and canned motor pumps have limited applicability and care must be taken when using such pumps in contaminated process streams, process streams containing particulate and higher pressures. It should also be noted that magnetic pumps typically have lower efficiency compared to conventional pumps, drawing more power for the same service. In end effect this transfers emissions from the pump (as VOC emissions) to the stack (as CO_2, SO_2, NO_2 emissions).
- piping of compressor seals, vent and purge lines to RFG or flare systems
- use of end caps or plugs on open ended lines and closed loop flush on liquid sampling points (no applicable with circulating fluid (pump discharge) or in tanks). Minimising the releases to air from process hydrocarbon analysers, by optimising sampling volume/frequency and venting to RFG or flare systems
- install a maintenance drain-out system to eliminate open discharges from drains
- using totally closed-loop in all routine samplers. To follow product quality, inspection requirements, environmental standards, etc. a sampling schedule is typically set up. With routine sampling is understood those that are frequently used or needed. For example, by routine samplers is understood, the samplers of effluent water quality, daily samples of processed crude fuel fired, fuel gas, certain feedstocks (i.e. FCCU), that are taken to analyse the sulphur concentration. and samplers from intermediates, final products, tanks, etc.

Achieved environmental benefits

Fugitive emissions are one of the largest sources of refinery hydrocarbon emissions. A leak detection and repair (LDAR) programme consists of using a portable VOC detecting instrument to detect leaks during regularly scheduled inspections of valves, flanges, and pump seals. Leaks are then repaired immediately or are scheduled for repair as quickly as possible. A LDAR programme could reduce fugitive emissions 40 to 64 percent, depending on the frequency of inspections.

Techniques to reduce VOC emissions are: efficient seals and valves, good maintenance programmes and monitoring of the emissions. Fugitive emissions can be reduced to 0.01 % weight when normal fugitive emissions has been calculated as 0.03 % weight on throughput. The investment cost for those techniques is negligeble and the operating cost is around EUR 0.1 million per year (accounting for 190 EUR per tonne of VOC recovered).

About 93 % of the sources of fugitive emission are accessible. The achievable emission reduction depends on the current conditions of the components, with typical reduction rates of at least 50 to 75 % related to average emission factors. The estimated efficiency for quarterly inspection and maintenance is 80 to 90 %. Higher efficiencies may be reached, when more intensive inspection and maintenance programmes are implemented.

A good inspection and maintenance programme for valves and flanges is a very cost-effective way to reduce NMVOC emissions in a refinery. Savings may reach 0.19 EUR/kg of hydrocarbon reduced.

Applicability
Fully applicable. See descriptions for applicability of each of the techniques.

Economics
A system for monitoring approximately 3000 refinery components (primarily pumps seals, valves inhigh liquid vapour pressure or gas services, and road/rail loading) is estimated to costs about EUR87500 excluding modification of poorly performing equipment and cost of labour.
For a reduction efficiency of 50 % by annual inspection for fugitive emissions, OECD estimated no additional costs, but a cost benefit due to hydrocarbon savings. A reduction of 80 % by quarterly inspection and maintenance will cost about 193 EUR/t NMVOC abated. A simple Inspection and Maintenance programme at a small plant may result in an annual cost of EUR 44000, whereas at a large plant with stringent requirements some EUR 875000 may have to be accounted.

The cost of leak detection and repair programme for pumps and compressors is 1.75 - 2.5 EUR/kg of hydrocarbon emissions reduced.

Emission Source	Refinery Process Units and Equipment (Installed and Retrofitted)
Control Technology	Leak Detection and Repair Programmes
Efficiency	50 - 90 %
Investment Costs	Moderate
Operating Costs	0.1 - 0.15 EUR million for 15 Mt/yr refinery(1) 0.06 EUR million for 5 Mt/yr refinery(2) 0.04 - 0.08 EUR million/yr for a 10000 ppm programme to 0.8 EUR million/yr for a 100 - 500 ppm programme(3)
Other Impacts	Costs of repair not included in above

Table 4.45: VOC control technique applied to refinery
Source (1) Industry Propriety Information
(2) UN-ECE EC AIR/WG6/1998/5
(3) Hydrocarbon Processing, September 1996, p 121

Driving force for implementation
Reduction of VOC emissions

Example plants
LDAR programmes have been used successfully world-wide to reduce VOC releases. Typical survey results show that leaks from glands on valves and pumps are responsible for 90 % or more of estimated fugitive releases and that a small proportion of valves, virtually all on gas or high temperature light material streams, contribute almost all of the total.

Reference literature
[107, Janson, 1999], [45, Sema and Sofres, 1991], [112, Foster Wheeler Energy, 1999], [79, API, 1993], [127, UN/ECE, 1998], [19, Irish EPA, 1993], [260, Sandgrind, 2000], [350, European Sealing Association, 2001]

4.23.6.2 Vapour recovery units (VRU)

Description
Vapour recovery units (VRUs) are installations designed for the emission reduction of volatile organic compounds (VOC) which are emitted during loading and unloading operations of light products. As VOC emission abatement by VRUs is only one aspect of total VOC control in a refinery, this section should be considered in combination with storage, handling and integrated Refinery management. Several commercial techniques are available for the recovery of VOC. Those techniques can be divided in two large groups according to the type of separation. One group includes techniques where the separation of the VOC from the air due to pressure swing adsorption on activated carbon, absorption by lean oil washing (kerosene), selective membrane separation or condensation by cooling or compression (this is a special case because separation and re-condensation are both achieved in a single process). The other group integrates those techniques that the VOC are separated by condensation to liquid state. It includes re-absorption into the gasoline or crude oil, condensation and compression. Follows a short description of those techniques.

- absorption: The vapour molecules dissolve in a suitable absorption liquid (water, lyes, glycols or mineral oil fractions such as reformate)
- adsorption: The vapour molecules adhere physically to activate sites on the surface of solid materials, like activated carbon (AC) or zeolite
- hybrid systems. Nowadays, combinations of the VRUs are on the market which are able to meet very low emissions standards. Examples are cooling/absorption and compression/absorption/membrane separation.

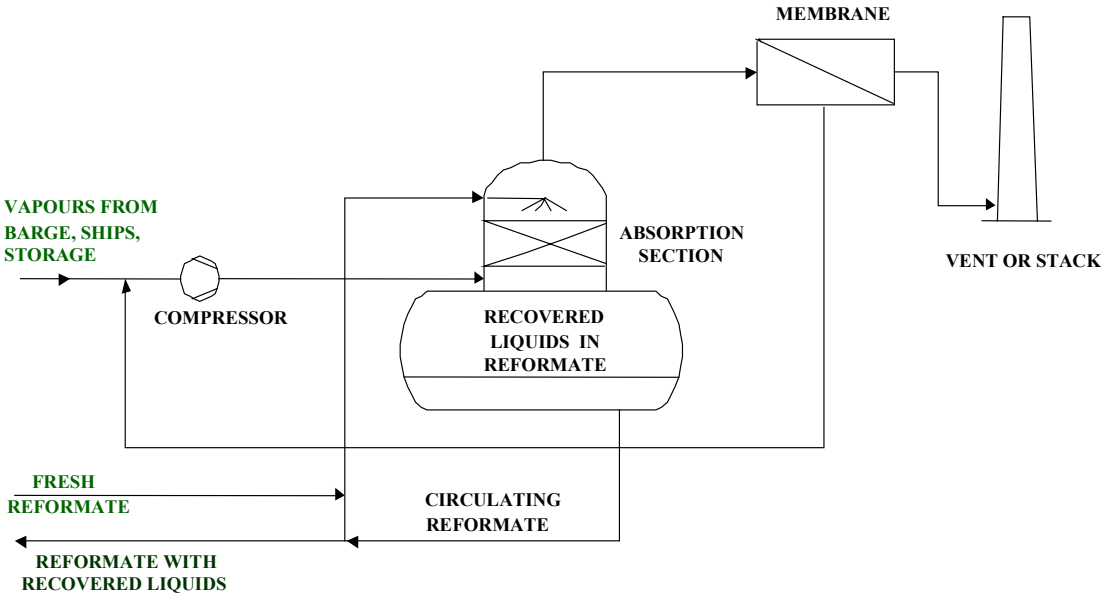


Figure 4.13: Simplified process flow scheme of a vapour recovery unit (Compression/absorption/membrane type)

- membrane gas separation: The vapour molecules dissolve into the membrane, move by diffusion to the other side and desorb into the support material, driven by a pressure difference. The concentration is higher at the desorption side of the membrane, as the vapour molecules are preferentially absorbed into the membrane compared to the gas molecules.
- refrigeration/condensation: By cooling of the vapour/gas mixture the vapour molecules condense and are separated as a liquid.

Achieved environmental benefits

VRU technique	VOC removal efficiency (%)
Absorption	99 - 99.95
Adsorption	99.95 - 99.99
Membrane gas separation	99 - 99.9
Refrigeration/condensation	99.8 - 99.95 This method can achieve low exit concentrations if the applied refrigeration temperature is low enough. A great advantage of condensation is that the vapours are recovered as pure liquids (no waste), which can easily be returned directly to the storage tank.
Ranges are due to the use of 1 or 2 stages. Higher removal efficiencies are only reached with high inlet loads.	

Emissions of the various systems are directly related to the reduction efficiency as reported above and can be as low as 10 mg/Nm^3 (without methane). An efficiency of 99.9 % concentrations of 150 mg/Nm^3 (without methane) or 2500 mg/Nm^3 (with methane) can be achieved.

Cross-media effects

Effluent is usually only condensate and is usually negligible.

VRU technique	
Absorption	If water is used regeneration of the absorption liquid is not necessary, as water can be treated in a waste water treatment plant. Regeneration more than doubles the investment + energy costs. The only waste generated is the exhausted liquid which need to be replaced once in many years.
Adsorption	Waste is only relevant in case absorption bed.

Operational data

The handling of VOC involves always safety measures in view of explosion risks (flame arresters) and the presence of toxic compounds such as benzene. VRUs are compact and require very little energy and process materials to operate. Usually operating times are longer than two years.

VRU technique	
Absorption	If reformate is used recycling to blending tanks is done.
Hybrid systems	Due to the complexity of operation it is difficult to maintain the high performance

Applicability

Vapour recovery units (VRUs) are installations designed for the emission reduction of volatile organic compounds (VOC) which are emitted during loading and unloading operations of light products. For a refinery this is particularly relevant to gasoline storage and loading as well as for products with equivalent volatility characteristics such as naphtha and BTEX.

VRU technique	
Adsorption	Due to heat of adsorption this method cannot handle high inlet concentrations (auto-ignition). At higher inlet concentrations the AC is quickly saturated, so regeneration is necessary. Normally, adsorption VRUs applies therefore to a two-stage system. The only waste generated is the exhausted activated carbons which need to be replaced once in many years.

VRUs occupy limited space. Usually they are preassembled and delivered skid mounted. Commercial VRU capacities range from 500 - 2000 Nm^3/h.

Scores of VRUs at gasoline (un)loading installations for VOC emission reduction have been built in W-Europe following Stage-1 legislation. Hybrid systems are popular due to simplicity, good operability and high performance.

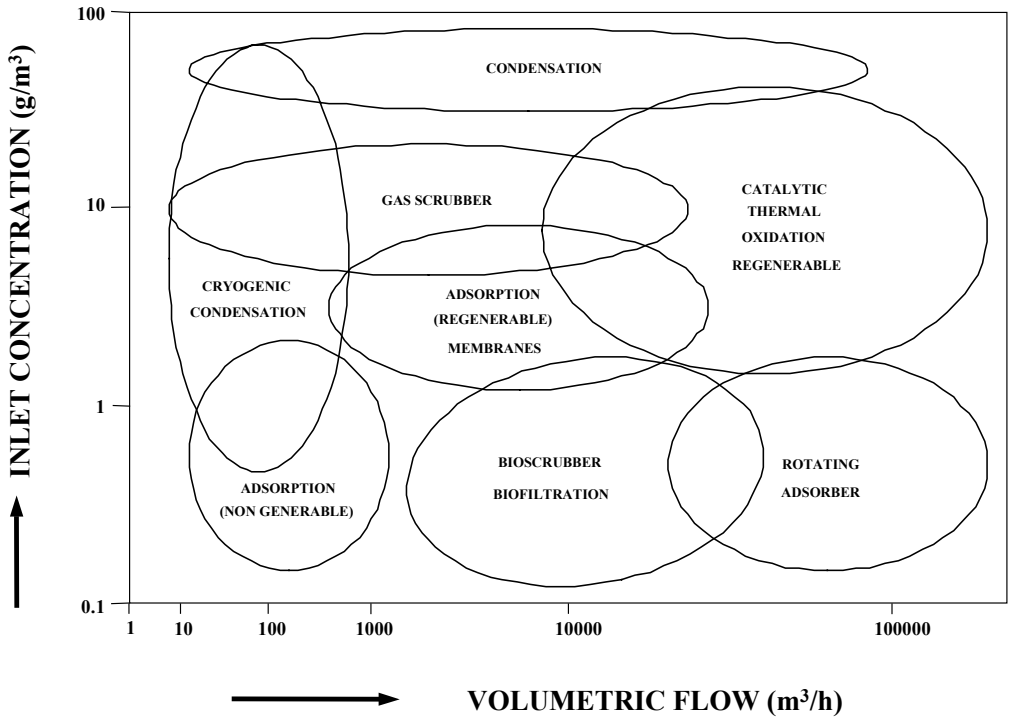


Figure 4.14: Applicability different techniques for end-of-pipe gas treatment for VOC removal

Economics

A typical VRU with a capacity of 1000 Nm^3/h involves a capital cost of EUR 2 million with an installation factor of 1.5 (as package unit) to 5 (in exceptional cases). Capital investment strongly depends on site-specific factors, such as the number of loading berths connected to the system, the distance between berth and the emission control facility (cost of ducting), the need for blowers, safety systems (explosion and flame arresters) systems. The capital costs can range from EUR 4 - 20 million for a VRU of 2000 Nm^3/h capacity. The investment costs can range from EUR 2 - 25 million for an efficiency of 99.2 % implying a operating cost from EUR 0.02 - 1 million applied to loading operations (slurry, road, rail and internal refinery movements). The cost for a VRU unit of 2000 Nm^3/h capacity and applying utilities is shown as follows:

DESCRIPTION		k EUR	%
INDIRECT COSTS			
230	Detailed Engineering	275	7
213	Field Supervision	137	3
213	Inspection	83	2
260	PMT - NPQC - Owner	424	10
	Subtotal	919	22
DIRECT COSTS - EQUIPMENT			
311	Heat Exchangers	0	0
314	Towers	0	0
315	Drums	0	0
316	Reactors	943	22
324	Pumps and Drivers	13	<1
326	Tanks and Spheres	0	0
347	Cooling Towers	0	0
	Subtotal	956	22
DIRECT COSTS - NON EQUIPMENT			
208	Scaffolding	25	<1
209	Cleanup Construction	8	<1
216	Construction Equipment	16	<1
307	Excavation & Cable Trenches	142	3
308	Concrete Work and Paving	216	5
309	Piling	33	1
313	Piping	1179	28
318	Structural Steel	77	2
322	Instrumentation	285	7
328	Roads, Walks, Fences	15	<1
337	Electric Power and Light	107	3
345	Communication Equipment	0	0
348	Insulation	3	<1
349	Paint	167	4
380	Standby Equipment (Cap. Spare)	0	0
	Subtotal	2273	54
	Total Capital	4148	98
EXPENSE			
101	Dismantling	17	<1
102	Site Clearance	0	0
103	Relocation	7	<1
104	Reconditioning	0	0
105	Temporary Bypasses	0	0
111	Gas Freeing & Cleaning	8	41
165	Owner Expense Charges	81	2
	Subtotal	113	2
	Final Total	**4261**	**100**

Table 4.46: Total erected cost of a Vapour Recovery Unit

Driving force for implementation

In some European countries, some programme applies to storage and loading operations of liquid hydrocarbons with a vapour pressure > 1 kPa (10 mbar) at ambient temperature. Moreover, the specific requirements on gasoline storage and loading are laid down in the national legislation following the Stage-1 Directive. For refineries the VOC emissions of gasoline and their abatement is by far the most important due to the high vapour pressure (>27.6 kPa), the large throughput and the large number of transshipments by truck, rail and barge.

Example plants

VRU technique	
Membrane gas separation	This new technology is now used at a number of refineries.

Reference literature

[258, Manduzio, 2000], [181, HP, 1998], [115, CONCAWE, 1999]

4.23.6.3 Vapour Destruction (VD)

In addition to vapour recovery also vapour destruction can be applied.

Description

Two systems are relevant in this respect:

- oxidation: The vapour molecules are converted to CO_2 and H_2O either by thermal oxidation at high temperatures or by catalytic oxidation at lower temperatures. The stage 1 directive only allows oxidation in special situations, e.g. when energy is recovered by a gas motor
- biofiltration: Decomposition to CO_2 and H_2O is achieved at temperatures slightly above ambient by micro-organisms located in a solid humidified mass.

VOC collection and destruction

Another control technique is to collect VOCs from vents, pumps and compressors and to route them to a flare system.

Achieved environmental benefits

Thermal oxidation: 99 - 99.9 %, Catalytic oxidation 95 - 99 %, Biofilters 95 - 99 %. The efficiency of the biofilters is normally a controversy. Since high removal efficiencies are only reaqched with high inlet loads, emission concentrations well below 50 mg/Nm^3 NMVOC are rarely achieved.

Biotreatment: The units are rugged, silent, need minimal maintenance and no inputs. No fuel or chemicals are required. Biofilters remove and destroy aliphatic and aromatic hydrocarbons, other VOC, H_2S and odors in off-gases from process streams, tank vents, relief valves, soil vapour extracion, waste water treatments, etc.

Cross-media effects

Thermal oxidation can give unwanted combustion products such as NO_x, requiring extra treatment. Catalytic oxidation requires less energy to arrive at combustion temperatures, and can be competitive with thermal oxidation at low inlet concentrations. Thermal oxidation requires good primary and/or secondary safety measures to prevent explosions, while the efficiency of catalytic oxidation may be reduced by catalyst poisoning and ageing. Incineration of VOC also generates CO_2. Combustion of streams with low concentrations and for preheating of catalysts additional fuel is consumed.

Waste is only relevant in case biofilters are exhausted. No secondary pollutants or wastes are created.

Operational data

Usually operating times are longer than two years. Biofilters: Input air should be 5 - 55 ºC and moist.

Applicability

Biofilters: Any gas that can burn in air will oxidise in biofilters. Installation for the treatment of flows of 17 m^3/h up to 135000 m^3/h are found in the literature.

Bioxidation: The method is highly suited for treatment of continuous constant-composition air streams with low concentrations of organic pollutants. The method is not suitable for the direct treatment of the vapour/air mixtures often encountered in transshipments, because such mixtures have mostly higher vapour concentrations (>1 % v/v) and appear as sudden peak flows during the rather infrequent unloading operations. Biotreatment facilities are certainly sensitive to poisoning by presence of unexpected compounds in the incoming vapour stream. Consequently most of those systems needs continuous monitoring to prevent the entrance of undesired compounds.

Economics

Thermal oxidation of VOCs. The economics of a thermal oxidation system with heat recovery will depend on many factors, including the calorific value of the waste stream. If a thermal oxidiser is furnished with a gas-to-gas heat exchanger that has an efficiency of 60 % and a gas

flow of 4720 l/s, the payback for heat recovery will be impressive. Assume natural gas, used as supplementary fuel, costs \$20/ million of kcal and electric power cost \$0.08/kWh. If a system runs 24 h/day, 350 d/yr, the payback for the 200000\$ additional capital investment for a plant-type heat exchanger would be less than five months.

Biofilters: Biofiltration costs significantly cost less than the other air pollution control techniques. Capital costs vary with flowrate and the destruction/removal efficiency. Capital costs start at about \$15/m^3/h. Operation and maintenance costs are extremely low because no fuel or chemicals are required.

Emission Source	Refinery Process Units and Equipment (Installed and Retrofitted)
Control Technology	Collection of atmospheric VOCs and relief valves to flare/incineration system
Efficiency	up to 99.5 % destruction efficiency in incineration
Investment Costs	1.3 EUR million for 5 Mt/yr refinery
Operating Costs	3.0 EUR million
Other Impacts	Increase in CO_2 emissions due to combustion

Table 4.47: VOC control technique applied to refinery
Source: UN-ECE EC AIR/WG6/1998/5

Driving force for implementation
Reduction of VOCs

Example plants
Thermal incineration: More than 107 units operaring in the world and over 76 portables.

Reference literature
[118, VROM, 1999], [181, HP, 1998]

4.23.7 Flares

Description
Flares are used for safety and environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situation or upsets. The flare is usually required to be smokeless for the gas flows that are expected to occur from normal day-to-day operation. This gas flow is usually designed at 15 to 20 percent of the maximum design flow. Flares may become an important SO_2 emitter when clean fuels are used within the refinery.

Flare systems normally can be divided into two main sections, i.e. the flare collection system with a flare knock out drum and the flare stack itself. When dealing with large refinery complexes separate knock-out drums may be installed in different process areas with 'blocking-in' facilities to allow maintenance during shut downs of these areas.

In Figure 4.15 a simplified process flow diagram of a flare system is shown.

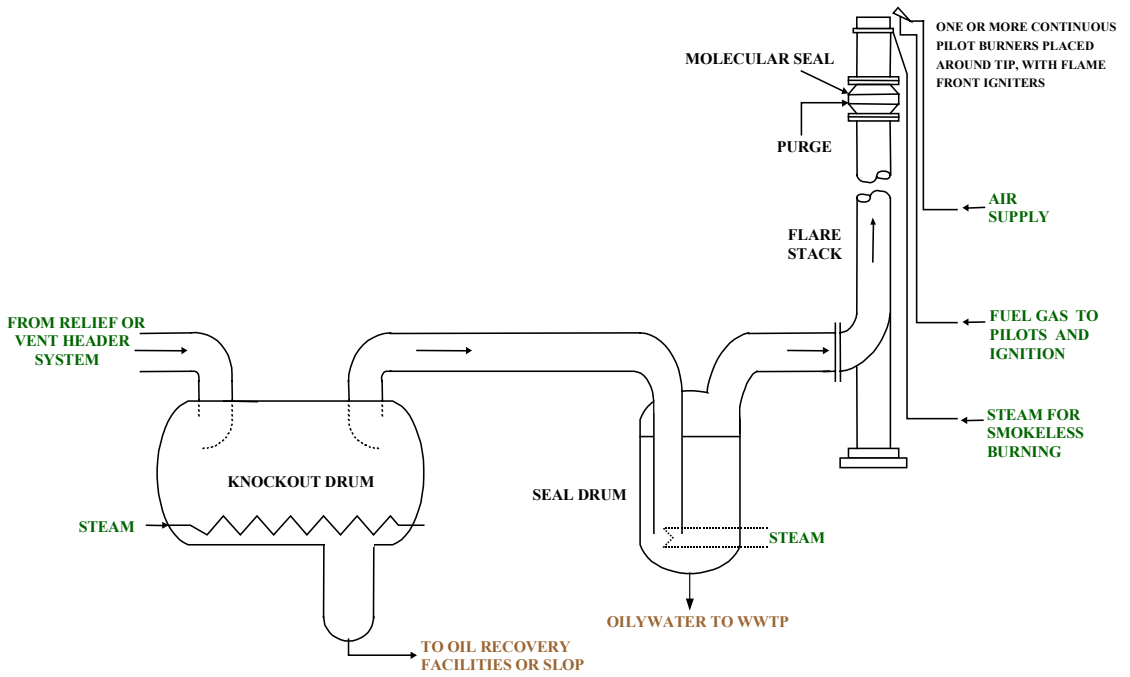


Figure 4.15: Simplified process flow diagram of a flare system

Techniques to be applied to flares that may reduce emissions:

- the pilot burners give more reliable ignition to the vent gases because they are not affected by the wind
- steam injection in flaring stacks can reduce particulate matter emissions
- coke formation in flare tips should be prevented
- surplus refinery gas should be flared not vented. Knock-out pots to remove liquids should be provided, and with appropriate seals and liquid disposal system to prevent entrainment of liquids into the combustion zone. Water streams from seal drums should be routed to the sour water system
- flare-gas recovery systems have been developed due to environmental and economic considerations. The flare gas is captured and compressed for other uses. Usually recovered flare gas is treated and routed to the refinery fuel gas system. Depending upon flare gas composition, recovered gas may have other uses. Reductions of flaring to ratios of 0.08 - 0.12 % of production in one natural gas plant in Norway have been reported.
- with the increasingly strict requirements regarding flame visibility, emissions, and noise, enclosed ground flares can offer the advantages of hiding flames, monitoring emissions, and lowering noise. However, the initial cost often makes them undesirable for large releases when compared to elevated systems. A significant disadvantage with a ground flare is the potential accumulation of a vapour cloud in the event of a flare malfunction; special safety dispersion systems are usually included in the ground flare system. For this reason, instrumentation for monitoring and controlling ground flares is typically more stringent than with an elevated system.

Achieved environmental benefits

Well operated refinery flares typically optain a conversion of 98 % to CO_2, 1.5 % to partially combustion products (almost all CO) and 0.5 % unconverted. Ground flares have reduced noise and smoke compared to elevated flares.

Cross-media effects

Flare seal water is typically in need of treatment before release.

Operational data
Since air present in the stack can create a potentially explosive mixture with incoming flare gas during low-flare gas loads, a continuous stream of purge gas is required. Also in a lot of cases a molecular water seal is employed which allows using a smaller purging rate.

Applicability
Flaring of toxic gases (never via a ground flare) requires special considerations. To ensure safe operation during periods when the flare may not have a flame present, ground level concentration calculations for hazardous components should be performed assuming the flare as a vent only. Other safeguards may be necessary to mitigate groundlevel exposure hazards. Reliable continuous pilot monitoring is considered critical when flaring toxic gases.

There are basically two types of flares, an elevated flare and a ground flare. Ground flares are used when it is necessary to conceal the flare (for various reasons), otherwise the elevated flare is commonly chosen, because it can handle larger flow releases more economically. Sometimes a refinery has both a ground flare and an elevated flare. In that case the ground flare is used to combust small amounts of continuous vents and small relief loads.

The elevated flare is always a vital part of the refinery complex, its primary purpose being safety. This flare system is designed to conduct easily ignitable and toxic vapours from the process area to a remote elevated location. The elevated flare system includes a seal drum to prevent the flame from flashing back into the process units, and an elevated stack with pilot-ignition and steam nozzles at the tip. Due to different burning characteristics of the gases, a separate sour gas flare is usually provided; this flare could be equipped with different burners than the hydrocarbon flare to allow more efficient combustion of sour gases (H_2S).

Driving force for implementation
The purpose of the flare system is to collect and process vent gases (e. g. pressure relief from the fractionator should pass to flare) and (large) quantities of fluids during emergency situations or upsets: when safety relief valves are open, during depressurisation operations and purging of process units in case of an emergency situation, during start-up of certain process units or prior to a scheduled shut down. Provisions are available to separate the liquids from the gases and to incinerate relieved vapours. The liquids are usually returned to the process units or tanks. Pilot burners are normally installed to take care of constant ignition of released vapours. Moreover, well controlled steam injection systems have been applied to achieve smokeless burning.

Flare-gas recovery systems often are installed to comply with local regulatory limits on flare operation and, therefore must be sized to conform to any such limits.

Example plants
Flares are common in refineries

Reference literature
[101, World Bank, 1998], [19, Irish EPA, 1993], [117, VDI, 2000], [118, VROM, 1999]

4.23.8 Combined techniques to abate air pollutants

Description
The SNOX plant removes SO_2, NO_x and particulate from the flue gas produced by the coal-fired boilers at the Gela refinery power plant.

The SNOX plant is based on catalytic processes where the only additional material necessary is the ammonia used for the NO_x removal. Furthermore, natural gas and water are needed, besides small quantities of silicone oil for the acid mist control unit.

The process produces 94 - 95 % pure sulphuric acid (H_2SO_4) for sale. The system employs a catalytic converter to oxidise SO_2 to SO_3 at a temperature of 400 - 420 °C. This temperature level allows a deNOx, operating at 380 °C, to be well fitted in the process. High NO_x removal at high NH_3 slip is possible with no risk of precipitation of ammonium sulphates, as the reactor temperatures are above the decomposition temperature (350 °C) and any NH_3 slip is destroyed in the SO_2 / SO_3 oxidiser. The process produces no waste water or waste products, nor does it consume any chemical apart from ammonia for NO_x control. The high removal of dust is demanded by the H_2SO_4 production step. Dedusting with an efficiency consistently at 99.9 % is required as to avoid frequent clean-up of the SO_2 / SO_3 converter and to maintain good product quality. The flue gas train subsequently comprises an air preheater, a high-temperature ESP, the cold side of the regenerative heat exchanger, the deNOx reactor, a heat supply, the SO_2/ SO_3 converter, hot-side regeneration heat-exchanger, the acid condenser (operating between 240 - 100 °C, hydrating SO_3 and condensing the resulting acid product) which heat is used as the first step in preheating combustion air. The recovered heat, produced by the conversion process, is substantial and make up for the power demand when the sulphur content in the fuel (oil or coal) is 2 - 3 %. Areas relating to dust that require attention in operation are the HTEP, the SO_2 / SO_3 converter and the acid falling-film condenser (made of borosilicate glass tubes).

The SNOX process is divided into four main steps:
- dust removal (ESP). More information in 4.23.4
- selective Catalytic Reduction (SCR) of NO_x. More information in 4.23.3.3
- catalytic oxidation of SO_2
- condensation of H_2SO_4

Dust removal (ESP)
An extensive dust removal from the flue gas is necessary to obtain:
- a long life of the deNOx catalyst
- a long running time between screening of the SO_2 oxidation catalyst
- a high purity of the produced sulphuric acid.

Catalytic Oxidation of SO_2
From the SCR reactor the flue gas is distributed uniformly over the sulphuric acid catalyst in the SO_2 converter. Here the SO_2 initially present in the flue gas is oxidized into SO_3 according to the following reaction scheme:
1) $2\ SO_2 + O_2$ ----> $2\ SO_3 + 23.6$ kcal/gmol SO_2

Condensation of H_2SO_4
The SO_3 rich flue gas from the SO_2 converter is cooled from approximately 422°C down to 260°C in the gas/gas exchanger, by heat exchange with the cold unconverted flue gas.
Then the SO_3 gas is condensed in the WSA heat exchanger.
When the SO_3 rich gas is cooled, the SO_3 is hydrated to vapours sulphuric acid according to the following reaction scheme:
1) $SO_3 + H_2O$ ----> $H_2SO_4 + 24.1$ kcal/gmol SO_3
The cleaned gas is discharged into the atmosphere through the stack at 106°C.

Achieved environmental benefits
- process qualified for treating high SO_2 concentration flue gas (as in Gela refinery)
- high removal of SO_2, together with NO_x and particulate removal
- low environmental impacts: no raw material required (only ammonia consumption for NO_x control), no waste water or waste production
- no cooling water consumption
- production, as by-product of the process, of H_2SO_4 commercial grade for sale
- high heat recovery.

Particulate removal rate	less than 10 mg/Nm^3 at ESP outlet
NO_x removal rate	90 - 94.7 %
SO_2 removal rate	94 - >96 % with 5 % v/v O_2 and a temperature of 410°C inlet the SO_2 converter.

Cross-media effects

H_2SO_4 production (95 % w/w H_2SO_4 concentration)	13 tonne/h with a 5.5 % w/w sulphur pet-coke

Applicability
The Gela Refinery SNOX plant was designed for cleaning the flue gas produced in the boilers at power plant burning a mixture of high sulphur Fuel Oil and high sulphur Petroleum Coke.

Economics
A SNOX plant designed for a flue gas load of 1.0 million Nm^3/h at the exit of the existing induced draught fans had a cost of EUR 100 million.

Driving force for implementation
Environmental Italian regulations (D.P.R. 203/88) imposed very severe limit on emissions (particulary on SO_2), so AgipPetroli had to search a way to be able to continue to burn high sulphur pet-coke in its power plants in Gela refinery.

Example plants
GELA AgipPetroli Refinery Start up September 1999

Reference literature
[297, Italy, 2000]

4.23.9 Odour preventing and control techniques

Description
Scrubber with hypochlorite ion is used for odour/low-level VOC abatement.

4.23.10 Noise prevention and control techniques

Description
Flares, compressors, pumps, turbines and air coolers require particular attention as regards sources of noise. Abatement measures in refineries usually focus on these types of equipment.

4.24 Waste water treatments

This section together with the previous one and the next section are dealing with the end-of-pipe processes that appear in a refinery. Deeper information about the techniques included in this section can be found in the Common waste water and wastegas treatments BREF. The reason why those techniques are appearing here is to give an overall description of the techniques and to avoid repetition. Description of end-of-pipe techniques does not appear in the previous sections. In this Section, general information on environmental benefits, cross-media effects, operational data, applicability is described here. Prevention or minimisation techniques applied to different process activities are found in each of the sections dealing with those production processes. Complementing water management systems that may be found along the document, this section contains the waste water treatments. Those techniques are only discussed in this section within this document.

Refinery waste water streams that require purification prior to discharge comprises mainly two streams. The first effluent is process water generated in various refinery units as a consequence of steam injection and/or washing hydrocarbon fractions with water. The direct contact with hydrocarbon fractions usually results in a high concentration of dissolved organics. Process water is treated in a sour water stripper (SWS) when it contains hydrogen sulphide and ammonia and is subsequently re-used as wash water for the desalter. The resulting effluent is high in oil and solids, has a high chemical oxygen demand (COD 300 - >600 mg/l) and might contain also specific contaminants for which legal limits apply. The second significant effluent stream that requires treatment is contaminated rainwater, referred to as surface water run-off, which usually requires only removal of free oil and solids as COD is usually below 100 mg/l. Prior to effluent treatment proper segregation and process water integration should be considered. Other waste water streams that appear in a refinery are the cooling water blowdown, tank water bottoms and ballast water. This section only includes the end-of-pipe processes that appear in treatment of waste water in refinery. Deeper information about the techniques included in chapter can be found in the Common waste water and wastegas treatments BREF.

Waste water treatment plants are advanced environmental protection systems for the control of surface water pollution. The purpose of waste water treatment is to remove floating and dispersed oil, suspended solids, dissolved oil, notably BTEX and phenol and other specific compounds such as sulphides, cyanides, heavy metals, phosphate (when polymerisation is present) and nitrogen compounds and other COD. Additionally, the treated effluent can be rendered suitable for re-use in the refinery process. The principle of waste water purification is based on (1) dedicated separation techniques for the dispersed and floating oil and suspended solids from the waste water and (2) removal of dissolved compounds by biological treatment or further treatments.

4.24.1 Management of waste water within a refinery

This section try to give some indication on what can be done in a refinery with the management of the waste water. In other words, it is better to combine waste waters from different processes or is better to process them independtly in some independent waste water plant. Topics related with the storage of waste water is also included here. This section deals with process waste water, cooling water and sanitary waste water, ballast water, cleaning water, accidentally oil contaminated water, continuous oil contaminated water, etc.

Process water integration can be applied at any industrial site, be it a refinery or a combined refinery and petrochemical complex. In this document the concept and practical tools for preparing a process water integration scheme for a refinery is presented in Section 4.15.7.1. Reference is made to a EU BREF document on waste water treatment.

Description
Some techniques to consider in that respect are:

1. use of sour water can be used to the maximum extend possible as desalter wash water or as wash water in overhead FCC main column
2. process water from the dimerisation process should be treated properly because the high content on phosphate that waste water from this process typically have
3. use of equalising tanks for the storage of waste water
4. tanks for storage of ballast water may cause large VOC emissions. A way to prevent those emissions is to cover the equalising tanks of the waste water treatment systems with floating roofs. Technique to consider also included in the Section 4.21.13
5. the temperature of the waste water is controlled in order to reduce volatilisation and to secure the performance of the biological treatment
6. rainwater from polluted plant areas (storm water) should be collected and routed to a treatment plant. For collection a "first flush" scheme may be used. Depending on the initial degree of pollution (mainly oil), the contaminated water should be treated in oil/water/solids separation systems (API, flotation units, sandfilters) and/or biotreatment units. Non-contaminated water may be discharged directly or re-used in order to save costs. It is necessary that the WWTP is able to handle high quantities of rainwater. For this purpose sufficient buffer capacity need to be installed (storm water tank). In locations with low rainfall segregation of streams is less relevant
7. control of surfactants in waste water - Surfactants entering the refinery waste water streams will increase the amount of emulsions and sludges generated. Surfactants can enter the system from a number of sources including: washing unit pads with detergents; treating gasolines with an end point over 400 degrees (F) thereby producing spent caustics; cleaning tank truck tank interiors; and using soaps and cleaners for miscellaneous tasks. In addition, the overuse and mixing of the organic polymers used to separate oil, water and solids in the waste water treatment plant can actually stabilise emulsions. The use of surfactants need to be minimised by educating operators, routing surfactant sources to a point downstream of the DAF unit and by using dry cleaning, high pressure water or steam to clean oil surfaces of oil and dirt
8. install high pressure power washer - Chlorinated solvent vapour degreasers can be replaced with high pressure power washers which do not generate spent solvent hazardous wastes
9. use non-hazardous degreasers - Spent conventional degreaser solvents can be reduced or eliminated through substitution with less toxic and/or biodegradable products.

Achieved environmental benefits

1. re-use of water within the refinery

   Process effluent volume can be compared to the volumes of process effluent discharged (excluding once through cooling water). Although related, the values are not identical given that there are other sources of water to the effluent system including rainwater on plant surfaces, water separaged from crude, ballast water, etc. On the other hand, some water will evaporate, be used in chemical reactions, etc. The correponding figures for effluents for 63 European refineries are (all annual averages):

Annual average effluent volume	3.6 million m^3/ year
Range	0.07 – 21 million m^3/year
Average effluent per tonne throughput	0.53 m^3/ tonne throughput
Range	0.09 to 1.6 m^3/ tonne throughput

   Other data from an EU+ country with many refineries gives the following ranges depending on the type of refinery:

   0.1 – 0.3 m^3/ tonne throughput for pure refineries
   0.3 – 0.5 m^3/ tonne throughput for lubricant refineries
   0.5 – 0.8 m^3/ tonne throughput for bitumen refinery

   Other data from another EU+ country gave a range from 0.18 – 0.21 m^3/ tonne throughput for three refineries in his country.

2. proper treatment of phosphates
3. action has been taken in order to reduce the amount of oil to reach the API separators
4. reduce the VOC emissions from waste waters
5. reduce the VOC emissions and secure the performance of the biological treatment.

Driving force for implementation
Re-use water, reduce the hydrocarbon charge to the waste water treatment and reduce VOC emissions.

Reference literature
[118, VROM, 1999], [197, Hellenic Petroleum, 1999], [107, Janson, 1999], [262, Jansson, 2000], [268, TWG, 2001]

4.24.2 Sour water stripping (SWS)

Sour water from the various refinery units is for the main part stripped in a SWS and can normally be re-used together with crude distillation unit overhead wash water as desalter wash water. This is the main process water source in refineries.

Description
Most sour water strippers are *single stage*, requiring one stripping column. Figure 4.16 shows a typical single stage sour water stripper. The sour water streams from the process units are collected in a sour water collection vessel. This provides both hold-up for feed and acts as a settler, where oil separation takes place. From this vessel sour water is pumped via a feed/effluent exchanger, to the top of the stripper column. The sour water is counter-currently stripped in the column by steam, either injected live or generated in a reboiler. This column is usually refluxed to reduce the water content in the sour gas. Operating pressure in the column varies from 0.5 to 1.2 barg depending on the destination of the off-gas. Often pH control is applied to maximise either H_2S or NH_3 removal.

Sour off-gases from a stripper unit can be routed either to a sulphur recovery unit (SRU), to an incinerator, or to the sour flare. Since off-gases routed to an incinerator or a flare contribute to the release of SO_2 and NO_x, routing to a SRU unit is preferred and now commonly practised. Normally the off-gas from the sour water stripper, leaving the reflux drum contains approximately 30 mol% water.

Two stage stripping:. The two-stage sour water stripper differs from the single stage stripper by operating the first column at a lower pH (6), removing H_2S over the top and NH_3/water via the bottom, and the second stage at a higher pH (10), removing the NH_3 over the top and a stripped water stream over the bottom. These results in much lower H_2S and NH_3 concentration in the stripped water to be discharged to the effluent treatment plant.

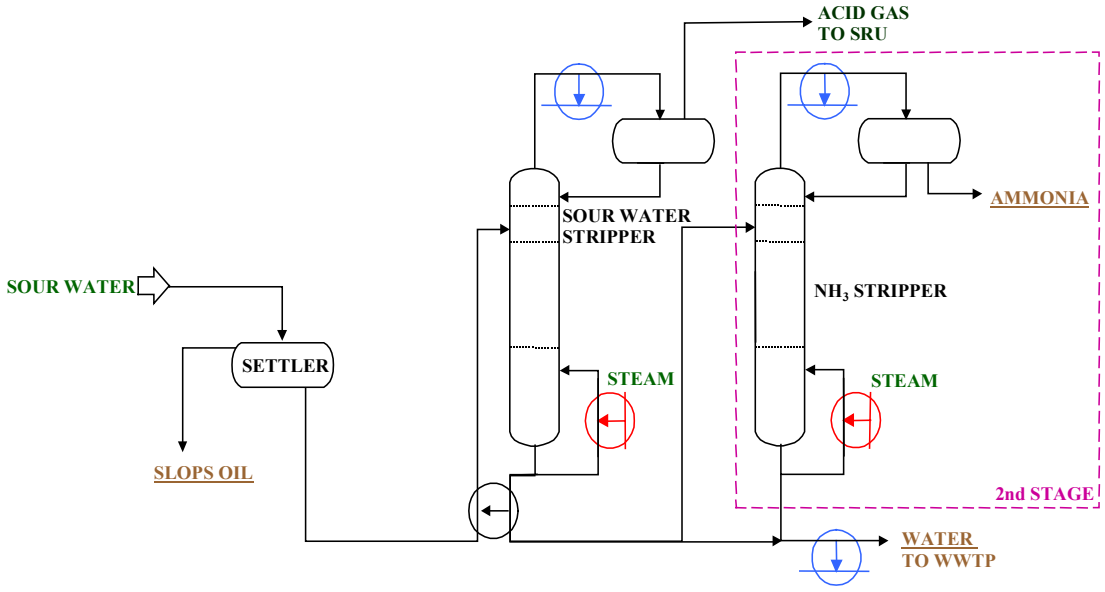


Figure 4.16: Simplified process flow diagram of a sour water stripping unit (SWS)
Note: The section enclosed in the dotted box is the second stage of a two stage SWS

Other techniques to consider are:

- standby stripping facilities or additional storage to be provided for sour water. Duplication of the SWS
- sulphide rich effluents streams should be stripped prior to discharge to effluent treatment. Most commonly SWSs have a surge drum to remove entrained hydrocarbons that can cause upset in the downstream SRU.

Achieved environmental benefits

The SWS produces sour off-gas and stripped effluent which are routed to down stream units. Next table shows the achievable levels for a 1-stage SWS.

	Source	**Flow**	**Composition min/max**	**Comments**
Emissions: sour gas	SWS off-gas to be routed to SRU	plant specific	Mainly H_2S and NH_3. Content depends on crude quality and refinery configuration	SRU
Effluent: stripped sour water (SSW)	SWS effluent to be used as desalter wash water or routed to WWTP.	20 - 50 m^3/h in a 5 Mt/yr refinery	COD: 500mg/l H_2S: 10 mg/l Phenol: 30 - 100 mg/l NH_3: 75 - 150 mg/l	SSW can be reduced by limiting live steam injection in process units and increasing the use of a reboiler

Stripped sour water can be routed to the process units for re-use or to the waste water treatment plant, after appropriate cooling if necessary. Normally stripped sour water can be used as desalter wash water, provided its contaminants levels are adequate (NH_3 less than 150 ppm and H_2S less than 20 ppm). These limits are required to avoid corrosion in downstream units (i.e.: CDU overhead system).

Two stage stripping: In the first one, H_2S is separated, whereas in the second one NH_3 is removed from water and concentrated to a solution containing 10 % NH_3, which can be re-used to reduce NO_x emissions. Exemplary data of this two stage stripping are given in the following table.

Values (mg/l)	Supply H_2S-Stripper-Column 1	Efflux NH_3-Stripper-Column 2	Efflux from WWTP
COD	14400	599	37
Hydrocarbons	98	4	1.1
N tot. Inorg.	1373	6	7
NH_4-N	1372	5	5
Phenols	182	141	0.1
Sulphide	1323	5	0.5

The two stage SWS process can reach an overall H_2S and NH_3 recovery, of 98 % and 95 % respectively. Hydrogen sulphide: 0.1 - 1.0 mg/l; Ammonia: 1 - 10 mg/l. Ammonia generated in the two stage SWS process can be used within the refinery.

Other benefits are that the reduction of ammonia and sulphur content in the waste water by SWS. Reduction of ammonia entering the waste water system reduce the need for a nitrification / denitrification process.

The addition of a sour water tank homogenises the different water streams, it further removes oil that may cause plugging in the stripper and it helps to produce acid gas of constant composition for the SRU. Because less hydrocarbon enters to the SRU, less coking of catalyst results.

Cross-media effects

Routing the off-gases from the stripper unit can influence negatively the efficiency and the running conditions of the SRU mainly due to the NH_3 content in the gas

Combination of 2 stage sour water stripping and re-use of NH_3-rich effluent for reduction of NO_x from CO-boiler achieves reduction of NO_x by 180 t/yr, NH_4-N by 250 t/yr and solid waste from WWTP by 10 % at Holborn refinery.

Operational data

Electricity (kWh/t)	Steam consumed (kg/t)	Acid and caustic consumption
2 – 3	100 - 200	n.a.

Most commonly SWSs have a surge drum to remove entrained hydrocarbons, that can cause upsets in the downstream SRU. The SWS feed is normally preheated by feed/effluent exchangers to a tower inlet temperature of 100°C to save stripping steam. A higher feed temperature than 100°C is not advisable since flashing of the feed on entry to the stripper tower is to be avoided.

Decreasing the water content in the off-gas below 30 mol% is not practised as problems with salt deposition from the vapour phase can occur. This salt deposition particularly occurs when CO_2 is present in the sour gas, and the level of corrosive ammonium bisulphide (NH_4HS) in the condensate refluxed to the stripper column increases beyond the level acceptable from a materials and corrosion perspective.

The use of a second stripping column consume extra chemicals for pH control (acid, caustic) and extra energy.

Applicability

Two stage stripping: In case the SWS bottoms are not re-used but sent to biotreating it may still contain too much NH_3. In order to solve this in the SWS unit, the Sour Water Stripper Column can be either equipped with a larger number of stages or a two stage stripper can be installed (Section enclosed in dotted box in Figure 4.16). The more or less pure ammonia stream from the second stripper top might be sent to the CO boiler of the FCCU for deNOxing purposes or to the hot flue gas of a furnace.

Economics
The cost for new steam strippers depends on the flow rate and range from about EUR 0.525 - 0.700 millions.

The investment costs for expansion of existing sour water stripping in the NH_3 stripper were about EUR 3.3 million. Annual operating costs (steam, energy, cooling water, sulphuric acid, caustic lye, fuel gas) for the entire plant is approximately EUR 0.45 million. In contrast to the annual operating cost for operation of only H_2S strippers (EUR 0.35 million), the annual operating cost are approximately 75000 EUR because the expansion of the NH_3 stripper.

Other data shows the following costs for different sour water strippers:

Year built	Design NH_3 effluent conc. (mg/l)	Actual performance (mg/l NH_3)	Design flow rate (m^3/h)	Capital cost (EUR million)	Operating cost/yr (EUR·10^3)
1996	18		22	2.7	–
1996	10		30	4.0	21
1992	max 150	13	20	0.6	97
1993	50		25	5.4	43
1995	50	35	32	5.3	175
1992	100		50	10.9	–

Table 4.48: Economics and performance of Sour Water Strippers

Driving force for implementation
Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia and hydrogen sulphide) and/or steam condensate, that will be contaminated with hydrocarbons. Sour water needs stripping prior to further treatment or re-use as wash water. A typical composition of the sour water is 900 mg/l of hydrogen sulphide, 2000 mg/l ammonia, 200 mg/l phenols and 15 mg/l hydrogen cyanide.

Example plants
Two-stage stripping is seldomly applied in refineries. In the Holborn refinery in Germany a two stage SWS is integrated as an alternative to an effluent denitrification stage in the WWTP. Also in the new Mider refinery a two-stage SWS unit has been installed.

Reference literature
[19, Irish EPA, 1993], [257, Gilbert, 2000], [118, VROM, 1999], [211, Ecker, 1999], [127, UN/ECE, 1998], [302, UBA Germany, 2000], [181, HP, 1998], [316, TWG, 2000], [115, CONCAWE, 1999]

4.24.3 Reduction and recovery of hydrocarbons from waste water

Description
Benzene, phenols and hydrocarbons in general in waste water can often be treated more easily and effectively at the point it is generated rather than at the waste water treatment plant after it is mixed with other waste water. Consequently the identification of hydrocarbon sources is the first measure to consider.

1. *Nitrogen or air stripping* for benzene recovery from waste water. Nitrogen stripping can be used to strip benzene and other low aromatic compounds from waste water. The mixture is treated by activated carbon beds that capture the organic allowing cleaned nitrogen to recycle to the waste water stripper. Peridiocally, the carbon bed is insitu regenerated with live steam: desorbed organic vapours are carried by the steam to a condenser and

subsequently decanted into organic and water layers. Organics are returned to refinery as valuable feed
2. *Liquid-Liquid extraction* from waste waters for phenol extraction from waste water
3. Reduction of hydrocarbons and aromatic compounds
4. *High-pressure wet air oxidation*. Water is intensively mixed with air and organic compounds are oxidised in the presence of a catalyst at high temperature and high pressure (250 ºC, 7 MPa). Sulphur containing substances are oxidised to sulphates; amines and nitriles are converted to molecular nitrogen
5. *Low pressure oxidation*. Persistent organic compounds are treated with oxygen and are mineralised in a biological treatment plant. (BOC Gases)
6. *Supercritical water oxidation process*. Supercritical water (373 ºC, 221 bar) is used to dissolve organic compounds, which are oxidised in a reactor by injection of oxygen
7. *Energy absorption technology*. Sources of contamination with hydrocarbons are desalters (40 %), storage tanks (20 %), slop-systems (15 %) and other processes (25 %). It is possible to recognise type and extent of water contamination directly at the source by use of electromagnetically high frequencies (EA – Energy Absorption Technology).

Achieved environmental benefits

1. A refinery has used that system to reduce 1895 l/d of waste water containing benzene 50 ppm, 100 ppm toluene/xylenes and 100 ppm of other hydrocarbons liquids. The recovery unit consistently reduced benzene to below 500 ppb. About 35000 kg of hydrocarbon liquid are returned to the refinery feedstock annually. This technique can be also applied to remove MTBE
2. Recoveries greater than 99 % or raffinate concentrations well below 1ppm can be achieved. With this technique waste water containing > 1 % phenols was treated to get purified water with a phenol content lower than 1 ppm (Efficiencies: higher than 99 %; Koch Process Technology, Inc.). Phenol containing waste water may also be treated microbiologically
3. The efficiency of this process is stated to be 99 % for a COD of 30000 mg/l. Sodium sulphide of spent caustic can be reduced from 3 % to <1 mg/l (160°C; 0.9 MPa)
4.
5. Efficiency is higher than 99.9 %
6. With this system emissions of hydrocarbons to water could be reduced (e.g. benzene contamination: minus 80 %).

Operational data

1. Nitrogen stripping has several advantages over air. No oxygen reduces biological fouling of the stripper and reduces the risk of refinery upsets creating explosive mixtures in the recovery unit.
2. Utilities: typical per m^3 water feed
Electricity 159 kWh
Steam, 20.7 barg, 15.6 kg
Steam, 2.07 barg, 103 kg
Water tempered at 45 ºC, (ΔT = 19 ºC) 5.6 m^3
cooling at 29 ºC, (ΔT = 11 ºC) 2.5 m^3

Applicability

1. This technology is used for the treatment of desalting water and waste water from BTEX-plants (Texaco Development Co; AMCEC, Inc.).
2. They can be designed to handle waste water streams with phenol levels from several hundred ppm to saturation (approx. 7 %) and above.
3. This method is not applied for high flows.

Economics

1. Economics: The design and equipment supply cost of about $1250000. Annual utility costs are around $85000.

2. Economics: Cost effective for levels of phenols higher than 1 %. A base case example for a waste water stream of 27.2 m^3/h containing 6 % phenol was treated with 4.3 m^3/h solvent in a four-column system. The overall phenol recovery was 99.3 %.
Investment, extractor only, \$1.32/m^3
complete system, \$3.43/m^3
Recovered value \$3.96/m^3
3. Method very expensive

Driving force for implementation
Reduction and recovery of hydrocarbons

Example plants
1. More than 15 systems ranging from 800 to 12000 l/min are now operating in various USA refineries. Air stripping for the removal of MTBE has been used succesfully at least in one European refinery.
2. This system is typically applied when phenol concentrations are high.

Reference literature
[181, HP, 1998], [211, Ecker, 1999], [316, TWG, 2000], [321, Helm, Spencer et al., 1998]

4.24.4 Primary treatments

Process water coming from the SWS is the main process water source in refineries. Moreover, some incompatible process effluents and drains from off-sites (flares and tanks) add to the total flow of process water. This effluent has to pass first an oil/water separator (CPI, PPI or API) for free oil and solids removal and an equalisation tank where sometimes further oil skimming can be accomplished.

Description
Emissions to air of VOC (including benzene) and odorous components (hydrogen sulphides and mercaptans), however, are not uncommon and cannot always be controlled fully by up-stream measures. Therefore APIs, CPIs can be provided with covers as an emission reduction measure, sometimes with off-gas treatment (biofilter or re-injected into the aeration basin). Safety aspects (explosiveness of VOC-air mixtures) are to be attended.

The next level of control is to install water seals (traps) on sewers and drains and gas tight covers on junction boxes in the system. The use of covers on oil/water separators with good oil removal facilities will prevent or reduce evaporation of liquid hydrocarbons from exposed surfaces. Alternatively, incineration of the vapours coming from the API could be achieved from a covered API separator.

Achieved environmental benefits
Performance of CPIs and APIs as regards oil removal suggests 50 - 100 ppm oil in the outlet.
NMVOC emissions from oil separators can be reduced to 3 g/m^3 by cover the CPI and API.

Emission Source	Oily water sewers/sumps/separations and drainage operations			
Control Technology	Automatic drainage facilities	Fixed/floating covers on APIs/sump	Incineration	'dry' oil collection systems
Efficiency	80 %	80 - 90 %	98 %	90 %
Investment Costs	0.002 - 0.03 EUR million/tank (1)	0.001 EUR million/m^2 (1)	1EUR million(1)	n.a.
Operating Costs	Small	Moderate	0.1 EUR million/yr(1)	n.a.
Other Impacts Comments	May not be suitable for all tank stocks	Limitation on access to APIs. Fixed covers may require purging systems	Assumes API is covered	n.a.

Table 4.49: VOC controls in oily water operations
(Installed and Retrofitted)
(1) Source: Industry propriety information

The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [117, VDI, 2000]:

- 20 g/m^2 per hour for open oil separator
- 2 g/m^2 per hour for covered oil separator

Cross-media effects
When API or PPI separators are covered the flammability/explosion limits may easily be reached. Consequently safety and environmental protection should be considered.

Operational data
Covers present problems with skimming of free oil.

Applicability
Those systems are fully applicable. CPI are easier to cover than API.

Economics
Costs are estimated with about 460 EUR per kt of HC emissions reduction by provision of floating covers for waste water separator bays. The investment for the installation of two 200 m^3 floating slab-covers is about EUR 75000 and the total annual operating costs about EUR 42800 per year.

Driving force for implementation
Reduction of VOC emissions and maximise the collection of oil. It has been estimated that between 0.5 and 4 % of the crude oil processed in a refinery can be found in the waste water before any treatment, depending on the complexity of a refinery. Consequently, oil is always recovered from the drainage system before the waste water is passed for final treatment.

Example plants
Well proven technologies. In some European refineries, the API and PPI separators have been covered.

Reference literature
[107, Janson, 1999], [115, CONCAWE, 1999], [258, Manduzio, 2000], [127, UN/ECE, 1998], [247, UBA Austria, 1998]

4.24.5 Secondary treatments

The next step after the primary treatments waste water is processed for the removal of dispersed oil and solids by air flotation where with the aid of polyelectrolytes flocs are formed which capture oil and suspended solids (sometimes a sandfilter is used for this duty). The thus formed sludge is brought to the water surface by air flotation whereby tiny air bubbles are also captured by the sludge flocs. The sludge is skimmed off and the water is routed to a biotreater.

Description
Emissions to air of VOC (including benzene) and odorous components (hydrogen sulphides and mercaptans), however, are not uncommon and cannot always be controlled fully by up-stream measures. Therefore DAF units can be provided with covers as an emission reduction measure, sometimes with off-gas treatment (biofilter or re-injected into the aeration basin). Safety aspects (explosiveness of VOC-air mixtures) are to be attended.

Other techniques to consider are:
- treat DAF float separately, rather than sending it to the slop oil system
- use continuous slip-stream filtration to remove amine degradation products.

Achieved environmental benefits
Flotation units achieve 10 - 20 ppm of oil.

Operational data
Chemicals utilisation includes acid and/or alkali for pH correction, polyelectrolyte or $FeSO_4$ or $FeCl_2$ flocculant requirements of the floculation units. In practice pH correction and polymer dosing to the flocculation flotation unit needs daily attention and fine tuning if needed. The energy requirement for the WWTP is relatively low, the aeration compressor being the largest consumer.

Applicability
Fully applicable

Economics

Year built	Type	Design flow rate (m^3/h)	Capital cost (EUR x 10^6)	Operating cost/yr (EUR x 10^3)
1995	DAF	80	0.2	18
1994	DAF	300	1.4	20
1989	IAF	400	2.4	47
1993	DAF	350	8.0	683
1996	IAF	818	0.4	112
1996	DAF	50	3.1	–
1996	DAF	800	1.5	–

Driving force for implementation
Reduce the hydrocarbon contents from waste water.

Example plants
Well proven technologies

Reference literature
[113, Noyes, 1993], [115, CONCAWE, 1999]

4.24.6 Tertiary treatments

Description
After the sludge is skimmed off in the flotation process, the water is routed to a biotreater, usually an activated sludge unit or to a trickling filter. By means of bacteria nearly all dissolved hydrocarbons and other organics are removed. In case deep nitrogen removal is required, denitrification in a biotreater is an option. Oxygen using (aerobic) bacteria is able to convert ammonia into nitrate and in a so-called anoxic stage (without aeration) in the biotreater other bacteria are able to convert nitrate into atmospheric nitrogen, which escape as bubbles. The generated biomass or biosludge is allowed to settle in a clarifier and for the main part recycled to the biotreater. Primary sludge from the flocculation-unit and excess biosludge are usually sent to a thickener prior to dewatering and disposal (Figure 4.17). Air Flocculation Flotation processes can be operated with Dissolved or Induced Air (DAF or IAF resp.).

Other techniques to consider are:

- heterotroph denitrification combined with autotrophic sulphide oxidation (the reductive potential of sulphide is used to eliminate nitrogen via denitrifiction, simultaneously sulphide oxidised, so that sulphide precipitation in subsequent biological treatment unit is unnecesary)
- granular activated carbon (GAC). Pollutants are adsorbed and biologically treated in an oxygen rich atmosphere. (attainable COD: <100 mg/l)
- powdered activated carbon (PAC). Similar to GAC
- cover of the waste water treatment plant. Fixed covers are to be avoided for loss prevention purposes (building up of explosive vapours)
- emissions to air of VOC (including benzene) and odorous components (hydrogen sulphides and mercaptans), are not uncommon and cannot always be controlled fully by up-stream measures. Therefore sometimes the aeration basins of biotreaters can be provided with covers as an emission reduction measure, sometimes with off-gas treatment (biofilter or re-injected into the aeration basin). Safety aspects (explosiveness of VOC-air mixtures) are to be attended, however they are less dangerous than in up-stream units.

Achieved environmental benefits
A biotreater can remove 80 - 90 % of dissolved oil and COD as well as 90 - 98 % BOD under normal operating conditions. Natural nitrogen removal is normally about 10 % in an activated sludge unit (ASU), 70 - 80 % in a nitrification/denitrification biotreater (DNB) and up to 90 % in a tertiary (add-on) denitrification unit. For MAH/phenol >95 % removal can be achieved based on a well-adapted biological system. Oxygen aireation in activated sludge plants can be up to 50 % more efficient than air aeration techniques.

Cross-media effects
Energy consumption, activated carbon wastes when GAC or PAC are appplied and methanol consumption when denitrification is applied. Waste water treatment generate sludge. If waste water treatment is not properly operated the amount of sludge can be increased.

Operational data
If a denitrification biotreater is applied pumping energy is relatively high. If a tertiary treatment unit is used for ammonia removal by biological nitrification, methanol can be used as in a subsequent denitrification stage as an oxygen receptor for denitrifiying bacteria. In some refinery biotreaters powdered activated carbon is dosed for meeting discharge specs. The sensitivity of a biotreater against shock loads (peak discharges) of toxic compounds (e.g. sulfolane, MTBE, phenol, cyanide, sulphide) is relatively large and should be avoided by spill prevention measures, good housekeeping and equalisation in a buffer tank.

Applicability
Fully applicable. Toxic streams should not enter a biotreater.

Economics
A complete API, equalisation tank, DAF, DNB biotreater, clarifier train for 125 m^3/h requires an investment cost of about EUR 15 million provided the up-stream drainage infrastructure is available. Operating costs are in the order of EUR 1.5/m^3.

Floating cover: Capacity of the process 800 m^3/h of oily water may emit up to 1000 t/yr
Efficiency: 90 % of recovery of the VOC
Investment cost EUR 0.6 million
Operating cost: EUR 0.03 million per year

Driving force for implementation
Denitrification biotreaters are usually applied in environments sensitive to nitrates.

Example plants
Well proven technologies. Nitrification/denitrification biotreater installations are operational at Harburg, Godorf and Gothenburg refineries.

Reference literature
[181, HP, 1998], [45, Sema and Sofres, 1991]

4.24.7 Final treatments

In countries where water is a scarce resource it is sometimes economically attractive to further improve the quality of the effluent in order to re-use the water as wash water or even as a source for the preparation of boiler feed water (BFW). In that case sand filtration (SF), followed by a combination of ultrafiltration (UF) or activated carbon filtration (AC) and reverse osmosis (RO) for salt removal generates sufficiently pure water for entering the demineralisation unit of the BFW preparation unit. Other techniques are ozonation/oxidation, ion exchange and incineration.

Description
Techniques for the reduction of salt contents of the waste water: Ion exchange, Membrane processes or Osmosis.
Metals may be separated by Precipitation, Flotation, Extraction, Ion exchange or Vacuum distillation.

Achieved environmental benefits
See Section 4.24.8

Cross-media effects
Energy consumption, wastes from exhausted activated carbon, membranes and metal sludges.

Operational data
Activated carbon is needed if AC filtration appears in the system.

Economics
When the WWTP is extended with SF and AC, the operating costs of the resulting WWTP is doubled in reference with a WWTP without those systems (base case). With UF and RO both the investment costs and the operating costs will approximately triple the base case.

Driving force for implementation
These systems have been installed at some locations only in BFW preparation. Applied in refineries where shortages of water supply may occur.

Example plants
Sandfilters, ultrafiltration, activated carbon and reverse osmosis are proven technologies.

Reference literature
[181, HP, 1998].

4.24.8 Refinery waste water treatments

This section contains what emission values can be achieved by an overall waste water treatment of refineries. The waste water system considered contains primary, secondary and tertiary treatment.

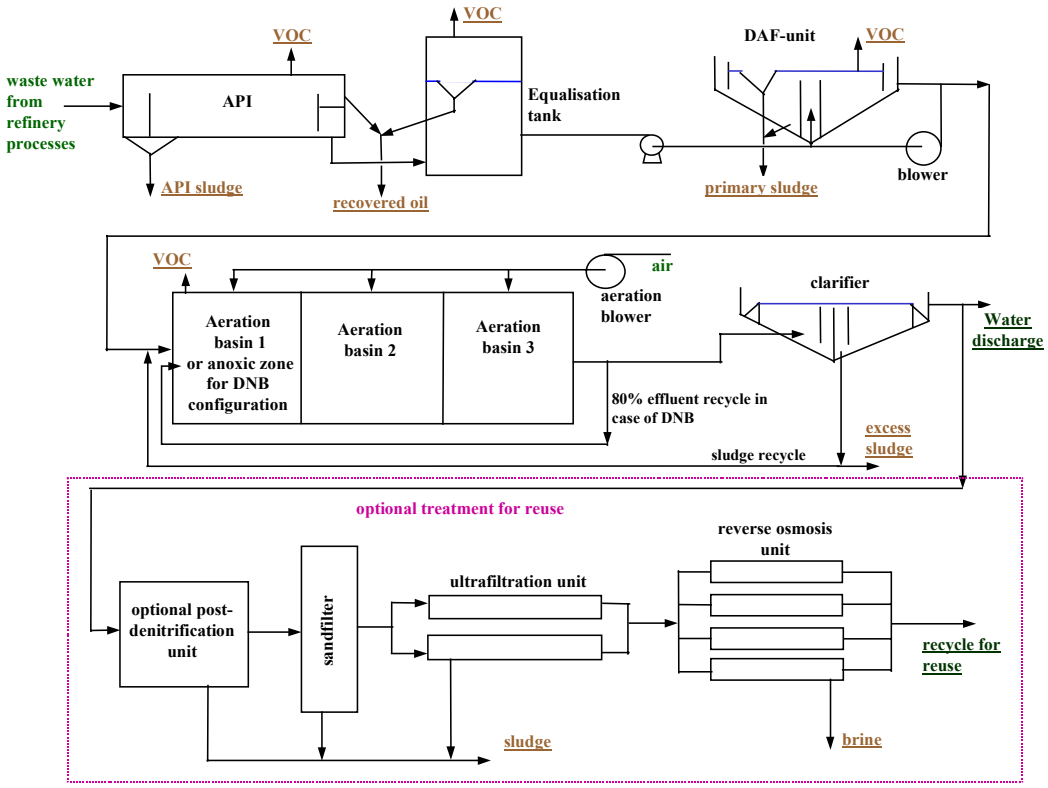


Figure 4.17: Simplified process flow diagram of a typical refinery waste water treatment plant, including denitrification/nitrification biotreater.

Achievable levels
The following ranges of release levels are considered to be achievable for key water parameters typically used to characterise a refinery release to water using a good combination of techniques described in this section.

Parameter	Concentration (mg/l)	Load (g/tonne crude oil or feedtocks processed) (Yearly average)
Temperature	30 - 35 ºC	
pH	6.5 - 8.5	
Total hydrocarbon oil content	0.05 - 5	0.01 - 3
Biological oxygen demand (5 day ΔTU @ 20 ºC)	2 - 30	0.5 - 25
Chemical oxygen demand (2 hour)	30 - 160	3 - 125
Ammoniacal nitrogen (as N)	0.25 - 15	0.1 - 20
Total nitrogen (as N)	1 - 100	0.5 - 60
Suspended solids (dried @ 105 ºC)	2 - 80	1 - 50
Cyanides	0.03 - 0.1	0.06
Fluor (refineries using HF alkylation)	1 - 10	
Nitrates	2 - 35	
Nitrites	2 - 20	
Phosphates (as P)	0.1 - 1.5	
Total P as P	1 - 2	0.6 - 1.2
Sulphides	0.01 - 0.6	0.3
Sulphite	< 2	
AOX as Cl	< 0.1	< 0.06
Benzene	<0.001 - 0.05	
Benzo(a)pyrene	< 0.05	
BTEX	<0.001 - 0.1	0.001 – 0.005
MTBE (lower levels for refineries not producing MTBE)	<0.001 - 0.1	
Phenols	0.03 - 0.4	0.01 - 0.25
Tensioactives (ionic and anionic)	< 2	
As	0.00055 - 0.1	
Cd	0.0009 - 0.05	
Total Cr	< 0.5	
Cr (VI) as Cr	< 0.1	
Co	< 0.5	
Zn	< 0.5 - 1	
Pb	0.024 – 0.5	
Fe	< 3 - 5	
Cu	0.003 - 0.5	
Ni	0.006 - 0.5	
Hg	< 0.0001 –0.05	
V	< 1	
Levels given within this table are ranges of achievable levels from the effluent treatment plant. Some of the concentration values have been reported for different average periods. No distinction have been done in here. They are given on the basis of 95 % of values not exceeding the relevant level. The water flow is calculated for process water and purging water of the closed loop cooling system. References: [101, World Bank, 1998], [181, HP, 1998], [262, Jansson, 2000], [257, Gilbert, 2000], [118, VROM, 1999], HELCOM and OSPAR recommendation, [268, TWG, 2001]		

Table 4.50: Emission concentration and loads found in good operated WWTP

Effluent treatment units are designed such that the most important key parameters (suspended solids, TOC, COD and BOD) can be monitored automatically leading to limited operator attention and even less if sufficient up-stream water management measures are being taken to ensure a constant quality and flow of water and adequate buffering. TOC and COD can be monitored continuously whereas BOD need several days for the analysis.

Applicability

WWTP usually occupy a significant space at refineries, particularly the biotreater due to the relative slow biodegradation process. In order to save space it is advisable to integrate water management principles into the design leading to a compact. A full train WWTP occupies a space of 1 ha, not including an observation basin which many refineries have installed as a last line of defense. The amount of rainwater depends of course on the local climatic conditions and the size and layout of the refinery.

4.25 Waste management

This section together with the two previous ones are dealing with the end-of-pipe processes that appear in a refinery. The reason why those techniques are appearing here is to give an overall description of the techniques and to avoid repetition. Description of end-of-pipe techniques does not appear in the previous sections. In this Section, general information on environmental benefits, cross-media effects, operational data, applicability is described here. Prevention or minimisation techniques applied to different process activities are found in each of the sections dealing with those production processes. Complementing waste minimisation and prevention of generation of waste that may be found along this chapter, this section contains the waste management systems that may be found within refineries. Those techniques are only discussed in this section within this document.

Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash. Other waste fractions are waste from flue gas desulphurisation, fly ash, bottom ash, spent activated carbon, filter dust, inorganic salts as ammonium sulphate and lime from water pretreatment, oil-contaminated soil, bitumen, sweepings, spent acid and caustic solutions, chemicals, among others. Treatment of these wastes includes incineration, land treating off-site, land filling onsite, land filling off-site, chemical fixation, neutralization, and other treatment methods.

4.25.1 Establishment of a waste management programme

Description

The establishment of an Environmental Management System (Section 4.15.1) should contain elements to prevent waste generation and some pollution prevention techniques that help to prevent pollution of soil and groundwater. Some techniques that may be included are:

- implementation of a sludge master plan with the aim to reduce the sludge generated.
- provide enclosed sampling loops
- clean and assembly only in especially constructed and dedicated areas
- provide dedicated drainage systems
- physical barriers such as clay walls or plastic membranes can be installed around the site boundary. To be effective at containing oil pollution, these have to extend below the water table. Monitoring wells will also be required to ensure that if oil does build up behind the barrier, it can be removed before it has a chance to escape under the barrier. A second form of barrier is a ditch also extending to below the groundwater table. Any oil leaving the site can be observed floating on the water in the ditch and recovered. The outer face of the ditch can be sealed with an impervious layer such as concrete, plastic, clay, steel piling etc
- groundwater, like surface water basically flows downhill. Therefore, groundwater can be prevented from leaving a site by lowering the level inside the site by pumping so that it is lower than the level outside. Water will then flow into the site rather than outwards. The pumped water has obviously to be disposed of. It may be possible to use this water for supply purposes on site. If it is to be discharged, then monitoring will be required to ensure that it is not contaminated. If it is, then it will have to be treated in which case, this method will be limited by the capacity of the effluent treatment system
- minimisation of underground piping. Underground piping can be a source of undetected releases to the soil and groundwater. Inspecting, repairing or replacing underground piping with surface piping can reduce or eliminate these potential sources. Retrofitting can be very expensive
- perform a risk analysis to rank in order of significance cases where accidental leak may occur (elements to consider are the product in the tanks/pipes, the age of the equipment, the nature of the soil and groundwater that would be affected). Prioritise areas where impermeable floors are needed most. Produce a multiyear master plan to program necessary steps
- periodically screening of leaks in sewers and pipes.
- correct conditioning of a catalyst during a run extends catalytic life

- control of sodium content in visbreaker feedstock reduces coke formation
- process optimisation leads to less off-specification product and hence less recycle
- recycling caustic sufficiently can ensure it is completely spent
- Sorting waste mixes e.g. concrete and scrap metal. could be cost-attractive (cheaper disposal routes for some components) and eliminates risk of unwanted components
- asbestos lagging: special equipment for compaction & packing
- TEL/TML scale & sludge: permanganate treatment eliminates TEL/TML traces
- oiled solids (soil): de-oiling in an oil extractor.
- neutralisation: mixing polymerisation catalyst (H_3PO_4) with lime
- Process treatment by steaming, flushing or regeneration prior to disposal: clay and sand filters; catalysts
- Solids released to the waste water sewer system can account for a large portion of a refinery's oily sludges. Solids entering the sewer system (primarily soil particles) become coated with oil and are deposited as oily sludges in the API oil/water separator. Because a typical sludge has a solids content of 5 to 30 percent by weight, preventing one kg of solids from entering the sewer system can eliminate 3 to 20 kg of oily sludge. The Amoco/USAEPA study estimated that at the Yorktown facility 1000 tonnes of solids per year enter the refinery sewer system. Methods used to control solids include: using a street sweeper on paved areas, paving unpaved areas, planting ground cover on unpaved areas, re-lining sewers, cleaning solids from ditches and catch basins, and reducing heat exchanger bundle cleaning solids by using antifoulants in cooling water.
- A significant portion of refinery waste arises from oily sludges found in combined process/storm sewers. Segregation of the relatively clean rainwater runoff from the process streams can reduce the quantity of oily sludges generated. Furthermore, there is a much higher potential for recovery of oil from smaller, more concentrated process streams.

Achieved environmental benefits
The aim of such a programme is to prevent contamination of the soil and the groundwater as well as reduce the amount of waste generated.

Reference literature
[195, The world refining association, 1999], [316, TWG, 2000], [115, CONCAWE, 1999]

4.25.2 Sludge management and treatment

Description
Sludges are defined as emulsions of oil in water, stabilised by the presence of solids. In refineries a number of different types of sludges are generated at the following sources: crude and product tanks (bottoms), API separation units, flocculation and flotation units, DAF, contaminated soil. Biological sludges represent an important different category of sludges in terms of oil content and dewaterability. According to CONCAWE, in 1993, 44 % of the European refinery sludges were incinerated, 9 % was land farmed and 30 % land filled. It is foreseen that land filling and land farming of sludges will be increasingly prohibited by forthcoming EU legislation, which means that the scope for sludge prevention reduction but also for incineration at third parties will increase in the future.

The purpose of sludge treatment by dewatering, drying and/or incineration is to reduce the volume and the residual hydrocarbon content in order to save costs in subsequent processing or disposal. The principle of mechanical dewatering by decanters is based on centrifugal forces and on the density difference between water, oil and solids. The principle of the thermal treatment steps is based on a combination of evaporation by indirect heating and/or destruction of the organic constituents by thermal oxidation (incineration).

Decanter centrifuges are the most widely used for dewatering both oily and for biosludges. Steam dryers are almost exclusively applied for biosludge and function often as a pretreatment

step for incineration. Landfarming of sludge cakes is still being practised but is increasingly restricted in view of emissions and soil contamination risks.

Decanter centrifuges are widely used in sludge dewatering and deoiling applications throughout the (refining) industry, either as fixed facilities or as a mobile service rendered by contractors. Dewatered biological and oily sludges can be further processed using drying and/or incineration techniques resulting into virtually oil free residues for which useful applications are available.

Oily sludge dewatering is only applied at refineries that dispose of sludge cakes outside their premises in order to reduce the volume and associated disposal cost. Disposal to cement kilns, coal fired power plants, dedicated sludge incinerators, municipal and hazardous waste incinerators are all practised. Drying is currently hardly employed by refineries due to safety risks. de-oiling/dewatering of sludges gives small volume of solid, low solvent waste, (centrifuging or filtration). De-oiling/dewatering of sludges gives small volume of solid, low solvent waste, (centrifuging or filtration).

In Figure 4.18 a simplified process flow diagram is shown of a decanter combined with a fluidised bed incinerator (FBI) being the most appropriate technique for sludge incineration. The feeding of sludge cake into the sand bed of the FBI can be accomplished with a positive displacement pump. The oxygen for incineration is provided by air injection into the bed via a wind box and a perforated floor. An air ventilator enables the sand in the bed to fluidise. The burned out ash particulates leave the bed and are removed by flue gas treatment. This can consist of a waste heat boiler (WHB), an electrostatic precipitator (ESP), a scrubber section, a flue gas heater (to avoid a visible steam plume), a flue gas ventilator and a stack. The ash is transported by a chain/bucket conveyor combination or pneumatically to a hopper, and it usually requires dedusting by water spray and agglomeration in a double paddle mixer. At smaller incinerators a water quench is used to cool the flue gas from 850°C to about 150 °C prior to fabric (bag) filtration.

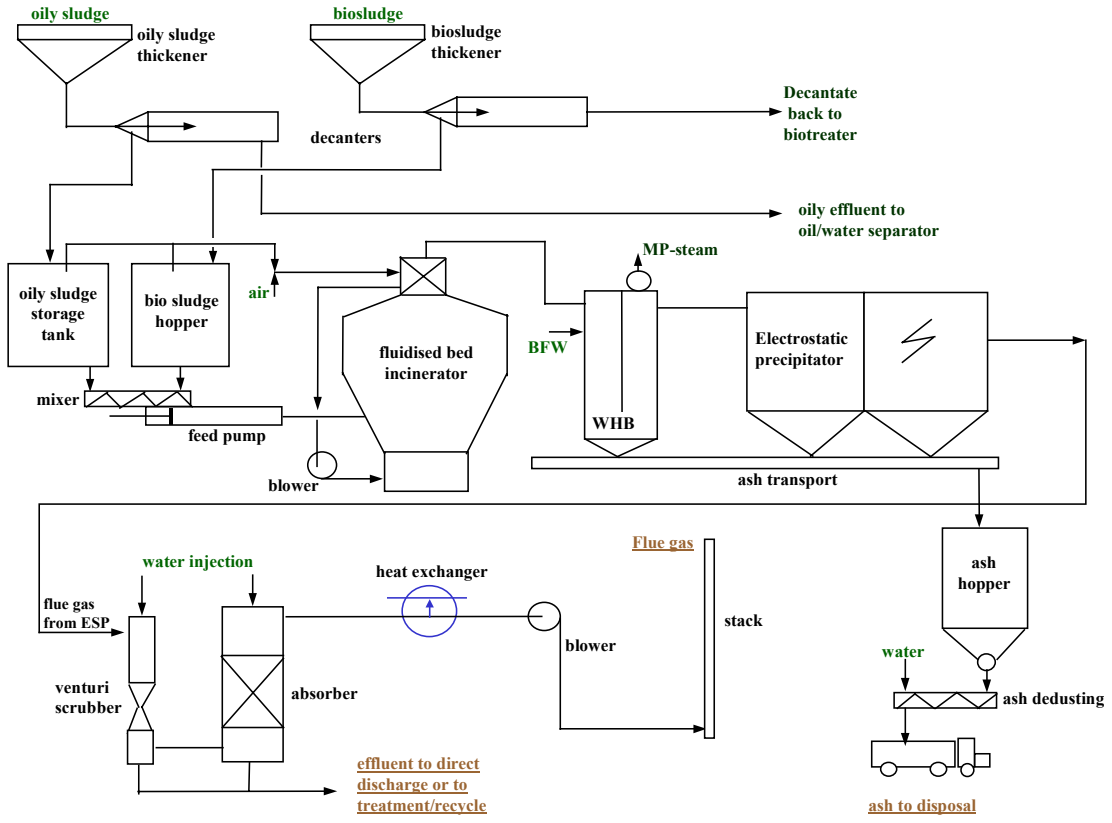


Figure 4.18: Simplified process flow diagram of sludge handling and incineration

Operating temperatures of the bed can be controlled at respectively 800 – 850 °C and 850 – 950 °C. The WHB operates between 250 and 450 °C, the ESP at 220 °C and the scrubber between 200 and 50 °C. In a FBI all ash is carried over the top with the flue gas, which provides a large dust loading (typically 50000 mg/Nm^3) to the WHB and ESP. Some 50 % of the dust is collected in the WHB, which can be regarded as a settling chamber. The catchment efficiency of an ESP is typically 99 %, leaving the (venturi) scrubber system to eliminate ± 500 mg/Nm^3 to the stringent CEC limit of 5 mg/Nm^3. The ash might find a useful outlet in concrete or asphalt dependent on the quality.

It should be mentioned that the emissions of SO_2, NO_x, CO, organic compound, PAH, heavy metals generated by those systems should be properly controlled by suitable abatement techniques.

Achieved environmental benefits
Generation of sludges can be minimised and can be maintained to values between 0.1 to 0.5 kg per tonne of feedstock processed within the refinery.

Cross-media effects
Scrubbing might require caustic if acidic (SO_2 and NO_x) components are present in the flue gas in concentrations which need to be removed to legal limits. The FBI with flue gas treatment and ash handling is a closed system, with fully automated control. The system is kept under slight negative pressure. The described system is regarded state-of-the-art for sludge incineration and is able to fulfil all legal stack emission requirements. Dioxins (PCDD/F) could be an issue at high chlorine loading combined with sub-optimum operation conditions. In flue gas treatment systems of domestic sludge incinerators impregnated activated carbon filters (ACF) or zeolites are installed for mercury/dioxin control. Effluent from the scrubber system can be substantial. Recirculation of scrubber water is only a cost effective proposition if treatment is required prior to discharge.

Operational data
Safety issues are associated with start-up and (planned or emergency) shut-down, for which a flame control interlock and a nitrogen purging system is required. Anaerobic and pyrophoric sludges (tank bottoms) can cause safety problems during storage and drying. The energy requirements of sludge drying and incineration depend strongly on the sludge cake characteristics (water and residual oil contents). Energy integration with FBI is two fold: air preheating of the primary fluidisation air is standard, and steam generation can be economically accomplished with systems able to generate >8 tonnes of MP steam/hour. An intrinsic disadvantage of FBI is the relatively large excess of air utilised in order to keep the bed fluidised.

Applicability
Because its high cost, options as reduction/recycling of waste are more typical waste minimisation options to be applied before waste incineration. Fluidised bed incinerators may be an option for third-party waste industry receiving waste streams.

Economics
For a FBI with a capacity of 4 t/h sludge cake (20 % dry solids) a footprint of about 50x100 m is required including tankage and complete flue gas and ash handling. The installation is normally 12 - 15 m high (tanks, incinerator, WHB, ESP, ash hopper) and the stack height is usually at least 40 m, dependent on ancillary installations. The above-described system would be suitable for a large 20 Mt/yr refinery and requires a capital investment of about EUR 37.5 million (including installation). The operational costs could amount to EUR 500 - 700/tonne dry solids. If large scale domestic sludge incinerators are available, which are entitled to take industrial sludges, the installation of a dedicated sludge incineration system is not economically justifiable. This certainly would be the case for smaller refineries, indicating that contract dewatering, drying and incineration are competitive to own processing.

A combination of decanters with an advanced drying system for oily sludge occupies only 10 - 15 % of the above indicated space, and would involve a capital investment of EUR 5 million due to the fact that expensive flue gas treatment is avoided.

Driving force for implementation
At some locations it has become common in the last 5 - 10 years to minimise sludges, collect them in tanks or basins and recover as much as possible the oil and water phases after gravity settling.

Example plants
Decanter centrifuges are reliable, advanced and proven technology with minimum emissions. At refinery locations permanent decanter centrifuges have for example been installed at refineries in Godorf, Gothenburg and Stanlow. A few times per year contractors are hired in either for on-site sludge processing or for collection and off-site processing (decanting, drying, incineration in cement kilns, power plants or in industrial/domestic waste or dedicated sludge incinerators).

Sludge incineration plants using the fluidised bed system are state-of-the-art but require advanced design and process control. At several refineries Mobil, Wilhelmshafen, Shell Pernis and Godorf, Esso Botlek these systems were already built in the 1970s. Some of them have been dismantled due to the current availability of more economic options as compared with necessary investment and operation in additional flue gas cleaning equipment. For oily sludges mixing with other wastes and use as secondary fuel in cement kilns and/or power plants represents an attractive disposal route if those plants use appropriate abatement techniques. International sludge contractors employ either mobile decanter and drying systems for oil recovery (Impex, EPMS, Soil Recovery A/S) or fixed oily sludge treatment systems (ATM).

4.25.3 Spent solid catalyst management

A BREF on Non-Ferrous metals has been already published. In that BREF the techniques used for the recovery of metals from secondary materials (e.g. refinery catalysts) is extensivelly treated.

The use of catalytic processes in refineries has increased significantly in the last 20 years. This increase is mainly due to the introduction of catalytic residue conversion processes such as heavy oil residue cracking, hydrocracking and residue hydroconversion, hydrodemetallisation and hydrofinishing and also Hydrogen production. Since 1980 a significant expansion has taken place of the hydrotreating and hydrodesulphurisation capacity as well as of sulphur recovery units and associated tail gas treatment, which processes also utilise catalysts. Traditional catalytic processes such as fluid catalytic cracking, catalytic reforming and isomerisation are also generators of spent catalysts.

Description
The purpose of spent catalyst management is to minimise environmental and health impacts. To achieve this goal spent catalysts are carefully handled, safely removed, carefully packed and sent for reactivation or metal reclamation. Metal recovery aims at conversion of spent catalysts into useful products, which can be recycled and re-used with minimum impact on the environment.

The principle of spent catalyst management is a scheduled, strictly regulated and safe handling of the materials involved, usually executed by specialised contractors during plant turn-arounds. Arrangements with the supplier of fresh catalyst can sometimes be made for them to take back the spent catalyst.

Regeneration of hydroprocessing catalysts is usually possible 3 or 4 times. The ultimate spent catalysts are almost exclusively reworked by third parties into commercial metal oxides or metal salt solutions. Although a regeneration process has been developed for spent FCC catalysts, this

process is hardly used due to the availability of cheaper alternatives. The catalyst carrier (alumina and/or silica) can sometimes be converted into products or is disposed of otherwise. Some refineries practise storage of spent catalysts at the refinery site with permission of the authorities. Spent catalysts are distinguished by type, process, composition and recyclability. A summary is given in Table 3.78.

Co/Mo catalysts from hydrodesulphurisation, hydrocracking, hydrotreating. Extensive regeneration and reclamation options are available.

Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. Regeneration and reclamation capacity is available.

Ni/W catalysts are used in lube oil hydrofinishing. This category experiences limitations to dispose off in view of the high Tungsten content (24 % w/w).

FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries. Outlets in road building are becoming available.

Reformer and Isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved.

Hydrodemetallisation catalysts typically have high vanadium contents (10 - 20 %) and are currently alumina based (used to be silica). Direct disposal to the steel industry is possibly the most cost-effective option.

Zn containing beds from H_2 plants are typically recycled to the Zn-industry where ZnS ores are processed. Amounts are some 50 t/yr.

The applied regeneration processes are based on pyrometallurgical techniques (roasting-, calcination, smelting-, sintering- and reduction furnaces) for thermal destruction of the inorganic matrix and on hydrometallurgical methods (aqueous/acid extraction, crystallisation, precipitation, separation and drying) for recovery/purification of metal salts either in dry form or as liquid metal concentrates.

The reclamation plants (more information in Non-Ferrous BREF) are typically operated in batch mode and contain many different unit operations. From the total spent catalysts only some 5 % pure products are produced. The remainder is either ferro-alloy feed or ceramic raw material. The plant usually processes relatively small batches. Spent hydroprocessing catalysts can vary considerably in composition. Hence the plants have limited process automation.

Achieved environmental benefits
Recover of metals from catalyst

Cross-media effects
The management of spent catalysts is an area of environmental concern because prolonged uncontrolled storage may lead to soil and groundwater contamination with heavy metals.

If the refinery has taken proper catalyst management measures the environmental concerns focus usually on the spent catalyst regeneration facilities. Most of these plants currently operate with proper flue gas and effluent treatment facilities and comply with present day emission standards. This is an important requirement for being acceptable for oil companies to make use of these spent catalyst reclamation contractors. Covering spent catalyst reception facilities is operational or being considered.

Operational data
Safe handling of chemicals is an important issue for spent catalyst metal reclaimers as toxic and pyrophoric materials are being handled. For the refinery utilisation of energy and process materials during spent catalyst handling are not particularly relevant.

Economics
Cost for processing and metal recovery depend strongly on the composition of the spent catalyst concerned. For high metal waste even a recovery fee will be paid to the waste generator. Current processing costs for an average HDS catalyst could be in the order of EUR 500/tonne. Recent stringent internationally accepted legal procedures, amongst which special packaging (for rent 2 m^3 containers at EUR 5/day), labelling and acceptance requirements as well as transportation costs could add considerably to these costs. On-site processing of spent catalysts is not economic for a refinery.

Spent FCC catalysts with limited V/Ni concentrations are accepted with consent of authorities, by raw material suppliers to the road building industry. The material is sometimes used in cement and as asphalt filler.

Example plants
The regeneration of spent catalysts started in the early 1980s. All processors use pyro- and hydrometallurgical processes with varying degrees of sophistication, recovery capabilities and environmental performance. The pyro- and hydrometallurgical processes currently applied are considered acceptable and proven technology.

Reference literature
[118, VROM, 1999; 122, REPSOL, 2001]

4.25.4 Recovery and recycling waste

Recycling and re-use of wastes minimises the quantity for disposal.

4.25.4.1 Treatment of heavy residues

Heavy residues generated by refineries are the heaviest fractions from the different units (distillation, conversion) and that have not application for products and are typically re-used within the refinery. Those residues have a calorific value that can be exploited. Follow a list of treatments that may be applied to reduce the amount of those residues. All these techniques are already analysed in other sections but they are put together here to help the reader to understand what refineries may do with their heavy residues.

1. **Methods to increase the hydrogen content (hydrogenation)**

   - **Catalytic hydrogenation** (included within Section 4.13) as Resid Fining, RCD UNIBON, Unicracking, HYVAHL-ASVAHL hydrotreatment, AUROBAN, H-Oil, LC-Fining, HYCON.

   - **Non catalytic hydrogenation** (included within Section 4.22) as Hydrovisbreaking, Dynacracking, Donor Solvent Visbreaking.

2. **Methods to increase the C-content**

   - **Catalytic cracking** (included within Section 4.5) as Reduced crude cracking (RCC), Heavy oil Cracking, VEBA combi cracking (VCC), Deep catalytic cracking (DCC).

- **Non catalytic cracking** (included within Section 4.7 and 4.22) as Delayed Coking, Fluid Coking, Flexicoking, LR-Coking, Deasphalting: DEMEX, Rose-Technology, Visbreaking, Thermal Cracking, Partial Oxidation.

4.25.4.2 Improve recovery of oils from oily sludges

Because oily sludges make up a large portion of refinery solid wastes, any improvement in the recovery of oil from the sludges can significantly reduce the volume of waste. There are a number of technologies currently in use to mechanically separate oil, water and solids, including: belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll centrifuges, disc centrifuges, shakers, thermal dryers and centrifuge-dryer combinations.

4.25.4.3 Regenerate or eliminate filtration clay

Clay from refinery filters must periodically be replaced. Spent clay often contains significant amounts of entrained hydrocarbons and, therefore, must be designated as hazardous waste. Techniques that may be applied are:

- Back washing spent clay with water or steam can reduce the hydrocarbon content to levels so that it can be re-used or handled as a nonhazardous waste.
- Another method used to regenerate clay is to wash the clay with naphtha, dry it by steam heating and then feed it to a burning kiln for regeneration.
- In some cases clay filtration can be replaced entirely with hydrotreating (See Section 4.20.4).

4.25.4.4 Reprocessing off-specification products

It is customary in refineries to have dedicated tankage (so-called “slops”) for the collection of hydrocarbon streams/intermediate products that cannot be blended into final products for the market. These slops are generally reprocessed, often by injection into the crude oil feedstock to the crude distilling unit or to the coker. Often segregation is practised between wet and dry slops. The wet slops tank is equipped with facilities to separate (drain) water from oil. (to prevent slugs of water coming into the crude distiller). In some refineries separate slops processing(distillation) facilities are installed [259, Dekkers, 2000].

Streams from water treatment units (e.g. oil/water mixtures from interceptors) can be routed to the wet slops tank. Oil from sludge thickeners (centrifuges/decanters) can be routed to the slops tanks. In that way also the oil in sludges from DAF units can be recovered [259, Dekkers, 2000].

4.25.4.5 Recycle / Re-use outside the installation

Some options to reduce the waste generation is the recycle or re-use of them. Follows some examples that can be considered as good environmental practices:

- some catalysts for metal recovery (reforming, desulphurisation) (See Section 4.25.3)
- waste lubes: re-refining (See Section 4.25.4.6)
- drums/containers: reconditioning
- spent caustic can be used: (See Section 4.20.2)
- alkylation process: CaF_2
  - for HF production
  - as a fluxing agent (steel industry)
- resale of polymerisation plant catalyst as a fertiliser (4.18.2)
- sale of gypsum or sulphuric acid from flue gas desulphurisation units

- dust: In the regenerative flue gas desulphurisation process according to Welmann Lord NH_3 is injected to prevent the formation of SO_3. Therefore up to 80 % of the ash consists of $(NH_4)_2SO_4$, which can be used as a fertiliser or as a basic material for NH_3 production [250, Winter, 2000].
- paper, wood, glass, scrap metal
- construction/demolition debris:
  - concrete to a crusher, for use in road building etc.
  - asphalt scrapings re-used, e.g. in road building

It has to be mentioned that re-use of waste fractions/residues outside the company is only an option, if these waste fractions meet certain criteria (such as concentration of pollutants in a fertiliser) and do not alter the original product characteristics (e.g. when using gypsum in the cement industry).

4.25.4.6 Re-use of waste lubes

Description
Waste lubes can be re-used within the refinery as fuel component or as feedstock for re-refining. Controlled incineration of waste lube oils is another alternative.

Achieved environmental benefits
Reduce the amount of waste lubes produced within the refinery and act as a receiver of waste lubes.

Cross-media effects
Waste lubricating oils are generally undefined and may contain all kind of additives and contaminants.(even PCB's). Inclusion of contaminated waste lubes into commercial fuel oil would expose the customer to high risks. Inclusion of this waste in refinery fuel poses a safety risk.

Applicability
Some applicability problems have been detected. For example, waste lubricating oil from garages may contain organic chlorides used as degreasers; in hydrotreaters they will be converted into HCl and cause severe corrosion in this high pressure unit filled with hydrogen. Only by application of well-controlled pretreatment techniques, the treated waste oil can be upgraded to a fuel component. Such a pretreatment activity is normally not compatible with refinery operations and is done outside the refinery by specialized companies, which also do the collection of the waste oils. The only exception to the use of waste lubes as fuel component is for waste lube oil that is generated in the refinery itself and of which its composition is beyond any doubt.

Driving force for implementation
Reduce the amount of waste lubes

Reference literature
[259, Dekkers, 2000].

4.25.4.7 Recycle lab samples

Lab samples can be recycled to the oil recovery system.

4.25.5 Biodegradation of wastes

This section contains methods for the biodegradation of refinery wastes that may be used specifically within refineries on-site. This section does not contain methods for the remediation

of contaminated soils. As it was stated in the scope of this document, soil remediation techniques are considered out of the scope of this document.

Description
Many hazardous chemicals present in refinery waste can be converted by microbiological methods to harmless compounds such as water and carbon dioxide. In general, the microbiological degradation of contaminants in soil is very slow in nature, because process conditions for such degradation are seldom favourable. To accelerate degradation a number of conditions have to be fulfilled.

Current techniques for biological decontamination are based on optimisation of the process conditions for microbiological degradation. The appropriate micro-organisms for microbiological degradation may already be present in the waste to be treated or may have to be added. The latter is necessary if special micro-organisms are required. These special micro-organisms can be obtained by selection and adaptation.

Operational data
The most important factors are the availability of temperature control, sufficient oxygen, nutrients, and the appropriate micro-organisms. Also important are the concentration level of the contaminants and the variation in concentration. The presence of toxic compounds can disturb the degradation process. Sometimes the presence of natural organic compounds has a positive influence on the biodegradation process.

In summary the following conditions have to be met in order to optimise the degradation rate of a waste generated by a refinery:

- sufficient number of micro-organisms of the right strains
- non-toxic concentrations of contaminants or other compounds
- adjustment of an accurate water content
- presence of sufficient nutrients (mainly P and N in ratio 1:10)
- presence of sufficient oxygen for aerobic processes and a full depletion of oxygen for anaerobic processes
- favourable temperature (20 - 30°C)
- pH 6 - 8
- temperature control
- measures have to be applied to prevent emissions into air by volatile contaminants or degradation products (by covering the area and by treating the exhaust air) and to prevent emissions into water and soil (by sealing the floor and re-use of excess water).
- sufficient availability of contaminants (preferably without high peak concentrations) to the micro-organisms including good mixing of nutrients, waste, inert (e.g. soil) and contaminants.

Reference literature
[115, CONCAWE, 1999]

4.25.6 Stabilisation/solidification of waste

Description
The following processes are commonly used:

Solidification – A process in which materials are added to the waste to produce a solid. It may involve a solidifying agent that physically surrounds the contaminant (i.e. cement or lime), or it may utilise a chemical fixation process (i.e. sorbents). The resulting waste is usually an easily handled solid with low leachability. Several processes exists:

- *Cement-based processes.* In this process the slurried waste is mixed with cement and during the hardening process is incorporated in the rigid concrete matrices. In the same line, spent catalytic cracker unit (FCCU) catalyst may be used as an additive in cement manufacturing. When the cement is used, the catalyst component forms insoluble hydrates with the chalk present in the cement mixture, which also gives beneficial fixation of heavy metals.
- *Thermoplastic techniques.* In general the use of thermoplastic solidification techniques is restricted to dry solid materials.
- *Mixing with bitumen.* The processing of waste with bitumen is applied in the oil manufacturing industry as a disposal method. This process allows treatment of soils with high levels (up to 10 %) of high boiling range hydrocarbons.

Stabilisation – The conversion of a waste to a chemically stable form that resists leaching. This may be accomplished by a pH adjustment. Stabilisation also generally results in a solidification of some sort (monolith or dry granular solid).

- *Chemical Stabilisation.* These processes are based on the reaction of lime with waste materials and water to form a chemically stable product. When compacted, the porosity to water is very low. This reduces the risk of leaching.

Encapsulation – Complete coating or enclosure of a waste with a new, non-permeable substance. Two type of encapsulation techniques exists: Micro-encapsulation and macro-encapsulation.

The *micro-encapsulation* techniques are based on the reduction to surface-to-volume ratio of the waste by formation of monolithic, hard mass with a very low permeability.
Macro-encapsulation is the enclosing of a relatively large quantity of waste, such as an entire waste container. Wastes are macro-encapsulated by surrounding them with a stiff, weight-supporting matrix, and a seam-free jacket.

Achieved environmental benefits
Stabilisation and solidification are treatment processes designed to improve waste handling and physical characteristics, decrease surface area across which pollutants can leach, or limit the solubility of hazardous constituents.

Applicability
Cement-based processes: The process is especially effective when the waste contains metals because at the high pH of the cement mixture most metal compounds are converted into insoluble metal hydroxides. In the case of spent catalyst, most metal compounds are present as hydroxides which as such may also increase the strength and stability of the waste containing concrete. On the other hand, the presence of organic impurities may act as interfering agents to the curing of the concrete and this limits the application of this disposal route.

Thermoplastic techniques. In general the use of thermoplastic solidification techniques is restricted to dry solid materials. This technique is not suitable to be used for wastes, containing:
- organic chemicals (these may act as solvents)
- oxidising salts (these can react with the organic material causing deterioration to the matrix material; at elevated temperatures these mixtures are extremely flammable)
- dehydrated salts (e.g. sodium sulphate easily dehydrates at temperatures required to plasticise bitumen; when the bitumen matrix is soaked in water, rehydration of the sodium sulphate can occur, and this can cause the bitumen to swell and split apart).

Mixing with bitumen. It is applied as a disposal method for spent FCCU catalyst and used for the production of a filler component in road asphalt where the catalyst is present as a minor component. The catalyst particles are completely encapsulated which makes aqueous extraction unlikely. This process allows treatment of soils with high levels (up to 10 %) of high boiling range hydrocarbons. The soil is mixed with bitumen to produce a stable end-product suitable for use in road construction.

Chemical Stabilisation. This technique is suitable to immobilise watery sludges to yield a powdery hydrophobic product which can be compacted. The immobilised product, is water-repellent and hardens with time and often has very good properties for civil engineering applications like foundations, tank bases, bundwall and road making.

Encapsulation is suitable for on-site treatment of disposal sites of accumulated spent acid tars and oily sludges which are difficult to transport and to dispose of by other means. A disadvantage is that the treated product occupies a larger volume than the original sludge. Because it can be applied on-site, the encapsulation process may be considered for single applications like rehabilitating refinery sites after decommissioning or cleaning up an oil-polluted site after a spill. The decision to apply the process depends on the future use of the site and local legislation. The process is less attractive for the treatment of regularly produced sludges, because of the increased mass generated for disposal.

Reference literature
[115, CONCAWE, 1999]

4.25.7 Waste storage

Wastes awaiting disposal should be stored in an environmentally acceptable manner, as approved by the local control authority. Storage should not give rise to secondary environmental problems such as odour or pollution of groundwater due to rainwater percolation through or run-off from the site. Storage should best be in closed vessels, containers or bags, on a site surrounded by a bund wall or toe wall, with drainage to a prepared system. Special precautions are of course required for pyrophoric materials to eliminate the risk of fires; they must be kept wet, sealed or blanketed with inert gas.

5 BEST AVAILABLE TECHNIQUES (BAT)

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: "How to understand and use this document". The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the Mineral Oil refinery and Natural Gas Plant sectors
- examination of the techniques most relevant to address those key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of these techniques
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels "associated with best available techniques" are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of "levels associated with BAT" described above is to be distinguished from the term "achievable level" used elsewhere in this document. Where a level is described as "achievable" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapters. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation.

In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

In order to complement what has been said above, the approach followed in this document for the BAT assessment can be summarised in the following steps:

1) Environmental performance - balanced with cross-media environmental effects - is the main criterion used to determine BAT. Moreover, a technique considered to be BAT should have a demonstrated applicability within the refinery sector or in another industrial sector. In the latter case, the expert judgement of the TWG members should be that there is no technical limitation on its implementation in the refinery sector.
2) A technique considered to be BAT needs to be economically viable within the sector. For this assessment, it is considered economically viable within the refinery sector if it has already been applied on a certain number of occasions (the more complex and more expensive the technique, the higher the number of proven operating experiences needed) within the refinery sector or other similar industrial sectors.
3) Operational data and applicability are criteria considered as limitations for the implementation of BAT in certain circumstances. Some of those limitations are mentioned together with the BAT (e.g. new vs. existing). General applicability problems in the implementation of techniques in existing installations (e.g. space, operational problems) are not mentioned in this chapter unless they are considered very specific (but are mentioned in Chapter 4).

As mentioned in the above paragraphs and in the Preface, Chapter 5 contains, where possible, the range of emission or performance levels associated with the use of a technique or group of techniques considered to be BAT. All emission levels associated with BAT given in this chapter are daily averages unless stated otherwise. Gaseous concentrations are corrected to 3% O_2 and in dry conditions unless stated otherwise. Where BAT is currently represented by only one technique, the emission or performance level cannot be defined as a single number because of differences in practical situations of feedstock, degree of integration, process variations or other circumstances. Where BAT is a group or combination of techniques, each single technique within that group has its own range of associated levels. However, the ranges appropriate for each technique are combined in a single range, typically wider than those related to a single technique. In some cases, some of the extreme values of the range have only been reported to be reached by a combination of at least two techniques.

The ranges given contain the lowest level of emissions found in Chapter 4, unless the lowest level has been achieved in special local circumstances. The upper end of the range does not generally correspond with the highest value found in Chapter 4. This upper value is determined from the better environmental performance levels reported but also takes account of the cost of reducing emissions and the process requirements constraints. In this respect, the proposed range is in accordance with the definition of BAT. For certain techniques, reduction percentages are given as well as associated emission levels. The reduction percentage (based on data in previous chapters) relates to the potential of the technique; it is acknowledged that, if a more contaminated feed is processed, a higher reduction percentage needs to be applied to reach the BAT associated emission values. Each range has its own purpose and importance and can be of help during the permit process.

In the determination of the upper value of the associated emission range in this chapter, a split view has been expressed by industry and two Member States. The split view is that they consider that the upper value in Chapter 5 should correspond with the upper value found in Chapter 4. Their rationale is that if a technique considered BAT is already applied in an installation and achieves a certain value, that value should be considered in the range of associated emission values.

Some key findings to help users/readers of this document

During the preparation of this document, several important issues were raised and considered by the TWG that may help future users/readers of this document.

- Due to the complex nature of refineries, the diversity in different refinery configurations and the high degree of process integration, it is strongly advised to read Chapter 5 in conjunction with Chapter 4 when determining the most appropriate solution for an individual refinery. To help the reader in this subject, references to Chapter 4 have been included in Chapter 5.

- Since the likelihood of new facilities being built in Europe is low, environmental improvement in the sector is normally achieved by applying BAT to existing installations. This retrofitting is often referred to as "revamping". This document takes account of the differences between new and existing installations, where relevant and quantifiable.

- For an integrated approach in refineries, it is important to note that integration includes both the integration of environmental aspects of a single unit and the integration of the environmental aspects over the refinery as a whole. This can be illustrated by the fact that if a refinery plans to build a new unit or replace an existing unit, the new unit is likely to influence operation of most (if not all) other units within the refinery and thus influence the environmental performance of the refinery as a whole.

- Certain prevention techniques (e.g replacing an alkylation process by another) that appear in the following sections may be very difficult to implement in existing installations. The reason is that the change from current practice to a more environmentally friendly technique has certain environmental and economic costs (e.g. decommissioning) which may outweigh the environmental and economic advantages of applying that technique. Thus, application is only justified in major rebuildings or changes and new installations. Existing installations may have factors such as space or height limitations that prevent full adoption of some of those techniques. A proper assessment can only be done at local/site level.

- Without prejudice to the preceding paragraph, the control and abatement techniques that appear in this chapter are widely applicable to both new and existing plants in the refinery sector.

- Many factors influence decisions about whether or not a refinery should have a certain process technique or pollution abatement technique. Factors such as the refinery's products, type of crude oil processed and type of refinery will need to be taken into account when using this document at local level. Similarly, actual costs for a technique in one location/site may differ from those in another; even in the same location the cost for an identical technique may differ widely depending on specific situations. (e.g. differences in furnace layout, in space availability). Independent assessments, by e.g. engineering contractors, may resolve issues when they arise and can only be done properly at local level.

- For an existing plant where the actual environmental performance is close to a BAT performance, it may be appropriate to consider the marginal cost-effectiveness of implementing a new measure in order to reach the BAT level. (See below for more information on cost-effectiveness analysis.)

- In addition to the BAT referenced in this chapter, BAT for a refinery contains elements from other IPPC documents and international regulations. In this context, special attention is drawn to the Storage and Handling BREF, Industrial Cooling BREF, Monitoring BREF and BREF on Large Combustion Plants when commercial fuels (e.g. natural gas, commercial fuel oil, gasoil) are used in the refinery.

BAT related issues
There were several key findings during the writing of this document, and they are relevant for the overall understanding of this chapter.

Basis for comparing refineries
All refineries are different in their configuration, process integration, feedstock, feedstock flexibility, products and product mix, unit size and design, control systems and environmental facilities. In addition, differences in owner's strategy, market situation, location and age of the refinery, historical development, available infrastructure and environmental regulations are amongst other reasons for the wide variety in refinery concepts, designs and modes of operation. However, there are approaches that attempt to normalise refineries by assigning e.g. the so-called complexity indeces (See Section 1.3.1) to a refinery as an aid to comparing the performance of refineries of different complexity (See application in Sections 3.1.2 and 3.10.1).

Cost- effectiveness
In judging whether a technique included in Chapter 4 and 5 is "available" in general, the concept of cost-effectiveness - taking account of investment and operating costs - is a useful tool for the BAT assessment of the respective technique as compared to alternative techniques that can achieve comparable levels of pollution prevention or control. Levels of cost-effectiveness (e.g. the cost to reduce one tonne per year of SO_2 emission) can be useful in setting so-called "reference values for cost-effectiveness". Such indicators of cost-effectiveness are sometimes used in other industries. Some data provided by the TWG in this respect are found in some techniques in Chapter 4 as well as in Annex IV.

BAT and environmental approaches
A most important issue during the preparation of this document has been how to tackle the process integration issue within a refinery. This issue can be approached in two different ways:
a) The so-called *bottom-up approach*, which matches the detail analytical approach followed in this document. In this case, each process/activity found in the industrial sector is analysed from the environmental point of view. This approach already recognises that some issues are common or integrated all over the installation (so called horizontal activities such as energy system, storage, cooling and integrated refinery management) and they need to be analysed across the whole installation.
b) The so-called *top-down* or bubble approach, where a certain environmental goal is given to the whole installation. The bubble approach is currently applied in environmental regulation of refineries, in particular for air emissions. More information is provided in Section 4.15.2.

The discussion among the experts of the TWG reflected differences of opinion that go beyond purely techno-economic considerations. Basically they may be considered to reflect differences in legislative and administrative procedures in Member States, which in turn are basically the result of differences in administrative and legislative cultures. The differences in approach should therefore not be classified as right or wrong within the IPPC legal structure. Both approaches should be respected as having their own merits in the permitting procedure and can be used in a complementary rather than contradictory manner. However, several important conclusions were drawn from the discussion on both approaches:

- The bottom-up approach has the advantage that the assessment of the emission values associated with the application of individual techniques on a separate process unit is more straightforward and more in line with the approach used in other BREFs. It provides the licensing authority with a clear picture of what it is considered to be the best environmental performance of a single refinery process/activity and how the goal can be achieved. This approach subsequently requires that the aspects of integration of the refinery as whole should be built from the individual processes/activities. If this is not performed correctly, it may result in a sub-optimal solution. This approach recognises that this integration aspect and the calculation of the bubble level can only be assessed properly at site level.

- The top-down approach can be used as an effective management tool to prioritise the application of environmental techniques in installations without becoming entangled in the complex technical-economic interrelationships in the refinery. However, it does not provide the licensing authority with guidance on what environmental goals may be achieved in certain processes/activies or on how a certain environmental goal can be achieved. The flexibility on how to achieve a goal is largely given to the operator with this approach.

- Both approaches recognise that the overall reduction of emissions is typically achieved in practice by a combined effort focused on the performance of the 'processes/activities' (e.g. improved SRU efficiency, application of low NO_x techniques) and on the performance of the 'integrated/whole' installation (e.g. energy efficiency, fuel management, sulphur balance). As a result of the high variability between refineries, the set of measures that leads to the lowest overall emissions at acceptable costs may also vary significantly from one refinery to the other.

- A certain direct relationship has been recognised between the two approaches. The more environmental measures that are applied, the lower the bubble level can be. Annex V gives some examples of calculation of the bubble figure considering BAT associated emission values for single processes/activities.

Some aids to understanding the remainder of this chapter
In subsequent sections of this chapter, the BAT conclusions for the Mineral Oil Refinery and Natural Gas Plant sector are set out on two levels. Section 5.1 deals with generic BAT conclusions that are generally applicable to both sectors as a whole and Section 5.2 contains the more specific BAT conclusions for the various processes and activities under analysis. So, BAT for any specific refinery is the combination of the non-unit-specific elements applicable to refineries as a whole (generic BAT) and the unit-specific-BAT applicable to the particular case. Both these approaches are complementary rather than contradictory in practical situations.

5.1 Generic (whole refinery) BAT

A refinery consists of a number of single process units. The way these single units are built up into an integrated refinery can have a considerable effect on the emissions. A well-integrated refinery will be characterised by a comparatively low overall level of emissions of pollutants. In determining BAT, the environmental effects of the single units and of the whole refinery have to be considered. This section provides the elements for BAT determined for refineries as a whole. It includes the determined BAT applicable to Mineral Oil Refineries and Natural Gas Plants for environmental management and the reduction, in a general sense, of emissions to air, emissions to water and solid waste. This chapter reflects the fact that emissions to air are the most important environmental concern of refineries.

BAT for Good Housekeeping and Environmental Management:
With reference to subsections of Section 4.15 a number of environmental management techniques are determined as BAT. They are techniques for continuous improvement of

environmental performance. They provide the framework for ensuring the identification, adoption of and adherence to BAT options that, whilst often down-to-earth, are important. These good housekeeping/management techniques/tools often prevent emissions.

BAT is to:

- implement and adhere to an Environmental Management System (EMS) (See Section 4.15.1). A good EMS could include:
  - the preparation and publication of an annual environmental performance report. Such a report will also enable the dissemination of performance improvements to others, and will be a vehicle for information exchange (Art. 16 of the Directive). External verifications may enhance the credibility of the report.
  - the delivery to stakeholders on an annual basis of an environmental performance improvement plan. Continuous improvement is assured by such a plan.
  - the practice of benchmarking on a continuous basis, including energy efficiency and energy conservation activities, emissions to air (SO_2, NO_x, VOC, and particulates), discharges to water and generation of waste. Benchmarking for energy efficiency should involve an internal system of energy efficiency improvements, or intra- and inter-company energy efficiency benchmarking exercises, aiming for continuous improvements and learning lessons.
  - an annual report of the mass balance data on sulphur input and output via emissions and products (including low-grade and off-spec products and further use and fate). (See Section 4.23.5)
- improve stability of unit operation by applying advanced process control and limiting plant upsets, thereby minimising times with elevated emissions (e.g. shutdowns and start-ups) (see Section 4.15.5)
- apply good practices for maintenance and cleaning (More information in 4.15.3).
- implement environmental awareness and include it in training programmes (More information in Section 4.15.4).
- implement a monitoring system that allows adequate processing and emission control. For more information on monitoring, refer to Section 3.26 and the Monitoring BREF. Some elements of a monitoring system could include:
  - continuous monitoring of pollutants for high volume flows with a high variability in pollutant concentrations
  - periodic monitoring or the use of emission relevant parameters for flows with a low variability
  - regular calibration of measurement equipment
  - periodic verification of measurement by simultaneous comparative measurements.

Reduction of Emissions to Air

The overall reduction of emissions to air is typically achieved in practice by a combined effort on the performance of the 'processes/activities' (e.g. improved SRU efficiency, application of low NO_x techniques) and on the performance of the 'integrated/whole' installation (e.g. energy efficiency, fuel management, sulphur balance). However, there is no consensus on a range of emission values under the bubble concept which could be associated with BAT. The reasons are: a) the different perceptions of emission ranges for individual processes, b) the different perceptions of the bubble parameters (e.g. concentrations vs. loads, yearly vs. daily, include or exclude certain processes), c) the way the flexibility issue is resolved, d) the environmental concern (e.g. how the parameters of the bubble should be set), e) the variety of refineries in Europe (e.g. simple vs complex, oil refineries vs. specialised refineries, 100 % gas vs. high percentage of liquid fuel, type of feedstock, etc). Annex V gives several examples of those reasons. However, Chapter 5 contains the different proposals or benchmarks given by the TWG. Those benchmark ranges are given together with the time span qualification (very important, as described in 4.15.2).

BAT is to:

- improve the energy efficiency (reduction of all air pollutants generated by combustion) by enhancing heat integration and recovery throughout the refinery, applying energy

conservation techniques and optimising the energy production/consumption (more specific information on how this can be achieved is found in Section 5.2.10). Three methods have been identified for the quantification of energy efficiency (see Section 3.10.1 and 4.10.1.1). Appropriate use of such data would be benchmarking between facilities in order to determine possible areas for improvement taking into account local differences in operations. The TWG provided data on EII for only ten EU+ refineries (See Figure 3.7). Data about this index show that the index for the world refineries ranges between 55 and 165. Lower values correspond to more energy-efficient refineries. Data reported by those ten EU+ refineries range from 58 to 94, all except one below the world average (92). Lower values are typically achievable under local circumstances where low grade heat can be externally exchanged. The TWG recognises that a transparent and standarised method for the calculation of energy efficiency is required to compare energy performance within the sector (See Concluding Remarks chapter).

- use clean RFG and, if necessary to supply the rest of the refinery energy demand, liquid fuel combined with control and abatement techniques (see Section 5.2.10) or other fuel gases such as natural gas or LPG. Where gaseous fuels replace liquid fuels, the reduction of SO_2 and NO_x emissions as a result of the fuel switch is not complicated to calculate for single processing units and for the refinery as a whole (see Section 4.15.2). Information on cross-media effects and applicability restrictions of a full gas switch is in Section 4.10.2.1

- reduce sulphur dioxide emissions by:
  - quantifying the sulphur emissions from various refinery sources to identify the main emitters in each specific case (See Section 3.26). This quantification is an element of the sulphur balance. More information about sulphur balance is in 4.23.5.
  - using BAT applicable to SO_2 emission reduction in the energy system, catcrackers and cokers (see Sections in 5.2)
  - efficient operation of the sulphur recovery unit according to 5.2.23.
  - reducing SO_2 emissions from typically small contributors when they become a significant part of the total emission and if cost-effective (e.g. flaring, gases from vacuum ejector gas burnt in furnaces) (See Section 4.23.5.7)

  The TWG has not been able to identify a single range of emissions associated with the application of BAT under the bubble concept (see reasons within the introduction to BAT for Reduction of Emissions to Air). However, several benchmarks were identified (See Section 4.15.2):

  For the concentration bubble approach (all in mg/Nm^3 and @ 3% O_2):
  - One Member State proposed that the full implementation of BAT results in a bubble of 60 - 200 (daily average).
  - Two Member States proposed that the implementation of BAT results in a bubble of 100 - 600 (monthly average) based on the calculations in Annex V.
  - One Member State proposed a bubble value of 850 (daily average)
  - Two Member States proposed a bubble range of 800 - 1200 (monthly average) based on current practice.
  - Industry proposed a bubble range of 1000 – 1400 (yearly average) based on current European refinery performance.

  For the load bubble approach (all in t SO_2/Mt of throughput):
  - One Member State proposed that the full implementation of BAT result in a bubble range of 50 – 230 (yearly average)
  - One Member State proposed a bubble range of 50 – 210 (yearly average) based on the upper quartile of specific emissions from 40 existing EU refineries.

  The above data demonstrates the wide variety of proposed ranges and the inconsistency when daily-monthly-yearly values are compared (yearly values should be the lowest values).

One Member State does not agree with the above approach of dealing with the sulphur dioxide emissions in the refinery as a whole. Their proposal is to follow their national methodology for BAT determination and implementation.

- reduce nitrogen oxides emissions by:
  - quantifying the NO_x emission sources in order to identify the main emitters (e.g. furnaces and boilers, the FCC regenerators and gas turbines) in each specific case (See Section 3.26)
  - using BAT applicable to NO_x reduction in the energy system and catcracker (see correspondent sections in 5.2)

The TWG has not been able to identify a single range of emissions associated with the application of BAT under the bubble concept (see reasons within the introduction to BAT for Reduction of Emissions to Air). However, several benchmarks were identified (See Section 4.15.2):

For the concentration bubble approach (all in mg/Nm^3 and @ 3% O_2):

- One Member State proposed that the full implementation of BAT results in a bubble of 70 - 150 (daily average).
- One Member State proposed that the implementation of BAT results in a bubble of 100 - 200 (monthly average) based on calculation in Annex V.
- One Member State proposed that the implementation of BAT results in a bubble of 150 (monthly average) and 200 daily.
- Two Member States proposed a bubble range of 250 – 450 (monthly average) based on current practice.
- Industry proposed a bubble range of 200 – 500 (yearly average) based on current European refinery performance.

For the load bubble approach (all in t NO_x/Mt of throughput):

- One Member State proposed a bubble range of 20 – 150 (yearly average) based on the upper quartile of specific emissions from 40 existing EU refineries.
- One Member State proposed that the full implementation of BAT results in a bubble range of 80 – 170 (daily average)

The above data demonstrate the wide variety of proposed ranges and the inconsistency when daily-monthly-yearly values are compared (yearly values should be the lowest values).

One Member State does not agree with the above approach of dealing with the nitrogen oxides emissions in the refinery as a whole. Their proposal is to follow their national methodology for BAT determination and implementation.

- reduce particulate emission by:
  - quantifying the particulate emission sources (especially furnaces and boilers, the FCC regenerators and cokers) in order to identify the main emitters in each specific case (See Section 3.26)
  - minimising the particulate emissions from solids handling situations (catalyst loading/unloading, coke handling, sludge transport) by applying good housekeeping and control techniques (see Sections 4.5.9.4, 4.7.8, 4.7.11, 4.25.1&3)
  - using BAT applicable to particulate reduction in the energy system, catcrackers and cokers (see Section 5.2)

The TWG has not shared so much information on values on particulate emission under the bubble concept. The reason is because the bubble concept it is less applied for particulates emissions than for the case of for SO_x and NO_x emissions. For this reason no figures appear here. However, several benchmarks were included in Section 4.15.2.

- reduce volatile organic carbons emissions by:
  - quantifying VOC emission sources (e.g. by DIAL) in order to identify the main emitters in each specific case (more information in 3.26)
  - executing LDAR campaigns or equivalent. A good LDAR includes the determination of the type of measurement, frequency, type of components to be checked, type of compound lines, what leaks should be repaired and how fast the action should be taken (more information in 4.23.6.1)
  - using a maintenance drain-out system (See Section 4.23.6.1)
  - selecting and using low-leakage valves such as graphite-packed valves or equivalent (especially important for control valves) for lines containing product with a high vapour pressure (See Section 4.23.6.1).
  - using low leak pumps (e.g. seal-less designs, double seals, with gas seals or good mechanical seals) on product lines carrying fluid with a high vapour pressure (See Section 4.23.6.1)
  - minimising flanges (easier to apply in the design stage), installing sealing rings on leaking flanges and use of high integrity sealing materials (fire safe) in flanges (very important for heat exchangers) (See Section 4.23.6.1)
  - blinding, plugging or capping open-ended vent and drain valves (See Section 4.23.6.1)
  - routing relief valves with high potential VOC emissions to flare (See Section 4.23.6.1)
  - routing compressor vents with high potential for VOC emissions back to process and when not possible (e.g. vent compressor distance pieces) to refinery flare for destruction (See Section 4.23.6.1)
  - using totally closed loop in all routine samplers (see Section 4.23.6.1 for what is understood by routine sampler) that potentially may generate VOC emissions
  - minimising flaring (see flaring in 5.2.23)
  - e.g. covering separators, basins and inlet bays and by routing off-gases in the WWTP. Implementation of some of those techniques may compromise efficient operation of WWTP or cause safety concerns if they are not properly designed and managed. For these reasons, this technique may have technical problems when retrofitted. Consider as part of an odour abatement programme. (Section 4.24.4)
  - using BAT applicable to VOC reduction in storage and handling (see 5.2.21)

<u>BAT for Reduction of Discharges to Water is to:</u>

- apply a water management scheme (as part of the EMS) aimed at reducing
  - the volume of water used in the refinery by:

Type of water	**Benchmarks for water volume consumption and emission (annual averages) (m^3/t throughput)**
Fresh water usage [1]	0.01 – 0.62[2]
Process effluent volume [1]	0.09 – 0.53[2]

Notes:
1 Definition of what each type of water does and does not contains is found in Section 3.15. As mentioned in 4.15.7.1 and 4.24.1, those values are very dependent on the type of refinery and they cannot be related to the use of BAT. They should be seen as references.
2 Upper value of these ranges corresponds to the average of 63 European refineries. See Section 4.24.1.

    - water stream integration options including water optimisation studies(see Section 4.15.7.1).
    - re-using as much as possible the cleaned waste water (see Section 4.15.8.1)
    - applying techniques to reduce waste water generated within each specific process/activity (see Section 5.2)

- the contamination of water by
  - segregation of contaminated, low-contaminated or non-contaminated water streams and, where possible, drainage systems (Section 4.15.6, 4.24.1). This entails the complete system of fresh water supply, rainwater, ballast water, sanitary water, process water, boiler feed water, cooling water, groundwater as well as effluent collection, storage and the various (primary, secondary and tertiary) waste water treatment systems. Many of those waters end up in a single waste water treatment where they may be mixed after they have been appropriately (pre)treated. In existing installations, this segregation may be very costly and may require space for implementation.
  - segregation of "once-through" cooling water from process effluent until after this has been treated (Section 4.8.1)
  - good housekeeping in operation and maintenance of existing facilities (as part of the EMS. Reference to Section 4.15.3)
  - spill prevention and control (4.25.1, 4.15.3)
  - applying techniques to reduce contamination of waste water within each specific process/activity (see Section 5.2).

- achieve the following water parameters in the WWTP effluent (see Table 4.50 in Section 4.24.8)

Parameters	Concentration (mg/l) (monthly average)[2]	Load (g/tonne crude oil or feedstocks processed)* (yearly averages)
Total hydrocarbon content	0.05 – 1.5[1]	0.01 – 0.75[1]
Biochemical oxygen demand (5 day ATU @ 20 ºC)	2 – 20	0.5 – 11
Chemical oxygen demand (2 hour)	30 – 125[3]	3 – 70[3]
Ammoniacal nitrogen (as N)	0.25 – 10[4]	0.1 – 6
Total nitrogen	1.5 – 25[5]	0.5 – 15[6]
Suspended solids (dried @ 105 ºC)	2 – 50[7]	1 – 25
Total metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, Zn)#	<0.1 – 4	

It should not be understood from this range that the amount of very toxic metals (e.g. As, Cd, Hg, Pb) can reach concentrations of this order of magnitude. More information on achievable levels for these metals can be found in Table 4.50 of Section 4.24.8. Two Member States claimed that the group of metals should be split into two groups according to their toxicity. One Member State claimed that the ranges should be given for individual metals. These last two requests came after the agreement in the TWG meeting on total metals.

* The lower load values are real refinery loads provided by the TWG. The upper load values have been calculated according to benchmarks on the process effluent volume of 0.53 m^3/t (average of 63 refineries). The load figures for a specific refinery can be easily calculated with the concentration value and the real effluent rate. One Member State disagrees with the upper values of this column because they should represent actual refinery figures that are lower that the ones represented here. On the other hand, industry believes that the load values set here should not be associated emission levels at all, but rather benchmark values since they are dependent on refinery water use and calculated on an arbitrary selection of the average water use at 63 refineries (which itself is presented only as a benchmark value on page 399 of the BREF). As stated in the * footnote in this table, the actual loads for a refinery can be "easily calculated with the concentration value and the real effluent rate", and can then be compared to the benchmark values that these should be.

1 There is some disagreement on the analytical methods to assess hydrocarbons. One Member State and Industry claim that 3 mg/l as upper value is representative of actual operations data of existing refinery facilities in Europe with 3-step Waste Water Treatment Plant currently in place. One Member State proposed an upper value of 5 based on current observe performances in existing facilities in their country.

2 One Member State claims that those values should be daily averages because those figures can easily be achieved with a well designed and operated WWTP. Industry claimed that the average should be yearly because all their data are based in yearly averages.

3 One Member State claims that the upper level in concentration should be 75 and the upper value for load should be 45 because a standard biotreater reduces the COD content by 90-97 %. As a consequence 75 is easy to achieve in a well designed and operated biox.

4 One Member State claims that the upper level should be 5. Those levels can be reached by strippers and biological nitrification/denitrification step.

5 Industry believe that, where nitrogen is not a pollutant of concern in the receiving waters, denitrification cannot be BAT as the environmental benefit to the receiving water is very low, while the cost both in Euros (Capital Expenditure) and the CO_2 emissions are high.

6 One Member State claims that the upper level of the range should be 8. They demonstrated (based on actual data) that a figure below 8 can easily be achieved with a stripper or a nitrification/denitrification step.

7 One Member State claims that the upper level should be 30. The reason is that the use of sedimentation, flotation, filtration or a combination of these techniques can reduce the suspended solids by 60 – 99.99%.

- by a suitable combination of:
  - a three-step waste water treatment plant consisting of gravity separation, advanced physical separation (e.g. FFU) and biotreater (See Section 4.24.4-6)
  - a nitrification/denitrification process (See Section 4.24.6)
  - ensure design of WWTP includes sufficient capacity to prevent toxic shock loads to the biotreater e.g. by the use of a buffer tank, diversion tank, oversized reactor, etc.(See Section 4.24.1).
  - good process practices and housekeeping to prevent contamination of the waste water (see BAT above table)

- combination of waste water from several processes with comparable qualities for pretreatment (e.g. treatment of sour water from primary distillation unit, catalytic cracker, coking and from other sour water sources by stripping; see Section 4.24.1).

BAT for Solid Waste Management is to

- implement a solid waste management system (as part of the EMS) (See Sections 4.25.1-2 and 4.15.1,3). This includes:
  - annual reporting of waste quantities
  - implementing a plan with measures for waste reduction including recycling and/or recovery
  - operating the WWTP so as to maximise performance, with the minimum of sludge production (Section 4.24.6)
  - implementing good housekeeping activities
  - applying BAT determined on forthcoming waste BREF
- minimise oil spills and exclude oil spills that contaminate the soil (as part of the good housekeeping activities (see 4.25.1)). This includes, among other things:
  - implementing a plan to exclude leakage from pipework and tanks (part of the EMS). This plan may include inspection, corrosion monitoring, leak detection instruments, double bottoms etc. (see Section 4.25.1)
  - performing a risk analysis to rank in order of significance cases where an accidental leak may occur (elements to consider are the product in the tanks/pipes, the age of the equipment, the nature of the soil and groundwater that would be affected). Prioritise areas where impermeable floors are needed most. Produce a multiyear master plan to programme necessary steps (Section 4.25.1 and 4.15.6)
  - designing new installations with the minimum of underground piping. In existing installations, include underground pipes in risk assessment process referred to above (Section 4.25.1, 4.21.22)
- apply techniques to reduce solid waste generated within each specific process/activity (see Section 5.2).

5.2 BAT for process/activity

This section presents BAT elements for each process/activity covered in this document. Numbers in the headings of the following BAT sections correspond with the numbers used in previous Chapters.

The analysis of production techniques from an environmental perspective is a task that is required for this BREF as well as comparisons between alternative production techniques, where they exist. The latter has only been possible to a limited extent because of a lack of the information.

2. BAT for Alkylation is to use either:

- HF alkylation. Because of the use of HF, this technique may represent a high risk for the operators and neighbourhood. Associated with BAT is the reduction of regular HF emissions to levels < 1 mg/Nm^3 by scrubbing, to levels of 20 – 40 ppm F in the discharges to water after AlF_3 or CaF_2 precipitation. It is not clear from the information provided by the TWG what fluoride levels may be reached in the waste generated by this technique. (Section 4.2.1)
- sulphuric acid alkylation. This technique includes as BAT the minimisation and regeneration of the spent sulphuric acid. Regeneration may imply transportation and storage of spent sulphuric acid waste. Waste water generated by this process should be neutralised before routing to the WWTP. (Section 4.2.2)

3. BAT for Base Oil Production:

Note: BAT for Vacuum Distillation Units and Hydroprocessing units are determined under their respective activities (Primary distillation and Hydrogen-consuming techniques).

BAT is to:

- use triple effect evaporation systems in the solvent recovery sections of deasphalting, extraction and dewaxing process units. In some instances, for technical reasons (increase in temperature and pressure) it is not feasible to go from double to triple effect. Triple effect systems are typically used in non-fouling feedstocks (e.g. wax). (see 4.3.1)
- use N-methyl pyrrolidone (NMP) as solvent in the aromatic extraction. In some cases, the switch from furfural to NMP may not be justified environmentally or technically especially when producing lower boiling point base oils (e.g transformer oil distillates). Because a solvent switch typically requires different temperature, pressure and solvent volumes, they are typically very costly (See 4.3.2). Industry claims that considering the information within this document, both NMP and furfural are equally viable solvent candidates. In Industry's opinion, no clear case has been made in the BREF to arrive at one preference.
- use hydrotreating for clean-up of the base oil streams and wax finishing if final clean-up is required. Clay treatment may be justified in some cases because product quality cannot be achieved by hydrotreating, but it produces solid waste. (see 4.3.4,5)
- consider the application of a common hot oil system for these solvent recovery systems to reduce the number of furnaces (see 4.3.10) In stand-alone lube refineries, this will facilitate application of flue gas treatment where liquid fuel is used (See 5.2.10)
- apply prevention techniques for VOC emissions from solvent-containing systems (e.g. storage). Practise benchmarking of solvent consumption (See 4.3.6-7)
- apply BAT on sulphur recovery units in stand-alone lube refineries (see 5.2.23)
- review the possibility of waste water stripping from aromatic extraction before re-use (see 4.3.9)
- consider the effect of solvents when designing and operating the WWTP. This BAT can be seen as a part of a water management scheme (See Section on generic BAT and 4.3.2)
- apply leakage prevention measures for solvent-containing systems, to prevent soil and groundwater contamination with the water-soluble solvents employed. This can be seen as a part of the waste management system (See Section on generic BAT and Section 4.3.7)

4. BAT for Bitumen Production is to:

- reduce aerosol and VOC emissions (considered as a part of the odour abatement programme) by selecting between:
  - recovering the liquid element of the aerosol that is directed to vents from storage and during the blending/filling operations of bitumen (e.g. wet electrostatic precipitator, oil scrubbing). This technique is easier to apply when the storage and blending/filling operations of bitumen are close enough. (More information in Section 4.4.2.3)
  - incineration at a temperature over 800 ºC or in process heaters. (More information in Section 4.4.2.2-3). Fitting such a system into an existing incinerator package may be difficult technically.
- apply leakage prevention measures (as part of the waste management) to prevent waste generation (see 4.4.4)
- apply BAT on sulphur recovery units in stand-alone bitumen refineries (see 5.2.23)
- apply the following techniques if bitumen blowing is applied:
  - treat the overheads from the oxidiser for removal of air contaminants (e.g. oil, solid, VOC) (as part of the odour abatement programme). If water scrubbing is used, water used in the wet scrubber need to be cleaned before being re-used. If incineration is used, the blow gas can be used in process heaters (see 4.4.2.1).
  - send the accumulated water condensate to a sour water stripper. In some cases, because of the quality and quantity of the water generated and a possible resizing of the SWS, this may not be justified economically (see 4.4.3).
  - route the condensed hydrocarbons to the refinery slops oil system or alternative recovery method (e.g. sludge recovery) (see 4.4.22).

5. Catalytic Cracking

A catalytic cracking unit is usually part of a processing complex that includes a gas plant, amine treating of the light (incl.C_3/C_4) gases and treatment of various product streams. BAT determinations for these associated activities are dealt with in the respective parts (gas separation processes, hydrogen-consuming processes and waste gas treatments) of this section. For the catcracker itself (reactor, regenerator, fractionator, catalyst receipt, storage/loading, wet gas compressor, absorber and debutaniser) the main specific BAT determinations are given above. Solutions and measures should be considered in an integrated way with measures and solutions in other units.

In this respect BAT is to:

- include a CO-furnace/boiler for partial oxidation conditions. Under those conditions and without abatement measures associated CO emission levels are 50 - 100 mg/Nm^3 and for NO_x emissions are 100 – 300 mg/Nm^3 (see 4.5.3). Low figures for CO and NO_x are not typically achieved at the same time. One Member State claims that the associated emission range should be 300 – 450 mg/Nm^3 if those low levels of CO need to be reached. Industry remains of the view that the range should be 100 – 500 mg/Nm^3 to cover the whole range reported in Section 4.5.3.
- monitor and control O_2 (typically at 2%) for full combustion plants, resulting in a CO emission level of 50 - 100 mg/Nm^3 and 300 – 600 mg NO_x/Nm^3 in absence of a downstream CO boiler. Low figures for CO and NO_x are not typically achieved at the same time (see 4.5.1).
- increase energy conservation by:
  - applying power recovery (expander) to the regenerator gas. This technique may not be economically or environmentally justified in small or low-pressure unit expanders (see 4.5.5)
  - using waste heat boiler to recover part of the energy content of the flue gas from the catcracker (see 4.5.5)
- reduce NO_x emission to 40 – 150 mg/Nm^3 (lower end is only applicable when SCR and low sulphur feedstock are used) by a suitable combination of:
  - modification of the design and operation of regenerator, especially to avoid high temperature spots. This technique may raise the CO emissions and cannot be environmentally justified if a major or complete revamp is necessary.
  - hydrotreatment of the feedstock if it is economically and technically viable (see 4.5.4). This technique is easier to implement when amine scrubbing and Claus capacities and hydrogen are available (see 4.5.4)
  - using SNCR on the regenerator flue gas, achieving a NO_x reduction of 60 - 70 % (see 4.5.8.2)
  - using SCR on the regenerator flue gas, achieving a NO_x reduction of 85 - 90 %. Associated emissions of ammonia slip is 2 – 5 mg/Nm^3. Ammonia slip concentrations may increase at the end of the catalyst life (see 4.5.8.1).

  Three split views from Member States appeared on the range of the NO_x emissions. One Member State claims that the application of an SCR is always possible and that the upper value should be therefore 100. One Member State claims that the range should be 300 – 450 mg/Nm^3 because the FCC technology is chosen according to the crude oil processed, the refinery configuration and the product demand. So NO_x emissions cannot drive the production operations. One Member State specifies that the range should be 10 – 450 because SCR and SNCR are not applicable to all existing units.

- reduce particulates emissions to 10 – 40 mg/Nm^3 (upper end of the range applicable to feedstocks with very low sulphur/metal content. Because of poor reliability of the particulates monitoring system and technical difficulties in upgrading the existing ESPs, the upper range can be difficult to reach. In those cases 50 is seen as a more achievable level) by a suitable combination of:

- tertiary and multistage cyclones (4.5.9.1)
- applying an ESP or scrubber to the FCC regenerator gas. Efficiencies associated with BAT range are 95 – 99 %. Upper range has not been reported to be achieved with scrubbing (4.5.9.2, 4.5.10.2)
- containing catalyst losses to atmosphere during loading/unloading (4.5.9.4)
- hydrotreatment of the feedstock if it is economically and technically viable (see 4.5.4). This technique is easier to implement when amine scrubbing and Claus capacities and hydrogen are available (see 4.5.4). It has an impact on the metal content of particulates
- selecting attrition-resistant catalyst to decrease the frequency of replacement and reduce the particulate emissions (see 4.5.6). This may adversely affect the performance of the FCCU (see waste paragraph)

- reduce SO_2 emission to 10 - 350 mg/Nm^3 (lower end of the range only achievable when both low sulphur feedstock and FGD are used) by a suitable combination of:
  - hydrotreatment of the feedstock if it is economically and technically viable (see 4.5.4). This technique is easier to implement when amine scrubbing and Claus capacities and hydrogen are available (see 4.5.4).
  - using DeSOx catalyst additive (see 4.5.10.1)
  - using FGD (techniques mentioned in Sections 4.5.10.2-6) of the regenerator gas with 95 – 99 % efficiency (emission target depends on uncontrolled level) especially if hydrotreatment of feedstock is not applicable.

  One Member State maintains that FGD is always applicable and that the range should therefore be changed to 10 – 100.

- reduce discharges to water by:
  - hydrotreatment of the feedstock if it is economically and technically viable (see 4.5.4). This technique is easier to implement when amine scrubbing and Claus capacities and hydrogen are available (see 4.5.4).
  - minimising water use by recycling and the application of a cascading system, observing corrosion constraints (see 4.5.7)
  - re-using waste water in desalters or ultimately routing it to the WWTP (see 4.5.7)

- reduce waste generation by
  - reducing uncontrolled catalyst losses (to air, from ESP, product and slurry tank bottoms) by spent catalyst management. Applying benchmark performance (see 4.5.12)
  - selecting attrition-resistant catalyst to decrease the frequency of replacement and reduce the particulate emissions. This may adversely affect the performance of the FCCU (see 4.5.6)

  One Member State does not agree with the approach followed in this section for the SO_x and NO_x emissions. Their proposal is to follow their national methodology for BAT determination and implementation.

6. BAT for Catalytic Reforming is to:

- route the regenerator gas generated during the catalyst regeneration to a scrubbing system. Send the bleed stream from the scrubbing system to the WWTP. (Section 4.6.4)
- optimise the amount of chlorinated promoters in the regeneration of the catalyst (See 4.6.3)
- quantify the dioxin emissions from the catalyst regenerator. More information about dioxin removal is given in Section 4.6.6. Since all techniques are quite new and not widely used yet, futher data gathering on dioxin clean-up techniques are necessary (see Concluding Remarks)

7. BAT for Coking Processes is to:

- use waste heat boilers to recuperate some of the heat produced during the coking/calcining process (see 4.7.1, 4.7.3-4)
- consider the use of flexicoking (fluid coking + gasification) to maximise the production of fuel gas and increase the heat integration in the refinery. For applicability, this option needs to meet refinery product requirements (see 4.7.4)
- use cokers as an alternative (others are e.g. CDU in Section 5.2.19) to destroy oily slops and sludge (see applicability restrictions in 4.7.5)
- convert COS from the coke gas of flexicokers to H_2S (see 4.7.6)
- route sour gas produced from cokers to sulphur treatment (see 4.7.6)
- reduce particulate emissions (containing metals):
  - by collecting and recycling, as much as possible within the refinery the coke fines generated in the coking processes (see 4.7.8 and 4.7.11.1)
  - by proper handling and storing of coke including construction of wind breaks around the green coke pit or storing it in completely enclosed facilities (see 4.7.8)
  - by covering the conveyor belts and de-pressurising with filters (see 4.7.8)
  - by enclosing loading areas, keeping them under negative pressures and exhausting the collected air through bag filters or by using dust extraction incorporated with the loading equipment (see 4.7.8).
  - to 10 - 50 mg/Nm^3 by applying ESP and/or cyclones and/or filters from the different flue gases containing particulates (see Section 4.7.9.1). Industry claims that ESP is not applicable because the conductivity of the coke particles is high and consequently the higher value of the range should be 100.
- reduce SO_2 emissions from the calcination flue gas to 25 to 300 mg/Nm^3 by applying FGD techniques (efficiency >90 %) (see 4.7.9.2). Industry claims that with the application of FGD and with 90 % removal is not possible to achieve the upper value because the sulphur in the feed may be very high. Their proposal is to increase the value to 500.
- reduce emissions to water by:
  - using treated water from the waste water treatment as cooling/cutting water in the delayed coking/calcination processes (see 4.7.7)
  - stripping waste waster generated in coking processes before sending it to the WWTP (see 4.7.10.1)
- reduce waste generation by enhanced separation of oily coke fines (more information in 4.7.10.2).

8. BAT for Cooling Sytems is to:

- apply BAT from the cooling BREF
- reduce cooling demand in the refinery by applying an integrated approach and heat optimisation analysis (related with BAT in Section 5.2.10, second bullet. See 4.10.1.3)
- maximise the heat recovery by application of low-level heat utilisation schemes (e.g. district heating, industrial heating) where local demand is identified and economic results favourable (See 4.10.1.3)
- during design, consider the use of air cooling. Applicability limitations are noise, space and climatic conditions (see 4.8.2)
- eliminate as far as possible oil leakage into cooling water discharges (once-through or from circulating systems) (see 4.8.3)
- segregate once-through cooling water and process waters until after treatment of the latter (see 4.8.1)

9. BAT for Desalting is to:

- use multistage desalters for new facilities. The switch from existing desalters to multistage desalters may not be environmentally or economically justified (See Section 4.9.1)

- apply good desalting practices (described in Section 4.9.1-3) that result in optimum downstream processing (minimal corrosion, meeting product specifications and reducing catalyst contamination) and waste water quality (oil and N content)
- maximise the use of already-used refinery water as desalting water (see 4.9.4).

10. BAT for the Energy System:

As mentioned in the previous chapters, this section comprises all units where energy (either electricity or heat) is produced. Consequently this section should be read together with any process/activity section or even when energy issues are analysed within a refinery as a whole.

BAT is to:

- adopt an Energy Management System as part of the Environmental Management System (described in Generic BAT section) (see 4.10.1.2). The aim is to increase the refinery energy efficiency (see below). As elements mentioned in the EMS section, a good Energy Management System could include:
  - reporting the energy efficiency of the refinery and the plan to increase it (as part of environmental performance report described in EMS)
  - an energy consumption reduction plan (as part of environmental performance report described in EMS)
  - participation in ranking/benchmarking activities in energy consumption (as part of benchmarking described in EMS)
- improve the refinery energy efficiency (see Generic BAT). Techniques that help to improve the overall efficiency are:
  - application of efficient energy production techniques such as use of gas turbines, combined cycle power generation/co-generation plants (CHP), IGCC, efficiently designed and operated furnaces and boilers and replacement of inefficient boilers and heaters. In the implementation phase of the replacement of inefficient boilers and heaters, consideration should be given tothe retrofitability, size, actual amount of emissions, age and remaining life in order to evaluate the cost-effectiveness and the timing for the action. (see 4.10.3)
  - application of combustion improvement campaigns (see 4.10.1.2)
  - matching energy production and consumption with computerised control systems (see 4.10.1.3)
  - optimised use of steam in the stripping processes and the use of steam traps (see 4.10.1.4)
  - enhancing the heat integration through processes/activities by energy optimisation analysis (see 4.10.1.3)
  - enhancing the recovery of heat and power within the refinery (see 4.10.1.3)
  - using of waste heat boilers to reduce the use of fuel for the production of steam (see 4.10.1.3)
  - identifying and using, if possible, opportunities for synergy outside the refinery fence (e.g. district/industrial heating, power generation) (See 4.10.1.3)
- use clean RFG and, if necessary to supply the rest of the refinery energy demand, liquid fuel combined with control and abatement techniques (see Section 5.2.10) or other fuel gases such as natural gas or LPG. Where gaseous fuels replace liquid fuels, the reduction of SO_2 and NO_x emissions as a result of the fuel switch is not complicated to calculate for single processing units and for the refinery as a whole (see Section 4.15.2). Information on cross-media effects and applicability restrictions of a full gas switch is in Section 4.10.2.1
- increase the proportion of clean fuels used. This can achieved by a suitable combination of:
  - maximisation of the use of refinery fuel gas (RFG) with low H_2S content (20 - 150 mg/Nm^3 by amine treating) (see 4.10.2.1-2 and 4.23.5.1). One Member State claim that for existing refineries the range should be <500 – 1000 ppm because the H_2S content in RFG is negligible if the bubble limit is respected.

- balance and control of the RFG system between suitable pressure limits to give system flexibility, with make-up available from sulphur-free sources such as LPG or imported gas (see 4.10.2.1)
- use state-of-the-art controls to optimise the performance of the RFG system (see 4.10.11.3 and 4.10.12.1)
- use flaring of RFG only during start-up/shutdown/upset/emergency conditions. During normal operation give a constructive use to the RFG, including sale (related to flare section at the end of this chapter) (see 4.23.7)
- upgrading and cleaning heavy fuel oil used in the refinery to low-sulphur liquid fuel. As mentioned in the SO_2 emission section below, the abatement of emissions after firing liquid fuels is also considered BAT (see 4.10.2.3).

- reduce CO_2 emissions by:
  - increasing the refinery energy efficiency (see above and Generic BAT section)
  - increasing the use of gaseous fuels that have higher hydrogen-to-carbon ratios (see 4.10.2.1)
- reduce CO emissions by application of efficient combustion techniques
- reduce NO_x emissions:
  - by reducing fuel consumption (increase the energy efficiency, see above)
  - by replacing existing burners with low-NO_x types during major outages. The lowest-NO_x burners suitable for individual applications should be used (see 4.10.4.1.2)
  - from boilers and heaters using gas fuel to 20 - 150 mg/Nm^3 (lower levels for natural gas and higher ones for small heaters with primary measures. Two Member States claim that the upper value should be 100 because it can be reached with the implementation of primary measures and SCR) by applying a suitable combination of:
    - high thermal efficiency heater/boiler designs with good control systems (e.g. oxygen trim) (see 4.10.3.1)
    - low-NO_x burner techniques (see 4.10.4.1-2)
    - flue gas circulation in boilers (see 4.10.4.3)
    - reburning technique (see 4.10.4.5)
    - SCR/SNCR. Ammonia slip considered associated with the use of SCR is 2 - 5 mg/Nm^3. The lower value is achievable with new catalysts and ammonia slip typically increases with catalyst life. (see 4.10.4.6-7)
  - from boilers and heaters using liquid fuel to 55 - 300 mg/Nm^3 (the lower levels relates only to boilers with SCR and the higher levels only to small heaters with primary measures. One Member State claims that small heaters (<50MW) can reach 200 and with the big heaters and boilers (>50MW) the installation of SCR is justified and consequenly values of less than 100 can be reached. One Member State claims a level from 200 – 400 because of the nitrogen content in the fuel) by applying a suitable combination of:
    - fuels with low nitrogen content (related with low sulphur content) (see 4.10.2.3)
    - low-NO_x burner techniques (see 4.10.4.1-2)
    - flue gas circulation in boilers (see 4.10.4.3)
    - reburning technique (see 4.10.4.5)
    - SCR/SNCR to liquid fuels heavier than gasoil type. Ammonia slip considered associated with BAT is 2 - 5 mg/Nm^3. The lower value is achievable with new catalysts and ammonia slip typically increases with catalyst life. (see 4.10.4.6-7)
  - from gas turbines to 20 – 75 mg/Nm^3@ 15 % O_2 (lower levels for natural gas and higher levels for small gas turbines and RFG. One Member State claims that the upper value should be 35 based on primary measures and SCR) by applying a suitable combination of:
    - diluent injection (see 4.10.4.4)
    - dry low-NO_x combustors (see 4.10.4.2)
    - SCR. Ammonia slip considered associated to BAT is 2 – 5 mg/Nm^3. The lower value is achievable with new catalysts and ammonia slip typically increases with catalyst life. (see 4.10.4.6-7)
- reduce particulate emissions (particulates from liquid firing contain Ni,V) to 5 - 20 mg/Nm^3 by applying a suitable combination of:

- reducing the fuel consumption (increasing the energy efficiency. See above)
- maximising the use of gas and low ash content liquid fuels (see 4.10.5.1)
- steam atomisation on the liquid fuels (see 4.10.5.2)
- ESP or filters in the flue gas of furnaces and boilers when heavy liquid fuel is used (see 4.10.5.3-4)

One Member State claims that the range for particulates should be 30 – 50 because those values are consistent with a 95% abatement. Industry rationale for the range 5 to 50 mg/Nm^3 is that this is consistent with the whole range reported in Chapter 4.

- reduce sulphur dioxide emissions:
  - by reducing the fuel consumption (increasing the energy efficiency)
  - from combustion processes (boilers, heaters and gas turbines):
    - by increasing the proportion of clean fuels used (to low-sulphur residual fuel, to gasoil, ultimately to gas) (See BAT on clean fuels at the beginning of Section 5.2.10)
    - to 5 – 20 mg SO_2/Nm^3 when using fuel gas by cleaning refinery fuel gas (20 to 150 mg H_2S /Nm^3) including monitoring of the sulphur content of the refinery fuel gas. Refer to split views given on the H_2S concentration in BAT for refinery fuel gas.
    - to achieve an average emission value of 50 – 850 mg SO_2/Nm^3 (lower end of the range is for the implementation of FGD and deep hydrodesulphurisation to all liquid fuels) for the total refinery liquid fuel pool by applying a suitable combination of:
      - hydrodesulphurising the necessary amount of liquid fuel (See section 4.10.2.3)
      - applying flue gas desulphurisation (See Section 4.5.10 and 4.23.5.4). This technique is more cost-effective in large furnaces and boilers.

      One Member State claims that the use of FGD is always possible and that the upper value should therefore be 200. One Member State and Industry claim that the limit should be no lower than 1700 mg SO_2/Nm^3 which is equivalent to a 1 % sulphur level in fuel oil with no abatement.

      The Commission has noted the divergent views of the TWG concerning the average sulphur dioxide emission levels when burning liquid fuels, associated with the use of BAT. The Commission further notes that Council Directive 1999/32/EC on the sulphur content of certain liquid fuels prescribes a maximum emission limit value of 1700 mg/Nm^3, which equates to 1 % sulphur in heavy fuel oil, as a monthly mean value averaged over all plants in the refinery from 1 January 2003. In addition, the more recently adopted Directive 2001/80/EC on large combustion plants provides for emission limit values in the range of 200 to 1700 mg/Nm^3 depending on the characteristics of plants covered by that directive.

      In this perspective, the Commission believes the range of 50 to 850 mg/Nm^3, as average sulphur dioxide emission levels when burning liquid fuels to be consistent with BAT. In many cases, achieving the lower end of this range would incur costs and cause other environmental effects which outweigh the environmental benefit of the lower sulphur dioxide emission (reference in Section 4.10.2.3). A driver towards the lower end could be the national emission ceiling for sulphur dioxide as fixed in Directive 2001/81/EC on national emission ceilings for centain atmospheric pollutants or if the installation is located in a sulphur sensitive area.

- reduce water use by:
  - re-using condensate water as de-areator feed water. Where the condensate and the de-areator are located far apart, their integration is not always cost effective. (see 4.10.3.2)
  - preheating the boiler feed water with waste heat. Where the BFW and the available waste heat are located far apart, their integration is sometimes too costly compared with the environmental benefit (see 4.10.3.2)

One Member State does not agree with the approach followed in this section for the SO_x and NO_x emissions. Their proposal is to follow their national methodology for BAT determination and implementation. Another Member State does not agree with the approach followed in this Section because they claim that the bubble approach should drive the Energy BAT Section.

11. BAT for Etherification is to:

- apply heat integration either in the unit itself or within the refinery (See 4.10.1.3)
- use a storage tank or production planning to control waste water generated, to prevent any upset of the biotreater (See 4.11.2)

12. BAT for the Gas Separation Processes is to:

- enhance the heat integration with upstream plant streams using low-level heat streams (see 4.12.1)
- re-use the fuel gas used for the regeneration of molecular dryers (See 4.12.4)
- preventing any release of odorant to any environmental medium during storage and handling (e.g. blanket storage) (see 4.12.5, 4.21.21)
- reduce VOC fugitive emissions (See 4.12.3 and Generic BAT)

13. BAT for Hydrogen consuming Processes is to:

- design and retrofit (where possible) hydrocracker units (reactor and fractionation section) to highly heat-integrated equipment, applying energy optimisation analysis and four-stage separator system (see 4.13.6)
- use heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting down liquid) (4.13.1-2,6-7)
- route off-gases containing H_2S to amine systems and SRUs (see 4.23.5.1)
- route waste waters containing H_2S and N-compounds to the appropriate waste water treatment (see 4.24.1 and 4.15.6)
- use on-stream catalyst replacement for high-metal feedstocks (see 4.13.4)
- promote catalyst regeneration options in co-operation with the catalyst suppliers/manufacturers where possible (see 4.25.3).

14. BAT for Hydrogen Production is to:

- consider the use of gas-heated steam reforming technology for new plants, including recovery of heat from the steam reformer flue gas and heat integration around the solvent absorber and the methanator (see 4.14.1)
- recover hydrogen from the gasification processes of heavy fuel oil and coke if the technology is applied in the refinery (see 4.14.2)
- apply heat integration schemes in the hydrogen plant (see 4.14.1)
- use PSA purge gas as fuel gas within the refinery (see 4.14.3)

15. BAT for Integrated Refinery Management

- BAT determined from Section 4.15 appears in Section 5.1 (generic BAT).

16. BAT for Isomerisation is to:

- use active chloride-promoted technology if sufficient guarantees can be given on feedstock quality and contamination levels (see 4.16.1), or
- use other catalytic systems (e.g. zeolite) (see 4.16.2)
- optimise the use of chlorinated organic compounds used in maintaining the catalyst activity (see 4.16.1)

17. BAT for Natural Gas Plants is to:

- apply Generic BAT (Section 5.1) including good housekeeping and Environmental Management and BAT related to reduction of air, water and solid emissions
- apply BAT related to the Energy system (see Section 5.2.10)
- apply BAT for Waste Gas Treatments (see Section 5.2.23)

- use as fuel preferably gas that is of saleable quality (typically less than 5 mg of H_2S/Nm^3) (see 4.17.1)
- consider, particularly for large carbon dioxide flows, alternatives to direct releases of CO_2. (See Section 4.17.3)
- dispose of mercury recovered from raw natural gas (if present) in an environmentally acceptable way (Refer to Section 4.17.7)

18. BAT for Polymerisation is to:

- optimise the catalyst consumption (Section 4.18.1)
- re-use phosphoric acid (catalyst) within the refinery as much as possible e.g. biotreater (see 4.18.2)
- properly manage the unused on-site catalyst for disposal or re-use off site (see 4.18.2).

19. BAT for Primary Distillation Units

The main refinery process is the Atmospheric Crude Distiller. In fact, it is a complex process, normally including a desalter, a gas plant, hydrotreaters, amine treaters, a sour water stripper and sometimes also an integrated high-vacuum unit. So the respective BAT as determined for the specific processing units (gas plants, hydrotreaters etc.) need to be observed.

BAT is to:

- maximise heat integration by selecting between:
  - design highly integrated units (e.g. progressive distillation) (see 4.19.1)
  - increase heat integration between the atmospheric crude distiller with the vacuum unit or with other refinery process units (4.19.2-3). Some techniques that could be used are:
    - application of energy optimisation analysis to the crude preheat train
    - increasing crude distillation column pumparounds. Reboiling sidestrippers with a heat transfer oil rather than by steam stripping.

- maximise the use of liquid ring vacuum pump and surface condensers in place of some stage steam jet ejectors on the vacuum tower overhead. Especially applicable to the last vacuum stage which gives the most environmental benefit avoiding contamination of water. Minimise waste water flow/transfer of hazardous substances from vacuum pumps applying water recycling/waste water-free technique. See applicability restriction and more information in Section 4.19.4.
- apply advanced process control to optimise energy utilisation (see 4.19.2-3)
- use crude distillation units as an alternative (other is in 5.2.7 third bullet) to reprocess slop. This technique may generate problems in the desalter or may foul up the heat exchangers (see 4.19.8).

20. BAT for Product Treatments is to:

- hydrotreat products where olefins and colour bodies need to be removed for new plants (see 4.20.4)
- consider the use catalytic dewaxing for new plants (see 4.20.6)
- implement a good management system of the caustic solutions with the aim of minimising the use of fresh caustic and maximising the use of spent caustic. (see 4.20.1-2). Techniques that could be used:
  - for recycling are cascading of caustic solution and the re-use of spent caustic solutions by stripping.
  - for destruction are injection to desalters (this option may enhance the coke formation e.g. in visbreakers as seen in Section 5.2.22 forth bullet) or incineration of remaining spent caustic solutions when COD is high (e.g > 100 g/l).
- incinerate the spent air from sweetening processes (as a part of an odour abatement programme) (see 4.20.3).

21. BAT for Storage and Handling of refinery materials:

Note: In this section, refinery materials mainly relates to hydrocarbon compounds. Storage of other materials in a refinery such as water, caustic, acids, etc is not covered here.

BAT is to:

- apply the BAT determined in the BREF on Storage
- ensure the liquids and gases stored are in appropriate tanks or vessels based upon the true vapour pressure of the stored material (see Storage BREF).
- implement containment BAT (see storage BREF)
- use high-efficiency seals in floating roof tanks (see storage BREF)
- bund all stored chemicals, with separate bunding for incompatibles (see storage BREF)
- apply emission reduction measures during tank cleaning (See 4.21.10-11)
- apply concepts of good housekeeping and environmental management (see Section 5.1 and 4.15.3)
- minimise number of tanks and volume by a suitable combination of: application of in-line blending, integration of processing units, co-operation with partners in industry. This technique is much easier to apply on new facilities. (see 4.21.7, 4.21.14, 4.15.5)
- enhance vapour balancing and back venting during loading/unloading processes, e.g. by vapour balance lines that transfer the displaced vapour from the container being filled to the one being emptied. Incompatibility of tank vapours and applicability to external floating roofs tank are some examples of restrictions of application. Applicability needs to reflect economics, the type and size of vessel to be used (e.g. tank, truck, railcar, ship), type of hydrocarbon fraction and frequency of use of the tank. Because this technique is related to the next one, both should be evaluated together when implementing on a specific site. (see 4.21.18)
- apply vapour recovery (not applicable to non-volatile products) on tanks, vehicles, ships etc. in stationary use and during loading/unloading. Achieved emission levels are very dependent on the application, but recoveries of 95 - >99 % are considered BAT. If VRUs are not considered appropriate for certain streams, vapour destruction units are considered BAT. Properties of streams, such as type of substance, compatibility of substances or quantity need to be considered in the applicability of this BAT. Applicability needs to reflect economics, the type and size of vessel to be used (e.g. tank, truck, railcar, ship), type of hydrocarbon fraction and frequency of use of the tank. Because this technique is related to the above one, both should be evaluated together when implementing on a specific site (see 4.21.16 and 4.23.6.2)
- reduce (risk of) soil contamination by the implementation of an inspection and maintenance programme that could include implementing good housekeeping measures, double-bottom tanks, impervious liners, good housekeeping practices (draining, sampling, tank bottoms) (as part of the EMS) (see 4.21.8 and 4.21.13)
- install self-sealing hose connections or implement line draining procedures (see 4.21.13)
- install barriers and/or interlock systems to prevent damage to equipment from the accidental movement or driving away of vehicles (road or rail tank cars) during loading operations (see 4.21.13)
- implement procedures to ensure that arms are not operated until inserted fully into the container to avoid splashing where top loading arms are used (see 4.21.13)
- apply instrumentation or procedures to prevent overfilling (see 4.21.13)
- install level alarms independent of normal tank gauging system (see 4.21.13).

22. BAT for Visbreaking is to:

- apply deep thermal conversion, hydrovisbreakers or soaker visbreakers (see 4.22.1-3)
- sweeten the gas from visbreaking (See 4.22.4)
- treat gas and effluent water because of the presence of sulphur compounds (see 4.22.4)
- reduce the coke formation. It may be reduced by controlling the sodium content in the visbreaker feedstock or by using additives that decelerate the coke-formation. (See 4.22.5)

23. BAT for Waste Gas Treatments:

Abatement techniques for air pollutants are not included in this section. They are included in the Generic BAT section and in the BAT for each of the process/activities mentioned above. The following table gives a summary of where the main air pollutants can be found in this Chapter:

Air pollutant	*Section of this chapter where specific BAT-related air pollutants are mentioned*
CO	Catcracker, energy system
CO_2	Energy system
NO_x	Generic, catcracker, energy system
PM	Generic, catcracker, reformer, coker, energy system
SO_x	Generic, catcracker, coker, energy system, product treatments, visbreaker
VOC	Generic, bitumen, gas separation processes, NG plants, storage

BAT for amine treating is to (see 4.23.5.1):

- use regenerative amine process
- re-use amine solutions wherever possible
- reduce the concentration of H_2S in the refinery gas to levels of 20 - 150 mg/Nm^3 (See for split views on the upper value within Section 5.2.10 third round bullet)
- have sufficient capacity to allow maintenance activities and upsets (e.g. have redundancy equipment, apply load shedding, emergency amine scrubbers, multiple scrubber systems) (related with second BAT on SRU)
- use a storage tank or production planning to control waste water generated, to prevent any upset of the biotreater. (See BAT on reduction of discharges to water).

BAT for sulphur recovery units (SRU in 4.23.5.2) is to:

- apply a staged SRU, including tail gas treatment with a recovery efficiency of 99.5 % - 99.9 % (based on acid gas feed to the SRU). Range depends on cost effectiveness considerations. Those efficiencies ensure a SO_2 concentration range in the flue gas after incineration of 2000 – 400 mg/Nm^3. (See Section 4.23.5). One MS claims that FGD can be used when concentrations from SRU are over 2000 mg/Nm^3 and they represent a significant amount of SO_2 emissions within the refinery. One Member State claims that the recovery efficiencies mentioned as BAT are for new plants. They claim that BAT for existing units is 98.5 – 99.5% recovery.
- have an SRU configuration with sufficient capacity for the H_2S feed to the unit. This may be achieved by having, for example, at least two parallel SRU's of sufficient total capacity satisfactorily to cover all normal operating scenarios, including the sourest crude feed slate expected to be processed on the site
- have enough SRU capacity to allow the scheduled maintenance activity to proceed every two years, without a significant increase of sulphur emissions
- have a utilisation factor of at least 96 %, including major planned turnaround maintenance
- use state-of-the-art control and monitoring systems. Use of a tail gas analyser linked to the process control system (feedback control) will aid optimum conversion during all plant operating conditions, including changes to sulphur throughput
- use a good furnace burning-zone design and effective furnace temperature and oxygen control systems where sour water stripper off-gases are a feed stream, because the process must also be designed and operated to complete the destruction of ammonia. Ammonia breakthrough may lead to deposition and blockages of catalyst beds by ammonium salts (eg carbonate/sulphate) and these SRUs need to be monitored for evidence of this.
- apply alternative H_2S/SO_2 recovery/removal techniques (e.g. iron chelating, solvent extraction, NaOH adsorption, molecular adsorption) in those installations where the H_2S production is small (< 2 t sulphur per day if incineration is acceptable). Those options have important cross-media effects such as waste generation and energy consumption. This BAT is especially relevant for stand-alone lubricant refineries, bitumen refineries and some natural gas plants (see 4.3.5 and 4.3.8).

BAT for flaring is to (see 4.23.7):

- use flaring as a safety system (start-up, shutdowns and emergencies).
- ensure smokeless and reliable operation
- minimise flaring by a suitable combination of:
  - balancing the refinery fuel gas system
  - installing a gas recovery system
  - using high-integrity relief valves
  - applying advanced process control
- reducing relief gas to flare by management/good housekeeping practices

24. BAT for Waste Water Treatments is:

- see Generic BAT Section

25. BAT for Solid Waste management is:

- See Generic BAT Section

6 EMERGING TECHNIQUES

Emerging technique is understood in this document as a novel technique that has not yet been applied in any industrial sector on a commercial basis. This chapter contains those techniques that may appear in the near future and that may be applicable to the refinery sector.

Refinery activities overview

Throughout its history the refining industry has continuously developed new and improved processes in response to changes in feed quality, product specifications, product slates, new product outlets and economic and environmental requirements. These developments have slowed down in recent years for the following reasons:

1. Large oil companies are cutting down on their R&D budgets, and are more and more relying on third parties for new developments in refinery technology and catalytic processes. These third parties develop techniques for licensing income or for income from catalyst sales. Developments are reported in the technical literature (Hydrocarbon Processing, Chemical Engineering Progress, Oil and Gas Journal, Erdöl, Gas und Kohle, Petroleum Technology Review) and during seminars and conferences (World Petroleum Congress, WEFA, Hart's Fuel Conference, European Refining Technology Conference, NPRA and API specialist meetings) for the dissemination of those techniques.
2. Technological developments are concentrating on optimising current systems for higher yields (e.g. more selective catalysts and solvents), higher energy efficiency (e.g. improved reactor design and better heat integration) and shorter downtimes (e.g. scavenging of impurities, automatic cleaning systems) rather than novel processes;
3. The current tool box of conversion, separation, treatment and environmental technologies seems adequate and sufficient to meet any desired product slate and product specifications for the coming decade as well as meeting stringent regulatory requirements;

Meanwhile, the upgrading process of the refinery sector to implement existing techniques for meeting new product specifications will continue. The rationalisation process in the refining industry will also continue and low margins will force refineries to look for cost savings.

Alkylation

Most of the safety and environmental concerns are related to the potential for a large release of HF or H_2SO_4. A solid acid catalyst would potentially overcome most of the drawbacks associated with liquid acid catalyst systems and open up a new area of marketing for alkylation. Numerous companies are putting a large R&D effort into the development of a new solid catalyst for the alkylation process.

Catalyst	**Technology**
BF_3/Al_2O_3	Grignard
SbF_5/SiO_2	Circulating bed + washing
Zeolite H-b	Grignard
CF_3SO_3H fixed in a porous carrier (silica)	Haldor Topsoe A/S

[61, Decroocq, 1997], [330, Hommeltoft, 2000]

Technology providers claim that these techniques will be ready in the market in one to two years.

Base oil production

A recently published new technology is the application of membranes for solvent recovery in the solvent extraction/dewaxing processes. Driving force is the reduction in energy consumption. [259, Dekkers, 2000]

Catalytic cracking

Some promising lines of investigation for the improvement of the environmental performance of catcrackers are:

- the capability to process heavier feedstocks, containing more contaminants (catalyst deactivators) such as vanadium and nickel and having a higher Conradson Carbon Residue (CCR) content. Responses that are being developed are: continue the development of more active catalysts and more effective (e.g. two-stage) catalyst regeneration. Driving forces are the reduction of residue (i.e. enhanced upgrading) and higher overall refinery efficiency (e.g. the elimination of high vacuum unit operation) [259, Dekkers, 2000].
- deNOx additives in catcracker regenerators. low-NO_x additives. NO_x removal additives are an emerging technology that may have future applicability for NO_x control from FCC regenerators. The additives are added to the regenerator of the FCC to promote the destruction of NO_x by reaction of nitrogen oxides with carbon monoxide or coke. They are often especially promoted SO_x removal additives, providing the ability to simultaneously reduce the NO_x and SO_x emissions from the FCC regenerator. They have been investigated under laboratory conditions but have not been commercially demonstrated. These additives are attractive since they need no capital investment, although the operating cost for additive replacement is expected to be large. Some trials in USA have achieved NO_x reductions of 50 %.
- hot ceramic filters can be retrofitted to the underflow of third stage cyclones. Ceramic filters are only applied in niche applications.
- improvement of the catalyst separation by use of a magnet (Kellogg Tech company) [247, UBA Austria, 1998]
- other flue gas desulphurisation includes CanSolv's amine scrubbing system for SO_2 removal. It has not commercially proven application in FCC, but it's process appears quite promising and cost effective, especially at high sulphur.

Catalytic reforming

The current practice of application of continuously improved catalysts (supplied by catalyst manufacturers) is expected to continue. [259, Dekkers, 2000]

Energy system

Some promising lines of investigation for the improvement of the environmental performance of the energy systems are CO_2 abatement techniques (more information within the waste gas treatments). Others are the heat integration. The search for further energy improvements is continuing, with the current focus on attractive cogeneration opportunities and more complex heat integration.

Hydrogen production

Some promising lines of investigation in hydrogen production technologies are:

- the hydrocarb process, in which the residual oil is essentially cracked to carbon and hydrogen. This process can be seen as an internal source of natural gas for a refinery. The process produces carbon, hydrogen and methanol. It has been calculated in a refinery of 4.98 t/yr that this process can increase by 40 % the total gasoline production, 1150 m^3/d of methanol and 795 m^3/d of C/H_2O slurry [12, Steinberg and Tung, 1992].
- methane pyrolysis, which takes advantage of the thermal decomposition of natural gas and the direct production of hydrogen while sequestering the carbon or using the carbon for other commodity purposes. Consequently the CO_2 generation is completely eliminated [12, Steinberg and Tung, 1992], [281, Steinberg, 2000].

Hydrogen-consuming processes

Some promising lines of investigation for the improvement of the environmental performance of energy systems are:

- residue hydrotreating and hydroconversion processes (e.g. slurry bed technology). This process has only been demonstrated at semi-commercial scale and no commercial plants are in operation yet.
- gasoline deep desulphurisation techniques with a lower hydrogen consumption are currently under development. Parameters are not yet available.

Integrated refinery management

Leak detection technology.
Smart LDAR. This device is able to detect (using laser technology) fugitive hydrocarbon emissions by real time video imaging of the equipment under surveillance. It allows the user to identify at a refinery the zones in which the greatest emissions are located so that an LDAR using sniffing techniques can focus on the high emission items. An API study has shown that 90% of fugitive emissions comes from 0.13% of the piping components (API analysis of refinery screening data. Publication 310, November 1997). This technology is under development and a number of technical issues need resolving before it is ready for use as a routine tool. The approach would considerably reduce the cost / benefit of a LDAR program by identifying swiftly the high leakers. Nevertheless these developments over conventional LDAR programmes are likely to come to fruition in the future term and progress should be monitored to see when they can be accepted as a good technique [115, CONCAWE, 1999].

Product treatments
A development to be mentioned is the biodesulphurisation of gas oil and even crude oil [259, Dekkers, 2000]

Waste gas treatments
Some developments to be mentioned are:
- sulphur dioxide removal by SO_2 capture from flue gas and conversion into liquid sulphur.
- biological H_2S removal [181, HP, 1998]
- particulate abatement techniques by new developments including ceramic filters (e.g. NGK, Japan) and a rotating particulate separator (Lebon & Gimbrair, the Netherlands)
- CO_2 abatement techniques.

Assuming refinery utilisation gradually increases and that product specification and abatement requirements continue to be more stringent, then CO_2 releases, if unabated, are likely to continue to rise, since measures to meet these requirements will require energy. In principle CO_2 emissions can be reduced by separation, collection and finding a useful application. Injection of CO_2 aiming at secondary and tertiary oil recovery is a potential possibility. Injection into sub-soil formations for storage or supply to greenhouses as a gaseous fertiliser product has also been suggested. However, considering the large quantities of CO_2 involved these projects will be very costly indeed. Moreover, these types of solutions can only partly alleviate the CO_2 emission issue.

Removal of CO_2 from Flue Gas Streams
Wet scrubbing using caustic soda for the removal of SO_2 / NO_x will effectively remove CO_2 as a carbonate. It should be noted, however, that to apply wet gas scrubbing for the sole purpose of removal of CO_2 would be largely self-defeating as the scrubbing process itself and the production of the scrubbing agents both require energy. A number of other licensed processes are available which will remove CO_2 from flue gases using a solvent that can be recycled, typically methylethylamine (MEA). After absorbing the CO_2 in a scrubbing system, the solvent is thermally regenerated, releasing the CO_2. This could then be compressed, liquefied and sent to underground disposal. Present indications are that the high energy requirements of this type of scheme will discourage its general use.

Disposal of CO_2
Unlike the abatement of other pollutants no feasible technology exists for the removal of carbon dioxide from flue gases. A number of disposal options are, however. under scientific consideration. For technical, ecological and economic reasons, a viable solution is not yet available, but this option is currently being investigated by certain major operators and the International Energy Agency (IEA).

Emerging technologies under consideration are:

- disposal in the deep ocean
- disposal in deep aquifers
- disposal in exhausted oil and gas reservoirs
- disposal as a solid in an insulated repository.

7 CONCLUDING REMARKS

Some general concluding remarks
The environmental situation of European refineries varies greatly across the European Community, so the starting point for each case is very different. Different environmental perceptions and priorities are also evident.

Timing of the work
The work on this BAT Reference document started with a kick-off meeting on 10 and 11 June 1999. Several consultations were made to the draft of the BREF or parts of it to the Technical Working Group (TWG) for consultation. The first draft of Chapters 1 to 4 and 6 onwards was sent out for consultation in February 2000. A plenary meeting was held in June 2000 where it was agreed to issue another draft of chapter 4 and introduction to chapter 5 for consultation. That partial draft was sent for consultation on October 2000. The second full draft was issued in January 2001 and the work concluded after another TWG meeting on 6 - 8 June 2001. After that meeting another consultation was done on Chapter 5, Executive Summary and Concluding Remarks.

Sources of information
More than 350 items of information were used for the preparation of this document. Eight reports from authorities and industry were used as the main sources of information. Complementary to that information, 17 site visits, sub-group meetings and much other information from suppliers and general literature were collected. In the later stages, comments on draft documents have represented the main source of information, complementing, qualifying or adding to the information into the BREF.

Most of the information on techniques submitted by TWG was focused on abatement techniques in general. Very little information was made available on the performance of production techniques to be considered in the determination of BAT, and especially on achieved emission and consumption levels that those production techniques may achieve. Most commonly, this type of data came from technology providers or from general literature.

Level of consensus
The refineries sector is a large and complex one, spread across all Member States except Luxembourg. This size and complexity are reflected in the number of processes / activities addressed in the BREF and the number (200+) of BAT it contains. The fact that agreement has been reached on all but 27 of those 200+ BAT is a measure of the broad commitment of TWG members to the conclusions reached. One corresponds to the general introduction to Chapter 5, eleven to the Generic BAT and fifthteen to Specific BAT. All of them are listed below.

	BAT where the split view is addressed	Split view from	Split view
1	Introduction to Chapter 5	Ind + 2 MS	In the determination of the upper value of the associated emission range in this chapter, a split view has been expressed by industry and two Member States. The split view is that they consider that the upper value in Chapter 5 should correspond with the upper value found in Chapter 4. Their rationale is that if a technique considered BAT is already applied in an installation and achieves a certain value, that value should be considered in the range of associated emission values.
GENERIC BAT			
2	reduce SO_2 emissions	1 MS	One Member State does not agree with the approach of dealing with the sulphur dioxide emissions in the refinery as a whole. Their proposal is to follow their national methodology for BAT determination and implementation.

	BAT where the split view is addressed	Split view from	Split view
3	reduce NO_x general	1 MS	One Member State does not agree with the approach of dealing with the nitrogen dioxide emissions in the refinery as a whole. Their proposal is to follow their national methodology for BAT determination and implementation.
4	Water emission table. *Total Metals*	3 MS	Two Member States claimed that the group of metals should be split into two groups according to their toxicity. One Member State claimed that the ranges should be given for individual metals. These last two requests came after the agreement in the TWG meeting on total metals.
5	Water emission table. *Monthly:*	1 MS + Ind	One Member State claims that those values should be daily averages because those figures can easily be achieved with a well designed and operated WWTP. Industry claimed that the average should be yearly because all their data are based in yearly averages.
6	Water emission table. *Calculation of upper value of the load range.*	1 MS + Ind	One Member State disagrees with the upper values of this column because they should represent actual refinery figures that are lower that the ones represented here. On the other hand, Industry believes that the load values set here should not be associated emission levels at all, but rather benchmark values since they are dependent on refinery water use and calculated on an arbitrary selection of the average water use at 63 refineries (which itself is presented only as a benchmark value on page 401 of the BREF). As stated in the * footnote in the BREF, the actual loads for a refinery can be "easily calculated with the concentration value and the real effluent rate", and can then be compared to the benchmark values that these should be.
7	Water emission table. *Total hydrocarbon content:*	2 MS + Ind	One Member State and Industry claim that 3 mg/l as upper value is representative of actual operations data of existing refinery facilities in Europe with 3-step Waste Water Treatment Plant currently in place. One Member State proposed an upper value of 5 based on current observe performances in existing facilities in their country.
8	Water emission table. *COD:*	1 MS	One Member State claims that the upper level in concentration should be 75 and the upper value for load should be 45 because a standard biotreater reduces the COD content by 90-97 %. As a consequence 75 is easy to achieve in a well designed and operated biox.
9	Water emission table. *NH_3.*	1 MS	One Member State claims that the upper level should be 5. Those levels can be reached by strippers and biological nitrification/denitrification step.
10	Water emission table. *Total N.*	Ind	Industry believes that, where nitrogen is not a pollutant of concern in the receiving waters, denitrification cannot be BAT as the environmental benefit to the receiving water is very low, while the cost both in Euros (Capital Expenditure) and the CO_2 emissions are high.
11	Water emission table. *Total N load:*	1 MS	One Member State claims that the upper level of the range should be 8. They demonstrated (based on actual data) that a figure below 8 can easily be achieved with a stripper or a nitrification/denitrification step.
12	Water emission table. *TSS:*	1 MS	One Member State claims that the upper level should be 30. The reason is that the use of sedimentation, flotation, filtration or a combination of these techniques can reduce of the suspended solids by 60 – 99.99%.
SPECIFIC BAT			
13	Base oil production. Use of NMP	Ind	Industry claims that considering the information within this document, both NMP and furfural are equally viable solvent candidates. In Industry's opinion, no clear case has been made in the BREF to arrive at one preference.

	BAT where the split view is addressed	Split view from	Split view
14	Catcrackers under partial oxidation conditions	1 MS + Ind	One Member State claims that the associated emission range should be 300 – 450 mg/Nm^3 if those low levels of CO need to be reached. Industry remains of the view that the range should be 100 – 500 mg/Nm^3 to cover the whole range reported in Section 4.5.3.
15	Catcrackers. NO_x emissons	3 MS	Three split views from Member States appeared on the range of the NO_x emissions. One Member State claims that the application of an SCR is always possible and that the upper value should be therefore 100. One Member State claims that the range should be 300 – 450 mg/Nm^3 because the FCC technology is chosen according to the crude oil processed, the refinery configuration and the product demand. So NO_x emissions cannot drive the production operations. One Member State specifies that the range should be 10 – 450 because SCR and SNCR are not applicable to all existing units.
16	Catcrackers. SO_x emissions	1 MS	One Member State maintains that FGD is always applicable and that the range should therefore be changed to 10 – 100.
17	Catcrackers. SO_x and NO_x emissions	1 MS	One Member State does not agree with the approach followed in this section for the SO_x and NO_x emissions. Their proposal is to follow their national methodology for BAT determination and implementation.
18	Cokers. Particulates	Ind	Industry claims that ESP is not applicable because the conductivity of the coke particles is high and consequently the higher value of the range should be 100.
19	Cokers. Calciner. SO_x	Ind	Industry claims that with the application of FGD and with 90 % removal is not possible to achieve the upper value because the sulphur in the feed may be very high. Their proposal is to increase the value to 500.
20	Energy system. Sulphur content of RFG	1 MS	One Member State claim that for existing refineries the range should be <500 – 1000 ppm because the H_2S content in RFG is negligible if the bubble limit is respected. BAT repeated in two more places within Chapter 5.
21	Energy systems. NO_x from boilers and heaters with gas fuel	2 MS	Two Member States claim that the upper value should be 100 because it can be reached with the implementation of primary measures and SCR.
22	Energy systems. NO_x from boilers and heaters with liquid fuel	2 MS	One Member State claims that small heaters (<50MW) can reach 200 and with the big heaters and boilers (>50MW) the installation of SCR is justified and consequenly values of less than 100 can be reached. One Member State claims a level from 200 – 400 because of the nitrogen content in the fuel)
23	Energy systems. NO_x from gas turbines	1 MS	One Member State claims that the upper value should be 35 based on primary measures and SCR.
24	Energy systems. Particulates emissions	1 MS + Ind	One Member State claims that the range for particulates should be 30 – 50 because those values are consistent with a 95% abatement. Industry rationale for the range 5 to 50 mg/Nm^3 is that this is consistent with the whole range reported in Chapter 4
25	Energy systems. SO_2 emissions from liquid fuel pool	2 MS + Ind	One Member State claims that the use of FGD is always possible and that the upper value should therefore be 200. One Member State and Industry Industry claim that the limit should be no lower than 1700 mg SO_2/Nm^3 which is equivalent to a 1% sulphur level in fuel oil with no abatement.

	BAT where the split view is addressed	Split view from	Split view
26	Energy systems	2 MS	One Member State does not agree with the approach followed in this section for the SO_x and NO_x emissions. Their proposal is to follow their national methodology for BAT determination and implementation. Another Member State does not agree with the approach followed in this Section because they claim that the bubble approach should drive the Energy BAT Section.
27	SRU	2 MS	One Member State claims that FGD can be used when concentrations from SRU are over 2000 mg/Nm^3 and they represent a significant amount of SO_2 emissions within the refinery. One Member State claims that the recovery efficiencies mentioned as BAT are for new plants. They claim that BAT for existing units is 98.5 – 99.5% recovery.
Ind: Industry; MS: Member State			

Recommendations for future work

The TWG recognised the interrelationship between emissions from the refinery itself and those arising from the use of the refinery products. It appears important that regulators are informed of this indirect environmental impact. For example, a reduction in the sulphur content in a fuel means that refineries need to handle more sulphur. Consequently, the TWG advises the relevant European and International bodies to consider this important issue in order to reduce the overall environmental impact of the industry sector as a whole. Additionally, it advises European bodies that when considering new product specifications, they should consider the impact on the emissions generated by refineries.

Very few data were exchanged on production techniques and related good environmental practices (e.g. current emission and consumption levels, performance, consumption benchmarks or economics for improvement). That is the main reason why few production techniques appear in Chapter 5. For future BREF reviews, all TWG members and interested parties should continue, or start, to collect these data for all production processes. The data should be expressed as concentrations as well as loads and, where appropriate, in relation to the amount of input and/or output material.

TWG recognises that technology providers or European technology providers associations (e.g. European Sealing Association) can give excellent input to the BREF, especially to give their expertise in new applications in the refinery sector. Consequently it is recommended that they be formally involved in the next revision of the BREF. The TWG advice is to start the review of this document in 2006.

For fugitive VOC emissions, a guide at the EU level covering equipment performances and good practices would be useful. It can be compiled as a preparatory step for the next BREF revision in partnership between member states, European environmental bodies, suppliers and industry representatives.

Information on plants and actual performance data are scarce; for the revision of this document the missing information should be provided. Apart from data missing in general, as mentioned above, the following comments relate to specific areas where data and information are missing:

a collect and analyse more data on split views with the intention to solve them
b try to achieve consensus in the definition of the bubble and try to collect technical support for the BAT associated values under the bubble concept for the main air pollutants.

c energy efficiency has been recognised as one of the most important issues in the BREF. The reason is because refinery processes are very energy intensive. In the next revision, a further analysis of the methods and quantification of energy efficiency needs to be done. The development and promotion of a transparent methodology for the calculation of energy efficiency should be promoted.
d provide data on decommissioning of processes
e provide data on mass balance of the metals contained within the crude oil. Mass balance on sulphur is typically done in refineries, but no information on mass balance of metals has been reported. Volatile metals such as mercury, contained within the crude oil are an issue that needs to be explored. Where do they go and how can they be abated?.
f data on characteristics of particulates such as unburnt hydrocarbons, metals (e.g. Ni, V) and PM_{10} need to be qualified
g very little information has been provided about noise levels or techniques to reduce them
h no information has been provided on odour abatement. It is recognised that odour abatement is linked to VOC abatement (typically sulphur compounds), but there is no identification of compounds and where they may come from. In other words, analysis of the VOC needs to be done.
i collect data on dioxin emissions and on the effect of catalyst regeneration processes and some clean-up facilities
j an important issue when considering refinery waste is that there are still many differing definitions between countries, which makes comparisons of waste difficult. Make a catalogue of types of wastes produced by refineries to make comparison easier and more accurate.
k collect information on NO_x and SO_x emissions from the flaring system
l collect information on NO_x emissions from coking processes
m very few information have been exchanged on natural gas plants. This can partially be justified because the number of those plants are much smaller than Mineral Oil Refineries. However, some concrete data on how those plants can be improved environmentally need to be exchanged.

Suggested topics for future R&D projects
The following topics might be considered for future Research and Development projects:

It has been recognised that the cross-media issues that may be generated by some process techniques are very difficult to assess. For example, alkylation productions raises the difficult question of which is the better process: HF alkylation (more energy efficient but very toxic catalyst) or sulphuric alkylation (less energy efficient and the waste generated needs to recycled, but less toxic). It may be worthwhile to develop some methodology to compare two or more technologies.

A study to compare energy efficiency in the refinery sector world wide. This needs to consider the different types of refineries. During this study, a transparent methodology needs to be defined. The study should also include an analysis of the techniques already used within the refinery sector to improve their energy efficiency and how they affect the efficiency, cost and environmental benefit.

No much information about the physical and chemical characteristics of dust (e.g. content of unburnt hydrocarbons, content of metals and content of PM_{10}) has been found during the work. Because those analyses are difficult to do, they can be supported by an R&D project to standardise them.

A study of the fugitive emissions from refineries. This should include the collection of fugitive VOC emission data from the refinery sector. This may be based on the information gathered by the Commission under Article 15 (European Pollutant Emission Register, EPER). This should also include an analysis of the monitoring methods and an analysis of techniques to reduce those VOC emissions in order to quantify emission reduction capabilities and cost. This programme

can also focus on the different types of equipments that could be used, their performances and their cost, or on the need to develop new equipment presenting a better trade-off between performance and cost or allowing fugitive VOC emissions to be identified and characterised at a lower cost than the actual LDAR programmes.

Refineries handle harmful products like aromatics (benzine, etc…). Some studies should be promoted to better evaluate the emissions of these products, their impact on the environment and the different ways to solve these problems. This is to some extent connected to fugitive VOC emissions, except that here there is a need to characterise these emissions.

There is a need expressed by the permitters to get more precise technical information in this area. A lot of recommendations are made concerning the seals of different equipment. It could be particularly useful to study more precisely their efficiency and their implementation conditions and to set up good practices and methodologies concerning the type of seals to recommend, the way to check their efficiency, their utilisation conditions and the relevant replacement interval.

The flameless oxidation mode has begun to be used more widely in sectors such as iron and steel and ceramics. Studies and experiments should be promoted to encourage similar work in the refinery sector. This technique seems to offer higher energy efficiency and low NO_x emissions.

It has been very difficult to express environmental performances for this sector in mass flow or specific mass flow that are highly representative of the environmental impact. This is because the energy consumption of a refinery increases with its complexity and the degree of conversion of the products. In parallel, the rate of sulphur recovered increases with the complexity and the energy consumption. A methodology to facilitate a benchmarking in specific mass flow, considering for example several kinds of refineries, would be useful.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

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9 GLOSSARY

Symbols

~	Around, more or less
ΔT	Increase of temperature, temperature rise
€	EUR (EU currency)

A

AC	Alternating Current
AC	Activated Carbon
Amylenes	Pentenes
AOC	Accidentally Oil Contaminated
°API	Density unit (specific density = 141.5/(°API+131.5))
API	American Petroleum Institute
API separator	Oil/water/sludge separator (developed by American Petroleum Institute)
ASU	Activated Sludge Unit
atm	Atmosphere. Pressure unit equal to 101.3 kPa
Auto-Oil I,II	Co-operative programmes between the EU and the oil and motor industries to find the most cost-effective way to improve air quality in Europe. These have led to Directives on fuel properties and vehicle emissions.

B

bbl	US barrel (159 litres)
bar	Pressure unit equal 100 kPa (1 bar = 0.987 atmospheres)
barg	Bar gauge (relative pressure over the atmospheric pressure)
BBU	Bitumen Blowing Unit
BFO	Bunker Fuel Oil
BFW	Boiler Feed Water to produce steam
BOD	Biological Oxygen Demand
bpcd	Barrels per calendar day (average flow rates based on operating 365 day per year)
bpsd	Barrels per stream day (flow rates based on actual on-stream time of a unit)
BREF	Best Available Techniques reference document (Documents developed by the EIPPCB on different IPPC sectors)
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BTX	Benzene, Toluene, Xylene

C

cat	catalytic
catcracker	catalytic cracker (typically refers to fluid catalytic cracker)
CCGT	Combined Cycle Gas Turbine
CCR	Conradson Carbon Residue (See under Concarbon more information)
CDD/CDF	Chlorodibenzoparadioxins/furans
CDU	Atmospheric Crude Distillation Unit
CEC	Comission of the European Community
CHP	Combined Heat and Power (co-generation)
COC	Continuously Oil Contaminated
COD	Chemical Oxygen Demand
Concarbon	Conradson carbon = measurement of carbon residue (expressed in % w/w). Measurement of the tendency of a hydrocarbon to form coke.
CONCAWE	European Refinery Association for Environment, Health and Safety
Corinair	European Air Emissions inventory
CPI	Corrugated Plated Interceptor
C_x	Hydrocarbons with x number of carbons
CW	Cooling Water
Currencies	http://fxtop.com/en/adv.htm

D

d	day
DAF	Dissolved Air Flotation
dB(A)	Noise unit
DC	Direct Current
DCU	Delayed Coker Unit
DEA	Diethanol Amine
DG	Direction General from the European Commission
DGA	Diglycolamine
DIAL	Differential absorption light detection and ranging
DIPA	Di-isopropanol amine
DNB	Nitrification/denitrification biotreater
DS	Dissolved Solids

E

EC	European Community
EFRT	External Floating Roof Tanks
EIA	Environmental Impact Assessmente
EII	Energy intensity index (Solomon index. See Section 3.10.1)
EIPPCB	European IPPC Bureau
EMS	Environmental Management System (see Section 4.15.1)
EOP	End-of-pipe
EP	European Parliament
ETBE	Ethyl tert-butyl ether
EU+	EU countries plus Norway and Switzerland
EUR	Euro: EU currency

F

FBI	Fluidised Bed Incinerator
FC	Flue Control
FCC	Fluidised-bed Catalytic Cracking
FCCU	Fluidised-bed Catalytic Cracking Unit
FFU	Flocculation/flotation unit
FGD	Flue Gas Desulphurisation
FGR	Flue Gas Recirculation
FOE	Fuel oil equivalent (1 tonne FOE = $4.25 \cdot 10^{10}$ J)

G

GAC	Granular activated carbon
GO	Gasoil

H

h	hour
HC (1)	Hydrocarbon
HC (2)	Hydrocracker/ing
HCU	Hydrocracker Unit
HDM	Hydrodemetallisation
HDS	Hydrodesulphurisation
HFO	Heavy Fuel Oil
HGO	Heavy Gasoil
Horizontal BREF	BAT reference documents prepared to deal with topics common to more than one IPPC industrial sector (namely storage, cooling, waste water and waste gas and monitoring)
HORC	Heavy Oil and Residue Catalytic cracking
HP	High Pressure
HSE	Health, Safey and Environment
HT	High Temperature

HVU	High Vacuum Unit
Hydrofiner	Selective hydrocracking

I

I-TEQ_{DF}	International toxic equivalent of dioxins/furans
IAF	Induced Air Flotation
IFRT	Internal Floating Roof Tank
IGCC	Integrated Gasification Combined Cycle
IMO	International Maritime Organisation

K

k--	kilo
kero	kerosene
KjN	Kjendahl nitrogen (Measure of the total nitrogen content)
kt	kilotonne (10^6 kg)

L

LCO	Light Coking Oil
LCP	Large Combustion Plant BREF
LDAR	Leakage Detection and Repair Programme (see Section 4.23.6.1)
LGO	Light Gasoil
LP	Low Pressure
LPG	Liquefied Petroleum Gas
LT	Low Temperature
LVGO	Light Vacuum Gasoil
LVOC	Large Volume Organic Chemicals BREF

M

M---	Million
MAH	Mono Aromatic Hydrocarbon
MDEA	Mono diethatnolamine
MEA	Mono ethanolamine
MP	Medium Pressure
MS	EU Member State
MTBE	Methyl Tert-buthyl Ether
Mt/yr	Million of tonnes per year
MWe	MegaWatts electric (energy)
MWth	MegaWatts thermal (energy)

N

n-	normal, linear organic compound
N---	Normal (refers to volume of gases under normal conditions (temperature 0 ºC and pressure of 1 atmosphere (101.3 kPa)))
n/a	not applicable
n.a.	not available (typically for data not available within the document). Highlighted within the document to help next revisions.
N-Kj	Nitrogen analysed by Kjendahl method.
Naphthenic	The naphthenes contain one or more saturated rings of 5 or 6 carbon atoms in their molecules to which paraffinic-type branches are attached.
NOC	Non-oil contaminated
NO_x	Nitrogen Oxides (NO + NO_2, normally expressed as NO_2)

P

Pa	Pascal (N/m^2). SI unit for pressure: 1 atm=101.3 kPa
PAC	Powdered activated carbon
PAH	Polyaromatic Hydrocarbons
PC	Pressure Control

PCDD/F	Polychlorodibenzoparadioxins/furans
Platformer	Type of catalytic reformer
PM	Particulate Matter (any finely divided solid or liquid material emitted into the air)
PM_{10}	Particulate matter of size less than 10 µm
Poly-unit	Polymerisation unit
PPI	Parallel Plate Interceptor
ppm	parts per million (weight)
ppm v/v	parts per million in volume
PPS	Pressurised cross flow plate separation of the desalting unit
PSA	Pressure-swing adsorption used for purification of hydrogen
psi	pounds per inch (British pressure unit 1 bar = 14.5 psi)
psia	pounds per inch (absolute pressure)

R

RCC	Residue Catalytic Cracker
Residue	This term is used in this document as the heaviest fractions of the distillation and conversion units. These fractions are used as feedstock in other processes or as liquid refinery fuel.
RFG	Refinery Fuel Gas
RO	Reversed Osmosis
RON	Research Octane Number
RSH	Mercaptan
RVP	Reid Vapour Pressure

S

S	Sulphur
SF	Sand Filter
SO_x	Sulphur oxides (SO_2 and SO_3)
SRU	Sulphur Recovery Unit
SS	Suspended Solids
SW	Sour Water
SWS	Sour Water Stripper

T

t	Tonne (1000 kg)
t/yr	Tonnes per year (annum)
t/d	Tonnes per day
TAME	Tertiary Amyl Methyl Ether
TCDD/F	Tetrachlorodibenzoparadioxins/furans (toxicity reference for dioxins)
TEL	Tethra ethyl lead
TGT	Tail Gas Treatment of the sulphur recovery unit
TML	Tethra methyl lead
TOC	Total Organic Carbon
TSS	Total Suspended Solids (water)
TWG	European Technical Working Group on refineries

U

U	Unit (used together with names of processes)
UF	Ultrafiltration
Ultraformer	Type of reformer
USAEPA	Environmental Protection Agency of the USA

V

v/v	volume by volume
V.I.	Viscosity Index (see Section 2.3)
VBU	Visbreaking Unit

VOC	Volatile Organic Compound
VR	Vacuum Residue
VSBGO	Visbreaking Gasoil

W

w/w	weight by weight. Ratio expressed in weight
WHB	Waste Heat Boiler
WWTP	Waste Water Treatment Plant

Y

yr	year

10 ANNEXES

Six annexes have been prepared to complement the information provided in the document. The information provided is the following:

Annex I Environmental legislation and emission limit values applied to refineries.

Annex II Refinery configurations.

Annex III Refinery feedstock, intermediates and products.

Annex IV Submitted examples of cost-effectiveness and implementation of environmental technologies.

Annex V Background information from TWG members for the different proposals of SO_2 and NO_x emission under the bubble concept.

Annex VI Proposals from some Member States on the implementation of BAT in the refinery sector

10.1 Annex I. Environmental legislation and emission limit values applied to refineries

Refineries generate emission to the air, discharges to water and also waste. Most pollutants are emitted to streams that are transboundary in nature. As consequence many of the environmental policies and regulations with respect to oil refining are to a large extent influenced by international developments (EU-directives and other international regulations). These regulations focus on product quality, refinery emissions and, more recently, on environmental reporting. The issue of emergency procedures is normally included in the external safety report and in the permit for the location.

10.1.1 EU and other international legislation

Table 10.1 gives a summary of some of the main EU legislation that it is applied to refineries.

Name	Concerning	Location	Emission limit values
Directive 96/61/EC	integrated pollution prevention and control	Official Journal L 257, 10/10/1996 p. 26 BGBl. I, 1997, S. 542	None
Directive 88/609/EEC and last amended by Directive 94/66/EC	limitation of emissions of certain pollutants into the air from large combustion plants	Official Journal L 336, 07/12/1988 p. 1	Yes
Directive 75/442/EEC as amended by Directive 91/156/EEC	waste	Official Journal L 194, 25/07/1975 p. 39	
Directive 91/689/EEC	hazardous waste	Official Journal L 377, 31/12/1991 p. 20	
Council Directive 84/360/EEC	on the combating of air pollution from industrial plants	Official Journal L 188, 16/07/1984 p. 20	
Directive 67/548/EEC	on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances	Official Journal L 196, 16/08/1967 p. 1	
94/904/EC: Council Decision	establishing a list of hazardous waste pursuant to Article 1 (4) of Council Directive 91/689/EEC on hazardous waste	Official Journal L 356, 31/12/1994 p. 14	
Directive 94/63/EC	on the control of volatile organic compound (VOC) emissions resulting from the storage of petrol and its distribution from the terminals to service stations	Official Journal L 365, 31/12/1994 p. 24	
Directive 96/82/EC	on the control of major-accident hazards involving dangerous substances	Official Journal L 10, 14/01/1997 p. 13	
Council Directive 1999/13/EC	on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations	Official Journal L 085, 29/03/1999 p. 0001 - 0022	

Name	Concerning	Location	Emission limit values
Council regulation (EEC) No 1836/93	allowing voluntary participation by companies in the industrial sector in a Community eco-management and audit scheme	Official Journal L 168, 10/07/1993 p. 1	
Directive 94/9/EC EC of the European Parliament and the Council	on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres	Official journal NO. L 100, 19/04/1994 P. 0001-0029	
Directive 94/63/EC	on painting of petrol tanks		

Table 10.1: Main EU legislation affecting refineries

Legislation affecting product specifications

Product specifications (Auto-Oil programmes and IMO)
Concern about the environmental and health impact of fuel combustion has caused changes in environmental regulations with special focus on gasoline and diesel fuel composition as the largest products (Auto-Oil specifications in Table 1.4). The main restrictions on diesel fuels impose limits on sulphur and polynuclear aromatics content. Gasoline specifications include not only sulphur and total aromatics content but also limits for specific compounds, such as benzene, olefins, maximum RVP and, in the USA, minimum oxygen for areas with CO problems.

The specifications for heavy fuel oils are regulated in Council Directive 1999/32/EC relating to the reduction in the sulphur content of certain liquid fuels and amending 93/12/EC. OJ L121/13, 11 may 1999 EU B. For heating oil, the Directive entails a reduction of the sulphur content to 0.1 % in 2008 and for landtrade fuel oils a limitation of the sulphur content to 1 % from 2003 onwards. For seagoing vessels the regulations of Annex VI of the MARPOL treaty, once ratified, imply that as of 2003, in so-called SO_x emission control areas, the use of fuel oils may be restricted to fuel oils with a maximum sulphur content of 1.5 %.

Legislation affecting emissions to air

Legislation	Concerning
National Emission Ceiling Directive	Important Directive for the reduction of CO_2, SO_2, NO_x and VOC
Air Pollution Protocol (Gothenburg Protocol, 1 December 1999).	Important protocol for the reduction of SO_2, NO_x and VOC
VOC prevention during transfer of liquids	When transferring liquids to vessels at atmospheric pressure, the vapour phase (often air, but also inerts) in the receiving vessel is often emitted to atmosphere. Such loading operation is recognised as having an impact on the environment due to the presence of VOC. EU Stage 1 Directive 94/63/EC prescribes emission reduction measures and the application of Vapour Recovery Units (VRU) or Vapour Recovery Systems (VRS) to prevent escape of vapours to the atmosphere.
Air Quality Directive (AQD)	The Air Quality Directive gives limit values. PM emissions has been agreed upon by the Council of Ministers in second reading and will be published shortly.

Legislation	Concerning
EC Large Combustion Plant Directive	New units (ie units which came into existence on or after 1 July 1987) with individual furnaces greater than 50MWth or multiple heaters where aggregate thermal input is greater than 50MW, come within the scope of the EC Large Combustion Plant Directive, and must comply with its requirements. However the Directive does not cover direct refinery processes, e.g. FCCU regenerators, coking processes or SRUS, nor gas turbines. The Directive requires Member States to introduce programmes for a successive reduction of sulphur dioxide and oxides of nitrogen emissions from large combustion plants operating, or licensed, before 1 July 1987.

Table 10.2: Main legislation affecting emissions to air

Table 10.3 lists, by compound, legislation affecting emissions to air

Compound		Legislation
Carbon dioxide	International	Post-Kyoto Protocol UN/Greenhouse gas convention
	EC Directives	93/76/EEC 93/389/EEC
Particulate	International	EU/UN-ECE
	EC Directives	Large Combustion Plant Directive (LCPD), Integrated Pollution Prevention Control Directive(IPPC) Air Quality Directives (AQFD)
	Other:	UN-WHO USAEPA
Sulphur oxides	International	EU/UN-ECE, Acidification Strategy
	EC Directives	Large Combustion Plant Directive (LCPD), Sulphur in Liquid Fuels Directive(SLFD) Integrated Pollution Prevention and Control Directive (IPPC).
	Air Quality Directives	Sulphur protocol (incl. Bunkers) Air Quality Framework Directive (AQFD) National Ceilings Directives
	Other	UN-ECE/- World Health Organisation (WHO) USAEPA/ 1990 Clean Air Act
Nitrogen oxides	International	EU/UN-ECE Acidification Strategy
	EC Directives	LCPD IPPC Air Quality Directives: AQFD N-protocol (93/361/EEC) National Ceilings Directives
	Other	UN-ECE/-WHO USAEPA/ 1990 Clean Air Act
Volatile organic compounds	International	EU/UN-ECE UN-ECE/VOC Protocol Stage I (Marine VR), Stage II MARPOL Convention Annex VI IMO-MARPOL 73/78
	EC Directives	Air Quality Directives AQFD 94/63/EC National Ceiling Directives Ozone Strategy
	Other:	UN-WHO USAEPA/1990 Clean Air Act Draft EC-Long range transboundary air pollution

Compound		Legislation
Carbon monoxide	International	UN/Greenhouse gas convention
	EC directives	IPPC
	Other	UN-WHO
Methane	International	Post-Kyoto Protocol UN/Greenhouse gas convention
	EC directive	(93/389/EEC)
Halon and CFC	International	UN Montreal Protocol (94/84/EC)
Nickel	International	UN-ECE protocols on Heavy Metal
	EC directives	Air Quality Directives, AQFD IPPC
Benzene	EC directives	Air Quality Directives AQFD IPPC
PAH	EC directives	Air Quality Directives AQFD IPPC
	Others	UN-ECE POP protocol

Table 10.3: Air pollutants affected by main legislation

Legislation affecting emissions to water

There is an OSPARCOM Decision (89/5) which sets an oil limit for refinery discharges.

Legislation affecting other issues

Environmental Impact Assessment (EIA)
An important tool for proactive Environmental Management as imposed by international authorities (in Europe per EC directive) is the Environmental Impact Assessment. Prior to each investment project the expected emissions, waste water and waste and the necessary abatement measures will be defined and the effects and impacts of the projected activities on the environment will be assessed and reported. An approved EIA report is a prescribed input for the permitting procedure for new installations.

External safety
On the basis of the post-Seveso guideline of the EU (82/501) refineries are nowadays obliged to prepare an external safety report. The Seveso-1 guideline was implemented in 1999, and involves further requirements on safety reporting. It applies to the refinery as a whole.

Some EU and international emission limit values

Compound	
SO_2	The EC directive on large combustion plants regulating the sulphur content in liquid fuels sets an overall limit of 1700 mg/Nm^3 (bubble) for existing plants in the refinery. For new refinery plants the directive on the reduction of emissions from large combustion plants limits the SO_2 emission to 1000 mg/Nm^3 flue gas. Moreover, the proposed revision of this directive includes a proposal to lower the SO_2 emission limit for new refinery installations to 450 mg/Nm^3.
Particulates	The EC directive for large combustion plants applies a limit to total emissions of particulate matter (PM) of 50 mg/Nm^3.

10.1.2 EU+ national legislation and emission limit values

The remaining tables in this section give a brief summary of the environmental legislation and/or emission limit values affecting refineries in some of the EU+ countries.

Austria

Medium	Legislation	Scope
Air	Feuerungsanlagenverordnung (BGBl. II 1997/331)	Ordinance for Firing Installations
	Luftreinhaltegesetz für Kesselanlage (LRG-K, BGBl. 1988/380 i.d.F. BGBl. I 1998/158)	Clean Air Act for Steam Boilers
	Luftreinhalteverordnung für Kesselanlagen (LRV-K, BGBl. 1989/19 i.d.F. BGBl. II 1997/324)	(Clean Air Ordinance for Steam Boilers)
Water	"Allgemeine Abwasseremissionsverordnung" (BGBl. 1996/186)	The discharge of waste water in running water or the public sewerage system in Austria is regulated by this ordinance
	Other ordinances based on the Austrian "Wasserrechtsgesetz" i.d.F. BGBl. I 155/1999 (water right act). Special ordinance of interest for oil refineries is Verordnung über die Begrenzung von Abwasseremissionen aus der Erdölverarbeitung BGBl. II 1997/344 (Ordinance for the limitation of waste water emissions from oil refining)	Other special ordinances for different industrial sectors.
Waste	The principles of waste management in Austria are regulated by the "waste management act" (BGBl. 325/1990 i.d.F. I 151/1998).	

Table 10.4: Summary of environmental legislation in Austria

Medium	Pollutant	Emission Limit Values	Units	Comments
Soil	Sludge	-		Limit according to regulation for landfilling
	Waste	-		Limit according to regulation for landfilling
Water (Ordinance regarding refining of crude oil)	Water	0.6	m^3/t	m^3/t crude oil throughput
	pH	6.5 - 8.5		
	Temperature	30 °C		
	Dissolved solids	-		
	Suspended solids	30	mg/l	
	COD	75	mg/l	
	BOD	20	mg/l	
	TOC	5	mg/l	
	H_2S	0.5	mg/l	as Sulphur
	NH_4+	5	mg/l	as Nitrogen
	Oil	2.0/3.0	mg/l	2.0 after biological treatment from 2005, today 10 mg/l
	Phenol	0.2	mg/l	
	Metals	0.5/3.0/0.5/0.5/0.02/1.0	mg/l	for Pb/Fe/Cu/Ni/Hg/V respectively
	SO_3	2.0	mg/l	
	Surfactants	2.0	mg/l	
	Toxicity	bacteria: 8 Gl fish: 2 Gf		
	Other	0.1/40/2.0/0.1/0.5	mg/l	for CN/total N/P/AOX/BTXE
Air	as regulated for the refinery in Schwechat		all values in mg/Nm^3	
	H_2S	10		for Claus-unit
	NH_3	10		for SNCR and SCR
	CO	100 fuel gas 175 liquid refinery fuels 2000 FCC		at 3 % 0_2, dry
	CO_2	-		

Medium	Pollutant	Emission Limit Values	Units	Comments
Air	SO_2	1700 FCC 800 Power station II, naphtha HDS, vacumm distillate HDS, SRU, VDU [4)] 200 Power station I		< 50/50 - 300/>300 MW at 3 % O_2 dry, [1) 2)]
	VOC	-		
	NO_x	200-300 fuel gas 100-150 power station I, 900 power station II (firing heavy residues) 300 FCCU regenerator		for the respective heat input and fuel at 3 % O_2 dry [1) 3)]
	Particles	50/35 10 gaseous fuels 50 FCCU 110 power station II (firing heavy residues)		for existing/new plants at >5 MW for heavy fuel oil
	Heavy metals	Ni: 1 Pt: 5 V: 5		for FCCU

Table notes:
1. for existing plants
2. 800 mg/Nm³ for refinery power plants
3. 900 mg/Nm³ for refinery power plants
4. 700 mg/Nm³ for 1 new boiler within power plant (recently installed)

Table 10.5: Emission limit values applied to Austrian refineries

Belgium

Air (Vlarem), water and ground water (Vlarem), waste and soil (Vlarem, Vlarebo and Vlaria) and noise (Vlarem).

Medium	Pollutant	Emission limit values[4]	Units	Comments
Soil		Measures against soil pollution related to e.g. the use and storage of chemicals, including construction conditions		not specific for refineries
		Periodic soil pollution test		Refineries are on the list of activities that entail risks for soil pollution
Noise		Immission levels are compared to quality objectives (e.g. industry fields 55 dB(A))		not specific for refineries
Waste		appropriate disposal and processing		not specific for refineries
		annual reporting to Waste Agency		list of 30 specific waste streams of refineries, annual reporting to Waste Agency
Water[3]	water	0.5	m³/t	m³/t crude oil throughput for simple refineries[1]
		0.6 – 1.2	m³/t	m³/t crude oil throughput for complex refineries[2,] (0.1 m³/t crude oil per addional treatment to a maximum of 0.7 m³)
	pH	6.5 –9.0	Sörensen	6.0 - 9.5 if discharged in sewer
	Temperature	30	°C	45 °C if discharged in sewer
	Dissolved solids	60	mg/l	1000 mg/l if discharged in sewer
	Sediment	0.5	ml/l	
	Hydrocarbons	20	mg/l	CCl_4-extractable, if discharged in sewer 500 mg/l (petroleum ether extractable)

Medium	Pollutant	Emission limit values	Units	Comments
Water	Detergent	3	mg/l	
	Oil and fat layers	not visible		
	BOD	35	mg/l	no limits if discharged in sewer
	Cr VI	0.05	mg Cr/l	
	COD	200	mg/l	250 for complex refineries[2]
	Phenol	0.5	mg/l	1 for complex refineries[2]
	Nitrogen	10	mg N/l	Kjeldahl, 30 mg N/l for complex refineries[2], no limits if discharged in sewer
	Sulphide	1	mg S/l	
	Total organic carbon	200	mg C/l	250 mg C/l for complex refineries[2], no limits if discharged in sewer
	Cr	0.5	mg Cr/l	
	P	2	mg P/l	
	Pb	0.05	mg Pb/l	
Air (ELV at 3% O_2)	SO_2	1300	mg/Nm³	bubble emissions for total of fuel and process emissions, including emissions from cogeneration plants; *ELV and scope currently under revision*
		1700	mg/Nm³	new large combustion installations, fuel oil, 50 to 300 MWth
		1700 to 400	mg/Nm³	new large combustion installations, fuel oil, 300 to 500 MWth
		400	mg/Nm³	new large combustion installations, fuel oil, >= 500 MWth
		35	mg/Nm³	new large combustion installations, fuel gas
	NO_x	450	mg/Nm³	bubble emissions for total of fuel and process emissions, including emissions from cogeneration plants; *ELV and scope currently under revision*
		450	mg/Nm³	new large combustion installations, fuel oil
		350	mg/Nm³	new large combustion installations, fuel gas
	dust	150	mg/Nm³	bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants
		50	mg/Nm³	new large combustion installations, fuel oil
		5	mg/Nm³	new large combustion installations, fuel gas
		50	mg/Nm³	fluid bed catalytic cracking regeneration (before 01/01/2005: 300 mg/Nm³)
	CO	150	mg/Nm³	bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants
	Ni	2	mg/Nm³	bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants

Medium	Pollutant	Emission limit values	Units	Comments
Air	V	7	mg/Nm³	bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants
	H_2S	10	mg/Nm³	
	Dioxins	0.5	ng TEQ/Nm³	new refineries, 0.1 ng TEQ/Nm³ emission objective
		2.5	ng TEQ/Nm³	existing refineries, 0.4 ng TEQ/Nm³ emission objective
	C	1 % of waste gas		flare efficiency of waste gases released at start-up and shutdown of installations

Table notes:
1. Following activities: storage, mixing, atmospheric distillation, vacuumdistillation, desalting, catalytic desulfurizing, reforming and/or sulphuric acid production
2. When one or more of the following activities takes place: catalytic cracking, hydrocracking, visbreaking, hydrogen production, gofining, coking, alkylation, sweetening, bitumen and asphalt production, acid treatment, naphtenic acid production, base oil quality improvement, production of methyltertiary butylether and other petrochemical processes, production of basic lubricating oils, isomerisation, polymerisation, production of solvents and/or mixing of oils, fats and additives
3. Limit values for water are sectoral discharge limits. In permits lower levels may be imposed e.g. as a result of local surface water quality objectives, for components for which there are no sectoral discharge limits often- as a rule of thumb - 10 times the surface water quality objectives are taken as limit values.
4. Belgium refineries are all located in the Flanders Region, Flemish Vlarem II regulation

Table 10.6: Summary of emission limit values in Belgium applied to refineries
Source: [268, TWG, 2001]

Denmark

Denmark has set SO_2 emission limit values of 1000 mg/Nm^3 for residual product fuels, with a maximum of 1 % S in the fuel oil. SO_2 limits for gaseous and LPG fuels have been set at much lower levels (35 mg/Nm^3 to 5 mg/Nm^3). NO_x levels have been set at 225 mg/Nm^3 for both liquid and gaseous fuels.

Finland

Media	Regulation	Pollutant	Scope	Limit value	Unit
Air:	VNp 889/1987	S-emissions	Refineries <3*10 ^{6} t crude/a	12	% of S-content in feed stock
			Refineries >3*10 ^{6} t crude/a	8	% of S-content in feed stock
	VNp 527/1991	NO_X	Nat. gas fired boiler P>50 MW	50	mg NO_2/MJ
			Nat. gas fired gas turbine P>50 MW	60	mg NO2/MJ
			Oil fired boiler 50<P<150 MW	120	mg NO2/MJ
			Oil fired boiler 150<P<300 MW	80	mg NO2/MJ
			Oil fired boiler P>300 MW	50	mg NO2/MJ
			Oil fired gas turbine 50<P<300 MW	150	mg NO2/MJ
			Oil fired gas turbine P>300 MW	60	mg NO2/MJ
	VNp 453/1992	S-content	Heavy fuel oil for boilers without S-remov.	1	%
	VNp 368/1994	Particles	Boilers P>300 MW	30	mg/m^3
			Boilers 50<P<300 MW	50	mg/m^3
			Boilers for gaseous fuel	5	mg/m^3
	VNp 468/1996	VOC	Petrol storages	0.01	% of throughput
	VNp 142/1997	S-content	Diesel fuel for domestic use	0.05	%
			Light fuel oil for domestic use	0.2	%
	VNp 101/1997	Cd	Burning of waste oil	0.2	mg/m^3
		Ni		1	mg/m^3
		Cr+Cu+V+Pb		5	mg/m^3
		HCl		100	mg/m^3
		HF		5	mg/m^3
		SO_2		1700	mg/m^3
		Particles		100	mg/m^3
	VNp 842/1997	CO	Burning of hazardous wastes	50	mg/m^3
		Particles		10	mg/m^3
		Org. subst.		10	mg/m^3
		HCl		10	mg/m^3
		HF		1	mg/m^3
		SO_2		50	mg/m^3

Table 10.7: Summary of environmental legislation and emission limit values in Finland applied to refineries
Note: VNp = Decision of Council of State

France

Air
The maximum allowable SO_2 refinery emission concentration (as bubble) permitted since 2000 is 1700 mg/Nm^3.

Water emissions.
According to the different refinery categories, the mass flow limits per tonne of product processed (crude, residues, etc…) are the following:

Type of refinery **Mass flow limit (monthly average)**	1	2	3
Water flow (in m^3/t)	0.25	0.65	1
Total suspended solids (in g/t)	6	15	25
COD (in g/t)	25	65	100
BOD_5 (in g/t)	6	15	25
Total nitrogen (in g/t)	5	12.5	20
Hydrocarbons (in g/t)	1.2	3	4
Phenols (in g/t)	0.06	0.15	0.25

Type of refinery **Mass flow limit (yearly average)**	(1)	(2)	(3)
Water flow (in m^3/t)	0.2	0.5	0.8
Total suspended solid (in g/t)	5	12.5	20
COD (in g/t)	20	50	80
BOD_5 (in g/t)	5	12.5	20
Total Nitrogen (in g/t)	4	10	16
Hydrocarbons (in g/t)	1	2.5	3
Phenols (in g/t)	0.05	0.125	0.2
Notes to the table: These emission limits will apply within 3 years after 2 February 1998. The water flow is calculated for process water and purging water of the closed loop cooling system. (1) : refinery with distillations, catalytic reforming and hydro-treatments (2) : (1) + catalytic cracking and/or thermal cracking and/or hydro-cracking (3) : (1) or (2) + steam cracking and/or lubes			

Table 10.8: Emission limit values applies to French refineries

French regulatory framework on on noise.
French approach: ordinance of the 23rd January 1997
Field: new or modified plants after 01/07/1997

Level of noise not to be exceeded at the limit of the plant
- during the day 70 dBA
- during the night 60 dBA

Consider the additional noise in regulated areas:

Level of noise in the regulated areas included the noise generated by the plant	**Additional noise limit**	
	Between 7 h and 22 h except Sundays and days of	Between 22 h and 7 h, Sundays and days of
From 35 dBA to 45 dBA	6 dBA	4 dBA
Greater than 45 dBA	5 dBA	3 dBA

Distance of 200 m from the plant limit where it cannot be applicable.
Monitoring method: AFNOR NF S 31010
- . bullet 6 expertise method
- . bullet 5 control method which need a difference greater than 2 dBA with the reference value to validate the difference.

Former ordinance of the 20 August 1985
Limit concerning additional noise 3 dBA (refineries 5 dBA)

Formula for the noise level requirement at the plant limit: 45dBA + ct (takes into account the different periods of the day) + cz (take into account the type of area)

Different periods of the day (ct):
- day: (+ 0dBA): 7 – 22 h,
- intermediate period: 6-7 h and 20-22 h (- 5 dBA),
- night: 22 – 6 h (- 10 dBA)

cz from 0 to + 25 dBA according to the type of area.
Other specific cases linked to impulsive and pure noises

Germany

Important regulations relevant for industrial installations in Germany are laid down in the Federal Immission Control Act [Bundes-Immissionsschutzgesetz - BImSchG], the Federal Water Act [Wasserhaushaltsgesetz - WHG] and the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG]. Germany uses a segregated media permitting system for different environmental media, but the final decision on an application is reached by the assessment of environmental impacts on all media by the local authorities. Also noise requirements are considered in the licensing procedure, whereby Germany aims at favouring pollution prevention. The "precautionary principle" has a legal status which permits the settings of standards. Legal standards are not subject to any negotiation in the licensing process in Germany. The cited regulations are currently amended according to the IPPC Directive.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may implement the administrative procedure differently. For new plants, that are regarded as relevant with respect to emissions and releases into the environment, also an environmental impact assessment is required during the licensing procedure (cf. Gesetz über die Umweltverträglichkeitsprüfung [UVPG]).

Table 10.9 gives an overview of the current German legal basis and regulations for environmental protection in German industry alongside the process chain. In the following, the most important acts and regulations are presented.

Area	Legal basis	Regulations and ordinances
Transport	Verkehrsrecht	- Gefahrgutverordnung Straße - Gefahrgutverordnung Schiene - Gefahrgutverordnung Binnenschifffahrt
Health and safety at work	Chemikaliengesetz (ChemG)	- Chemikalienverbotsordnung - Gefahrstoffverordnung
	Gewerbeordnung	- TA Lärm - Arbeitsstättenverordung und -richtlinien
Emissions into air	Bundes-Immissionsschutzgesetz (BImSchG)	- Bundes-Immissionsschutzverordnungen - Bundes-Immissionsschutzverwaltungsvorschriften - TA Luft - TA Lärm
Emissions into water	Wasserhaushaltsgesetz (WHG) Abwasserabgabengesetz (AbwAG)	- Abwasserverordnung (AbwV) - Abwassergesetze der Länder or Indirekteinleiterverordnungen - Anlagenverordnungen der Länder - Katalog wassergefährdender Stoffe - Klärschlammverordnung
WasteTreatment	Abfallgesetz (AbfG)	- Abfall- und Reststoffüberwachungsverordnung - Abfallbestimmungsverordnung - Reststoffbestimmungsverordnung - TA Abfall - TA Siedlungsabfall
	Kreislaufwirtschafts- und Abfallgesetz (KrW.-/AbfG)	

Table 10.9 Legal basis and regulations alongside the process chain

German regulations concerning the air quality

The basic law for air pollution control is the Federal Immission Control Act [Bundes-Immissionsschutzgesetz BImSchG]. The BImSchG is specified by ordinances and the Technical Instructions on Air Quality [TA Luft]. The Federal Immission Control Act and the Technical Instructions on Air Quality are currently being amended according to the IPPC Directive.

Technical Instructions on Air Quality Control (TA Luft):

The Technical Instructions on Air Quality Control (TA Luft) have been set up as general administrative regulations in connection with the § 48 BImSchG. The TA Luft further specifies the requirements to be met by installations subject to licensing. Therefore, it prescribes limit values for virtually all air pollutants as well as structural and operational requirements designed to limit fugitive emissions. For the new federal states, the requirements had to be met before 1996, and in special cases by 1999. Table 10.10 shows the limits for main emission control requirements or, if specific regulations for the mineral oil refineries exist, it gives the corresponding more specific requirements laid down in the TA Luft, which are aimed at the avoidance and minimisation of air pollution.

The emitted substances are split into 3 classes (vaporous or gaseous inorganic substances: 4 classes), whereby class I substances are the most toxic and Class III or IV are the least harmful. The emission limit values contained in the TA Luft represent the State of the art for technical measures for reducing emissions (last amended in 1986, currently being amended). These quality values were developed referring to scientific findings and research taking into account toxicological, bioaccumulative and epidemiological aspects. The required concentration limits are given in mass of emitted substances related to the volume of emitted gas under standard conditions (0°C, 1013 mbar) after subtraction of the water vapour content.

Emitted substance (TA Luft section)	Class	Substances		Mass flow threshold [g/h]	Concentration limit [mg/m³]
Total dust	-			< 500	150
				> 500	50
Inorganic dust	I	(e.g. Hg, Tl)	sum of substances	1	0.2
particles	II	(e.g. As, Co, Ni, Te, Se)	- " -	5	1
(3.1.4)	III	(e.g. Sb, Pb, Cr, F, Cu, Mn, Pt, Pd, Rn, V, Sn, substances which are strongly suspected to cause cancer)	- " -	25	5
	I+II		- " -		1
	I+III, II+III		- " -		5
Vaporous or	I	(e.g. AsH_3)	per substances	> 10	1
gaseous inorganic	II	(e.g. HF, Cl_2, H_2S)	- " -	> 50	5
substances	III	(e.g. Cl-compounds as HCl)	- " -	> 300	30
(3.1.6)	IV	(e.g. $SO_2 + SO_3$ as SO_2, $NO + NO_2$ as NO_2)	- " -	> 5.000	500 FCC: 700 (NO_2) FCC: 1700 (SO_2)
Organic substances	I	(e.g. Chlormethane)	Classification	> 100	20
(3.1.7)	II	(e.g. Chlorbenzene)	according to	> 2.000	100
	III	(e.g. Alkylalcohols)	Annex E of TA Luft	> 3.000	150
Carcinogens	I	(e.g. Cd[1)], As[1)], asbestos, benzo(a)pyren)		≥ 0.5	0.1
(2.3)		- sum of substances -			
	II	(e.g. Ni, chromium VI) - " -		≥ 5	1
	III	(e.g. Acrylonitrite, benzene)	- " -	≥ 25	5

[1)] Based on the decision adopted by the Conference of the Federal Government/Federal States Ministers for the Environment on 21/22 November 1991, an emission limit of 0.1 mg/m³ has been stipulated for Cd and its compounds, given as Cd, as well as for As and its compounds, given as As.

Table 10.10 Emission control requirements laid down in the TA Luft (1986)

If inorganic dust particles of several classes are present, the mass concentration in the emitted gas should not exceed a total of 1 mg/m^3 for coinciding class I and II substances as well as a total of 5 mg/m^3 for coinciding class I and III or class II and III substances.

If organic substances in several classes are present, the mass concentration in the emitted gas should not exceed a total of 0.15 g/m^3 with a total mass flow of 3 kg/h or more.

In case of high emission mass flows, emissions have to be monitored continuously.

No daily mean value of the respective emitted substances should exceed the required emission limits, 97 % of all half-hourly means should not exceed six fifths of the required emission limits, and all half-hourly means should not exceed the required emission limits by more than twice.

Because state of the art technology significantly proceeded since 1986, the local authorities in some cases demand stricter emission limit values than laid down in the TA Luft.

Technical Instruction on Noise Abatement:
The Technical Instruction on Noise Abatement [TA Lärm] sets the limits for noise emissions from the operation of a facility permitted in various areas. Permission for the construction, operation or altering of a facility is granted only if the emission limits allowed for a specific area are not exceeded and if state-of-the-art noise protection measures are employed.

German regulations concerning the water quality
The legal framework for water management is the Federal Water Act [Wasserhaushaltsgesetz - WHG]. The WHG applies to waste water generated by various industrial processes. The use of surface, coastal, and ground waters requires the approval of the competent authority. Discharges into water are regulated in the Waste Water Ordinance including its Annexes [Abwasserverordnung, AbwV] which is based on art. 7(a) of the Federal Water Act. Here, minimum requirements concerning waste water treatment, requirements concerning techniques of analysis and monitoring as well as limits for the content of specific substances are laid down for different industrial sectors.

Issued by the Federal Government in consent with the Federal States (Länder), these minimum requirements are binding for the authorities responsible for licensing and governmental control of the discharges. Depending on the local conditions, even more stringent requirements can be established. The minimum requirements are based on the 'emission principle' and the precautionary principle, i.e. application of stringent, technically derived emission standards irrespective of the loading reserves of the receiving water bodies resources or the potential effects of the various substances discharged. Additionally, the Federal Ministry of Environment publishes explanations and comments on the Waste Water Ordinance. Refining of petroleum is dealt with in Annex 45 of this regulation. Table 10.11 gives the main restrictions established in Annex 45 of the AbwV.

Parameter	Limit value*) [mg/l]
Phenol index after distillation and dye extraction	0.15**)
Total hydrocarbons	2
Total phosphorus	1.5
Cyanide, easily released	0.1**)
Sulphide sulphur and mercaptan sulphur	0.6**)
AOX	0.1**)
5-day biochemical oxygen demand	25
COD	80
Total nitrogen as the sum of ammonia, nitrite and nitrate nitrogen	40
*)Qualified random sample or 2 hours composite sample **) Requirements apply to the waste water prior to blending with other waste water Source: AbwV, Annex 45 „Petroleum Refining“	

Table 10.11 Limit values for discharges into water for petroleum refining plants

The required loads shall be production-specific loads in relation to the production capacity on which the water discharge licence is based. This should be determined by a qualified random sample or a 2 hour composite sample.

A qualified random sample should refer to a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, which are then blended. A composite sample should refer to a sample which is taken continuously over a given period, or a sample consisting of several samples taken either continuously or continuously over a given period and then blended. A random sample should refer to a single sample taken from a waste water flow.

Waste water from cooling systems for the indirect cooling of industrial processes is excluded from this regulation. Indirect cooling water is subject to the provisions laid down in Annex 31, AbwV. Table 10.12 gives the relevant requirements for discharges from cooling circuits in Annex 31. If the stated values are not reached, approval for the discharge of waste water will be denied.

Parameter	Minimum Requirements*)
COD	40 mg/l
Phosphor compounds, given as P	3 mg/l
Zinc	4 mg/l
AOX	0.15 mg/l
Available residual chlorine	0.3 mg/l
Chromium compounds	must not be contained
Mercury compounds	must not be contained
Nitrite	must not be contained
Metal organic Compounds (Metal-Carbon-Compound)	must not be contained
*)Qualified random sample or 2 hours composite sample Source: Annex 31, Abwasserverordnung	

Table 10.12: Requirements for discharges from cooling circuits of industrial processes

The WHG is complemented by the waste water charges act [Abwasserabgabengesetz - AbwAG]. The charges are related to the mass and possible hazard of the discharged waste water according to Table 10.13. For the discharge of sewage, that exceeds the mentioned threshold values for concentrations or annual loads, the discharging party has to pay a fee related to the given units of measurement.

Hazardous Substances	**Units of measurement (relating to a unit of hazard)**	**Threshold values**	
		Concentrations	**Annual freights**
Chemical oxygen demand (given as COD)	50 kg Oxygen	20 mg/l	250 kg
Phosphor	3 kg	0.1 mg/l	15 kg
Nitrogen	25 kg	5 mg/l	125 kg
Organic Halogen compounds as AOX	2 kg Halogen, calculated as Cl	100 µg/l	10 kg
Mercury & compounds.	20 g	1 µg/l	0.1 kg
Cadmium & compounds	100 g	5 µg/l	0.5 kg
Chromium & compounds	500 g	50 µg/l	2.5 kg
Nickel & compounds	500 g	50 µg/l	2.5 kg
Lead & compounds	500 g	50 µg/l	2.5 kg
Copper & compounds	1000 g	100 µg/l	5 kg
Fish toxicity	3,000 m^3 discharges divided by T_F	T_F =2 (dilution factor for non-lethal quantity for fish from the discharge)	
Source: Abwasserabgabengesetz			

Table 10.13: Thresholds according to the water charges act

German regulations concerning the waste management and disposal of hazardous materials

Regulations concerning the waste management and disposal of hazardous materials are laid down in the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG] and the Federal Immission Control Act [BImSchG]. According to the BImSchG, an operator of a waste generating installation which is subject to licensing, is obliged to avoid waste production or to make sure that the waste is environmentally soundly recovered. If that is technically or economically not reasonable, the waste has to be disposed of without any harmful effects. The federal States' working group on immission control (Länderausschuss für Immissionsschutz, LAI) has published examplary administrative regulations for particular industrial sectors containing measures for avoidance and recovery of wastes which are considered as technically and economically reasonable.

The KrW/AbfG states that installations generating more than 2 tonnes of hazardous waste or more than 2000 tonnes of non-hazardous waste (per waste key), must produce a waste management concept and yearly waste balances.

References to the German Legislation

- Abwasserabgabengesetz -AbwAG: Gesetz über Abgaben für das Einleiten von Abwasser in Gewässer, 3.11.1994
- Abwasserverordnung - AbwV: Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer und zur Anpassung der Anlage des Abwasserabgabengesetzes, 09.02.1999; last review 20.02.2001
- Bundes-Immissionsschutzgesetz (BImSchG): Gesetz zum Schutz vor schädlichen Umwelteinwirkungen durch Luftverunreinigungen, Geräusche, Erschütterungen und ähnliche Vorgänge, 14.05.1990, last amendment 19.07.1995

- Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG: Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der umweltverträglichen Beseitigung von Abfällen, 27.09.1994
- TA Luft: 1. Allgemeine Verwaltungsvorschrift zum Bundesimmissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft - TA Luft), 27.2.1986
- TA Lärm: 6. Allgemeine Verwaltungsvorschrift zum Bundesimmissionsschutzgesetz (Technische Anleitung zum Schutz gegen Lärm - TA Lärm), 26.08.1998
- UVPG : Gesetz über die Umweltverträglichkeitsprüfung - UVPG, 12.2.1990, last amendment 23.11.1994
- Wasserhaushaltsgesetz - WHG: Gesetz zur Ordnung des Wasserhaushalts - WHG, 12.11.1996

Ireland

Substance	Concentration (mg/m^3)	
	Petroleum Refining	**Gas Refining**
Hydrogen sulphide	5	5
Hydrogen fluoride	5	-
Particulates - Processing - Materials Handling	 100 50	-
VOCs (as Total Carbon) (excluding particulates)	Control by Load Minimisation	Control by Load Minimisation
NO_x	Control by Load Minimisation	350
SO_2 - Liquid refinery fuel - Vaporised LPG - Other gaseous fuel	 Control by Load Minimisation	 1700 5 35
NOTE 1: Achievement of ELV concentrations by the introduction of dilution air is not permitted. Notes to table: 1. The toxicity of the effluent shall be determined on an appropriate aquatic species. The number of Toxicity Units (TU) = 100/96 hr LC50 in % v/v so that higher TU values reflect greater levels of toxicity. For each TU at least 20 dilutions of the effluent volume must be available in the receiving system. 2. No substance shall be discharged in a manner which, or at a concentration which, following initial dilution causes tainting of fish or shellfish, interferes with normal patterns of fish migration or which accumulates in sediments or biological issues to the detriment of fish, wildlife or their predators. 3. Consent conditions for these parameters for discharge to municipal treatment plants can be established with the Licensing Authority, and different values may apply.		

Table 10.14: Emission limit values for air emissions applied in Ireland

Constituent group or parameter	Limit value
pH	6 - 9
Suspended Solids (mg/l)	30
COD (mg/l)	100
Number of Toxicity Units	5
EC List 1	As per 76/464/EC and amendments
Fish Tainting	No Tainting
BOD (mg/l)	20
Total Nitrogen (mg/l as N)*	10
Total Phosphorus (mg/l as P)**	3
Hydrocarbons	5
Notes to the table: These values apply prior to any dilution with e.g. uncontaminated stormwaters or cooling waters. Where appropriate, saline waters to be discharged to sea/lower estuary in compliance with the above standards. * All values refer to daily averages, except where otherwise stated to the contrary, and except for pH which refers to continuous values. ** Applicable to waters subject to eutrophication. One or both parameters may be limiting, depending on the receiving system.	

Table 10.15: Emission limit values for discharges to water applied in Ireland

Italy

The maximum allowable SO_2 refinery emission concentration (as bubble) permitted in 2000 will be 1700 mg/Nm^3.

Norway

Emission standards are not generally applied in Norway. The emission limits for the refineries are set according to each case. Norway has introduced a special tax duty to minimise emissions of CO_2 and SO_2. Heavy fuel oil with more than 1.0 % sulphur is prohibited in the twelve southern and southwestern counties of Norway. In the northern parts of Norway heavy fuel oil is allowed with a maximum 2.5 % sulphur. But due to high sulphur taxes, heavy fuel oil with up to 2.5 % sulphur content is more expensive than the 1.0 % oil, and is therefore hardly used. Noise is regulated to a limit of 45 dB(A).

Media	Pollutant	Emission Limit Values	Units	Comments
SOIL	Sludge	-		Limit according to regulation for landfilling, hazardous waste and groundwater
	Waste	-		Limit according to regulation for landfilling, hazardous waste and groundwater
WATER	pH	6-9		
	H_2S	0.5 - 1	mg/l	
	Oil	5	mg/l	
	Phenol	1	mg/l	
	NH_4+	10 - 15	mg/l	
	CN (total)	1	mg/l	
	Suspended solids	-	tonnes/year	[1] Not regulated but reported in the annual report
	COD [1]	-	tonnes/year	[1]
	TOC [1]	-	tonnes/year	[1]
	Metals [1]	-	kg/day	[1]
	P (total) [1]	-	tonnes/year	[1]
AIR	H_2S	15	mg/l	
	CO_2	-	tonnes/year	[1] Not regulated but reported in the annual report
	SO_2	650 – 1350	kg/h	
	SO_2	1000 – 2000	tonnes/year	
	NO_x	2150	tonnes/year	
	CN (total) (cracker)	5	mg/Nm^3	
	Particles (cracker)	50	mg/Nm^3	
	Particles (cracker)	25	kg/h	
	Particles (calciner unit)	30	mg/Nm^3	
	N_2O [1]	-	tonnes/year	[1]
	NMVOC [1]	-	tonnes/year	[1]
	Methane [1]	-	tonnes/year	[1]

The permit values vary from refinery to refinery due to design, age and local factors. The permits are planned to be under revision in 2001 and 2002.

Sweden

Air

The maximum allowable SO_2 refinery emission concentrations (as bubble) permitted in 2000 will be 800 mg/Nm^3. Use of high sulphur fuels (>0.5 %) is prohibited throughout the country. Sulphur recovery must be in excess of 99 % including the flaring of residual tail gas. NO_x and particulates must be reduced to the minimum feasible level.

The total permitted release levels for the Scanraff Refinery are 2000 t/yr SO_2 and 1000 t/yr NO_x. The absolute limit of particulates from the FCCU is 75 mg/Nm^3 (the crude capacity of the refinery is 10 Mt/yr))

The Netherlands

A characteristic of the Dutch regulations and permitting is “self-regulation within boundaries”. This characteristic stems from a broad support for achieving consensus, and includes as well the environmental policy, both in the way it was brought into existence and in the way it has been implemented.

Air emissions

Regulation	Affecting
Combustion Plant Emission Limits Decree (BEES)	SO_2, NO_x, particulates
Emission Guidelines for Air (NeR)	Sulphur Recovery Plants
Hydrocarbons 2000 programme (KWS2000)	VOC

The National Environmental Policy Plan (NEPP, 1997) states as a policy objective that by 2010 the refineries will be gas-fired, or that installations that are still oil-fired will be equipped with FGD, SCR and ESP. The KWS2000 measures comprise preventive maintenance and spills and leaks abatement. Furthermore, vapour recovery for inland barge loading operations of gasoline and double mechanical seals on floating roof tanks are specified as well as improved sealings of pumps, compressors, valves and flanges and covering of open basins. Measures for vapour recovery are also applicable for crude loading and unloading.

Table 10.16 summaries the emission limit values applied to different air contaminants.

	Load per year (year when the value is applicable)	Emission limit value or performance (New)	Emission limit value or performance (Existing)
SO_2	53 ktonne 36 ktonne (2000) 18 ktonne (2010)		1500 mg SO_2/Nm^3 1000 mg SO_2/Nm^3 (2000)
Sulphur Recovery Plants		99.8 % recovery	99 %recovery
NO_x(1)	15 ktonne (1997) 12 ktonne (2000) 5 - 7 ktonne (2010)	NG: 80 mg/Nm^3	NG: 150 - 500 mg/Nm^3 LF: 400 - 700 mg/Nm^3
Particulates	5 ktonne (1997) 0.5 - 1 ktonne (2010)	Combustion plants 50 mg/Nm^3	Catcrakers with ESP: 50 mg/Nm^3
VOC	8.8 ktonne in 2000 4.2 ktonne in 2010		
CO_2	11000 ktonne (2)		

NG: Natural Gas
LF: Liquid fuels
(1) Correction factors are used for the determination of the allowed emission level in relation to the quality of the fuel, the extent of air preheat and the prevailing bridge wall temperature.
(2) Emission reduction target for total Dutch economy for year 2010, not specifying individual sectors

Table 10.16: Dutch legislation, regulations and targets

Effluents (emissions to water)

Laws affecting water emissions are: The Surface Water Protection Act (Wvo), Dutch National Environmental Policy Plans (NEPP, NEPP-3), the Third and Fourth Document on Water Management, the Rhine Action Plan/North Sea Action Plan (RAP/NAP) and the ER-heavy metals and blacklist compounds (benzene, toluene, ethylbenzene, xylenes, PAH and heavy metals as Hg and Cd). Limits will be set for other compounds as well, such as nitrogen (total N), phenol, cyanide, sulphides and overall parameters such as COD, BOD and TOC. The PARCOM recommendations ratified by the Netherlands provide guidance with respect to refinery oil discharges:

Permits normally impose the following obligations on refineries:

- cooling waters should be separated from other waters and kept uncontaminated by oil
- storm waters from polluted plant areas should be collected and connected to treatment plants
- waste waters should be subjected to biological or equally effective treatment.

Permit values vary from location to location due to differences in design, age and other local factors. The authority aims at uniformity for future permit revisions. A number of permit parameters and typical compliance values for Dutch refineries are (1997): Oil 140 t/yr, Benzene 9 t/yr, Phenol 5 t/yr and N-total 540 t/yr. The parameters and compliance values refer to typical refinery effluent composition (ranges), having passed primary effluent treatment facilities but prior to secondary and/or tertiary treatments.

Waste
Hazardous waste in refineries mainly involves the management of oily sludges, spent catalysts and spent caustic. For these waste categories increased use is made of third-party waste contractors for off-site recovery or disposal. The Environmental Management Act (Wm) governs legal disposal and two EU-Directives cover the classification, packing and labelling of hazardous substances. As regards the export of hazardous waste a similar procedure exists as laid down in the Basle Convention on the Control of Transboundary Movements of Hazardous Waste and their Disposal.

Soil and groundwater
Contaminated soil and polluted groundwater are relevant environmental issues for refineries. The Dutch Soil Protection Act (Wbb) stipulates no risk to people and the environment, multi-functionality of the soil, the duty of care, prevention of migration of pollutants beyond location boundaries (isolate, manage and control) in case of historical soil pollution. Soil and groundwater cleaning is obligatory if the so-called intervention values, as defined per component and for each soil type, are exceeded and if the extent of the pollution indicates the seriousness of the pollution. The urgency of the clean-up is determined by the migration rate and the risk to the threatened objects in the actual situation. Contaminated soil is an increasing problem for refineries. In all refineries measures have been taken at least to make an inventory of the soil and groundwater pollution and, where needed, measures are taken to prevent migration. In one refinery preventive measures for soil pollution had been included right from the design stage.

Noise
The Netherlands has an integrated policy for noise, and aims for a proper inventory of noise sources and a planned abatement programme. Germany, Switzerland, Austria, France and the Scandinavian countries are developing similar policies on noise.

Nowadays noise level contour values and monitoring obligations are included in permit requirements of the refineries. Typical for industrial noise requirements in urban areas in most countries are maximum allowable limits between 55 and 73 dB(A) during daytime and 45-66 dB(A) during the night.

United Kingdom
The UK does not have standard emission limit values for refineries, but their guidance notes provide expected BAT levels for new plant units. Existing unit operations should meet BATNEEC standarts (Best Available Techniques Not Entailing Excessive Cost).

10.1.3 Non-EU+ legislation and emission limit values

Japan
There are three regulation levels: the State, the Regional Prefecture and the municipality. Japanish refineries are forced to use as liquid fuel an industrial gas oil (so called A-fuel) containing less than 0.1 % S.

State regulations on NO_x are: Refinery furnaces, 100 ppm; boilers, 150 ppm; hydrogen production unit, 150 ppm; and FCC, 250 ppm. Municipality emission limit value for NO_x is 85 Nm^3/h (equal to 1396 t/yr) [248, Ademe, 2001]

USA
Air
The US Environmental Protection Agency has set a limit for particulate matter in the FCC generator exhaust gas of 1.0 kg/1000 kg of coke burnt off in the catalyst regenerator (equates approximately to 75 mg/Nm^3). The coke burn-off rate is determined from the volumetric flow rate of regenerator exhaust gas and the content of CO_2, CO and O_2. The SO_2 emission limit for New Source Performance Standards is 700 mg/Nm^3.

Water
Strict limits apply to toxic and conventional pollutants for waste water, BOD, COD, TOC, ammonia, sulphides and phenolics.

World Bank
The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance; any deviations from these levels must be described in the World Bank Group project documentation. The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable. All the maximum levels should be achieved for at least 95 % of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. [101, World Bank, 1998]

Air Emissions

Parameter	Maximum value (mg/Nm^3)
Particulate matter (PM)	50
Nitrogen oxide (NO_x)* (as NO_2)	460
Sulphur oxide (SO_x) (as SO_2)	150 for sulphur recovery units and 500 for other units
Nickel and vanadium (combined)	2
Hydrogen sulphide	15
* Excluding NO_x emissions from catalytic units.	

Liquid effluents

Parameter	Maximum value milligrams per litre (mg/l)
pH	6 - 9
BOD_5	30
COD	150
Total suspended solids	30
Oil and grease	10
Chromium (hexavalent)	0.1
Chromium (total)	0.5
Lead	0.1
Phenol	0.5
Benzene	0.05
Benzo(a)pyrene	0.05
Sulphide	1
Nitrogen (total) (1)	10
ΔT (ºC)	Less than or equal to 3 (2)

(1) The maximum effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include hydrogenation

(2) The effluent should result in a temperature increase of no more than 3 ºC at the edge of the zone where initial mixing and dilution takes place. Where the zone is not defined, use 100 meters from the point of discharge provided there are no sensitive ecosystems within this range.

Note: Effluent requirements are for direct discharge to surface waters. Discharge to an off-site waste water treatment plant should meet applicable pretreatment requirements.

Solid Wastes and sludges

Wherever possible, generation of sludges should be minimised to 0.3 kg/tonne of crude processed with a maximum of 0.5 kg/tonne of crude processed. Sludges must be treated and stabilised to reduce concentrations of toxics (such as benzene and lead) in leachate to acceptable levels (such as levels below 0.05 mg/kg)

Ambient Noise

Noise abatement measures should achieve either the following levels or a maximum increase in background levels of 3 dB(A). Measurements are to be taken at noise receptors located outside the project property boundary.

Receptor	Maximum dB(A)
Residential; institutional; educational	L_{dn} 55
Industrial; commercial	L_{eq} (24) 70

The emission requirements given here can be consistently achieved by well designed, well operated and well maintained pollution control systems.

10.2 Annex II. Refinery configurations

Worldwide there are in total approximately 700 refineries. Every year on average between four and six brand-new refineries come on-stream, mainly outside Europe (China, India). On the other hand the origin of some of the oldest refineries still in operation dates back to the end of last century. Many of those refineries have been extended and modernised since. Basically there are about 25 typical refinery processes (excluding treatment) used in the refinery industry. The simplest type, the so-called hydroskimming refinery, comprises a minimum of five processing units. Some large and complex refineries can comprise up to fifteen different processing units or more.

In this section four of the most common refinery schemes or configurations will be discussed in detail. The classification of refineries into these configurations is slightly arbitrary. Other approaches do exist, but the main purpose is to illustrate the great diversity of refinery types in existence.

Configuration	Units included
1	Hydroskimming (Base Scheme) + Isomerisation Unit
2	Base Scheme + High Vacuum Unit + Fluid Cracking Unit + MTBE Unit + Alkylation Unit + Visbreaker
3	Base Scheme + High Vacuum Unit + Hydrocracker Unit + Isomerisation Unit (+ Delayed Coker Unit)
4	Large complex refinery comprising Scheme 2 + Hydrocracker (+ Hydrogen Residue Cracking unit + IGCC + Petrochemical feedstock production + Flexicoker)

The overall block flow diagrams of the above four configurations are shown in Figure 10.1 to Figure 10.4.

The first diagram is the aforementioned ‘Hydroskimming’ refinery including an Isomerisation Unit. Such a refinery merely produces fuels such as gasoline, kerosene (jet fuel), middle distillates (diesel and light heating oil) and fuel oil, in a ratio determined by the crude oil composition. By adding a Vacuum Distillation Unit and conversion units the atmospheric residue from the Crude Distillation Unit can be converted to lower boiling fuels with higher product values. Two schemes will be discussed, to cover the most commonly used conversion processes, i.e. Fluid Catalytic Cracking and Hydrocracking. The Fluid Catcracker (FCC) configuration (no. 2) may include on MTBE unit and an Alkylation unit to increase the production and to improve the quality of the gasoline. A Thermal Cracker or Visbreaker unit is often also included in this scheme to reduce the quantity of the heavy fuel oil. The Hydrocracker configuration (no.3) may include a Delayed Coker unit to reduce heavy fuel production and to maximise light fuels production. The last configuration included in this overview is a large, very complex refinery. Besides a Hydrocracker and an FCC unit, this refinery scheme includes units for the conversion of the vacuum residue, a Residue Hydroconversion unit and an Integrated Gasification Combined Cycle Unit.

The complexity of the above 4 configurations (Simple, Complex catcracking, Complex hydrocracking, and Very Complex) can be quantified and various approaches prevail in the Industry. One approach is to express each processing unit in its so-called “equivalent distillation capacity” (EDC), and calculate the sum of these EDCs as a total refinery EDC (the crude distillation unit has an EDC of 1 by definition). The complexity is than the sum of EDCs.

Another approach is to express the conversion (of residual material into distillates) of each conversion unit into its “catcracking equivalency”, and than to define the refinery complexity as the sum of all the catcracking equivalencies. In comparing refineries, both the configuration (which units are in) and the complexity (what is the capacity of these units) are important to consider.

Energy requirements will generally increase from configuration 1 to 4 and with complexity. Similar generalisations can be made regarding e.g. process water requirements, sulphur production (at same sulphur intake) etc., but qualifications often need to be made. In the schemes that represent the configurations in the following pages, processing units are abbreviated; for more details on these process units, see the Glossary.

10.2.1 Configuration 1: hydroskimming + isomerisation unit

This is the simplest type of refinery, producing fuels by straightforward operations (see Figure 10.1). This type of refinery has a very rigid product distribution pattern; the produced fuels are almost entirely fixed by the type of crude being processed. The production cannot be greatly influenced by changing the operating modes of the various processing units.

Many of the Hydroskimming refineries were built in the fifties and sixties when the demand for all fuels increased significantly, the cost of crude was relatively low and the demand for heavy fuel oil was relatively high. In the seventies and eighties the majority of the Hydroskimming refineries were expanded to include a cracking complex, but quite a lot of Hydroskimming refineries dating from that period are still in operation. In the Crude Oil Distillation Unit the crude oil is fractionated into straight-run naphtha overhead product, kerosene, gas oil side-stream products and atmospheric residue product from the bottom of the column. The straight-run unstabilised naphtha is passed to the Naphtha Hydrotreating Unit to make it suitable for Catalytic Reforming. The hydrotreated naphtha stream is split into a light and a heavy naphtha fraction.

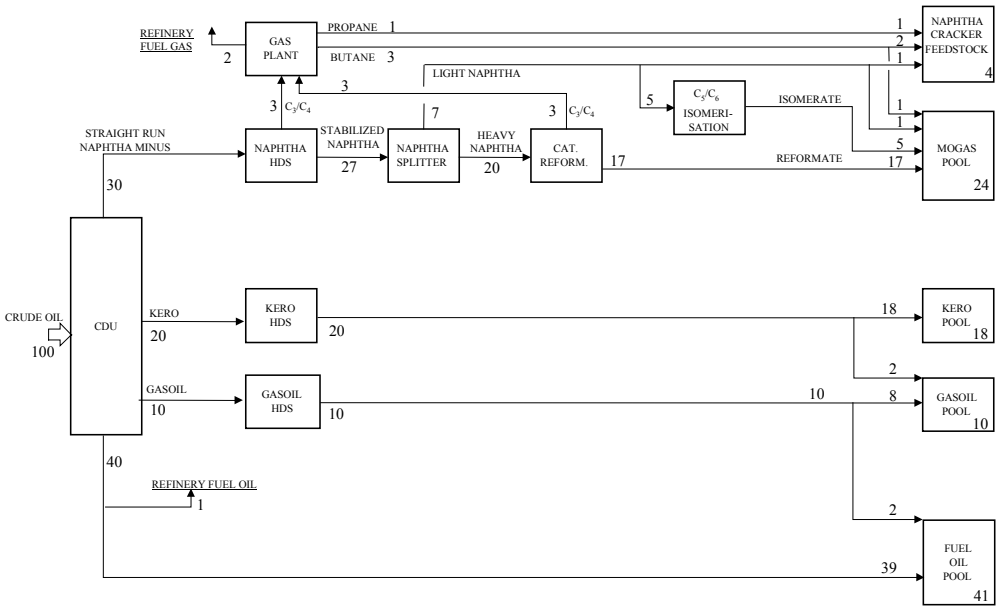


Figure 10.1: Scheme 1: Hydroskimming + isomerisation unit

In the past part of the light naphtha fraction was used as mogas (motor gasoline) blend component, and the balance was sold as feedstock to Naphtha Crackers. More recently, as a result of the lead (TEL) phase-out programme, many Isomerisation Units are included in the Hydroskimming refineries to isomerise the light naphtha stream. The isomerate produced has a roughly 20 - 25 higher octane number than its feed and compensates for the loss of octane resulting from the lead phase-out. This avoids the complete light naphtha stream being sold as low value feedstock to Naphtha Crackers. The heavy naphtha fraction from the Naphtha Hydrotreater is upgraded in the Catalytic Reformer to a high-octane gasoline-blending component. The hydrogen from the Catalytic Reformer is used to desulphurise the gasoil and naphtha. Normally two grades of gasoline are produced in a refinery, regular and premium gasoline. These grades of gasoline are produced by blending different ratios of isomerate,

reformate and butane. Saturated light hydrocarbons from the CDU Naphtha Hydrotreater, Isomerisation Unit and Catalytic Reformer Unit are sent to the Gas Plant. Propane from the Gas Plant is either sold directly as propane product or blended with butane to be sold as LPG. A proportion of the butanes produced in the Gas Plant is used as blend stock for the mogas pool, the remainder of the butanes are either blended with propane to be sold as LPG or directly sold as butane product. The components lighter than propane are sent to the refinery fuel gas system. Straight-run kerosene is often hydrotreated in the Kero Hydrotreating Unit (or kero HDS) and run down as jet fuel. Normally a portion of the hydrotreated kerosene is used as blending component for the automotive diesel oil pool.

Straight-run gas oil is hydrotreated in the Gas Oil Hydrotreating Unit to reduce its sulphur content. Automotive diesel oil is produced by blending desulphurised kerosene with desulphurised gas oil. Heating oil and marine diesel oil (MDO) are produced by blending desulphurised gasoil with straight-run gasoil. Both products have higher maximum allowable sulphur contents than diesel oil. Heavy fuel oil is produced from atmospheric residue with adjustment for viscosity and sulphur content by addition of desulphurised gas oil. In some cases the atmospheric residue is thermally cracked. This is not indicated in the configuration scheme. The sour off-gases from the Naphtha Hydrotreater, the Kerosene and Gas Oil Hydrotreating units (or Gasoil HDS) are treated in the Amine Treating Unit to remove H_2S and other sour components present, prior to being sent to the refinery fuel gas system. The sour LPG stream from the Naphtha Hydrotreater is also treated in the Amine Unit to reduce its sulphur content before combining with the sweet LPG stream from the Catalytic Reformers. Sour waste water from all process units is stripped, prior to utilisation as wash water in the Desalter and final purification in Effluent Water Treating facilities. The sour off-gas from the Sour Water Stripper is combined with the H_2S rich-off gas from the Amine Unit and sent to a Sulphur Recovery Unit (SRU), where the H_2S is converted to elemental sulphur, and a nearly sulphur-free off-gas is vented to the atmosphere.

10.2.2 Configuration 2: catcracker configuration

Scheme 2 is a configuration whereby the Hydroskimming refinery is extended with a High Vacuum Unit (HVU), a Fluid Catalytic Cracking Unit (FCCU) and a Visbreaker Unit (VBU). In this refinery configuration a considerable part of the atmospheric residue is converted into lighter fuel components (see Figure 10.2.). As a result the production of residual fuel oil and/or the export of atmospheric residue is considerably reduced. FCC units are specifically designed to increase the production of gasoline. Depending on the refinery market and strategy, a significant quantity of kerosene can also be produced, when the heavier fraction of the catcracked naphtha is separated and hydrotreated along with the straight-run kerosene product. The overall yield of middle distillates is also increased due to the production of ‘light cycle oil’.

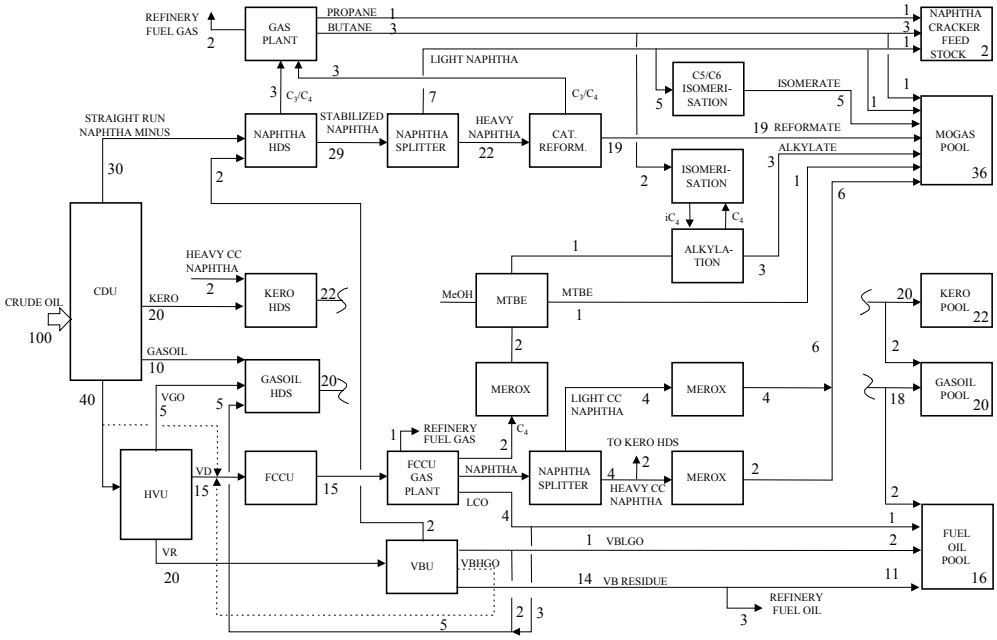


Figure 10.2: Scheme 2: Catcracker configuration

Many Catcracker refineries in Europe include a Visbreaker Unit to reduce the heavy fuel oil production. If no VBU is applied, significant quantities of high value gasoil components will have to be blended to the vacuum residue product, mainly to meet the viscosity specifications of heavy fuel oil. The VBU converts the vacuum residue into a residue which has a much lower viscosity and also produces some naphtha and gas. This type of refinery has a flexible product distribution pattern. The fuel slate can be significantly influenced by changing the operating modes of the various processing units and by the blending of products. This type of refinery configuration is predominant in Europe. Most of these FCC refineries were built in the fifties and sixties as a simple Hydroskimming refinery. In the seventies and eighties, a Catcracker complex was added to these refineries.

10.2.3 Configuration 3: hydrocracker configuration

Scheme 3 is a Hydroskimming refinery expanded with an HVU, Hydrocracker Unit (HCU) and e.g. a Delayed Coker Unit (DCU, see Figure 10.3.). In this configuration an even larger part of the atmospheric residue is converted into lighter fuel components together with reduced production of residual fuel oil. The addition of a Coker allows this refinery to eliminate the production of residual fuel oil completely. HCU units are specifically used to maximise the production of gasoline and middle distillates. A limited number of Hydrocracker refineries in Europe include a Delayed Coker Unit (DCU) to reduce heavy fuel production and maximise light fuels production. The DCU converts heavy residues in lighter hydrocarbon fractions and petroleum coke. Dependent on the quality, coke is used in the cement and steel or in the aluminium industry. The hydrogen necessary for the HCU is supplied by a Hydrogen Plant. A Catalytic Reformer does not normally produce enough hydrogen for the HCU. Alternatively, the supplemental hydrogen requirement can be provided via partial oxidation of heavy hydrocarbons followed by hydrogen separation.

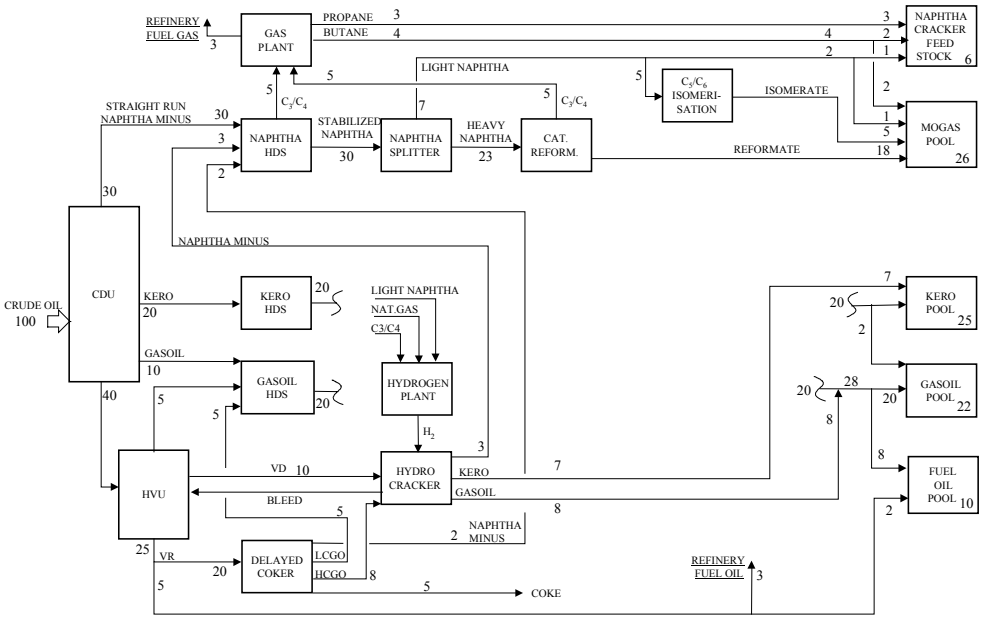


Figure 10.3: Scheme 3: Hydrocracker configuration

This type of refinery has a higher degree of flexibility with respect to either maximum gasoline or maximum middle distillate production, whereas a FCC configuration is primarily focused on increased gasoline production. About 15 % of the existing refinery complexes in Europe have already been extended with a Hydrocracker. It should be noted that such extensions require a relatively high capital investment and high energy consumption compared to the installation of a Catcracker.

10.2.4 Configuration 4: complex refinery with hydroconversion and IGCC

Scheme 4 is a refinery with a Hydrocracker and additional “deep conversion”. With a Residue Hydrocracker and/or a Gasification Unit (IGCC), so that even more conversion capacity for heavier feed stocks is introduced (see Figure 10.4). This is an example of a large complex refinery, and it includes some options to produce high value petrochemical feedstocks. This extended range of heavy residue conversion techniques can in principle eliminate the need for mixing heavy residue to the fuel oil pool or can process more heavy crude oils. The Residue Hydrocracker, i.e. Hycon, H-oil Unit or other types of Residue Hydrocrackers, converts vacuum residues to high-value transportation fuels e.g. gasolines, kerosene and diesel. The addition of a Residue Hydrocracker to a refinery provides considerable flexibility and increases production of gasoline and middle distillate fuels at the expense of fuel oil. The IGCC converts the visbreaker residue to power, steam, hydrogen, and some waste streams. The main advantage of this arrangement is the production of hydrogen by use of low-value vacuum residue instead of the more valuable light naphtha, other light hydrocarbon streams or natural gas. Moreover, the fuel oil production is reduced and the production of LPG and diesel fuels is increased.

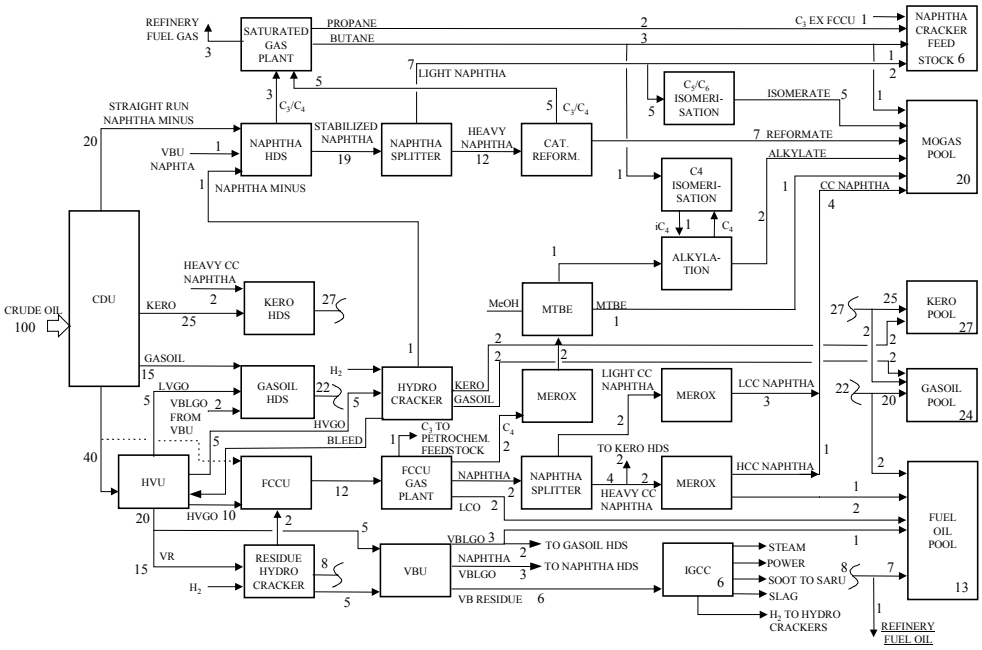


Figure 10.4: Scheme 4: Complex refinery with hydroconversion and IGCC

The visbroken residue is sent to the IGCC where it is converted into syngas (H_2/CO). The produced hydrogen can partly be used in the Hydrocracker and the Residue Hydrocracker. Remaining syngas may be combusted in a gas turbine followed by a steam turbine for electricity production and a boiler for steam production. This can be an energy efficient alternative to the classic heavy fuel-fired boilers. Waste streams from the IGCC are slag and soot recovered from the soot rework unit. The quantity and quality of the soot depends on the visbroken residue feed quality and ultimately on the crude oil processed.

10.3 Annex III. Refinery feedstock, intermediates and products

This section contains a brief explaination of the chemical and physical properties of feedstock, intermediates and products available within a refinery. Because some of the terms may vary from country to country, this annex gives a short description of how those names are used within this document. Moreover this annex gives a short overview for non expert readers.

10.3.1 Crude oil

Crude oil is a mixture of hydrocarbon compounds (95 - 99 % w/w) of different chemical composition and molecular structures with some impurities. Most of these impurities, such as sulphur, nitrogen, vanadium and nickel are chemically bound to the hydrocarbon structures. Others, such as sand/clay, water and water-soluble salts of zinc, chromium and sodium are present as inorganic material.

The hydrocarbons in crude oil are a mixture of three chemical groups: paraffins (straight and branched chains are called normal- and iso-paraffins), naphthenes (saturated rings or cycloparaffins) and aromatics (one or more unsaturated rings). The most used rough distinction between crude oil types is sweet or sour. Sweet crude is normally low in sulphur and lightly paraffinic. Sour crude is usually high in sulphur and heavily naphthenic.

The composition of the crude is the most important parameter in establishing the range and quality of products that may be produced from a refinery. The impurities of the crude, which usually make up 1 - 5 % of the total, are also very important in establishing the value of the crude and the difficulties in converting it into marketable products. The most important impurity of crude oil is sulphur, which is present largely in the form of organic compounds such as mercaptans and sulphides. Some elemental sulphur, H_2S, and FeS may also be present but only in small quantities. The total sulphur content may be as low as 0.04 % w/w or as high as 5 % w/w. Crudes containing more than 0.5 % w/w S are commonly referred to as 'sour' and the others as being 'sweet'. In general, the sulphur content increases in the higher boiling fractions.

Examples of crude types processed in European refineries are shown in Table 10.17. A distinct shift in crude oils processed in European refineries took place between 1993 and 1997, from Middle East crude oils to "North Sea" crudes. Market forces mainly caused this and this trend could therefore easily reverse. CONCAWE has reported that the average sulphur content processed in European refineries decreased from 1.45 % in 1979 to approx. 1.0 - 1.1 % from 1985 onwards. The availability and marketing of low sulphur crude oils has helped the European refineries to reduce SO_2 emissions and to some extent also the emissions of NO_x.

Crude origin	Crude Oil	density kg/m^3	kinnetic viscosity mm^2/s	sulphur %w/w	vanadium mg/kg	nickel mg/kg
Middle East	Arabian Light	864	5.18	1.91	23.7	4.6
	Iranian Heavy	870	7.85	1.67	68.2	21.4
	Arabian Heavy	889	14.54	2.92	69.8	22.3
	Iranian Light	860	5.11	1.46	55.2	17.0
	Kuwait	870	6.90	2.47	32.9	9.6
North Sea	Statfjord	830	2.70	0.26	1.5	0.7
	Oseberg	845	3.47	0.24	1.6	0.8
Russian	Ural	864	5.41	1.55	37.1	12.2

Table 10.17: Examples of crude oil types and compositions

The next two tables show the metal content of crude oil. Nickel and vanadium are present as porphyrin-systems in the crude oil. In order to determine heavy metals in crude, sampling is of crucial importance. More information about that can be found in [43, Dekkers and Daane, 1999].

Metal content of different crude oils

	Metals, ppm			
Source	Fe	Ni	V	Cu
East Texas	3.2	1.7	12	0.4
West Texas	5.1	4.8	7.9	0.4
Mirando	7.6	1.9	1.4	0.5
Jackson	4.4	1.8	0.9	0.1
Scurry County	3.4	1.0	0.8	0.2
Wilmington	28	46.0	41.0	0.6
Santa Maria	17	97.0	223.0	0.3
Kettleman	24	35.0	34.0	0.4
Ventura	31	33.0	49.0	1.1
Tibu-Petrolea	1.6	9.0	60.0	0.9
Kuwait	0.7	6.0	77.5	0.1
Mid-Continent	3.8	4.2	7.9	0.3
Kansas	5.8	5.8	20.8	0.4
Morocco		0.8	0.6	0.1
Redwater	3.4	10.6	4.5	0.1

Source: Speight, J 0 - The Chemistry and Technology of Petroleum, Marcel Dekker Inc. 1980

Range of metals content found in crude oils

Element	Concentration (ppm)
V	5.0 - 1500
Ni	3.0 - 120
Fe	0.04 - 120
Cu	0.2 - 12.0
Co	0.001 - 12
Si	0.1 - 5.0
Ca	1.0 - 2.5
Mg	1.0 - 2.5
Zn	0.5 - 1.0
Al	0.5 - 1.0
Ce	0.001 - 0.6
Zr	0.001 - 0.4
Ti	0.00l - 0.4
Sn	0.1 - 0.3
Pb	0.001 - 0.2
Hg	0.03 - 0.1
B	0.00l - 0.1
Ga	0.00l - 0.1
Ba	0.001 - 0.1
Sr	0.001 - 0.1

A recent report [43, Dekkers and Daane, 1999] has shown that the quantity of Cadmium, Zinc, Chromium, Copper and Arsenic in the crudes are indeed much lower than traditionally assumed. Reasons for this include improper analytical techniques and contamination during sampling. The following table shows the results achieved in the above-mentioned report.

Metal	Concentration (µg/kg)	
	[43, Dekkers and Daane, 1999]	Published data*
Arsenic	4 – 37	0.2 -26200
Cadmium	0.40 – 4.9	0.10 - 29.1
Chromium	12 – 240	1.5 - 3170
Copper	10 – 195	30 - 7180
Zinc	59 –1090	25 -19500
* Published data from several sources reflected in the report [43, Dekkers and Daane, 1999]		

Table 10.18: Content of certain metals in some crude compared to other published data

Physical properties and characteristics of crude oil

Crude oil is a mixture of many compounds and, apart from the lightest components, the characterisation by a complete chemical analysis is almost impossible. As a result, the general physical properties are expressed in terms of simple parameters, which can be quickly estimated. The underlying nature of the crude is then derived from this information by comparison with corresponding parameters from known feedstocks. Most of these parameters are not limited to crudes, but may be used for most petroleum products as well. One of the simplest crude properties to measure is the specific gravity, normally expressed in terms of the °API. Crudes are often classified as being 'heavy' or 'light' according to their °API, the heavy being less than about 28 - 32°API and the light over 32 – 35 °API.

10.3.2 Refinery intermediates and products

There are over a hundred of refinery products, including gaseous and liquid refinery fuels for domestic and industrial use, fuel for most forms of transport, lubricating oils for all types of machinery and the basic raw materials for the petrochemical industry. Individual refineries do not usually supply the full range of possible products, but try to select those most suited to the quality of the crude feed, the available processing equipment and the local market requirements. The composition of a product will vary between refineries, being a function of crude type and refining processes used, but the overall quality will meet the product specifications prevailing for a given market. The major refinery product groups are shown in Table 2.1 by refinery process unit. A short description of the product groups follows.

Refinery fuel gas (RFG)
Refineries use the C_1/C_2 fraction as refinery gas to cover part or most of their fuel requirements. Refinery gas can also contain H_2. An amine wash is normally used to extract H_2S.

LPG
Sometimes C_3 and C_4 components are also used for refinery fuel, but most of the C_3 and C_4 components will be sold as liquefied petroleum gas (LPG), which is used as a fuel for numerous applications. LPG is sold either as a mixed LPG fraction or as separated C_3 and C_4 fractions. The liquid propane normally contains a minimum of 95 %w/w C_3 compounds, the remainder being C_2 and C_4. Butanes and butenes are also used as a petrochemical feedstock for the manufacture of MTBE, acetic acid, solvents, polybutylenes, and rubber.

Naphtha and chemical naphtha
Naphtha is the raw gasoline range fraction from crude oil distillation. As well as gasoline production, in some cases, naphtha is used as the feedstock for petrochemicals production.

Gasoline
Gasoline, the fuel for motor cars and light aircraft, represents the highest volume and one of the more valuable refinery products. Automotive gasoline, which is by far the most important gasoline type, consists of a complex mixture of hydrocarbons ranging from C_4 to C_{10}, boiling

between 38°C and 205°C. Most refiners produce gasoline in three or four octane grades, the principal difference being the anti-knock performance. Mogas is a term normally used for motor gasoline.

Jet fuel (kerosene, avtur)
Jet fuel is the name given to kerosene or kerosene blends used as fuel in aviation turbines (hence also called Avtur) by both commercial aviation and military aircraft. For most refineries the primary source of jet fuel blending stocks is the straight-run kerosene fraction (C_8 - C_{12}) from the atmospheric crude unit. For a refinery with a Hydrocracker, kerosene boiling range hydrocarbons from this unit can also meet jet fuel specifications, and is a major contributor to jet fuel production. Hydrotreated light Coker gas oil and thermally cracked gasoil can also be used as blending stock. In some developing countries kerosene is still the primary fuel for cooking and domestic heating.

Diesel oil / heating oil / gasoil
Diesel fuels are produced by blending of kero and gas oil fractions from the crude distillation unit and gas oil fractions of the high vacuum unit and from conversion units. An upgraded and flexible processing scheme for desulphurisation of blending components is necessary in most refineries in order to arrive at the currently required and future sulphur specifications (500 ppm currently, 350 ppm from 2000 and 50 ppm from 2005 onwards). Light heating oils (kero/diesel fraction) are typically used for small domestic applications.

Middle distillates / distillate fuels
Alternative names for the fuels in the kerosene and gasoil boiling ranges.

Fuel oils
Fuel oils cover a very wide range of applications and are produced in a variety of grades. Gasoils are sometimes referred to as fuel oils, but in Europe the term is usually used to describe heavy fuel oils (atmospheric residue) which are used for electricity etc. Heavy fuel oil are used for electricity or power generation by utility companies, or sold as bunker fuel oil for seagoing vessels. Refineries use heavier fractions from crude oil distillation, from vacuum distillation or from visbreaking for generation of heat, electricity and steam in their furnaces and boilers.

Heavy fuel oils consist largely of the residue remaining from the distillation of crudes. These residues consist of large hydrocarbon structures containing components that require additional processing to convert them into more valuable, lighter products for use in gasoline and diesel engines. These residues generally have a high sulphur and ash content, are mostly very viscous and will therefore be blended with lighter gasoils in order to sell them as a commercial fuel for ships and utilities.

Lubricating oils, wax and greases
Lubricating oil feedstocks are produced from the atmospheric residue by fractionation under vacuum. The oil cuts produced from the vacuum distillation column are further processed to remove unwanted impurities (solvent extraction and dewaxing) and blended with miscellaneous additives (both organic and inorganic in nature) to give lubricating oils of various grades. Lubricating oils can be modified by mixing with thickening agents such as soap, clay or silica gel to produce lubricating greases. Dewaxing yields paraffinic or microcrystalline wax that is usually subjected to hydrofinishing to remove colours, odours and potentially carcinogenic hydrocarbons for domestic applications.

Bitumen
Bitumen (referred to as asphalt in the USA) is used mainly for paving roads but also for a number of other applications, such as materials for roofing. The basic source of bitumen is the residue remaining after vacuum distillation of crude. The residue can also be treated by blowing with air at high temperature (bitumen blowing process) to increase the asphaltene content.

Petroleum coke
Petroleum coke is the residue remaining after destructive distillation of petroleum residue in a delayed coking unit. It is widely used as fuel in the cement and steel industry. It can also be used as a fuel for power plants if the sulphur content is low enough. Coke also has nonfuel applications as a raw material for many carbon and graphite products.

Petroleum coke analysis used in oxygen-blown gasification [166, Meyers, 1997]	
Ultimate analysis	**% w/w**
Carbon	87.1 - 90.3
Hydrogen	3.8 - 4.0
Oxygen	1.5 - 2.0
Nitrogen	1.6 - 2.5
Sulphur	2.1 - 2.3
Proximate analysis	% w/w
Volatiles	9.0 - 9.7
Fixed C	80.4 - 89.2
Moisture	0.9 - 10.2
Ash	0.2 - 0.4

Sulphur
Sulphur is basically a by-product of refining resulting from the removal of sulphur compounds from the main hydrocarbon product streams. The quantity of sulphur produced by a refinery depends on the amount present in the crude and the desulphurisation and sulphur recovery capacity installed. It is a valuable product which is mainly used as the raw material for sulphuric acid manufacture.

Relationship between feed (typically crude oil) and products
As a broad generalisation it is true to say that any crude can be processed into any reasonable selection of products by a suitable choice of refining unit operations. The cost of production will depend on the refining units required, which in turn depend on the crude selected. In theory the production cost can be minimised by careful selection of the crude. In practice, however, refinery designs are often compromised by factors such as: the changing availability, price and composition of crudes and changing market demands for product slate and specifications. A few relatively simple crude properties can indicate the feasibility of processing a particular crude (mix) with a given refinery complex.

In general, it is found that the heavier the crude, the higher the quantities of sulphur, Conradson carbon and heavy metals, and the lower its hydrogen content. Heavy crudes are also more difficult to process. Heavy crude normally results in high fuel-oil production while light crude is more appropriate for a high gasoline and middle distillate production. Other simple property indicators are sulphur content and pour point.

In order to evaluate the properties of the various likely products such as gasoline octane rating, the aromatics content of kerosene, etc., it is necessary to distil the crude and analyse the fractions boiling within different boiling ranges. This will give information on the process units that may be required for quality improvement, such as desulphurisation facilities, a reformer unit or an aromatics extraction plant. The residue fractions can be similarly analysed to give more detailed information on the conversion units that may be appropriate.

10.4 Annex IV. Submitted examples on cost-effectiveness of implementation of environmental technologies

References: [115, CONCAWE, 1999], [268, TWG, 2001], [248, Ademe, 2001], [348, Ashworth Leininger Group, 2001]

It follows some examples submitted by the TWG on the calculation of some cost-effectiveness of the implementation of environmental technologies in the refinery sector. One feasibility study (Section 10.4.4) provided by a TWG member has shown that the cost and the technical solution for the achievement of the same environmental goal (e.g. bubble concept) depends on the local situation.

10.4.1 Calculation of the cost-effectiveness of the implementation of a technique in a hypothetical case

An important consideration of the cost of environmental technologies relates to the changing cost-effectiveness that results for a given technology depending on the point of control from which one starts the cost effectiveness calculation. Most studies on environmental technologies, present the cost and effectiveness (percent of emission reduction or tonnes of emissions reduced) of installing a technology or implementing a technique against an uncontrolled baseline operation. In this case it is easy to calculate the cost effectiveness of an environmental technology versus an otherwise uncontrolled facility by simply dividing the cost of the technique by the emissions reduction achieved. Table 10.19 shows a series of various hypothetical controls capable of reaching various percentage emission reductions. For example, technology C would provide a 50% reduction for a cost of 2000 k EUR while technology G would provide 99% reduction for 12000 k EUR.

Technology	Percentage of reduction (%)	Remaining Emission (tonnes)	Technology cost for a new installation (kEUR)
A	0	10000	0
B	20	8000	1000
C	50	5000	2000
D	60	4000	3000
E	90	1000	4500
F	95	500	7000
G	99	100	12000

Table 10.19: Example of abatement technology cost for a new installation, emission reduction and emissions remaining after the application of the technology.

Due to local regulations and/or corporate policies there are many situations where certain levels of control already exist within specific sites. In these cases the cost for achieving a given % emission reduction target is significantly increased over the initial cost effectiveness values. This needs to be accounted for in determining the cost effectiveness of a technology/technique. As can be seen in Table 10.19, if technology C is already in place at a location, the additional emissions reduction for going to technology G would be only 49%. The cost of implementing technology G therefore becomes 2.45 kEUR/tonne for the incremental emissions reductions, rather than the 1.21 kEUR/tonne when going to 99% control from 0%. If one were to go to technology G in a location where technology E was in place, the incremental cost would be 13.3 kEUR/tonne. In all of these instances the final situation is to be at 99% control of emissions. The actual cost for going to the 99% level in these situations, if done incrementally, would effectively be the cost of implementing Technology C plus E, plus G, to get the 99% reduction. Table 10.20 shows the resultant cost of applying various technologies starting from different levels of existing control.

Actual level of control Targeted level of control	0%	20%	50%	60%	90%	95%
20%	0.5	-	-	-	-	-
50%	0.4	0.67	-	-	-	-
60%	0.5	0.75	3	-	-	-
90%	0.5	0.64	1.12	1.5	-	-
95%	0.74	0.93	1.55	2	14	-
99%	1.21	1.52	2.45	3.07	13.3	30

Table 10.20: Cost effectiveness (kEUR/tonne abated) starting from different percentages of reduction and considering that the previous technology should be replaced 100%

10.4.2 Cost-effectiveness data for SRU

Next table gives the data on cost-effectiveness of the application of serveral sulphur recovery unit techniques.

Name of the technique	Specific cost (1) EUR/tonne SO_2	Specific cost (2) EUR/tonne SO_2
3rd reactor		32
Stand Alone Scot	321-538	32
Cascade Scot Common regenerator		32
Super Claus	155-228	32-161
Super Claus + Claus Stage		32-160
Clauspol	198-330	32
Sulfreen	174-288	32-160
Hydro-sulfreen	253-417	32-160
CBA/AMOCO cold real absorption	169-300	-

(1) [268, TWG, 2001]

Calculations for this column have been performed based on the following hypothesis:

- The TGCU selling costs include license fee, catalyst and chemical first loads. These investments are financed by a full reimbursable loan. This loan is based on a 10 years basis, with a yearly 6% interest rate.
- The catalyst life-time is 3 years (part of the operating costs). The related investment every 3 years is financed by a full reimbursable loan. This loan is based on a 3 years basis, with a yearly 6% interest rate.
- The solvent and chemical make-up (part of the operating costs) have been calculated on a yearly basis as a cash expense.
- The utilities consumption and production as well as the supervision manpower costs have been considered constant over the time.
- The sulphur selling price has also been considered constant over the time.

(2) [115, CONCAWE, 1999]
Claus plant with a capacity of 30000 t/yr sulphur production (sulphur recovery efficiency 94-96% for a two stage unit), a volume of gas treated of 60 million m^3/yr, and pollutant initial concentration: 34000 mg SO_2/m^3

10.4.3 Compendium of cost-effectiveness data for some NO_x abatement techniques

The following graph shows the cost to abate a tonne of NO_x in industry sectors as well as some reference values used in some countries [248, Ademe, 2001],

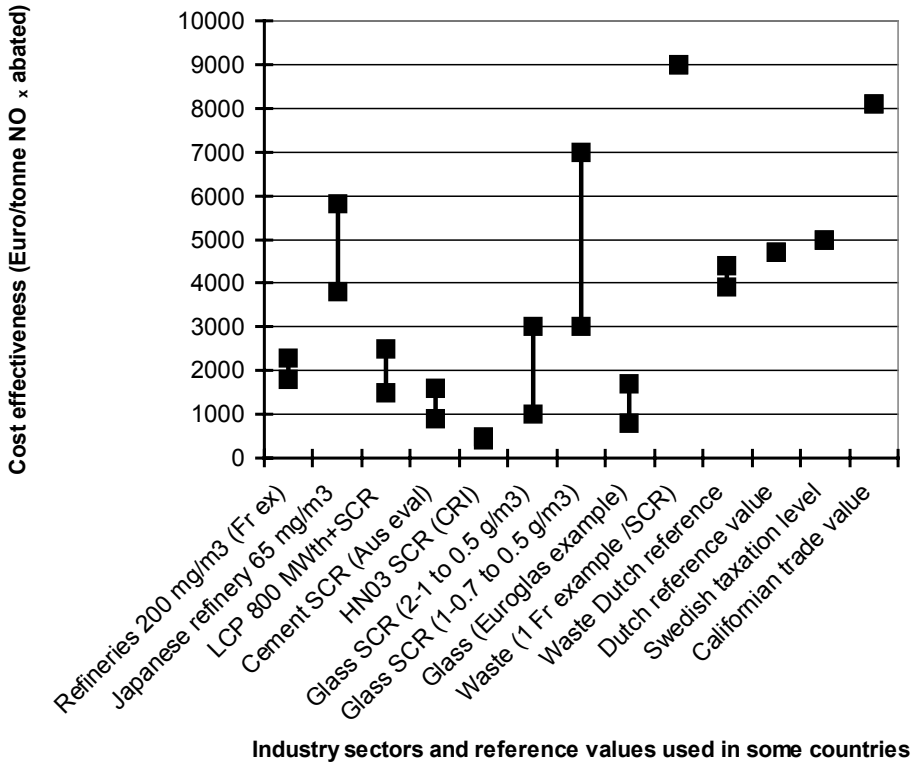


Figure 10.5: Some values on the cost for the abatement of NO_x in different industrial sectors

The following tables show data concerning cost-effectiveness for NO_x abatement measures.

NO_x Control for Fired Heaters and Boilers Firing Refinery Blend Gas

Basis: 100 Giga joules/hr installation
Retrofit of existing unit
Refinery blend gas firing
Uncontrolled NO_x emissions of 150 ppm at 3% oxygen (300 mg/Nm^3)

	Flue Gas Recirculation plus Low NO_x Burner [6]	Ultra Low NO_x Burners	SNCR	SCR	Ultra Low NO_x Burner plus SCR
Cost Effectiveness EUR/tonne NO_x Removed (incl. capital charge @ 15%)	2000-4300 [3]	650 [1] 600-700 [2] 1700-5000 [4]	2000-2500 [2] 1800-4300 [4]	8300-9800 [2] 12000 [3] 4200-9000 [4]	9100-10500 [2] 9000 [3]

(1) U.S. Environmental Protection Agency RBLC clearinghouse listing and California Air Resources Board BACT listing. These listings provide the permitted emission levels in permits granted within the United States or the State of California for alternative control technologies to meet RACT, BACT (Best Available Retrofit Control Technology) and LAER (Lowest Achievable Emission Requirements.) The listings cover the period to 1996.

(2) Alternative Control Techniques Document—Control of NO_x Emissions from Process Heaters, U.S. Environmental Protection Agency, EPA-453/R-93-015, February, 1993

(3) Proprietary industry studies

(4) CONCAWE Member Company Information

Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr have been used in this analysis.

NO_x Control for Fired Heaters / Boilers Firing Residual Fuel Oil

Basis: 100 Giga joules/hr installation
Retrofit of existing unit
Residual Oil firing
Uncontrolled NO_x emissions of 250 ppm at 3% oxygen (500 mg/Nm^3)

	Boilers			Heaters
	Low NO_x Burners (3)	SNCR	SCR	Low NO_x Burners (1)
Cost Effectiveness EUR per tonne NO_x Removed (incl. capital charge @ 15%)	500-1800	1500-2800 1500-4300 (2)	5000-8000 4500-10200 (2)	500-1800

Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr have been used in this analysis

(1) ULNB are not available for oil-fired fired heaters and boilers.

(2) California Clean Air Act Guidance, Determination of RACT and BARCT (Best Available Retrofit Control Technology), California Air Resources Board, July 1991

(3) ULNB are not available for oil-fired heaters and boilers

NO_x Control for Gas Turbines Firing Natural or Refinery Blend Gas

Basis: 85 MW output turbine (representative of a GE Frame 7 size unit) (electrical output)
-tural gas or refinery blend gas firing
Uncontrolled NO_x emissions of 250 ppm at 15% oxygen (350 g/GJ)

	Dry Low NO_x Combustors	Steam Injection	SCR	Steam Injection plus SCR	Dry Low NO_x Combustors plus SCR
Cost Effectiveness EUR/tonne NO_x Removed (includes capital charge @ 15%)	350 (1)	1500 (1)	1700-8000 (2)	3800 (3) 3600 (2)	7600 (4)

(1) Alternative Control Techniques Document— NO_x Emissions from Statio-ry Gas Turbines, U.S. Environmental Protection Agency, EPA-453/R-93-007, January, 1993

(2) Proprietary industry studies

(3) Costs from Reference (1) above for SCR increment only with NO_x entry to SCR following low NO_x combustor of 25 ppm.

(4) Dry Low NO_x combustors are not available for refinery blend gas containing more than 5 to 10% hydrogen

Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr have been used in this analysis.

NO_x Control for Fluid Catalytic Cracking Units
Basis: 30 k bbl/day FCCU with CO Boiler
800 mg/Nm^3 uncontrolled NO_x emission (1)

	SNCR	SCR	Feedstock Hydrotreating
Cost Effectiveness EUR/tonne NO_x Removed (includes capital charge @ 15%)	1900	2800-3300	28000 (2)

(1) Removal of NO_x from FCCU regenerator vent gases, Refining, PTQ Spring 1997. Analysis of SCR installation at Scanraff refinery, Lysekil, Sweden.
(2) Assigns all feedstock hydrotreating costs to NO_x control.
Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr used in this analysis.

Cost Effectiveness of some already applied NO_x abatement techniques in USA refineries.

	Low-NO_x Burners (LNB)	Selective Catalytic Reduction (SCR)	Selective Non-Catalytic Reduction (SNCR)
Cost Effectiveness EUR/tonne NO_x Removed	1260-4500	6300-21600 (for process heaters and boilers) Approx. 5940 for the FCCU described in the report	2070-6030 (for process heaters)

10.4.4 Feasibility study on the applicability of NO_x environmental measures in two different refinery sites

A French study, performed by an engineering consultant and sponsored by ADEME / Environment Ministry and French Oil Federation, evaluated the "pre-engineering cost" of BAT implementation by retrofitting for NO_x reduction on two existing refinery sites. The study explored the choice mechanism to implement IPPC directive.

For both sites, all the major existing units contributing globally for more than 80 % of the NO_x emissions from the site have been considered: furnace, boilers, regenerator, etc. The BAT candidates listed in the [115, CONCAWE, 1999] have been considered for each item at the technical, economic and maintenance levels.

Summary graphs are presented showing the variable efficiency of considered and validated techniques on different units: low-NO_x burners, flue gas recirculation, SNCR, SCR, reburning, etc. An estimated cost (about 30 %) is expressed for implementation of each BAT candidate in terms of cost per reduced NO_x tonne per year. A large variation of cost is observed on different units, for various techniques and with different impacts on the global NO_x emissions reductions of the two sites respectively.

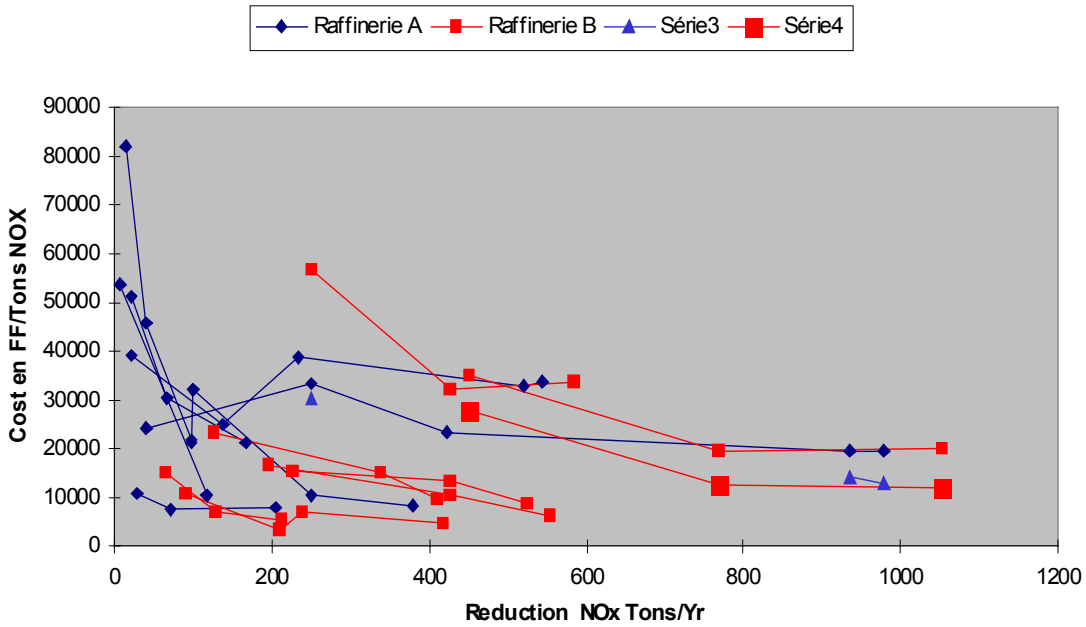


Figure 10.6: Variable efficiency and cost of retrofitting of existing units (FRF/tonne NO_x reduced)
Note: Using feasibility of NO_x BAT candidates study on two refinery sites (1 Euro = 6.56 FRF)

Finally, combined scenarios of the potential applicability of these BAT are presented for the both sites and for similar environmental objectives based on a global NO_x bubble concentration. Cost impact is different for each existing site to be retrofitted and is very expensive according to the environmental objectives to be reached.

This technical feasibility and economic considerations have to be remembered in the context of the BAT associated emissions levels to be proposed, taking into account the complexity of retrofitting due to the difference in the current European existing refinery sites.

	Objectives	**400 mg/Nm^3**	**300 mg/Nm^3**	**200 mg/Nm^3**
Site A				
Investment	kEuro	3000	6800	13000
Annual Cost	kEuro	1070	2150	4150
Cost/t NO_x abatted /yr	Euro	1170	1680	1860
	techniques	LNB - SNCR	LNB - 1 SCR	LNB - 3 SCR

	Objectives	**400 mg/Nm^3**	**300 mg/Nm^3**	**200 mg/Nm^3**
Site B				
Investment	kEuro	3800	8620	17900
Annual Cost	kEuro	930	2600	5350
Cost/t NO_x abatted /yr	Euro	1100	1770	2350
	techniques	LNB - recircul.	reburn - SCR	SCR with exch.

10.5 Annex V: Background information from TWG members for the different proposals of SO_2 and NO_x emission under the bubble concept

The calculation of the emission levels for the bubble concept that can be associated with applying BAT incorporates the various aspects presented in Section 4.15.2 (description of the bubble concept) and the elements described in Chapter 5. The following elements have to be taken into consideration, with due regard to the applicability of each of the elements or options in a particular situation:

- Increased energy efficiency of the various processes integrated with the refinery fuel management system;
- Decrease use of liquid fuels by increased use of gaseous fuels from within the refinery or, where applicable, from additional processing and conversion in the refinery, FCC, IGCC, coker, etc.;
- Lower the S-content of liquid fuels (e.g. hydrotreatment) used in the refinery;
- Use of clean gaseous fuels (-tural gas or cleaned refinery gas);
- Use of liquid fuels combined with control techniques to clean the flue gases, thereby reducing the emissions of SO_2 and NO_x;
- Apply BAT to single installations, especially to the sulphur recovery unit (SRU).

It follows some calculations, justifications for the proposals given by some TWG members.

10.5.1 Calculations based on BAT assumptions provided by the Netherlands

In order to illustrate the use of the bubble concept in a refinery, a number of cases and their relevant emissions are calculated along the lines outlined below. The following assumptions are used.

Gas-fired refinery:
There are a few full conversion refineries in Europe that are fully gas-fired. The main source of energy in these cases is cleaned refinery gas. In some cases also natural gas is used as supplementary fuel.

Assumptions for bubble calculation: Full conversion, fully gas fired refinery, processing 10 million tonne of crude oil with an annual fuel use of 700000 tonnes (7% on intake). SRU applies BAT with 99.8% efficiency and has an annual production of 100000 tonnes of elementary sulphur. The FCC has an annual throughput of 1.5 million tonne (consuming some 12% of the total refinery fuel consumption). The 100% gas case is presented in Tables 10.21-24.

Gas and Liquid Fired Refinery using low sulphur oil (0.5% S)
Most European refineries use a combination of gaseous and liquid fuels from within the refinery. The calculation of the technical achievable emission values in such a refinery is based on a) existence of a combined fuel management system in the refinery, and b) emission values of the combined fuel system with fuels that are either inherently clean (certain refinery gases or natural gas) or refinery gaseous or liquid fuels that can be cleaned relatively easy. It may also cover the situation of the cleaning of the flue gases from fuels that "untreated" will cause pollution to air.

Assumptions for the calculation: Medium conversion, partially gas fired refinery, processing 10 million tonne of crude oil with an annual fuel use of 400000 tonne (4% on intake). SRU applies BAT with 99.8% efficiency and has an annual production of 50000 tonnes of elementary sulphur. The FCC has an annual throughput of 1.5 million tonne (consuming some 20% of the total refinery fuel consumption). Several cases are shown (*70% gas*, *50%gas* and *30% gas*).

Gas and Liquid Fired Refinery using flue gas desulphurisation

The following calculations are based on actual data from a complex refinery firing heavy residues in the power plant, whereby all the liquid fuel firing of the refinery is concentrated and the installation is equipped with flue gas desulphurisation. The remaining installations are gas fired.

Assumptions for the calculation: Medium conversion, partially gas fired refinery, processing 10 million tonne of crude oil with an annual fuel use of 400000 tonne (4% on intake). SRU applies BAT with 99.8% efficiency and has an annual production of 50000 tonnes of elementary sulphur. The FCC has an annual throughput of 1.5 million tonne (consuming some 20% of the total refinery fuel consumption). Heavy residue (3.5 wt% S) is fired on the power plant, which is equipped with flue gas desulphurisation. Two desulphurisation efficiency cases are presented, *90% DeSOx* and *95% DeSOx*.

The results from the calculations are summarised in Table 10.21. The cases are elaborated in more detail in Tables 10.22-24. It should be explicitly noted that these bubbles are calculated from a technical basis and by taking the 'bottom up' approach. It does not take account of process upsets or outages.

Cases	SO_x Concentration bubble mg/Nm^3	SO_x Load bubble tonne/Mtonne crude	NO_x Concentration bubble mg/Nm^3	NO_x Load bubble tonne/Mtonne crude
100% gas	58 – 109	49 – 91	100 – 150	84 – 126
70% gas	258 – 334	124 – 160	105 – 162	50 – 78
50% gas	394 – 468	189 – 224	108 – 170	52 – 82
30% gas	529 – 601	254 – 289	111 – 178	53 – 85
DeSOx-90	353 – 426	169 – 204	110 – 175	53 – 84
DeSOx-95	203 – 276	97 – 133	110 – 175	53 – 84

Table 10.21: Summary of calculated SO_x and NO_x bubbles from the cases described in this section and presented in following tables

It should be noted that the 100% gas case is the only case that is a full conversion refinery. The other cases refer to medium conversion refineries, which has a considerable effect on the fuel consumption and thus also on the load bubbles.

Description	Unit	100% gas	70% gas	50% gas	30% gas	DeSOx-90	DeSOx-95
Refinery type	conversion	Full	medium	medium	medium	medium	medium
Crude throughput	million tonnes/year	10	10	10	10	10	10
Fuel consumption	% of feedstock input	7	4	4	4	4	4
Fuel consumption	tonnes per year	700000	400000	400000	400000	400000	400000
FCC fuel consumption	%	12	20	20	20	20	20
Other fuel pool	%	88	80	80	80	80	80
• Gas in fuel pool	%	100	70	50	30	37	37
• Oil in fuel pool	%	0	30	50	70	63	63
Flue gas from FCC*	10^3 m^3, ISO, dry, 3% O_2	1008000	960000	960000	960000	960000	960000
Flue gas from gas firing*	10^3 m^3, ISO, dry, 3% O_2	7392000	2688000	1920000	1152000	1420800	1420800
Flue gas from oil firing*	10^3 m^3, ISO, dry, 3% O_2	0	1152000	1920000	2688000	2419200	2419200
S-content fuel oil	wt. %	0.5	0.5	0.5	0.5	3.5	3.5
Flue gas desulphurisation	%	0	0	0	0	90	95
Ref. product desulphurisation	%	80	50	50	50	50	50
Delta S removed from product	wt. %	1.25	1	1	1	1	1
SRU efficiency	%	99.8	99.8	99.8	99.8	99.8	99.8
Sulphur recovery	tonnes per year	100000	50000	50000	50000	50000	50000

Table 10.22: Description of 6 different cases of refinery firing and flue gas treatment

* The flue gas flow is calculated from the assumption that the combustion of 1 tonne of oil or 1000 m^3 of gas yields a flue gas flow of 12000 Nm^3 (at 3% O_2)

SO_x* Description	FCC mg/Nm^3	Gas firing mg/Nm^3	Oil firing mg/Nm^3	FCC tonne/yr	Gas firing tonne/yr	Oil firing tonne/yr	SRU tonne/yr	Total tonne/yr	Concentration bubble mg/Nm^3	Load bubble tonne/Mtonne crude
100% gas	50 – 400	5 – 15	-	50 – 403	37 – 111	0	400	487 - 914	58 – 109	49 – 91
70% gas	50 – 400	5 – 15	850	48 – 384	13 – 40	979	200	1241 – 1604	258 – 334	124 – 160
50% gas	50 – 400	5 – 15	850	48 – 384	10 – 29	1632	200	1890 – 2245	394 – 468	189 – 224
30% gas	50 – 400	5 – 15	850	48 – 384	6 – 17	2285	200	2539 – 2886	529 – 601	254 – 289
DeSOx-90	50 – 400	5 – 15	595	48 – 384	7 – 21	1439	200	1695 – 2045	353 – 426	169 – 204
DeSOx-95	50 – 400	5 – 15	298	48 – 384	7 – 21	720	200	975 – 1325	203 – 276	97 – 133

* Concentrations are assumed from the application of BAT. Loads and bubbles are calculated accordingly.

Table 10.23: Assumed and calculated SO_2 emissions and bubbles for the different cases described in Table 10.22

NO_x* Description	FCC mg/Nm^3	Gas firing mg/Nm^3	Oil firing mg/Nm^3	FCC tonne/yr	Gas firing tonne/yr	Oil firing tonne/yr	Total tonne/yr	Concentration bubble mg/Nm^3	Load bubble Tonne/Mtonne crude
100% gas	100 – 150	100 – 150	–	101 – 151	739 – 1101	0	840 – 1262	100 – 150	84 – 126
70% gas	100 – 150	100 – 150	120 – 200	96 – 144	269 – 403	138 – 230	503 – 778	105 – 162	50 – 78
50% gas	100 – 150	100 – 150	120 – 200	96 – 144	192 – 288	230 – 384	518 – 816	108 – 170	52 – 82
30% gas	100 – 150	100 – 150	120 – 200	96 – 144	115 – 173	323 – 538	534 – 854	111 – 178	53 – 85
DeSOx-90	100 – 150	100 – 150	120 – 200	96 – 144	142 – 213	290 – 484	528 – 841	110 – 175	53 – 84
DeSOx-95	100 – 150	100 – 150	120 – 200	96 – 144	142 – 213	290 – 484	528 – 841	110 – 175	53 – 84

* Concentrations are assumed from the application of BAT. Loads and bubbles are calculated accordingly.

Table 10.24: Assumed and calculated NO_x emissions and bubbles for the different cases described in Table 10.22

10.5.2 Example provided by Austria

Hypothesis
The following calculations are based on a complex refinery firing heavy residues in the power plant, which is equipped with flue gas desulphurisation. To allow some flexibility a gaseous/liquid fuel ratio between 1 and 2 is assumed, which means that between 50 % and 33 % of the total energy used by the refinery is derived from combustion of liquid fuels (there are refineries existing with 100 % gas firing). Average S-content of the liquid fuels is assumed to be in the range of 2.8 – 3.5 %. Measures to increase energy efficieny are not included in these calculations.

- Range of input of liquid fuels:
  a) 303000 t with a S-content of 2.8 %: S-input in the power plant: 8484 t
  b) 500000 t with a S-content of 3.5 %; S-input in the power plant: 17500 t
- Range of efficiency of FGD: 90 – 95 %
- Highest SO_2 concentration in the off-gas of the Claus plant: 1350 mg/m^3

Calculations
Assuming the above given parameters, calculated bubble (including all installations, but without flares) concentrations for SO_2 are in the range of 109 mg/Nm^3 (case a; 95 % efficiency of FGD) and 338 mg/Nm^3 (case b; 90 % eff. of FGD). Case b together with an efficiency of FGD of 95 % results in a bubble concentration of 175 mg/Nm^3 (corresponding to 235 t/Mt crude throughput).

Corresponding loads are from 126 t SO_2/Mt to 455 t SO_2/Mt crude throughput.

10.5.3 Two examples provided a TWG member

CASE A: Reduction scenario developed in an existing refinery

Refinery characteristics
A complex refinery processing 15 Mt/yr of crude oil. 15% fuel oil at an average sulphur content of 1.3 %. 160000 tonnes of fuel oil and 840000 tonnes of gas (RFG + natural gas)

BAT assumptions
50% reduction of fuel emissions by switching fuel oil to low S fuel oil or by installing FGD on stacks with highest SO_2 fuel emissions.
50% reduction of catcracker emissions by reducint sulphur input to catcracker and/or by installing FGD on stacks of catcracker
High efficient SRU >99.5% sulphur recovery

Conclusions
Concentration bubble of 200 mg SO_2 /Nm^3

CASE B: Reduction scenario developed in an existing refinery

Refinery characteristics
A complex refinery processing around 12 Mt/yr of crude oil.
Fuel consumption: 156000 t/yr liquid at 3 % S
400000 t/yr of refinery fuel gas + natural gas
SRU at 99% SO_2 concentration 20000 mg/Nm^3

BAT assumptions
Improve the SRU to BAT levels
DeNOx in the main stacks

Conclusions
SO_x bubble concentration of 50 mg/Nm^3
NO_x bubble concentration of <100 mg/Nm^3.

10.5.4 Italian proposals and justification for the given bubble figures

With respect to environmental benefits, Italy and other mediterranean countries are characterised by a nearly full compliance with objectives for acidification and very marginal transboundary pollution. In other words we don't need very stringent emission ranges for SO_2 and NO_x.

From the technical and economic point of view, we should consider that the refining sector in the Mediterranean area is characterised as follows:

- 70 % of the European fuel oil market demand is located in the Mediterranean area;
- the current configuration of the existing refineries in this area derives from the actual petroleum products demand that is very different from the North Europe demand;
- the crude oil slate processed is mainly derived from Middle East crude oils that represent the best choice to fit both the market demand and the refinery configuration. The heavy fuel oil produced under these conditions needs to be used internally because any other options (deep conversion, desulphurisation, gasification, etc) are not economic sustainable

In conclusion we believe that the level associated with BAT should take into account the cost and the advantages associated to different emission ranges and, moreover, BAT must be techniques generally applicable otherwise the competitiveness inside the refining sector in Europe will be distorted.

On the basis of these considerations we propose the following bubble emission ranges:

- SO_2: 800-1200 mg/Nm^3 (monthly average all plants included)
- NO_x: 250-450 mg/Nm^3 (monthly average all plants included)
- Dust: 30-50 mg/Nm^3 (monthly average all plants included)

The ranges here proposed for SO_2 and NO_x are derived from the emission values associated to the BAT considered for the revision of the Large Combustion Plants Directive, recently approved at European level. The BATs adopted for this revision are the most stringent techniques applicable to the new and existing large combustion plants.

In the revision of the Large Combustion Plants Directive the SO_2 emission limit values for new and existing refineries are respectively 600 and 1000 mg/Nm^3. Having considered that the bubble emission levels in the BREF are referred to all plants, these emission limit values are slightly increased to include the SO_2 emission also from Claus and Catalytic Cracking plants.

The emission limit values for NO_x, in the revision of the Large Combustion Plants Directive are defined in the same range we proposed for refinery bubble and this seems enough to justify our proposal.

The above emission values ranges are coherent with the definition of general BAT and so the requirement of more stringent ranges do not have justification.

By the way the techniques that need to be adopted to meet the more stringent ranges will increase the refinery energy consumption and the associated CO_2 emissions.

10.5.5 Concawe proposals and justifications for the given bubble figures

SO_2 bubble calculations and scenarios

parameters	Ratio FO use	S content of FO	Combustion bubble	Global bubble
Base case	30 %	1.7 %	1000	1200
Scenario 1	30 %	1 %	590	*880*
Scenario 2	30 %	0.5 %	295	*650*
Scenario 3	100 %	1 %	1960	*1950*
Scenario 4	100 %	0.5 %	980	*1190*
Scenario 5 + FGD on all units	100 %	3 %	294	*650*
Scenario 6 + FGD on 75 % of emissions or major emitters	100 %	2 %	1130	*1300*
Scenario 7 + FGD on 75 % of emissions or majors emitters	100 %	1.7 %	960	*1170*
Scenario 8 + FGD on 50 % of emissions or majors emitters	100 %	1 %	*1030*	*1225*

Table 10.25: Variation of the Bubble Results from Use of Fuels with Varying Sulphur Content with and without FGD

SO_2 REFINERY CASE - daily figures

In terms of the regulatory point of view or operating conditions of a single site, the imposed or reachable bubble limit has to take into account the huge variable conditions of operations of a refinery site on a daily basis, particularly on the averaging time considerations.

Figure 2 shows the reported daily variation of a calculated SO_2 global bubble of a representative refinery, all units included, and the corresponding daily use of potential fuels within the site. The annual global average SO_2 bubble is 1200 mg/Nm^3, ranging from 500 to 2000 mg/Nm^3, the daily variation is given for each type of fuels use (low sulphur fuel oil, high-sulphur fuel oil, vacuum residue, refinery fuel gas).

In order to avoid making the graph over complex, it does not reflect the fuels sulphur content which is also varying according to the initial sulphur content in crude feedstock, we observe respectively:

- for LS FO, average S% of 0.7 %, ranging from 0.4 to 1 % by month
- for HS FO, average S% of 1.87 %, ranging from 1.1 to 2.3 % by month
- RSV, average S% of 1.94 %, ranging from 0.9 to 2.7 % by month
- fuel gas (average S% of 0.05 %)

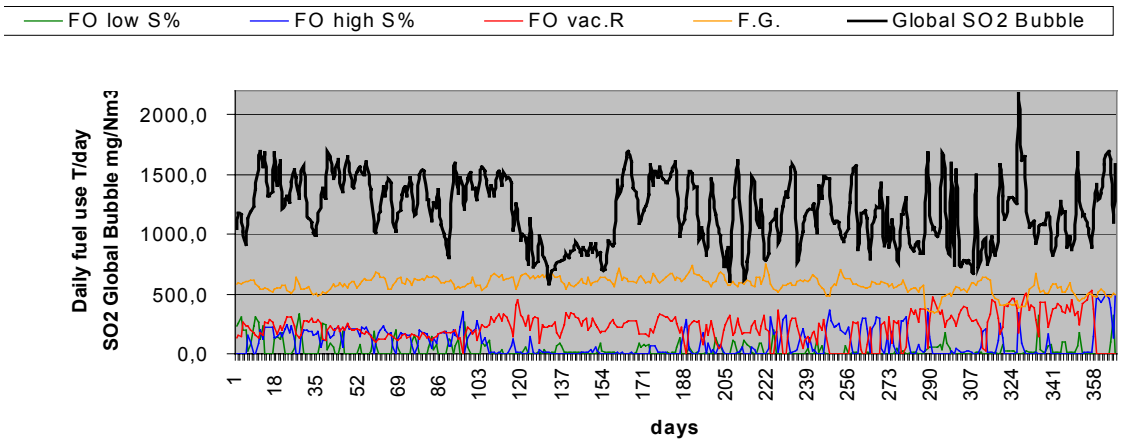


Figure 10.7: Daily SO_2 bubble variation and fuels breakdown – real refinery case (global annual average of 1200 mg/Nm^3)

Concawe SO_2 recommended figures

It is recommended, to consider yearly averaged value of the SO_2 bubble in order to maintain the flexibility of the process.

We would believe that very challenging global and annual bubbles for SO_2 in the future, based on local conditions and considering the SO_2 emissions of all the units, could range from 1000 to 1400 mg/Nm^3. This leaves flexibility to still respond to market constraints and opportunities on the crude oil, the supply/demand situation for oil products and to operate effectively in a very competitive environment. Individual refineries that have the local opportunity to burn gas only and still remain competitive can go to lower values than this.

In order to avoid any negative local impact on neighbouring communities, this daily variation can be locally controlled by alert procedures based on unfavourable weather forecast conditions, resulting in temporary specific operating constraints for the sites.

Achieved NO_x emissions levels

CONCAWE does not have survey data available on the NO_x emissions. These values are not only dependent on the fuels management but also from the operating conditions (excess air, temperature, etc.) and processes.

a) REAL NEW REFINERY CASE – Daily Variation of NO_x single stack ELV

As observed for an SO_2 bubble, similar large variations are observed on the short-term basis for single stack: the variation is very sensitive, even on a new built refinery, where feedstock is however not so varyiable.

Stack No	Unit	Equipment	max. heat perfor-mance (MW)	NO_x emission per year (mg/m^3) as NO_2			Range of NO_x emission as NO_2	
				daily limit	(average 1999)	(average 2000)	range daily values (mg/Nm^3)	range half-hour values
1A	Distillation (atm.)	Stack	130	100	56	44	35,5 - 98,7	10 - 130
1B	Distillation (vac.)	Stack	73	100	6	61	13,6 - 91,1	20 - 180
3A	Reformer	Stack	86	100	85	66	47,1 - 152,5	20 - 220
5	VGO	Stack	66,5	100	72	52	18,0 - 198,2	20 - 220
6	FCC	Regene-rator	-	500	89	53	20,3 - 250,2	70 - 420

Table 10.26: Real emissions and legal limits of a EU+ refinery
Source: [248, Ademe, 2001]

NO_x Recommended Figures

We would believe that NO_x annual bubble for a good performing existing refinery (mixed gas/liquid fired) could be 350 to 500 (based on low NO_x burners on fuel oil accounting for combustion air preheat). NO_x for a new refinery (gas fired) possibly 200 can be reached.

parameters	Ratio FO use	S content of FO	Combustion bubble	Global bubble
Base case	30 %	1.7 %	1000	1200
Scenario 1	30 %	1 %	590	*880*
Scenario 2	30 %	0.5 %	295	*650*
Scenario 3	100 %	1 %	1960	*1950*
Scenario 4	100 %	0.5 %	980	*1190*
Scenario 5 + FGD on all units	100 %	3 %	294	*650*
Scenario 6 + FGD on 75 % of emissions or major emitters	100 %	2 %	1130	*1300*
Scenario 7 + FGD on 75 % of emissions or majors emitters	100 %	1.7 %	960	*1170*
Scenario 8 + FGD on 50 % of emissions or majors emitters	100 %	1 %	*1030*	*1225*

Table 10.27: Variation of the Bubble Results from Use of Fuels with Varying Sulphur Content with and without FGD

10.6 Annex VI. Proposals from two Member States on the implementation of BAT in the refinery sector

Those are alternative text proposals given by the French delegation and the Italian delegation for some parts of chapter 5 related with the emissions of SO_2 and NO_x. The main conclusion, as it can be seen, is that the BAT sections on those two pollutants should be driven by the bubble concept. And consequently the BAT related with those pollutants should only be proposals for the achievement of those environmental goals.

10.6.1 French proposals for the structure of some parts of Chapter 5

GENERAL BAT. REDUCTION OF SO_2 EMISSIONS

The French delegation proposes reducing sulphur oxide emissions by the following steps:

1. Mass balance of sulphur, through the whole refinery, to identify the main sulphur streams (indicated in the graph in Figure 10.9 (see at the end of this Section)) and the overall percentage of sulphur recovered (OPSR) in an inert form or trapped in products in an inert form (OPSR: methodology tool used to appreciate the influence of a technical measure on the sulphur balance)

2. Quantification of the sulphur emissions of the different refinery sources being part of S2 and S4 in order to clarify the bubble concept and to identify the main emitters in each specific case,

3. Selection, among the different technical options indicated below (described more precisely in the specific BAT), the technical measures allowing to achieve the following global indicative reference values (bubble benchmark)

   600 mg/Nm^3 (Monthly average),
   850 mg/Nm^3 (Daily average),
   considering the possible cross-media (extra energy consumption, production of waste and water effluents, atmospheric emissions outside the refinery, increase of residue production, etc...) and the cost effectiveness.
   Possible technical measures which could be implemented to fulfill the global environmental goal include the following:

   - switch to gaseous fuels if no other reasonable option can guarantee a better evolution of the OPSR,
   - improvement of gaseous and liquid fuels and feeds characteristics,
   - use of flue gas desulphurisation promoting regenerative techniques or techniques leading to products which can be valorised and trapping sulphur in an inert form (This amount of sulphur has to be taken into account in the OPSR evaluation),
   - DeSOx catalyst for the FCC,
   - maximisation of the sulphur stream S6,
   - flaring optimisation,
   - treatment of non condensable gases from the vacuum ejectors

Due to the specific characteristics of the sulphur recovery units for flue gases, it is additionaly considered that BAT is also to apply the specific BAT defined for this type of unit (see Section 5.2.23).

The overall sulphur strategy should also lead to minimise S7 by increasing the conversion of products without specifications with processes like cokers, hydrocracking, gasification, etc…, by improving the characteristics of these products or by having an external use ensuring that the environmental impact is minimised (cement plants, conversion in another refinery for example). This kind of external use has also to be taken into account in the OPSR calculation.

GENERAL BAT. REDUCTION OF NO_X EMISSIONS

The NO_X BAT implementation process needs a prior quantification and characterisation of the emission sources. It follows, having in mind an environmental goal for the whole refinery (150 mg/Nm^3 (Monthly average), 200 mg/Nm^3 (Daily Average)), definition of the priorities to reduce the global emission level taking into account environmental benefits, cost effectiveness and cross-media effects.

Primary measures have generally the highest cost effectiveness but also limited performances especially for liquid fuels. These measures can easily be implemented for new units but may raise important integration problems with existing units. Given the limited cost of this type of measure its promotion may be encouraged where possible.

The limited performance of the primary measures makes necessary to consider secondary measures, whose cost effectiveness considerations are of great importance. Its implementation should be restricted to the main sources, e.g. those representing about 80% of the emissions of the whole refinery. Secondary measures includes three main abatement techniques: Reburning, SNCR (Selective non catalytic reduction) and SCR (Selective catalytic reduction) with a range of efficiencies (50 to 60%, 50 to 70 % and 80 to 90 %) and costs per tone of pollutant abated.

BAT can be considered an average abatement rate of 70 % for the sources representing 80% of the whole emission of a refinery. According to the principles described above, the combination of primary and secondary measures allows to reduce the global rough emission level of a refinery by 60-80 % and to achieve average emission levels in the range of 100-150 mg/Nm^3 on a long-term period.

Other techniques, such as catalytic combustion, or oxyfiring, may need also consideration and could represent relevant technical measures to achieve the global BAT emission level above-mentioned.

Other technical options have been implemented in some world areas to achieve lower emission levels. In a refinery in California there was a switch from liquid to gaseous fuels and implementation of secondary measures on gas fired units, achieving 20-30 mg/Nm^3. In Japan it has been applied hydrotreatment of liquid fuels and feeds combined with the implementation on an important number of SCR units, achieving 60-65 mg/Nm^3.

However, although this type of environmental goal may be locally justified, it is not considered that these experiences represent at the time of writing a general level of BAT in the EU framework because of the direct cost of these measures and the other investments required to manage the great amount of residues produced or to improve their characteristics.

CATALYTIC CRACKING NEW STRUCTURE

In most cases, the catalytic cracking is a source contributing to a large extend to the emission of SO_x, NO_x, dust, metals, CO and SO_2 of a refinery. Some measures on this specific unit may be considered fully justified from an environmental point of view in all cases but others have to evaluated in the global framework of the refinery. For this reason, this section has been splitted in specific BATs and technical options to consider in the global framework of the refinery.

The specific BATs include:

1. a CO-furnace boiler for partial oxidation conditions. The associated emission levels are less than 50 mg/Nm^3 for CO and between 100-300 mg/Nm^3 for NO_x (see Section 4.5.3),

2. a monitoring and control of the oxygen excess (around 2%) for the full combustion mode. The associated emission levels are between 50-100 mg/Nm^3 for CO and between 300 - 600 mg/Nm^3 for NO_x (see Section 4.5.1),

3. a reduction of particulates emission in the range 10 - 30 mg/Nm^3 (metals (Ni, V, etc...) less than 5 mg/Nm^3) by a suitable combination of the following techniques:

    - then BAT on particulate emissions
    - text BAT on energy conservation,
    - text BAT on reduce discharges to water,
    - text BAT on reduce waste generation,
    - a yearly monitoring of the N_2O emissions of the regenerator.

In addition, the FCC unit may be a major source of NO_x and SO_x. In this case, several technical options described below have to be considered and evaluated alone or in combination:

- the hydro-treatment of the feedstock (economical and technical viability are described in the Section 4.5.4). The main purpose of this technique is to reduce the sulphur content of the feed but this option has also a positive influence on NO_x, metals and on the product quality. Most units around the world (California for example) are designed to achieve 300 to 500 ppm in the feedstock,
- flue gas desulphurisation; depending on the process considered and the running conditions, the abatement rate may vary between 50 and 90 %. These techniques may produce large amounts of residues and water effluents,
- DeSOx catalyst. This technique may have a limited efficiency and involves an important consumption of catalyst. This option is probably more suitable to solve peak pollution problems,
- DeNOx measures such as SCR (abatement rate between 80-90%) and SNCR (abatement rate between 50 and 70 %) (these techniques have an associated emission of ammonia which can be limited to 10 mg/Nm^3 and it has to be pointed out that SCR is much more common for FCC units than SNCR) or modifications concerning the design of the unit which can induce a trade-off between NO_x and CO emissions.

These technical options allow thus to achieve ranges as low as 50 - 200 mg/Nm^3 for SO_x as SO_2 and 50 - 100 mg/Nm^3 for NO_x as NO_2. Their combination has to be optimised concerning performances in regard of the different parameters, energy consumption, waste and water effluents and cost effectiveness. They may not be justified in all refinery frameworks but have to be considered to fulfil the whole environmental goal of a refinery.

BAT PROCESS PER PROCESS ENERGY SYSTEM

The energy system is the main source of air pollution of a refinery, however, due to the diversity of the units used (boilers, furnaces, turbines), their characteristics (size, age, type of burners, purpose) and their running conditions (air preheat, fuels used, temperature requirements, oxygen excess and type of control), the strategy to reduce the environmental impact of these units can only be given by the general guidelines described below.

Firstly, it is necessary to have an overview of the fuels used by the refinery, types of combustion units, and characteristics of the air emissions (concentration and mass flow) for the main pollutants (SO_x, NO_x, dust, metals, carbone oxides).

On these bases, **the first step** is to consider technical options which seems totally justified from an economical point of view. This category includes specific BATs such as:

- the use of clean refinery gaseous fuels (H_2S content between 20 and 100 mg/Nm^3),
- the reduction of CO emissions below 50 mg/Nm^3 with efficient combustion techniques, the reduction of dust emissions in the range 10 - 20 mg/Nm^3 (metal content (Ni, V, etc...below 5 mg/Nm^3) applying the suitable following combination of techniques (improvement of fuel characteristics, steam atomisation for liquid fuels, ESP or bag filter),

- the use of primary DeNOx measures for new units, existing ones when these measures can be implemented quite easily and in the other cases during the major rebuilding of these units. The achievable emission levels with primary DeNOx techniques are the following: Gaseous fuels (30 to 100 mg/Nm^3 for boilers and heaters, 50 to 100 mg/Nm^3 at 15% O_2 for gas turbines - the lowest values are more likely achieved with natural gas and the highest with refinery fuel gas but a lot of other parameters may influence the performance level), liquid fuels (200 to 400 mg/Nm^3 for boilers and furnaces -the performance level is mainly influenced by the nitrogen content of the fuel even if other parameters need also to be considered).
- It is also considered in this category to (add Section 101).

The **second step** consists of analysing the relevancy of the following basket of techniques in the global framework of a refinery concerning NO_x and SO_x for the main sources (see SO_x and NO_x sections of the general BAT):

- improvement of liquid fuels and feeds characteristics,
- use of flue gas desulphurisation promoting regenerative techniques or techniques leading to products which can be valorised and trapping sulphur in an inert form,
- switch to gaseous fuels if no other reasonable option can guarantee a better evolution of the overall percentage of sulphur recovery (OPSR), of the amount of residue produced and of the SO_x, NO_x and dust abatement rates. It has to be reminded that gaseous fuels having a higher ratio H/C contribute to lower the SO_2 emissions,
- reburning (for boilers and furnaces), SNCR (Selective non catalytic reduction) and SCR (Selective catalytic reduction) with various efficiencies (50 to 60%, 50 to 70 % and 80 to 90 %) and costs per tone of pollutant avoided.

These last two techniques induce NH_3 emissions which can be kept below 10 mg/Nm^3. The application of these techniques or of a combination of these techniques may allow to achieve emission levels lower than 50 mg/Nm^3 for NO_x (as NO_2) and 100 mg/Nm^3 for SO_x (as SO_2) on any kind of the energy system sources, but the partial or complete implementation of these options on a specific unit has to be examined in the global framework of the refinery.

The technico-economical analysis may lead to select a less ambitious option concerning performances allowing nevertheless to achieve the global environmental target at the refinery level. On the contrary, better performances may be proposed through technical options like catalytic combustion for turbines (NO_x level lower than 2.5 ppm)

BAT FOR STORAGE

First proposal is to define an upper limit (volume and pressure) to store a liquid in another way than a pressurised tank designed to prevent any direct organic vapour loss to the atmosphere (connection to a vapour recovery unit with an efficiency of more than 95%). This limit could be 70 kPa concerning the pressure under storage conditions and 150 m^3 for the volume.

Then, a second limit (volume: 150 m^3 and pressure under storage conditions: 3.5 kPa) could be indicated concerning the following technical choices: pressurised tank designed to prevent any direct organic vapour loss to the atmosphere (connection to a vapour recovery unit with an efficiency of more than 95%) or external floating roof with two seals (one above the other) or for new fixed roof storages connection to a vapour recovery unit with an efficiency of more than 95% and for existing fixed roof storages installation of an internal floating- type cover with two seals or connection to a vapour recovery unit with an efficiency of more than 95%.

For storages non connected to a vapour recovery unit, BAT is also to paint the external walls and the roof with a material having a radiant heat reflection index of at least 70%. This BAT could apply to facilities that load organic liquids with a vapour pressure higher than 10500 Pa

under loading conditions. Continuous monitoring concerning the vapour recovery unit emissions should also be considered.

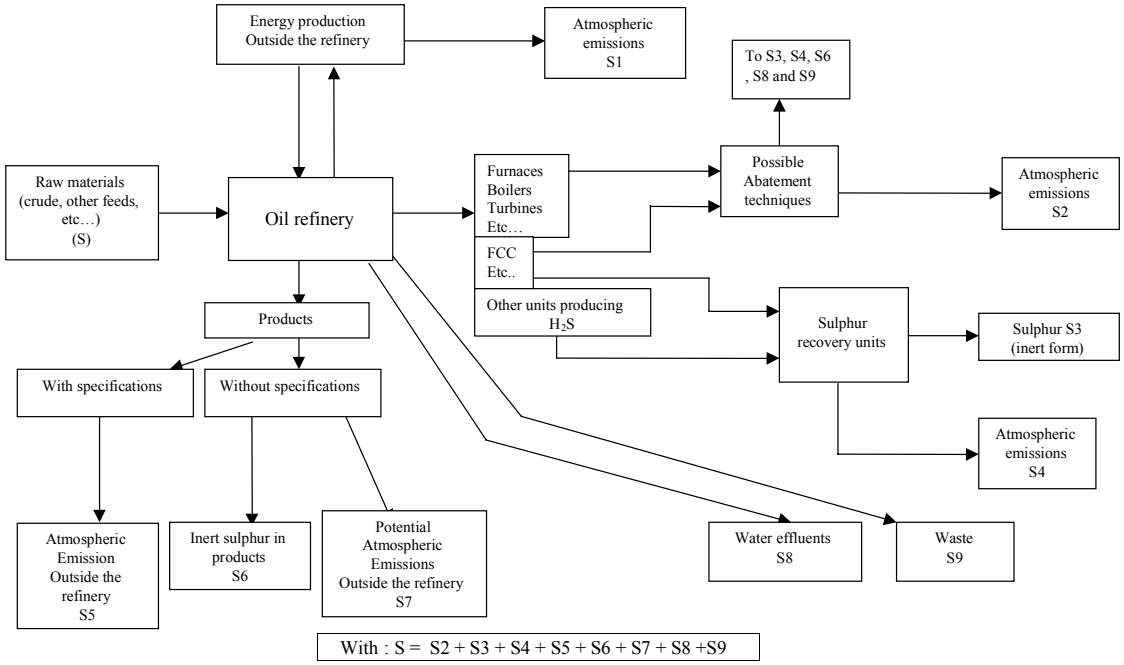


Figure 10.8: Global sulphur balance in a refinery

10.6.2 Italian proposals for the structure of some parts of Chapter 5.

BAT for the Energy System:

- Flue Gas Desulphurisation, SCR, SNCR, Electrostatic Precipitators should be considered only options that can be used to meet the bubble limits and not techniques that must be used in any case in conjunction with the high sulphur fuel oil.
- Providing that the bubble limits are respected, high sulphur fuel oil (3% max. sulphur content) can be used without any other limitation (FGD). High concentration emissions from one stack, can be balanced by low concentration emissions from other stacks. Possible health concerns for refinery workers should be considered at local level.