Integrated Pollution Prevention and Control (IPPC)

German notes on best available techniques in the Refinery Industry

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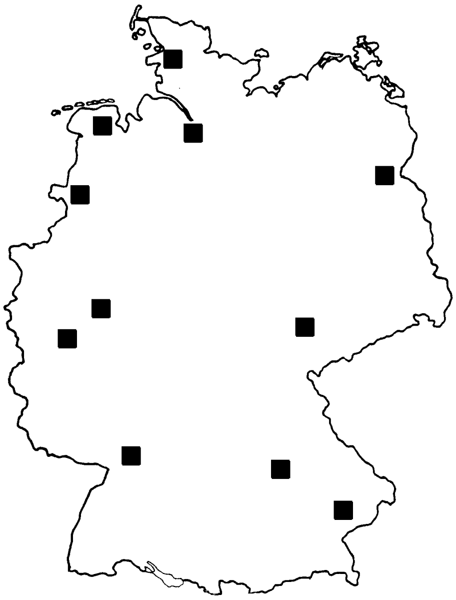
- The German Refinery Industry -



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Preface

In September 1996, the Council of the European Union issued the Directive 96/61/EG /E1/ for integrated prevention and control of pollution in the environment (IPPC, Integrated Pollution, Prevention and Control).

The Directive has, as its objective, the integrated prevention and control of environmental pollution resulting from industrial activities which are named in Annex 1 of the Directive. The refineries are also included in these activities.

A fundamental component of the Directive are the **Best Available Techniques (BAT)**, which are defined in Article 2.11 of the IPPC Directive as follows:

- ”best available techniques” designate 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 emissions in general, and their repercussions in the environment as a whole, or where that is not possible, to reduce and control them.
- ”techniques” mean the applied technology as well as the way in which the plant is designed, built, maintained, operated and decommissioned.
- ”available” refers to the techniques developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the cost/benefit ratio whether or not the techniques are used or developed within the Member State in question, as long as they are reasonably accessible to the operator.
- ”best” are the techniques which are most effective in achieving a high general level of conservation and protection of the environment as a whole.

This document deals mainly with the present plant techniques in German refineries which have proven themselves in reducing emissions.

The focus of this work is the collection of consumption and emission data from 5 representative German crude oil processing refineries and a lubricating oil refinery which concentrates mainly on functional units which were newly established or greatly modified, i. e. modernized in the last decade. As such the described plants are taken into consideration as the best available techniques.

This work restricts itself to the fundamental and manufacturing processes in the refineries. Processes which are not directly related to the production of mineral oil products such as, e. g. the manufacture of petrochemical products, are not included. This also applies to power stations.

Storage as well as loading and unloading mineral oil products in the refineries are considered although a BREF for the whole sector (horizontal) was made for the storage of dangerous substances. Because of the large quantities stored specific requirements which are not described in detail in the horizontal BREF are important for the storage of mineral oil products.

In contrast, cooling systems, for which a horizontal BREF also exists, are not part of the present work.

Further BREF's are important in connection with mineral oil refineries
- Treatment of waste water and waste gas
- Monitoring of emissions
- Large combustion installations

The distribution of mineral oil products, e. g. of fuels to service stations or the operation of pipelines are not considered.

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Synopsis

The best available techniques, as main results of the present study, are shown in Chapter 4 and 5.

In this chapter, the candidates BAT with a high environmental protection performance are summarized. Beside the most important individual measures, information about configuration of the plant in the context of BAT is given. It should be noted that the configuration of new plants can be adapted for integration of BAT. Because most refineries have grown over the past decades, fundamental changes in the structure of the refinery are not possible, especially because of economic reasons.
Refineries which meet the requirements of the BAT should have the following characteristics:

- The fuels in refinery furnaces and feedstocks in catalytic cracking plants, if possible, are low in sulphur or are desulphurized. For this purpose, suitable sulphur management is performed.
- The refinery has an adequate high capacity for hydrodesulphurization and, if necessary, is supplemented by a hydrocracker.
- The combustor in refinery furnaces correspond to state of the art with respect to primary emission reduction techniques.
- Secondary measures for air purification are taken during catalytic cracking and calcination. Beside the elimination of dust, denitrification and desulphurization are considered by correspondingly high loads.
- Optimized waste water management based on aimed recording of different loaded tributary waste water streams for effective treatment and maximal rate of re-utilization
- With respect to prevention and reduction of waste water generation and load, an optimal combination of process-integrated measures (e.g. regenerative gas scrubbing) as well as measures for waste water treatment in tributary waste water streams (e.g. sour water stripping) and in a waste water treatment plant with at least three stages
- Sulphur recovery with optimized effectiveness

1 General Information on the Mineral Oil Industry in Germany

1.1 Location and Capacity

At the present moment 14 crude oil processing refineries are operating in Germany. Their capacity was 110 million tonnes in 1998 which was extensively exploited. Germany therefore occupies the sixth position in the refinery capacity in the world /L40/.

The number of crude oil processing refineries in Germany decreased in the past years.

Table 1 shows an overview of the locations of the refineries in Germany together with the operating capacity of the atmospheric distillation, crude oil distillation, vacuum distillation and lubricating oil refining (Data from 1998, MWV /L41/).

Location	atmosph. dist. [in 10^3 t/a]	Vacuum distillation [in 10^3 t/a]	Lubricating oil-refining [in 10^3 t/a]
Wilhelmshaven	10.300	0	
Heide	4.000	1.600	
Wesseling (bei Köln)	6.000	2.800	
Godorf (Köln)	8.500	4.000	
Hamburg-Harburg	5.100	2.500	330
Burghausen	3.400	0	
Ingolstadt	5.000	1.690	
Hamburg	5.100	1.030	
Karlsruhe	14.000	7.200	
Gelsenkirchen	12.300	5.200	
Ingolstadt/Vohburg/Neustadt	12.000	4.410	
Lingen	3.800	1.900	
Spergau / Leuna	10.290	4.578	
Schwedt	10.500	5.500	
Lubricating oil refineries			
Hamburg Neuhof		740	230
Hamburg Grasbrook			250
Salzbergen		310	170

Table 1 Capacity of German refineries

The location of the crude oil processing refineries in Germany is depicted in the following map. The crude and the most important product pipelines are also shown.

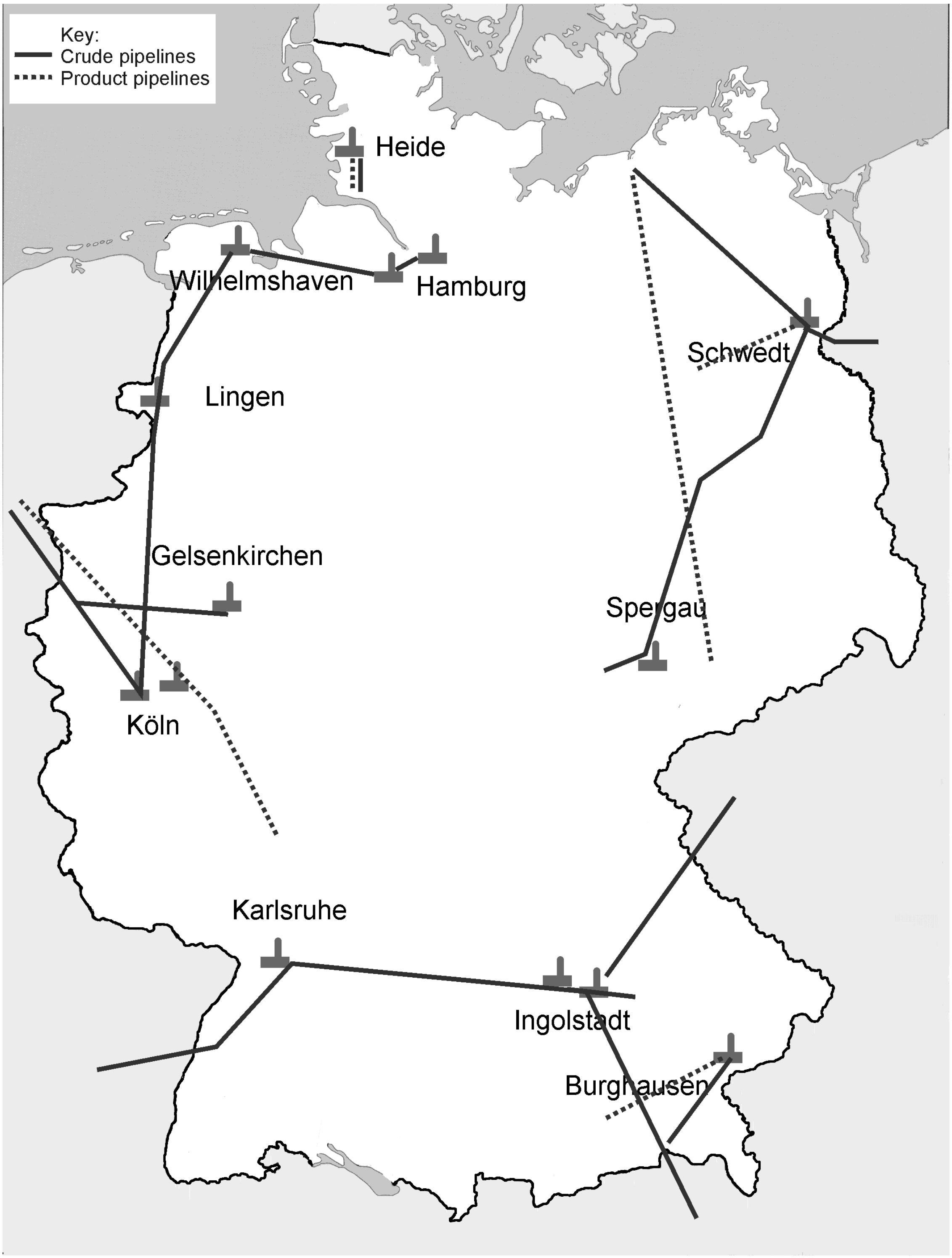

Figure 1 Location of refineries and pipelines in Germany

1.2 Legislative Regulations

Refineries are subjected to various legal regulations.

Besides the legal regulations, the Association for German Engineers (VDI) published Directives which are recognized as state of the art for the mineral oil industry.

- VDI 2440 Mineral oil refinery: Draft 07.99 /L32/
- VDI 3479 Marketing installation tank farm: Draft 2000 /L34/
- VDI 3454 Pages 1-3 Claus plants: 07.1989 /L33/

This document contains in Annexes 1 and 3 a comprehensive summary of the most important legal and technical regulations, standards and corresponding literature sources for the best available techniques. Literature sources with the grammalogue L are technical regulations, standards and miscellaneous literature (Annex 1), E represents Directives of the European Union and D stands for German Acts and Ordinances (Annex 3).

1.3 Economic Aspects

After rationalization measures in the eighties, the refineries in Germany are especially effective when compared on an international scale. Some of these refineries belong to the European leading group. Nevertheless, German refineries are in a difficult economic situation. This is illustrated by closure of the refineries in Wörth and Zeitz in 1995 as well as the consolidation of both refineries in Karlsruhe in 1996 and of two Bavarian refineries in 1997.
High transport, salary and energy costs, energy-political regulations and environmental-political requirements result in unsuitable conditions in German refineries as compared to competitive foreign refineries. In addition, the European-wide overcapacity in the refinery sector puts continuous pressure on the processing margins which German refineries cannot avoid on an international basis since imports for supply of the German market is essential and such supply pathways are also subjected to overproduction. Exploitation of the crude oil distillation capacity was high in 1997. The refineries in West Germany were completely employed to capacity whereas in East Germany more than 80% was achieved.

After the rationalization measures in the past years which was caused by high costs, approximately 50,000 jobs are directly or indirectly connected to refinery operations in Germany.

1.4 Environmental Account of the Refineries

The refinery industry is characterized by relatively few locations and a correspondingly high production capacity.

Compared to these capacities, the emissions nowadays are already reduced to a very low level via reduction measures according to state of the art. In 1990, the West German refineries contributed to 1.3% of the total SO_2 emission and 0.9% NO_x in Germany /L49/.
The main emission pathways from refineries are air, water and soil.

Typical emissions into the air can be:

- Sulphur oxide
- Nitrogen oxide
- Hydrocarbons (VOC)
- Special organic compounds (benzene)
- Dust and particle components

Typical emissions into water can be:

- Hydrocarbons
- special organic compounds (phenols)
- Nitrogenous compounds (inorganic, organic)
- Sulphur compounds (mercaptan, hydrogen sulphide)
- Special inorganic compounds (cyanide, in individual cases nickel)

In addition to the emissions from substances emissions from noise are also important. The determination of noise emissions depends largely on the specific location. They are especially very expensive if existing plants must be improved.
Waste is not an important factor in refineries. With respect to the quantity of products the amount of waste, especially the amount of non-usable waste, is relatively small.

1.5 Emission limit values

1.5.1 Air limit values

The emission limit values for operating plants in refineries are based on the TA Luft /D8/ incl. the Dynamierungsklauseln /D8a/ and the 13. BImSchV /D5/ including the UMK Beschlusses 1984 /D30/. Maintenance of these limit values must be monitored via continuously operating measuring instruments if fixed hourly loads or fixed heat production in refinery furnaces are exceeded.

The VDI Directive 2440 (Draft) /L32/ contains a detailed list of limit values for furnaces and different processing plants. As an example, table 2 shows the limit values for refinery furnaces with gas furnace (refinery gas if necessary substituted by natural gas) for different heat production.

Bubble concept
The "Bubble Concepts" for limiting emissions were introduced firstly in the USA /L1/ but are also applied today to some locations in Germany. The detailed stipulations are dependent on the location but always lead to low emissions in contrast to full exploitation of the limit values if these were single plants. For example, the following regulation is practiced:

Different plants are combined to form a bubble. Within the bubble, each plant can exploit the SO_2 -limit from 1700 mg/m³ as half-hourly mean or daily mean. The annual mean of all plants of the bubble may not exceed 680 mg/m³.

Air pollutant	**Reqirements under ambient pollution law (1/2-h means)**	**Remarks**
Dust emissions	5 mg/m^3	
Carbon monoxide	100 mg/m^3	
Nitrogen oxide, given as Nitrogen dioxide		
a) < 100 MW	200 mg/m^3	1)
b) 100 to 300 MW	200 mg/m^3	2)
c) > 300 MW	100 mg/m^3	2)3)
Sulphur oxide, given as Sulphur dioxide		
a) Liquefied petroleum gas	5 mg/m^3	
b) Refinery gas: < 100-MW-Plant	100 mg/m^3	
c) Refinery gas: ≥ 100-MW-Plant	35 mg/m^3	4)

1) The possibilities to further reduce emissions via furnace technical or other suitable measures according to state of the art are exploited /D8a/
2) In process refinery furnaces secondary measures are not tested
3) maintained in new plants, in renovated plants only 200 mg/m^3 can be maintained
4) Exceptions according to § 33 of the 13. BImSchV /D5/ are fundamentally possible

Table 2 Emission limits for refinery furnaces

1.5.2 Discharge limits for water pollutants

According to the regulations of the federal water act /D10/, the pollutant load of waste water is to be maintained as low as possible via methods according to state of the art. The necessary requirements to be considered are fixed in Annex 45 in the waste water ordinance /D13/. Table 3 shows an overview. The requirements of the parameter COD, BOD_5, $N_{tot,inorg.}$, P_{tot} and hydrocarbons apply to the discharge to surface waters, the other requirements are to be considered before mixing with waste water of a different origin (e.g. sanitary water). For waste water from dewaxing, an additional requirement of 0,5 mg/l for AOX in tributary waste water stream applies. Additional to the concentration limits listed, each pollutant's discharge freight may be limited on the basis of specific waste water production of 0,5m^3/t feedstock. For the manufacture of lubricating oil, a specific waste water volume of 1,3 m^3/t feedstock is fixed. The regulations for sampling, preparation and analysis which are to be applied for monitoring the maintenance of these requirements are defined in the waste water ordinance /D13/ (Annex "Analyse- und Messverfahren").

Pollutant	Qualified random sample or 2-hour-composite sample (mg/l)
Chemical Oxygen Demand (COD)	80 1)
5 Days Biochemical Oxygen Demand (BOD$_5$)	25
Nitrogen, total, as sum of Ammonia-, Nitrite and Nitrate Nitrogen (N$_{tot.}$)	40 2)
total Phosphorous,	1,5
total Hydrocarbons	2
Phenol index after Distillation and Dye extraction	0,15
Adsorbable organic halogens (AOX)	0,1 3)
Sulphide- and Mercaptan-Sulphur	0,6
Cyanide, readily released	0,1 3)

1) A higher concentration till maximal 100 mg/l can be authorized if the decrease in the COD load in the central waste water treatment plant is at least 80 % of oil separator effluent freight
2) A higher concentration till maximal 100 mg/l can be authorized if the decrease in the nitrogen load (given as TN$_{b)}$ in the central waste water treatment plant is at least 75 % of oil separator effluent freight
3) Random sample

Table 3 Emission limits for water pollutants

In the following section, the effect of pollutants on surface water is shortly commented /L13a/:

COD The chemical oxygen demand is a measure for the chemical oxidizing demand of contents. The COD is limited because, as governing parameter, it allows the determination of the degrading capacity of waste water treatment plants. With the COD, the low degradable organic substances are also included.

BOD$_5$ In the case of the biochemical oxygen demand, the biologically degradable organic content present in waste water is included. The BOD$_5$ is a suitable governing parameter for determining the biological purification capability. It is a measure for the expected oxygen uptake of substances introduced into waters.

Nitrogen (N$_{tot}$) (as sum of ammonia, nitrite and nitrate nitrogen) promotes, as a nutrient, the growth of algae and can become, besides phosphorous, a limiting factor for eutrophication.

Phosphorous; total (P$_{tot}$) promotes, as a nutrient, the growth of algae. It is a limiting factor for eutrophication in many waters.

Hydrocarbons; total are typical contents of waste waters from refineries. They occur in a dissolved, emulgated or in an undissolved form and can affect the waste water characteristic in different ways.

Phenols (phenol index after distillation and dye extraction) are typical contents of waste water from crude oil refineries. They are strongly toxic to aquatic organisms.

AOX Adsorbable organic-bounded halogen compounds (AOX) can, as governing parameter, include compounds which are toxic to aquatic organisms and are difficult to degrade biologically.

Sulphide and **Mercaptans** are typical contents of waste water from refineries. They are very toxic and extraordinary odour intensive.

Cyanides readily released occur in process waste water from crude oil processing (e.g. catalytic cracking, coking). They are very toxic.

Other Parameter Because of local conditions, often other parameters such as temperature and pH-value are limited. Furthermore, also certain heavy metals as well as toxicity to fish are limited.

2 Applied technical processes and methods

2.1 Feedstocks and products

2.1.1 Feedstocks

The main feedstock of a refinery is crude oil. It should be taken into consideration that different crude grades have a different composition since these differences can be relevant in relation to emissions into the air or water. In addition to the main components hydrocarbons, petroleum contains, according to origin, different quantities of sulphur, nitrogen and oxygen as well as traces of other elements such as vanadium, nickel and sodium.

Crude oil contains almost only hydrocarbons. The following basic types are differentiated:

- Alkanes (or Paraffins)
- Naphthene (or Cycloalkane)
- Aromatics(substituted or condensed)
- Heterosubstituted hydrocarbons (containing nitrogen, sulphur and oxygen)

The mineral oil in Germany originates from three sources:

- National crude oil (mainly from Niedersachen and Schleswig-Holstein)
- Imported crude oil
- imported mineral oil products

The German crude oil demand is met mainly by importing from countries of the former Soviet Union and the North Sea. Imports from OPEC countries contribute approximately 29% while the local crude oil contributes only a few percent.

Besides the feedstock petroleum a number of auxiliary substances are used in a refinery. Details concerning auxiliary substances are contained in Chapter 3.

2.1.2 Products

Table 4 contains the most important products of a refinery which can be produced in varying quantities according to crude oil and the configuration of the refinery. Information about manufacture and internal utilization are contained in Section 2.2.

Propane	Butane
Propylene, Butylene	Crude gasoline (Naphtha) for the petrochemical industry
Premium gasoline	Regular gasoline
Reformed gasoline and aromatics for the petrochemical industry	Diesel
Extra light heating oil	Jet fuels
Sulphur	Heavy heating oil
Lubricating oils	Paraffin
Bitumen	Petroleum cokes

Table 4 Refinery products

2.2 Production processes and Functional units

The production processes or functional units of a refinery are differentiated as follows

1) Refinery furnaces
2) Separation methods
3) Conversion methods
4) Refining methods
5) Tank farm processes
6) Other methods

The processes are briefly described in the following sections. The list corresponds extensively to the content of the VDI guideline 2440 /L32/. In this guideline, simplified diagrams of processes are shown.

2.2.1 Refinery furnaces

Plant components in refineries in which endothermic conversion processes are carried out or feedstocks must be warmed to a high temperature are heated with refinery furnaces. Furthermore, refinery furnaces are used to produce steam and electricity. Refinery furnaces contribute largely to the emissions from a refinery into the air. Hence, they play an important role in the determination of the best available techniques. As fuel, mostly desulphurized refinery gas, in certain cases natural gas and liquid conversion residuals from own processing (gas, oil and mixed furnaces) are used. In a refinery approximately 5-6 % of the throughput is used as fuels. The sulphur dioxide emissions of refinery furnaces depend directly on the sulphur content of the fuel.The flue gases from refinery furnaces are discharged via stacks. The height of the stack depends on the mass flow of the emission and the local geographic conditions. It is determined according to the regulations of the TA Luft.

2.2.2 Separation methods

2.2.2.1 Atmospheric Distillation

After prior desalting, processing starts with the heating of the crude oil to a temperature of about 370°C for distillation at atmospheric pressure or slight overpressure up to 3 bars. The fractionation of the crude oil in accordance with the boiling points of its constituents can be carried out in a single or multistage operation. The residue from this distillation can serve as an end product and in this case is termed heavy fuel oil.

The vapour/gas mixture leaving the top of the atmospheric column ("overhead product") separates after cooling into a gas fraction; a gasoline cut and an aqueous condensate, most of which results from the steam added to facilitate distillation. This condensate and the gaseous portion, which mainly consists of low-boiling hydrocarbons (methane, ethane etc.), contain hydrogen sulphide and mercaptans. In the aqueous condensate these substances are either dissolved or chemically bound; in the latter case they are mostly bound to alkaline substances (ammonia) added during atmospheric distillation to prevent corrosion.

The naphtha cut produced as an overhead product also contains dissolved hydrogen sulphide and mercaptans.

The gasoline, kerosene and gas oil fractions drawn off from the side of the column (sidestreams) are practically free of gases. All the fractions usually undergo further treatment.

2.2.2.2 Vacuum Distillation

If further fractional distillation of the higher-boiling crude oil components is required, this has to be effected at reduced pressure to achieve the necessary lower temperatures. The vacuum required to lower the boiling points of the hydrocarbons (up to approx. 10 hPa) can be generated in various ways. Steam jet pumps and vacuum pumps are used in most cases.

The temperature of about 400°C is barely exceeded during vacuum distillation because some of the hydrocarbons start to crack even at this temperature. The consequence of this is not only a reduction in the quality of the distillates but also processing difficulties. However, since cracking cannot be fully prevented even during gentle distillation, the waste gases from vacuum distillation usually have a characteristic unpleasant odour, which is attributable to the presence of olefins, and of sulphur and oxygen compounds.

The waste waters from vacuum distillation, which consist of the steam added to the column and the jet steam of the jet pumps, contain varying quantities of odorous gas depending on the pressure, temperature and, composition of the gas phase.

The distillate fraction generated as the overhead product of vacuum distillation may still contain dissolved gases (e.g. hydrogen sulphide) and is then treated appropriately. The remaining fractions (vacuum gas oils as the feedstock for catalytic cracking or the production of lubricating oil) may contain sulphurous compounds resulting from the processed crude oil although they are virtually free of hydrogen sulphide. The same applies to the vacuum residue, which is either used directly as bitumen or, by itself or blended with distillates, as fuel oil. Finally, if appropriate crude oils are used, the vacuum residue can serve as feedstock for the cracker or for the production of blown bitumen or petroleum coke.

2.2.2.3 Gas Separation

After gas scrubbing, the typical refinery gases containing hydrogen sulphide and the low-boiling hydrocarbons are further treated in a gas separating plant working at elevated pressure. The way in which the hydrocarbon mixture is separated depends on the nature of the desired products. It is assumed that, in addition to the naphtha fraction (pentane and higher-boiling hydrocarbons), butane and propane are to be separated individually from the gas. The remaining dry gas, consisting essentially of ethane and methane, is used as refinery fuel gas.

2.2.3 Conversion processes

2.2.3.1 Thermal cracking (visbreaking)

At temperatures of over 370°C, this process converts heavier, higher-boiling fractions (gas oil fractions and residues from atmospheric and vacuum distillation) into less viscous, lower-boiling products.

The gases generated by this process contain not only hydrogen but also saturated and unsaturated hydrocarbons as well as hydrogen sulphide, mercaptans and other odorous products of cracking. The aqueous condensate from this process also contains these substances in accordance with their degree of solubility.

Thermal cracking today is mainly applied in the mild form of visbreaking and in the vigorous form of coking. Furthermore, other methods for thermal processing of residues are available.

The distillates produced in this process (gasoline, gas oil) are always subjected to secondary treatment because of the unsaturated hydrocarbons they contain.

2.2.3.2 Petroleum coke production (delayed coking) and calcination

Residues from atmospheric and possibly also from vacuum distillation are heated in a refinery furnace to temperatures of over 490°C. The energy input in the furnaces is sufficient to induce cracking in the coking chamber. The distillates from the coking chamber (gases, gasolines, middle distillates and a heavy gas oil) are fed to a fractionating tower, separated, and supplied to secondary treatment for stabilization. Added to the feedstock, part or all of the residue is returned to the cracking process. The plant has two or more coking chambers. If one is filled with coke, the vapours are passed through the empty chamber. The chamber filled with coke is stripped, with most of the volatile hydrocarbons being expelled and cooled with water.

The petroleum coke ("green coke") is cut with water jets, before undergoing further treatment (crushing, classification, calcination) or for immediate use.

The cutting water is reused after separation of the coke particles. The stripping and cooling of the petroleum coke gives rise to gases and condensates which are returned to the process as well as waste water which has to be regenerated.

The hydrocarbons still contained in the petroleum coke are burnt at temperatures of up to 1400°C in the presence of air in rotary kilns or multiple-hearth furnaces (calcination).

The calcined coke is cooled and stored in silos until it is shipped for further use.

2.2.3.3 Fluid catalytic cracking (FCC)

In the presence of catalysts; the thermal cracking process can be specifically influenced to increase the yield of gasoline or middle distillate. These catalysts consist of aluminium silicates (zeolites) doped with rare earths (e.g. cerium, lanthanum). The catalytic cracking widespread today uses a fluidized-bed process. The catalyst in powder form circulates continuously in the plant and is kept in a quasi-fluid state in the reactor by steam, by the treated hydrocarbons themselves, and by air in the regenerator.

The feedstock (vacuum gas oils and possibly residue portions as well) is preheated and enters the reactor together with the hot regenerated catalyst via a riser. In the reactor, after the cracking process, the hydrocarbon vapours are separated from the catalyst by the addition of steam. Heavy metals in the feedstock act as catalyst poisons. The catalyst then flows into the regenerator for incinerating the coke deposited during cracking. Depending on the feedstock and the processing conditions, the waste gases contain catalyst fines, sulphur dioxide as well as carbon monoxide and nitrogen oxides. The sulphur dioxide content depends on the sulphur content of the feedstock. The carbon monoxide is burnt for heat recovery in a waste heat boiler (CO boiler) to form carbon dioxide, and the waste gas is then discharged via a stack.

The hydrocarbon vapours emerging from the reactor are conveyed together with water vapour to the fractionating tower. The overhead product fraction consists of gases, gasoline and aqueous condensate. Before further processing, the gases are compressed.

Besides hydrogen sulphide, all the products of the overhead product fraction contain odorous sulphur and oxygen compounds, including phenols in the aqueous condensate. The sidestreams can be returned to the feedstock or used as blending components. The bottom product (residue oil) is separated into two components, the catalyst-bearing component being returned to the feedstock. After treatment in a gas scrubber, the hydrogen sulphide generated with the cracker gases is fed to a Claus plant.

2.2.3.4 Hydrocracking

With the aid of hydrocracking, the product yield in the light and middle distillate boiling range is higher than that achieved with the cracking processes.

This process makes use of a hydrogen atmosphere in order to generate predominantly saturated hydrocarbons.

This process makes use of catalysts at temperatures between 350°C and 450°C and pressures of 100 to 200 bars.

The catalysts consist of metal components such as nickel (Ni), chromium (Cr), palladium (Pd) or tungsten (W) on a carrier, which may consist of aluminium oxide or special aluminium silicates.

A further development of the coal hydrogenation process facilitates almost total conversion, even of heavy distillation residues, at pressures of 250 to 350 bars.

The feedstock (e.g. vacuum gas oil) is mixed with residues from the fractionating tower and heated together with a circulating gas containing hydrogen. The mixture is passed, over catalysts where it is cracked and reacts with hydrogen. At the same time, compounds containing sulphur and nitrogen break down to release hydrogen sulphide and ammonia, similarly to the reactions taking place during hydrodesulphurisation.

After leaving the reactor, the mixture is cooled, washed with water, and separated in a high-pressure stage into liquid and gaseous phases. Hydrogen sulphide is removed from the gas phase, e.g. by washing with amines, and recycled. The liquid hydrocarbons are expanded at a low-pressure separator and then separated by distillation. The gas generated in the low-pressure expansion stage is scrubbed to remove the hydrogen sulphide and ammonia and then separated into fuel gas and liquefied petroleum gas (LPG).

The scrubbing water from the high-pressure stage contains ammonia sulphides and is fed to a waste water regeneration plant.

The hydrogen sulphide generated with the fuel gas is supplied to a Claus plant.

2.2.3.5 Production of blown bitumen

Some of the immediate residues from vacuum distillation (bitumen) are subjected to secondary treatment in the form of air blowing in a separate plant and, in some cases, with the addition of flux oil.

Various product characteristics of the blown bitumen are predetermined by partial oxidation at elevated temperatures (up to about 300^{o}C). This gives rise to blow gas and a condensate which are separated into an aqueous (sour water) and an oily phase. The blow gas and condensate contain hydrogen sulphide and other odorous compounds.

The oily phase is recirculated to the crude oil feedstock whilst the blow gas is generally incinerated in refinery furnaces.

2.2.3.6 Reforming

By reforming, a gasoline with a low anti-knock rating (octane number) is converted into a. reformed gasoline with a high anti-knock rating which is required for the production of motor vehicle gasolines. The gasoline hydrocarbons are subjected to isomerization, ring formation and aromatization, giving rise to large quantities of hydrogen. The reformate contains a considerable portion of light aromatics, including benzene.

Nowadays, catalytic processes are exclusively employed, which generally operate with multi-metal catalysts (mostly platinum and rhenium on aluminium oxide).

At temperatures of about 500°C and pressures between 5 and 15 bar, the feedstock is passed over the catalyst, where reactions take place at a relatively high partial pressure of hydrogen.

The reformers are preceded by hydrodesulphurization because the catalysts are susceptible to damage by sulphurous compounds and, to a lesser extent, by compounds containing oxygen or nitrogen.

The hydrogen arising during aromatization and the gaseous hydrocarbons arising from secondary reactions are continuously removed from the process. The gas mixture consisting primarily of hydrogen is the source of hydrogen for desulphurization in the refinery.

Depending on the catalyst type, plant and process conditions, the catalysts, whose activity is diminished by coke deposits, are regenerated by controlled burn off at temperatures between 400°C and 480°C. During the regeneration of discontinuous reformers, heated nitrogen is circulated over the reactors. When the reactor bed temperature reaches about 400^{o}C, a defined, constantly controlled quantity of air is added to the nitrogen and a corresponding quantity of circulated gas is released into the atmosphere. The released mixture consists of carbon monoxide, carbon dioxide and nitrogen. Release can be effected continuously or discontinuously, depending on the type of process.

2.2.3.7 Isomerization

This process is used for the production of gasoline components with a high anti-knock rating. Isomerization is generally carried out with the aid of a catalyst (usually platinum on aluminium oxide) at about 30 bar and temperatures of 150°C to 220°C in a hydrogen atmosphere. In this process, n-pentane and n-hexane are usually converted into their isomers. The spent catalyst is replaced. The platinum is recovered.

2.2.3.8 Production of MTBE

MTBE (methyl tertiary butyl ether) is a high-octane gasoline-blending component and is produced catalytically from methanol and isobutylene. The reaction takes place in mild conditions (approx. 80^{o}C) on an ion exchanger resin, e.g. polystyrene divinylbenzene copolymer, in the liquid phase. During downstream fractionating, the MTBE is separated from its coreactants and accompanying components. The process takes place without generating off gas. After relatively long periods of service, the catalyst becomes deactivated and must be replaced and disposed of.

2.2.3.9 Alkylation

During alkylation, unsaturated C_3 and C_4 hydrocarbons (propene and butenes) are dimerized on acid catalysts (hydrofluoric acid or sulphuric acid) to form a high-octane fuel component.

Conversion takes place at temperatures between 35°C and 39°C and at an overpressure of approximately 14 bars. Depending on the pretreatment of the feedstock, it may be accompanied by lighter hydrocarbons and hydrogen yielded at the head of the separation column for the product and unconverted components. This gas is scrubbed with an alkaline solution before leaving the plant.

2.2.4 Refining methods

2.2.4.1 Hydrodesulphurization

To remove sulphurous compounds from mineral oil fractions, the hydrogen generated in the reforming process is employed. During this process, the mineral oil fractions undergoing desulphurization are passed over a catalyst (cobalt-molybdenum, nickel-molybdenum on aluminium oxide) at a hydrogen pressure of 30 to 100 bars and at temperatures of 350°C to 400°C. The organic sulphur compounds are converted into sulphur-free hydrocarbons and hydrogen sulphide.

The hydrogen sulphide dissolved in the liquid products is expelled either by fractional distillation of the reaction product or by stripping. It arises either as a gas or in an aqueous condensate.

Depending on the design of the plant and the sulphur content of the feedstock, the dry gas leaving the plant may contain 20% v/v hydrogen sulphide. This gas is scrubbed.

The spent catalyst can either be replaced or regenerated. A catalyst can be regenerated with the aid of a mixture of superheated water vapour and air. The resultant gas mixture contains odorous components.

2.2.4.2 Mercaptan conversion (sweetening)

To convert odorous mercaptans into barely perceptible disulphides, light cracker components from the catalytic cracking plant are subjected to catalytic oxidation. The liquid catalyst (cobalt phthalocyanine) is brought into contact with caustic soda solution and the product in the presence of air. The waste gas is incinerated.

2.2.4.3 Gas scrubbing

Gases containing hydrogen sulphide are scrubbed with regenerable scrubbing solutions to remove the hydrogen sulphide.

As a rule, alkanolamines such as diethanolamine or diisopropanolamine are used as the absorbent. The scrubbing solutions charged with hydrogen sulphide are usually regenerated (desorbed) by heating, in the course of which the hydrogen sulphide is expelled and the scrubbing solution is returned to the process. The hydrogen sulphide is supplied to the Claus plant. Smaller quantities of gas or gases with a low H_2S content can be freed of hydrogen sulphide by scrubbing with an alkaline solution, for example.

2.2.4.4 Extraction

Solvent extraction Extraction processes with solvents are employed above all to extract aromatics of high purity from hydrocarbon mixtures containing aromatics, such as pyrolysis or reformed gasoline. The aromatics are extracted from the feedstock with the aid of a selective solvent. After this, the solvent/aromatics mixture is separated by distillation. The solvents employed are substances with high solvency for aromatics, have a significantly higher boiling point than the extracted aromatics, and are miscible with water.

The feedstock is fed through the extractor. The solvent in countercurrent extracts the aromatics. The entrained non-aromatics are separated from the solvent/extract mixture in an extract reflux column and returned to the extractor. In the solvent stripper, the extract is then separated by distillation from the solvent, which is recirculated to the extractor. The raffinate saturated with solvent passes through a water scrubbing plant in which the aqueous condensate of the solvent stripper is employed. The run-off from water scrubbing and the aqueous condensate from the extract reflux column are reclaimed in the solvent stripper. The end products are an aromatic extract of high purity and a low-aromatics raffinate.

Molecular sieve extraction This extraction method makes use of the specific adsorption properties of artificial zeolites known as molecular sieves. Molecular sieves are employed in the mineral oil industry to remove carbon dioxide, water, hydrogen sulphide, mercaptans, etc. from gases and liquids, and amongst other things to recover normal paraffins from mixtures of naphthenes, isoparaffins and aromatics or to recover p-xylene from xylene mixtures. The processes take place in the gas or liquid phase. According to the requirements of the specific process, desorption is mostly effected by reducing the pressure, increasing the temperature and/or the use of displacement media.

When, in plants operating at relatively high temperatures (up to 400°C), the adsorbency of the molecular sieves drops below an acceptab1e level due to coke deposits, the sieves can be regenerated in much the same way as reformer catalysts.

The plants consist of two or more adsorbers for alternating operation, or else of a single adsorber divided into sections which permits quasi-continuous operation with the constant alternation of the inlets and outlets of these sections. The charging time of adsorbers working on the alternating principle varies greatly, ranging from several weeks in some cases to as little as only a few minutes.

2.2.4.5 Lubricating oil production

The production of the various product categories in the lubricating oil sector (motor oils, transformer oils, white oils, etc.) demands the application of special process techniques suitable for the feed product and the intended application.

Vacuum distillates are processed with the following methods:

- Extraction
- Paraffin removal (dewaxing)
- Hydrogen treatment

During extraction, which is carried out on the principle described in 2.2.4.4, aromatic and heterocyclic compounds are removed from the feedstock with furfural, n-methylpyrrolidone or other selective solvents. The aromatic-rich extract is subjected to catalytic cracking or other processes and the paraffin contained in the raffinate is removed.

During paraffin removal, the feedstock is diluted with mixtures of methylene chloride/1,2-dichloroethane or methyl ethyl ketone/toluene and cooled. The crystallizing paraffins are filtered off and further processed, whilst the filtrate is a base oil resistant to low temperatures.

In the above processes, the solvents are regenerated and recirculated.

Hydrogen treatment for the final refining of base oils gives rise to residual gases and aqueous condensates which, depending on the nature of the feedstock and the intensity of treatment, contain varying quantities of hydrogen sulphide. Flue gases containing hydrogen sulphide are incinerated, as a rule, or are fed to the process furnace. This is basically a form of hydrodesulphurization, as described in 2.2.4.1, and in certain circumstances the hydrogenation of the remaining aromatic compounds in order to produce white oils. Given certain pressure and temperature levels, this process can replace the removal of aromatics by extraction.

Filtration with bleaching clay is used for the secondary treatment of special oils. The resultant "oil clay" is usually employed outside the refinery sector, e.g. in the production of cement.

2.2.5 Tank farm processes

2.2.5.1 Product supply

Crude oil is supplied either via long-distance pipelines or tankers. Mineral oil products are normally supplied by rail tankers, tanker ships or road tankers. Small quantities of auxiliary substances are also supplied in containers.

2.2.5.2 Loading and unloading

Withdrawal of crude oil and mineral oil products from the transport vessel is performed mostly via pipes and detachable hose connections using pumps.

Loading of mineral oil products generally occurs in ships, tank cars or tank lorries. Some refineries transport products using product pipelines (cf. Diagram 1).

2.2.5.3 Storage tanks

Storage of crude oil and liquid mineral oil products is normally done in above-ground tanks up to a size of approximately 100 000m³. The following technical variants with different concepts for reducing emissions are used:

- Fixed-roof tanks with coatings and/or overpressure/underpressure safety-valves
- Floating-roof tanks
- Fixed-roof tanks with floating covers
- Fixed-roof tanks connected to a gas collecting system

Liquefied petroleum gases are stored either aboveground in round vessels or in underground or also semi-underground tanks. Vessel sizes of up to 1500m³ are typical.

Bitumen is stored in heated fixed-roof tanks . The highly smelling tank flue gas is generally incinerated.

Petroleum coke is stored either in open spaces or in silos. When stored in open spaces petroleum coke is kept moist in order to minimize dust emissions.

Sulphur in a liquid state is stored in heated and heat-insulated fixed-roof tanks.

2.2.6 Other Processes

2.2.6.1 Sulphur recovery units

From the hydrogen sulphide produced in different functional units of the refinery elemental sulphur is produced in the sulphur recovery unit. Hydrogen sulphide is combusted with air to form sulphur dioxide (SO_2). In the Claus plants, only a partial combustion occurs in the oven whereby from three parts H_2S only one is turned to SO_2. The mixture produced from two parts H_2S and one part SO_2 already react in the oven but moreso in the reactor on the catalyst according to the equation

$$2\,H_2S \quad + \quad SO_2 \quad \rightarrow \quad 3\,S \quad + \quad 2\,H_2O$$

to sulphur and water. The sulphur precipitates in a liquid form and is recovered in a sulphur pit. Many consecutive connected reactors enable an almost complete run of the reaction. Subsequently, either a thermal or catalytic combustion occurs. The released energy from this reaction is used to produce steam. Besides the "classical" Claus process other methods for reduction of sulphur are used in the Claus plants in German refineries:

- Scot Process /L2/: Sulphur compounds in the flue gas from Claus plants are hydrated catalytically to hydrogen sulphide. The hydrogen sulphide is returned to the Claus process via regenerative amine scrubbing.
- Sulfreen Process /L3/: Variations of the Claus reaction; the rate of sulphur emission is reduced in a further catalytic stage.
- Wellmann-Lord Method /L3/: If a corresponding installation for the power plant is available, the flue gases from the Claus process can be included.

In lubricating oil refineries, no Claus plants are installed because, in contrast to crude oil processing refineries, a lot less sulphur is generated. H_2S-containing flue gases from waste water treatment is fed to an incinerator.

2.2.6.2 Flares

Flares are important safety facilities in a refinery since they prevent emissions from dangerous substances via pressure release valves directly into the environment.

One differentiates between elevated flares and ground flares. In order to decrease emissions from flares, flare gas collecting systems are installed which act as a buffer and after recompression can direct the flare gas into the refinery gas system. In this way, emissions via flares are minimized.

Flares are operated under steam. Control of the steam is an important factor which enables an extensive soot-free burning of the flare gases.

Flare heads with possibly small noise emissions are used /L39/.

2.2.6.3 Treatment of waste water

German refineries treat waste water generally in their own central waste water treatment plant. Only in exceptional cases treatment is performed together with waste water having a different origin in common sewage plants. Since refineries are often connected with further manufacturing processes in the same location (petrochemical industry, synthetic materials, fertilizers), generally waste water from different areas of the location are treated together in the central waste water treatment plant. Also, several refineries in different locations can be consolidated in a connecting system. Here, very different configuration of the processing plants can exist in the respective locations. This can lead to correspondingly different characteristics of the waste water to be treated from each location.

The main information on the generation and characteristic of waste waters as well as prevention and treatment, according to state of the art in Germany (fixed in the WHG as the best available technique), is summarized in the „Hinweisen und Erläuterungen zum Anhang 45“ /D13a/ (Section 3.6.3). In German refineries, waste water is treated mainly according to these principles. The exact expression in individual cases depends strongly on the characteristics of each location and the historical development there (Section 3.6.3.2).

2.2.6.4 Exhaust cleaning (Vapour Recovery)

Emissions are prevented during filling of transport vessels with mineral oils with a vapour pressure exceeding 13 hPa at 20 °C by collecting the vapour mixture and balancing, recovering or incinerating the hydrocarbons contained in it. In this process, consideration must be given to installations, safety risks and minimization of energy input.

The necessity for reducing emissions depend on the following parameters:

a) Vapour pressure of the supplied product,
b) Type of previous tank contents, which affects the concentration of the hydrocarbon/air mixture already contained in tanks.

To minimize the emissions , the following measures are applied:

Top-submerged loading/Bottom loading Mineral oils are loaded with the aid of filling arms which reach down to the bottom of the container’s tank compartment of; on ships these pipes are permanently installed. This technique of “top-submerged loading” prevents spraying of the products; as a consequence, the hydrocarbon content of the displaced air remains below the saturation concentration.

Further emission control is achieved via bottom loading with drip-tight couplings. This technique is only widely applicable, however, to road tanker loading because rail tankers used throughout Europe have not been standardized for this as yet.

Vapour balancing To prevent and reduce emissions, fixed-roof tanks and loading/unloading equipment can be connected with vapour balance lines. These permit a balance of the displaced gas volume.

The displaced vapour/air mixtures can be balanced via a vapour return line between the loading point and the tank being emptied as long as the latter does not have a floating roof. Installation of detonation protection and flame arrester equipment is necessary because of plant safety.

For **vapour recovery**, a vapour accumulator is installed in order to maintain a uniform stress in the plant. The following procedures are normally used:

- Condensation: The hydrocarbon/air mixture is cooled in a heat exchanger allowing a portion of the hydrocarbon to condense. The concentration of hydrocarbons in the flue gas depends only on the temperature achieved and not on the hydrocarbon load.
- Absorption: The hydrocarbon/air mixture is scrubbed in countercurrent by a liquid mixture of hydrocarbons (e.g. petroleum) at the operating temperature. The loaded scrubbing liquid can, according to local conditions, be fed to a production process or be degassed by heat-

ing in a further processing step. The expelled gases either have to be condensed, processed further or incinerated. For condensing mixtures containing butane, refrigeration plants are to be used.

- Adsorption: During adsorption the hydrocarbon/air mixture is passed through an adsorbent e.g. activated carbon. The hydrocarbons are deposited on the adsorbent. After a certain charging period, the adsorbent must be regenerated. Hence, adsorbent installations are designed two-staged for changing operations. The desorbate is taken up by a circulating gasoline or gasoline component current in a scrubbing column (or scrubbing stage). The residual gas is subjected to further treatment.
- Membrane method: Selective membranes separate the vapour/air mixture into a hydrocarbon-rich phase (permeate) which is then either condensed or adsorbed to form a depleted phase (retentate).

Incineration The hydrocarbon/air mixtures from loading processes can be burnt in gas engines or incineration plants as long as certain process conditions are complied with. These plants can be operated together with recovery plants.

Lean hydrocarbon/air mixtures require resaturation or auxiliary firing.

In all incineration plants, special attention must be devoted to safety installations (explosion areas, detonation protection and flame arrestor equipment).

3 Data about the emission situation for single processing stages and different locations

3.1 Method of collecting the data

The typical consumption and emission values of 5 representative German refineries and a lubricating oil refinery were determined using questionnaires which are shown as a sample in Annex 2.

In some locations, petrochemical plants are connected closely to the refinery plant. Emissions from the refinery’s own power plant (where available) or petrochemical plants in refinery locations were not considered. Because of a close connection between the petrochemical industry and refineries it was only sometimes possible to collect separate data for the refinery plants.

A questionnaire for the whole refinery (Questionnaire A) and one for functional units (Questionnaire B) (or refinery processes) were prepared. The considerations are oriented according to the revised version of the VDI Directive 2440 corresponding to the content in Chapter 2. An overview of the relevant functional units for the whole project is shown in Table 2 *Environmental account of production processes (Account Table).*

Questionnaires A and B have a similar table of content and address the following topics:

1. General information about refineries and functional units
2. Emissions into the air
3. Emissions into water
4. Wastes
5. Consumption of substances and energy
6. Other information
   a) Waste heat emissions
   b) Noise
   c) Costs, economic aspects

Questionnaires Part B for the processes require more detailed information than Part A.

The data were collected as follows:

1. Design of the questionnaires with representatives from the refinery and regulatory boards
2. Distribution of the questionnaires to 5 chosen refineries
3. Discussion of the data directly in some refineries
4. Participation of the monitoring and authoritative regulatory boards for the locations

For the processes lubricating oil refining and extraction, data from a lubricating oil refinery were also obtained. In order to limit the extent of the data collected, the processes were classified qualitatively according to their environmental account in the environmental compartment. The results are shown in Table 5. The following key is used:

X	high environmental account
0	low environmental account.
–	very low or no environmental account

The data of the processes with a high environmental account are emphasized.

In choosing the refineries, care was taken in also recording all processes with a high environmental account, i.e. that the plants were represented at least one time in a refinery. Table 6 shows the processes for which data was collected in the refineries. The selection consists mainly of plants that were constructed after 1990 or were greatly modified.

Some special measures which are applied in other German refineries are also included.

3.2 Origin of the Data

The questionnaires were prepared from the refineries mainly with the following basic information:

- Emission explanations in conformity with the 11. Ordinance of BImSchG
- Waste water balance, waste water register
- Waste balance, waste industry concepts etc.
- Internal reports of the expert departments for environmental protection
- Regulatory board licences
- reports according to the Environmental Statistic Law

Most of the data originate from 1998 but some are considered from 1996 and 1997.

Process/Functional unit	**Environmental compartment (Numbers in Quest. B)**						
	Air (2)	**Waste water (3)**	**Waste (4)**	**Substances and Energy (5)**	**Waste heat(6.1)**	**Noise (6.2)**	**Safety**
Refinery furnaces	X	-	0	X	X	X	X
Separation processes							
Atmospheric distillation	0	X	X	X	X	0	X
Vacuum distillation	0	X	0	X	X	0	X
Gas separation	0	0	0	0	0	0	X
Conversion processes							
Thermal cracking, (Visbreaking)	0	X	0	X	X	0	X
Petroleum coke production and calcination	X	X	X	X	X	X	X
Catalytic cracking (FCC)	X	X	X	X	X	0	X
Hydrocracking	0	X	X	X	X	0	X
Bitumen blowing	X	X	X	X	X	0	X
Reforming	0	X	0	X	X	0	X
Isomerization	0	0	X	X	X	0	X
MTBE production	0	X	X	X	0	0	X
Alkylation	0	X	X	X	0	0	X
Refining processes							
Hydrodesulphurization	0	X	X	X	X	0	X
Mercaptane conversion (Sweetening)	0	X	X	X	0	0	X
Gas scrubbing	0	X	X	X	0	0	X
Lubricating oil refining including dewaxing	0	X	X	X	0	0	X
Extractions							
- with solvents	0	0	0	X	0	–	X
- with Molecular sieves	0	X	X	X	0	–	X
Tank farming processes							
Product supply	–	–	–	–	–	0	X
Loading and unloading	X	–	–	–	–	X	X
Storage	X	0	X	0	0	–	X
Other processes							
Sulphur collection (Claus plant)	X	0	0	0	0	0	X
Flare	X	X	0	0	0	X	X
Waste water treatment	X	X	X	X	0	–	0
Exhaust purification (Exhaust gas recovery unit)	0	0	X	0	0	0	X

Table 5 Environmental account of refinery processes

Process/Functional unit	**Refinery**				
	1	2	3	4	5
Refinery furnaces		X			X
Separation processes					
Atmospheric distillation		X		X	X
Vacuum distillation		X	X	X	X
Gas separation		X			X
Conversion processes					
Thermal cracking, (Visbreaking)		1988 (HSC)			X
Petroleum coke production and calcination			X		
Catalytic cracking (FCC)		X	X		X
Hydrocracking	X (in construction.)			X	
Bitumen blowing		(X)		(X)	
Reforming				(X)	X
Isomerization		X			
MTBE production		X			
Alkylation		X			X
Refining processes					
Hydrodesulphurization		X	X		X
Mercaptane conversion (Sweetening)		X	X		X
Gas scrubbing		X			X
Lubricating oil refining and dewaxing	Data for the lubricating oil refinery 6				
Extractions					
- with solvents		1970			
- with molecular sieves					
Tank farm processes					
Product supply					
Loading and unloading					
Storage					
Other processes					
Sulphur recovery (Claus plant)		X	X	(X)	X
Flare		X	X		X
Waste water treatment	X			X	X
Exhaust purification (Exhaust gas recovery unit)		X		X	X

N. B.: Information in brackets originate before 1990 or are greatly modified

Table 6 Recorded processes in representative refineries

3.3 Data for the complete refinery

The capacity of the documented refineries range from 4 Mio. t/a to 12 Mio.t/a. The list of products is typical even though special processing units, e.g. for petroleum coke production, are not operated in all refineries. The main products are:

- Liquefied petroleum gas
- Benzene hydrocarbons
- Middle distillate
- Bitumen and heavy oils
- Sulphur
- Other products

Annex 5 contains chart diagrams which show schematically the configuration of the refineries considered with the most important stream of substances.

The quantity of sulphur produced in the refineries differs since it depends on the amount of sulphur contained in the crude oil feedstock. Values between 0.29 and 0.83 % of total throughput were determined (3 refineries).

3.3.1 Emissions into the air

The emissions of the relevant substances into the air are shown in the Table 7 as emission factors in relation to the crude oil throughput (without power plant and the petrochemical industry).

Pollutant	**Emissions/Crude oil feedstock (t/10^6 t Crude oil)**
Dust	9-18
SO_x as SO_2	240-620
NO_x as NO_2	100-283
Hydrocarbons/ Benzene	
1)Processing	11-100 / 0,1 - 0,5
2)Storage	7 - 70 / 0,02 - 0,6
3)Flare	0.1 – 9 /
4)Loading	0.06 – 5 / indetectable

Table 7 Emissions into the Air

Emissions from sulphur dioxide emerge from FCC and Claus plants and nitrogenous gases emerge largely from refinery furnaces. Dust is emitted mainly from FCC plants and calcination. The main emissions from hydrocarbons (VOC) arise in the area of processing and storage.

3.3.2 Emissions into waters

3.3.2.1 Quantity of waste water

The proportion of polluted waste water due to processing with respect to total waste water from a refinery depends heavily on the respective local conditions. (processing spectrum, proportion of rain water), type of cooling, method of supplying oils, ground water discharge etc.). The quantity of waste water due to production in all German refineries lies under the value of 0,5 m³/t feedstock (or 1,3 m³/t for lubricating oil refining) which is based on the load limits fixed in the waste water ordinance (Section. 1.5.2). The true value depends, in individual cases, not only on the degree of waste water separation and re-utilization but also on the available spectrum of the plant.

3.3.2.2 Waste water characteristic

The characteristics of waste water is analysed regularly within the scope of the official and refinery's own monitoring of plants and controlled with respect to maintenance of the fixed limit values in the water legislatory permit. For this purpose, generally the final treated process waste water is considered but can, however, be mixed with other waste water flows treated. For waste water streams for which different requirements hold and which are introduced together each standard requirement is determined through calculation of the mixed ratio for each parameter. If requirements of the location of generation of the waste water or mixing are demanded these are standard. Data for the characteristic of internal tributary waste water streams are only available as an exception.

If waster water treatment plants in refineries are designed according to state of the art the requirements of Annex 45 of the waste water ordinance (Section. 1.5.2) can be safely attained.

With corresponding loads, the degree of elimination of the central waste water treatment plant for COD lies by approximately 80 %. On average, values from 90 to 95 % are achieved. The degree of elimination for inorganic nitrogen in the central waste water treatment plant is fixed differently according to which proportion is already removed by pretreatment (sour water stripping). With respect to the total balance, elimination rates exceeding 90 % are achieved. A still higher level of purification performance is achieved with hydrocarbons (> 95 %), the rate of degradation of aromatic hydrocarbons and phenols can be >99 % through adapted biological cleaning.

3.3.3 Waste

3.3.3.1 Quantity of waste, Type of waste and Disposal

The collection of the data resulted in comprehensive information about wastes. It was also very difficult to classify waste (with the exception of spent catalysts and sludge from waste water purification) according to certain functional units.

The following summary limits itself to typical refinery wastes if they are produced in relevant quantities of > 10 t/a.

The following table shows the quantities of wastes in need of close monitoring which arose in the respective years in the refineries. The quantity is only 0.32 to 0.57 ‰ of total throughput and is small compared to other industrial manufacturing procedures.

Wastes in need of close monitoring	**5 Refineries**
In t / 10^6 t Rohöl	320 - 570

Table 8 Quantities of waste in need of close monitoring

The types of waste and the possible disposal for wastes in need of close monitoring are listed as follows.

Definition of waste	**Location of origin (Functional unit)**	**Waste code Nr. (EAK)**	**Utilization/ Disposal (Examples)**
Sludge-like tanks residues	Tank farm processes Distillation	05 01 03	Substitute fuel for cement factories
Acidic alkyl sludges	Alkylation	05 01 04	Substitute fuel for cement factories
Spilled oil	all	05 01 05	Substitute fuel for cement factories
Spent catalysts	FCC Dust filter	05 03 02	Cement production
Exhausted filter clay	Product, waste water, exhaust cleaning	05 04 01	manufacture of construction materials, Landfill
Solids from oil-/Water separators	water purification	13 05 01	Incineration
Sludge from oil-/Water separators	water purification, oil separation plants sewage system	13 05 02	Incineration
Oil mixtures not otherwise specified	Maintenance waste water plant	13 06 01	Incineration
Sulphuric acid and sulphurous acid	Desulphurization Alkylation	06 01 01	Production of SO_2
Aqueous washing liquids and mother liquors	Maintenance waste water treatment Loading	07 07 01	Phys.-chem. treatment
Oil-polluted materials	all plants	15 02 99 D1	Incineration
Polluted insulated material	all plants	17 06 99 D1	Landfill
Oil polluted soil	Leakages, abandoned polluted area	17 05 99 D1	Biological treatment

Table 9 Waste types and disposal for waste in need of close monitoring

The quantity of wastes in need of monitoring and other wastes for disposal and utilization cannot be completely recorded for the whole refinery; the quantity of the latter is normally less than that of wastes in need of close monitoring.

The types of waste and their possible disposal are listed as follows.

Wastes in need of monitoring and other wastes	**Location of origin (Functional Unit)**	**Waste code Nr. (EAK)**	**Utilization/ Disposal (Examples)**
Sludge from refinery's own waste water treatment	Waste water treatment plant	05 01 01	Incineration
Spent catalysts, containing noble metals	Process plants	05 03 01	Metal recovery
Other spent catalysts	Process plants	05 03 02	Regeneration, Incineration
Sulphurous wastes	Sulphur recovery	05 05 01	Landfill
Other filter cakes, spent absorbents	Activated carbon	07 01 10	Incineration
Spent linings and refractories	Furnaces	10 01 12	Landfill
Sludge from water softener	Water preparation	19 09 03	Cement production
Bitumen waste	Bitumen production and storage	17 02 03	Utilization
Mineral fibre waste	Insulating material	17 06 02	Landfill

Table 10 Type of waste and ways of disposal for wastes in need of monitoring and other wastes

The main quantities of typical wastes from refineries:

- Wastes containing or contaminated by oil
- Residues from tank cleaning
- Sludge from waste water purification
- Spent catalysts

Spent catalysts originate mainly from the processes catalytic cracking, hydrocracking, reforming and hydrodesulphurisation. Catalysts accumulate, depending on the refinery processes, in quantities up to 500 t annually normally after a period of several years.

Catalysts are disposed off as follows:

a) for recovery of metal externally
b) regenerated internally or externally
c) or a low percentage is disposed off

3.3.3.2 Measures to reduce waste

In German refineries, the following measures are used to reduce the amount of waste:

- Exploitation of the possibilities for harmless utilization of energy
- Slop systems with recirculation
- Minimization of wastes during tank cleaning through organizational measures and low waste-producing cleaning methods
- Separation of different types of wastes
- Recycling catalysts
- Exploitation of possibilities of utilization in the construction and cement industry

3.3.4 Substances and Energy

Data on the consumption of substances and energy were not collected for the complete refineries.

3.3.5 Other Data

3.3.5.1 Waste heat

Values for waste heat emissions in the refineries were not available. Data were collected indirectly from the temperatures of flue gas- and cooling water.

In different functional units, waste heat emission into the air can be estimated from the temperature and volume of the flue gas. Likewise, this is also possible using the difference in temperature of the cooling water.

For optimal heat utilization, the following measures are taken in all processing plants:

- Heat exchangers widely permit efficient use of energy
- Process heat is used to heat feedstock or for vapour recovery
- Functional units are heat-insulated

3.3.5.2 Noise and Vibrations

According to the german TA Lärm /D9/, the allowed values for noise emissions depend on the level at which the neighbourhood is classified.

Since refineries are operated continuously the standard emission values for the night is especially relevant. These values are 45 dB (A) for mixed areas and for pure residential areas 40 dB (A).

In German refineries, the following emission-reducing measures are applied in order to maintain the recommended values:

- Use of quiet sound sources (burners, pumps, compressors, control valves, ventilators)
- Sound protection hood, Sound absorbers
- Sound insulation measures
- Avoidance of vehicle traffic, start-up and shutdown during the night

The distance of some refineries to neighbouring residential and mixed areas are only a few 100 m. In such cases, further noise protection measures are required.

3.3.5.3 Costs

The costs of a refinery for environmental protection is difficult to determine because reliable information about determining which plant or functional unit is a measure for environmental protection does not exist. This applies for investments and especially for operating costs.

This problem would become clear based on the following question: Is the investment for constructing a hydrocracker with a high yield and its possibilities for the production of low-sulphur products an investment for environmental protection and, if yes, to what percentage?

According to information obtained from the mineral oil trade association /L42/, in the past years the German mineral oil industry used up to one-fifth of its investments for environmental protection. The annual operating costs for these plants are approximately 500 Mio. Euros. The major part of these investments is for air purification and water protection.

For a newly constructed refinery, e.g. approximately 10% of the total investments was used for emission reduction measures. This corresponds to more than 250 Mio. Euros. The total investment for environmental protection measures was even much higher.

In another refinery, approximately 400 Mio. Euros was invested from 1991 to 1998 for environmental protection measures. The investments for air purification contributed to 90 % of total investments, thus ranking number one. The operating costs for environmental protection was approximately 110 Mio. Euro in 1998.

3.4 Plant safety

3.4.1 Regulations

The refineries in Germany are subjected to the 12th Ordinance of the BImSchG /D4/ (Störfall-Verordnung) because this country, due to the type and quantity of materials, lies in the area of application of the Ordinance.

The legislations for preventing serious accidents will change in Germany and also in the other EU countries in the near future when the Directive 96/82/EG (Seveso-II Directive) /E9/ is revised in national law.

The new legislation will not have a major impact on the requirements of the refineries in preventing serious accidents. In the normal case, it is obligatory to prepare a safety report according to Article 9 of the Directive.

The measures for safety of plants in the refineries are specified in the safety analysis. Based on the characteristics of the substances, the danger of refineries for the environment, population and employees can be deduced:

- Explosions and fires due to highly flammable substances
- Release of toxic substances into the atmosphere
- Hazard for the environment due to pollution of soil and water

In order to combat the hazard, safety concepts were introduced in German refineries whose principles are outlined as follows. The concepts contain technical and organizational measures for plant safety.

3.4.2 Technical Measures

Principally, release of dangerous substances and with this explosions and fires are prevented when toxic, highly flammable and flammable substances are kept in closed and sealed systems according to requirements.

The functional units consist of suitable materials which are designed for operating stress and are adequately resistant against corrosion. If required, the plants are protected by constructive fire prevention measures with fire-resistant fittings or with local sprinklers for cooling. Safety relevant functional units such as pumps, compressors and heat exchangers are redundantly installed.

Protection areas are installed in which ignition sources are avoided. In the protection areas, the correct choice of electrical facilities is especially important. In construction plants overpressure systems, among other things, are installed which prevent entrance of explosive substances.

Release of toxic or explosive gases are detected by gas detectors. In especially safety-relevant plant sectors, alarms in the process conductive system and also parallel optical and acoustic alarms in the plant are disengaged.

Various warning, alarm and safety devices are installed in the processing plants. They sense a deviation of the processes from normal operation and, if necessary, automatically disengage safety measures after announcement of a pre- and main alarm. Here, it is especially important to monitor filling level, pressure, temperature and flow. During failure of the driving energy the measuring and controlling devices go into the fail-safe position. The flames in refinery furnaces and flares are monitored with reliable measuring devices. The operators in the plants are equipped with permanent walkie-talkie connection to the process control station.

As a rule, the central process control stations are constructively designed in such a way with safety and protection systems against flooding, explosions, overpressure and failure of energy supply so that they remain operative in case of damage. The plants are controlled with process control systems. Shut-Down systems are installed which allow safe shutdown of the plant or the specific functional unit during malfunctions. Shut-off systems between functional units limit disturbances and avoid Domino-Effects. In addition, an emergency shut-down-system consist of a central and a decentral emergency shut down switch with which individual plant components are switched off or complex emergency shut down programmes are deleted. The supply of electricity is redundant, additionally an emergency electricity supply exists for the Shut-Down and emergency shut down systems.

For fire prevention, an adequate number of stationary and mobile fire extinguishing facilities are present. In sensitive areas, local fire detectors are installed. An adequate amount of fire extinguisher is kept and or taken from neighbouring waters. To retain water used for fire fighting /D11/ an adequate volume is kept normally in vessels in the area of the waste water treatment plants.

Substances which are released from pressure venting devices, e.g. safety valves or rupture discs are carried into attached facilities which allow safe removal. Generally, these are flares but, in special cases, exhaust scrubbers e.g. are also considered.

Normally refineries have a fire brigade which, in the case of a fire, is immediately on location and can begin with fire prevention measures or can support the fire fighters.

3.4.3 Organizational Measures

Plans for alarm, hazard prevention and communication to external locations are present and are continuously kept current. Precise operating instructions demand normal operations. Training and instructions for the employees are done on a regular basis. Here, they are informed about hazards on the work place and for the environment.

By means of a monitoring plan the plants are inspected regularly from operators. A work’s protection force is in charge of controlling and monitoring access to the refinery and prevents intervention by trespassers. Safety instruction of the contractors are performed regularly.

The organizational measures can be regulated by management systems. I.e. the following regulations and standards come into question:

- Regulation EG 1836/93 (EMAS-Verordnung) /E11/
- Environmental management in conformity with the Standards of the Series DIN EN 14000 /L47/
- Quality control in conformity with the Standards of the Series DIN EN 9000
- Special, e.g. business-specific systems, QHSE-system.
- Future: safety management systems in conformity with the Seveso (II) Directive

Management systems are already introduced in most German refineries and, to some extent, further certification is being prepared.

3.5 Groundwater and Soil Protection

3.5.1 Regulations

For ground water and soil protection no extensive identical European regulations exist as yet.

In the Federal Republic of Germany, detailed regulations for preventive water protection, in contrast, exist since decades in the federal water act (WHG) /D10/ which is fixed in all Federal States through detailed requirements in Ordinances about plants as to handling substances which are hazardous to water and about specialized companies VAwS- /D12/. The regulations for preventive water protection are based on the legislative principle of *precaution according to which each possibility of water pollution or other disadvantageous changes to water from a plant must be excluded.

The legislative requirements of the VawS apply to plants for storage, filling and loading/unloading as well as for the processing units for production, treatment and use of substances which are hazardous to water. Besides construction-technical standards operating-organizational measures and the performance of plant controls are required which, with the exception of the WHG and the VAwS in administrative regulations to VAwS, are fixed in technical rules and standards, e.g: /D14, L5-8, L14,16,17, L21-27/.

3.5.2 Water hazard classes and hazard potential

Substances which are hazardous to water in Germany are grouped into a system of 3 water hazard classes (WGK 1 to 3, water hazard classes) because of their hazardous characteristics.
The system of water hazard classes serves to give the plant a hazard potential, depending on water hazard classes and plant size, according to which the material requirements of the plant are determined (requirements proportional to hazardousness). The system of water hazard classes correspond with the European regulations for dangerous substances.

Most mineral oil products belong to water hazard classes 2 or 3. If carcinogenic substances are present in a fraction or mixture at a concentration of more than 0.1 % products are classified in WGK 3. (Some mineral oil products because of their low solubility in water and despite their high content of carcinogenic substances are classified in a low water hazard class). Crude oil and numerous products and intermediary products of the refineries are classified according to Annex I of the Directive 67/548 EWG carcinogen cat. 2 (R-Phrase 45) if they contain carcinogenic components.

Carcinogenic substances in mineral oil products can be the following:

- (1,3)-Butadiene in slightly volatile fractions, gases
- Benzene in different fractions
- Benzo[a]pyren and other PAH in residues

3.5.3 Construction-technical measures for Water Protection

The construction-technical measures in German refineries for protecting waters are mainly the following:

- The restraining capacity for substances released during accidents are present. The restraining capacity is normally designed so large so that the largest volume released (e.g. the content of the largest storage vessel) can be collected /L6/.
- Impervious design of areas (e. g.) according to /L45/ which serve as components for collecting rooms or filling or discharging areas.
- Technical measures are taken to avoid overfilling of vessels or vehicles during loading and unloading /L29,30/.
- Underground tanks and pipelines for substances hazardous for water are double-walled and are constructed with leakage-monitoring systems.
- It is possible to restrain contaminated extinguishing water mostly as a component of the central waste water treatment.

The planned technical measures for the different types of processing plants in the refineries (plants for manufacture, utilization and treatment of substances which are hazardous to water) do not differ fundamentally from those for storage and filling. The main aspects are also areas impervious to substances and restraining capacity for released substances.

3.5.4 Renovation of flat-bottomed tanks

For storing mineral oil products, normally flat-bottomed tanks are used. In flat-bottomed tanks, the floor is a special risk because, without special protective measures, the substances which leak into the underground cannot be recognized early enough. For this purpose, a series of comparable techniques are appropriate for new as well as existing installations.

Primarily, a double-walled design with leakage monitoring e. g. with a vacuum system comes into question. Also other methods are available, e. g. high quality concrete coating of the collecting rooms or placing the vessel on a supporting grid so that leakages can be recognized.

Legislative requirements for new and existing plants according to the water act are principally similar. For renovating existing plants which do not correspond to the current standard, operators are given a longer deadline since renovation is connected with extensive investments.

The costs for renovation depends on material and size of the vessel.

For example, renovation of a flat-bottomed tank with a leakage protection layer made of synthetic material with a leakage detector costs approximately 150,000 Euro for a vessel size of 10,000 m^3 and approximately 500,000 Euro for a vessel size of 60,000 m^3.

Renovation of a 5 000 m^3 flat-bottomed tank with a double metal floor and leakage detector is estimated to be 135,000 Euro for a vessel size of 5,000 m^3 and 400,000 Euro for a vessel size of 40,000 m^3.

In order to spread the required investment over time, some refineries in Germany have developed middle-term renovation concepts in cooperation with the respective regulatory boards to renovate existing plants. The plants with the substances belonging to WGK 3 or with the highest hazard potential have first priority.

3.5.5 Organizational Measures for Water Protection

The organizational measures for soil and water protection are extensively identical with those which were already described for plant safety. This is supplemented by:

Plant controls are to be performed regularly by internal and independent external workers (experts). The deadline for control is governed by legislation.

Work in plants dealing with the way in which substances which are hazardous to water with a high hazard potential is handled is performed by specialized companies.

Current lists of storage and plans for measures after an accident (internal and external) are available.

3.6 Data for Functional Units

3.6.1 General measures for reducing emissions into the air

The following overview shows measures for all plants_which are used in German refineries to reduce diffuse emissions into the air. With these measures especially hydrocarbon emissions are reduced. Special measures, which refer to the processes, are shown in the following chapters if the emission account according to Table 5 is present. The measures for all plants regarding waste and noise were already listed in Chapter 3.3. Measures for reducing emissions into water are contained in Section 3.6.3.

Measures for reducing diffuse emissions

- Processing of mineral oil products in tight, closed plants
- Suitable sealing systems with
    - Pumps
    - Compressors
    - Shut-off and control fittings
    - Flange connections
- Closed sampling systems
- Minimization of the number of flange connections
- Inspection of the plants during initial operation and thereafter regularly

Emission values for released substances from different sealing systems are given in the VDI-Directive 2440 and can therefore be estimated. Typical values for diffuse hydrocarbon emissions from process plants with a high throughput (> 1 Mio t/a) were determined to be 0,5 - 1,5 kg/h.

The choice of the appropriate sealing system depends on the hazard potential of the substance. For toxic and carcinogenic substances, , high quality sealing systems are used, e.g.

- Multiple mechanical seal with buffer medium for pumps and compressors,
- Metalseals for flange connections.
- Metal bellows welded on both sides for shut-off and control fittings,

3.6.2 Emission data and measures for functional units to reduce emissions into the air

The emission data in the tables in the following chapters are listed as ranges. The smaller values are usually measured values; the higher values could also be legal limit values.

3.6.2.1 Refinery furnaces

Refinery furnaces for which data were collected in the refineries are mainly operated with refinery gas. Nevertheless, the data for pure gas furnaces are limited because the flue gases from different plants are discharged via common stacks and a bubble concept is applied.

Furthermore, emission data for 3 refinery furnaces which were operated with gas and oil were determined. The values given are valid for oil furnaces.

In the whole refinery, the proportion of gas- to oil furnaces is almost equal. A typical value is 2:1 gas /oil.

The following measures to reduce emissions are taken:

- Low-NOx -Burners
- Desulphurized refinery gas
- Optimized design burner/furnace
- Optimized burner adjustment air/fuel

For gas fuels the following concentration is measured or can be maintained in flue gases:

Refinery furnaces -Gas, 4 plants	
Flue gas temperature 200-270 °C	
Heat production 18.5 – 130 MW	
Pollutant	**Values achieved in continuous operation (½ hourly means and 24 hourly means) (mg/m³, standard conditions¹⁾)**
Dust	**1 - 5**
Sum Metals (Ni)	**-**
SO_x as SO_2	**5 – 100 according to fuel**
NO_x as NO_2	**63– 200**
Carbon monoxide	**1 – 100**

1) with respect to 3% (v/v) oxygen

Table 11 Emissions from gas furnaces

When using liquid fuels the following concentrations are measured or can be maintained in flue gases:

Mixed refinery furnaces - Oil , 3 plants	
Flue gas temperature 170 - approx. 250 °C	
Heat Production 20-140 MW	
Pollutant	**Values achieved in continuous operation (½ hourly means and 24 hourly means) (mg/m³, standard conditions[1)])**
Dust	**1,2 - 40**
Sum Metals, Ni	**-**
SO_x as SO_2	**670 – 1700**
NO_x as NO_2	**240 –450**
Carbon monoxide	**10 – 25**

1) with respect to 3% (v/v) oxygen

Table 12 Emissions from mixed furnaces

3.6.2.2 Petroleum coke production and calcination

During petroleum coke production the main emissions arise from the refinery furnaces. Therefore it is not dealt with further. The emissions during calcination are caused by the burning of remaining hydrocarbons.

The SO_2 emissions from calcination is optimized via sulphur management with reference to green coke. Furthermore, a flue gas desulphurization plant was operated in a refinery for many years. The flue gas is discharged via a flue gas filter to reduce dust emissions.

The following concentrations are to be maintained with the technique applied:

Calcination , 1 Plant	
Capacity 150 000 t/a Calcinate	
Pollutant	**Values achieved in continuous operation (½ hourly means and 24 hourly means) (mg/m³, standard conditions)**
Dust	**35 – 50**
Nickel +Vanadium	**-**
SO_x as SO_2	**1000 (300[1])**
NO_x as NO_2	**340 – 450**
Carbon monoxide	**5 - 100**

[1)] when using a flue gas desulphurization plant

Table 13 Emissions from calcination

3.6.2.3 Catalytic Cracking FCC

The main emissions during catalytic cracking arise from regeneration of the catalysts. For emission reduction the following techniques / measures are used:

- Dust removal from the regenerated flue gas: cyclone separator and/or electrostatic separator
- Desulphurization of feedstocks
- CO-Boiler

The following values for emission concentrations in regenerator flue gas were determined:

FCC Flue gas regenerator, 2 plants	
Capacity 1,3-2,8 Mio t/a	
Flue gas temperature 260-280 °C	
Pollutant	**Values achieved in continuous operation (½ hourly means and 24 hourly means) (mg/m³, standard conditions)**
Dust	**45 - 50**
Ni + V	**< 0,1 - 1**
SO_x as SO_2	**600 - 1200**
NO_x as NO_2	**100 -500**
Carbon monoxide	**50-125**

Table 14 Emissions from catalytic cracking

Besides the abovementioned measures the following secondary measures to reduce emissions are considered which were not applied in any of the plants investigated:

- DeSOx supplementation to catalysts
- SNCR: (Selective non-catalytic reduction)
- SCR (Selective catalytic reduction)

3.6.2.4 Production of blown bitumen

The values are derived from data from two plants which were constructed before 1990 or which were greatly modified.

As an emission reduction measure the thermal incineration of the flue gas is mentioned.

Emissions into the air arise from the production of bitumen during post-combustion in the incinerator. Hence, emissions mainly from fuel in the incinerator (as also in other refinery furnaces) are determined.

3.6.2.5 Loading

During loading and unloading as well as during transfer and blending emissions occur from fixed-roof tanks by the displacement of gas volumes from tanks or transport vessels. Hence, measures for reducing emissions were taken which mainly depend on the vapour pressure of the products.

The main measures for emission reduction from hydrocarbons during product supply and withdrawal as well as during transfer and blending are:

- Top-submerged loading, Bottom-loading

- Gas balancing
- Vapour recovery (VRU) for VOC

The emissions determined during loading are given as emission factors in the emission values for the entire refinery in Section 3.3.

The special effective techniques of vapour balancing and vapour recovery are used for products with a vapour pressure of more than 13 hPa at 20°C whereas during product supply and withdrawal of middle distillates and heavy fuel oil top-submerged loading is done.

Vapour balancing in plants is performed according to the state of the art mainly without emissions.

During vapour recovery hydrocarbon concentrations (without methane) of 100-150 mg/m³ and < 5mg/m³ benzene as 1/2-hourly can be maintained (Data from 2 single-stage adsorption plants with supplementary blower on activated carbon). Since during loading of gasoline the hydrocarbon concentration in unpurified flue gas is approx. 1000 g/m³ /L32/ an effectiveness of > 99.98 % is achieved.

3.6.2.6 Storage

Emissions from storage occur mainly by tank breathing. Depending on the characteristics of the substances, measures to reduce emissions are taken. On one hand the environmental pollution potential of the stored substance and on the other hand the physical characteristics of the substances, especially the vapour pressure, are important. According to the requirements of the TA Luft, special effective measures for the reduction of emissions are necessary for products having a vapour pressure of more than 13 hPa at 20°C.

During storage the following techniques for emission reduction are applied

- Floating-roof tanks with primary and secondary sealing
- Fixed-roof tanks with floating covers (only present in individual cases)
- overpressure/underpressure valves
- Fixed-roof tanks with tank coatings which reflect at least 70 % radiation heat
- Fixed-roof tanks with connection to a flue gas collection line
- Low-emission pumps (cf. Section 3.6.1)
- Vapour incineration during storage of bitumen

The technique applied alone or in combination depends on the vapour pressure as well as the hazard potential of the products.

During storage of liquefied petroleum gas emissions from normal operation are not considered.

During storage of mineral oil products and crude oil the following emission mass flows in the 5 refineries were determined:

Emissions during storage	
Storage capacity (m^3)	**435,000 – 2,500,000**
Hydrocarbons (kg/h)	**5 – 85**
Benzene (kg/h)	**0.2 – 0.6**

Table 15 Emissions from Storage

The correlation between tank farm volume and the emission values is poor. This could be due to the following reasons:

- Different volumes loaded and unloaded
-
- Different number and size of tanks
- Products are delivered partly via long-distance pipelines
- Data for storage without loading are sometimes not available
- The proportion of the petrochemical industry is partially recorded, in contrast, the storage of crude oil was not partially recorded

3.6.2.7 Sulphur recovery

Emissions from sulphur recovery plants are reduced when the following measures are taken

- Downstreamed stages (e.g. Scot)
- Incineration of tail gases
- Sulphur degassing

Through installation of Scot- or Sulfreen stages the degree of sulphur emission in the Claus plants is decreased. The Scot flue gas is incinerated thermally or catalytically in incineration plants in order to oxidize residual hydrogen sulphide. The following concentrations were determined:

Emissions from Claus plants, 4 plants	
Pollutant	**Values achieved in continuous operation**
SER 1)	**0.2 – 0.5**
SO_x as SO_2	**560 – 4300 mg/m^3**
H_2S	**< 1 – 8 mg/m^3**
CS_2 +COS	**<0.1 mg/m^3**

1) SER = Sulphur emission rate

Table 16 Emissions from Claus plants

3.6.2.8 Flares

Emissions from hydrocarbons (and also SO_2) from flare operations are small (Table 7). The minimization of flare operation is achieved by flare gas collection systems.

An effective burnout of the flare gases of >99% is achieved via controlled steam injection.

3.6.2.9 Waste water treatment

Data for emissions from the central waste water treatment into the atmosphere are not available. As emission reduction measures, mainly use of closed waste water canals and the covering of mechanical separators and waste water collecting pit come into consideration to reduce emissions from hydrocarbons.

One of the plants examined has an exhaust-cleaning installation (biofilter unit) for treatment of odour emissions from waste water.

3.6.3 General measures for reducing of emissions into the waters

The following summarizes the most important methods for waste water prevention and –treatment which are considered as state of the art in Germany. They are also shown essentially also in the "Hinweise und Erläuterungen zum Anhang 45" /D13a/.

3.6.3.1 Measures for preventing and reducing emissions and waste water

- **Desulphurization with hydrogen:** Through desulphurization with hydrogen (Hydrotreater/Hydrofiner) in combination with regenerative gas scrubbing and sulphur recovery (Claus plants) the pollutant load in waste water is greatly reduced, in contrast to the use of other methods such as caustic-/sour scrubbing or sweetening with copper compounds.
- **Regenerative gas scrubbing:** Through the use of alkanolamines (MEA, DEA, DIPA etc.) as medium for gas scrubbing to remove hydrogen sulphide because of their regenerative capacity the waste water production is greatly reduced in comparison to caustic washing.
- **Merox-Process:** Mercaptanes in petrol fractions can be removed with caustic soda. The caustic solution can be regenerated whereby a low waste water circulatory process is possible.
- **Re-utilization of waste water in crude oil desalting:** instead of fresh water, pretreated sour water is used in crude oil desalting.
- **Oil separation and –re-utilization:** Through installation of an oil separator in relevant waste water flow in which heavily oil-polluted waste water is regularly generated the waste water load can be minimized and the separated oil can be refed to the process via the Slop system

3.6.3.2 Measures for waste water treatment

a) Tributary waste water stream treatment (Process condensate, Sour water):

Heavily polluted process waste water with high concentrations of especially hydrogen sulphide, hydrolysable sulphides, ammonia, phenols, cyanides and aromatics are collected in the sour water system and are pretreated generally by stripping. These can be performed in one or two stages; steam is used as the stripping medium.

The separated volatile substances are burnt or fed to the gas scrubbing and the Claus plant for sulphur recovery. For removal of the ammonia from the stripping gas catalytic methods are used which allow a selective oxidation to elementary nitrogen and water or hydrogen. The pretreated sour water is used in crude oil desalting.

The following table shows, as an example, the operating data for three sour water strippers examined. A typical cleaning performance of at least 97 % is shown for sulphide and mercaptan as well as, if necessary, nitrogen in the form of ammonia.

Sour water stripping, 3 plants		
Capacity: 22-60 m³ /h		
Parameter	**Characteristic of sour waters (mg/l)**	
	Input	**Output**
Sulphide/Mercaptan	**6300 - 20000**	**1- 100**
N (sum inorg.)	**2500 - 17000**	**2- 500**

Table 17 Characteristic of sour waters

Pressure oxidation comes into question as an alternative for appropriate tributary waste water streams with which hydrogen sulphide and dissolved sulphide at high temperature and pressure are converted with oxygen from the air into thiosulphate and sulphate.

During extractions in lubricating oil refineries waste water strippers are used to remove solvents. In the case of two strippers examined values of <0,5 mg/l AOX (Dichloromethane /Dichloroethane) and <5 mg/l for furfurol were achieved.

b) Central waste water treatment:
– mechanical treatment: Separation and recovery of oil, separation of sedimented particles. Rough cleaning occurs via the heavy oil separator. For fine cleaning, a flotation plant is often installed.

– chemical treatment: Production of metal hydroxide flakes whereby the dispersed hydrocarbons and other waste water contents as well as hydrogen sulphide become flocculated or precipitated. These stages are often connected to a flotation plant.

– biological treatment: Biological treatment occurs, generally in an activated sludge process. It can limit itself to reduction of the carbon content only when nitrogen is already adequately eliminated via tributary waste water stream treatment (stripping); otherwise a nitrification/denitrification unit is included. In some cases, a supplementary biological treatment stage is installed in the conventional aerobic activated sludge plant (fixed film biology or aerated lagoon); as well as additionally a filter stage. In an investigated case, denitrification is combined with biological sulphide oxidation.

3.6.3.3 Waste water management

Of special importance with respect to efficient and economic waste water treatment and reutilization, besides the consequent application of the above-mentioned measures, also the meaningful recording of different loaded waste waters is included:

- Rain water which is definitely unpolluted can be discharged without treatment.

- Polluted rain water which is produced in the plant area can be re-used after treatment (oil separation, if necessary biological treatment) for operating purposes (cooling water, washing- and cleaning water, extinguishing water).
- Lowly-polluted process waste water with low salt concentrations and condensates can be directly re-used after treatment or, as in the case of polluted rain water, can be further used.
- Heavily organic-polluted process waters with high concentrations of especially hydrogen sulphide, hydrolysable sulphides, ammonia, phenols, cyanides and aromatics are collected in the sour water system and are pretreated generally by stripping. The pretreated sour water is used in crude oil desalting. The subsequent salty waste water cannot be further used or only after complicated supplementary treatment, it is transported to the central treatment plant.

A further important instrument are measures which are necessary to minimize peak loads. This applies to temporary increased waste water production as well to the occasional emergence of strongly one-sided or especially highly loaded waste water i.e. for situations which, without homogenizing measures, can lead to overload of the waste water treatment. The requirement for such measures is an adequate storage capacity flow to or bypassed to the central waste water treatment, corresponding facilities for monitoring the waste water quantity and characteristic fed to or bypassed to the central treatment plant as well as suitable facilities for controlling or regulating filling and emptying of the intermediate storage.

4 Techniques to consider in the Determination of BAT

4.1 General Remarks

The measures mentioned in Chapter 3 are considered in the determination of the best available techniques because the plants examined in which they were taken were almost exclusively newly constructed or greatly modified in the last decade. They therefore correspond to “state of the art”. The recommended limits in Germany are normally maintained and sometimes the emissions remain significant under these limits.

After a short introduction, the techniques used in German refineries in relation to the list in Chapter 3 are summarized in tables. When using the techniques described in the tables the emission values listed can be maintained. Furthermore, the compilation contains the remarks for environmental performance and "cross-media-effects".

The plants which are considered as BAT fulfil, as far as possible, the most important requirements for the best available techniques in refinery plants:

- Minimization of emissions into the atmosphere and waters
- Prevention of wastes or, if it is not possible, to utilize them
- Saving energy and protecting resources.

Techniques for emission reduction
In order to minimize emissions into the atmosphere and waters principally the following possibilities can be realised:

- Reduction and prevention of emissions with process-integrated techniques and
- Reduction of emissions with "end-of-pipe" techniques.

Measures for air pollution control are generally process-integrated (e.g. choice of the burner and the fuels in refinery furnaces). The use of low-sulphur-containing fuels reduces emissions but leads to partial transfer of incineration outside of the refinery. Secondary measures, for example, gas scrubbing for reducing the sulphur dioxide emissions in refinery furnaces are not state of the art and are not proportional.

The nitrogen oxide emissions do not depend directly on the bound nitrogen in the fuels since, during combustion, atmospheric nitrogen also contributes to the production of nitrogen oxides. Reduction of nitrogen dioxides in the flue gas is achieved by modern incinerating technology. Use of low-NOx furnaces is largely state of the art in Germany but renovation is not in all cases possible.

The secondary measures applied in other industrial sectors for reduction of NO_2 emissions, SCR (selective catalytic reduction) and SNCR: (selective non-catalytic reduction) are not state of the art for process furnaces and are not proportional.

The central waste water treatment plant as the main measure in limiting emissions into waters is an "end-of-pipe" technique. It is advisable and necessary since, as a relative flexible system, similar waste water collected from various different plant sectors can be treated with relatively low energy consumption and use of substances and also because of changes caused by standstill, extension and inspection etc. Prerequisites for an optimal waste water scheme are, however, process-integrated measures such as use of regenerative procedures for gas scrubbing or re-utilization of unloaded/purified waste water during processing.

In a similar way, the Claus plant must be considered as a meaningful and necessary „end-of-pipe“ technique.

Altogether, the ideal combination of process-integrated and „end-of-pipe“ technique must be found for each refinery location in the context of the specific local conditions.

Waste management

Special characterization of refineries is the closed material balance which means that almost no waste is generated (Section 3.3.3.1) because side products from individual processes are converted completely in other processes to products. Through sulphur management with respect to products and intermediary products material balance is closed and sulphur emission from the whole refinery is minimized.

For measures for reducing wastes and for internal or external utilization organisational measures are important which are based on the Waste Management plan. The Waste Management plan is seen by the lawmaker as an internal planning instrument. If wastes cannot be avoided, as is the case with refinery-typical oil sludges, sludges from waste water treatment and used catalysts, the possibilities for utilization must be examined. Typical routes are the thermal utilization (if necessary, also external) or feeding back to production (desalting, coking).

Energy and Substances

For energy management organisational measures likewise are important to, at first, identify the deficits and, secondly, to eliminate them.

In the general typical central facilities in refineries for steam production and distribution at different pressure levels the primary energy is effectively used.

Techniques for heat recovery in the form of steam or energy production in the form of steam or electrical energy are used.

In addition to primary energy carriers, auxiliary substances are used in refineries. These are mainly:

- Catalysts
- Chemicals for waste water treatment
- Acids and bases for different purposes
- Liquids for gas scrubbing
- Extractives
- Activated carbon for VRU

The capacity for reducing these quantities of substances is, because of its purpose, small as long as absorptions, extractions and similar processes proceed in a regenerative manner.

In conformity with Annex IV, the IPPC Directive demands that the BAT use "less dangerous substances". Accordingly, it should be examined if the solvents furfurol and halogenized hydrocarbons in extractions can be substituted by less harmful solvents or mixtures. If halogenized hydrocarbons are used they must be removed from waste water by stripping. Emissions into the air are not important in extractions because, according to BAT, regenerative and extensive emission-free techniques are applied.

Antagonistic or synergistic effects of environmental protection measures
In this section, environmental protection measures are judged under the aspect of multimedia complexity. Therefore, a main concern of the IPPU-Directive, namely the **integrated** concept, is considered. The following aspects are important:

- The effectiveness of special measures for common treatment of different environmental protection aspects.
- The requirements, if necessary, for special environmental protection aspects of specific measures should be compared to one another.
- Synergism of and independence of different environmental protection measures.

In this context, the following aspects, for example, are to be considered for refineries:

- The more products and intermediate products of a refinery are refined the more energy and auxiliary substances are needed. Hence, more wastes are normally produced and therefore also more waste water. A high quality of mineral oil products is required due to increasing demands (octane number, sulphur content).
- Reduction of the sulphur content of the feedstock in catalytic cracking or fuels in refinery furnaces serves to improve products or reduce SO_2 emissions into the atmosphere and is effectively achieved with hydrodesulphurization of the feedstock. In this process, on the other hand, hydrogen, catalysts and energy are used and sour waters are produced.
- Prevention of wastes has priority over waste utilization and elimination since secondary emissions emerge into the air or water during these processes.
- The tributary waste water stream treatment, e.g. H_2S stripping eases the central waste water treatment. For this purpose, additional energy is used and wastes and emissions from sulphur recovery are produced in the atmosphere.
- Water consumption is to be minimized which protects resources and also reduces the quantity of solid wastes from waste water treatment.
- By means of efficient energy management not only resources are protected but also emissions into the air, especially from carbon dioxide, are reduced.
- Through sulphur management with respect to products and intermediary products material balance is closed and sulphur emission from the whole refinery is minimized.

In the context of the integrated concepts according to BAT, the following components in the normal case should be compatible with available components in refineries:

- Hydrodesulphurization
- Regenerative gas scrubbing
- Tributary waste water stream treatment
- Effective central waste water treatment
- Effective sulphur recovery

4.2 Emissions into the air

The "achieved" values in the following tables are half-hourly or daily means when not otherwise stated. Because not only data from the survey are recorded the origin of the data is given under „Reference“.

4.2.1 Sulphur oxides

The main sources of SO_2-emissions are:

- Flue gas from refinery furnaces
- Flue gas from catalytic cracking plants
- Flue gas from sulphur recovery plant
- Petroleum coke production

Table 18 Candidates BAT for emission reduction of SO_2

Technique, *Measure*, (Reference Chapt. 3)	**Achieved Values**	**Environmental performance, cross-media effects, Remarks [Reference]**
Refinery furnaces (Chapt. 3.6.2.1)		
Use of low-sulphur fuels within the context of sulphur management process integrated	5 – 1700 mg/m³ according to fuel and furnace heat production	Together with the bubble concept leads to a reduction of sulphur emissions in the entire refinery, compared to exploitation of the single limit values. Conversion of heavy fractions into light fractions with the aim of obtaining products with a lower sulphur content requires higher energy consumption (higher CO_2- emissions), [Refineries 1-6]
Catalytic cracking plants (Chapt. 3.6.2.3)		
Use of low-sulphur feedstocks within the context of sulphur management *process integrated*	600 -1200 mg/m³	Together with the bubble concept leads to a reduction of sulphur emissions in the entire refinery, compared to exploitation of the single limit values.
Desulphurization of the feedstock *process integrated*	600 -1200 mg/m³	Reduction of SO_2 emissions in the regenerator flue gas by approximately. 70 - 80 %, also reduces the NO_2- and dust emissions, via supplementary step energy-consuming measure, produces sour waters and spent catalysts [Ref. 2,3,5].
$DeSO_x$ additive in catalyst *process integrated*		Reduction of the SO_2 concentration by approx. 30 to 50 %; because of high costs only used discontinuously in German refineries [Ref. 11]
Desulphurization of regenerator flue gas *end-of-pipe*	100-400 mg/m³	Reduction of SO_2 emissions in the regenerator flue gas by approximately 90 - 95%, also reduces the dust emissions, [/L50/], not used in German refineries

Sulphur recovery plants (Chapt. 3.6.2.7)		
Post-treatment of flue gases with Sulfreen stage *Process integrated/end-of-pipe*		Reduction of total SO_2 emissions (incl. previous stages) by approximately 99,5 % [Ref. 7]
Post-treatment of flue gases with Scot stage *Process integrated/end-of-pipe*		Reduction of SO_2 emissions (incl. previous stages) by approximately 99,8 % [Ref. 2,3,4]
Coke production and Calcination (Chapt. 3.6.2.2)		
Low-S green coke as feedstock during calcination in the context of sulphur management *Process integrated*	1000 mg/m^3	[Ref. 3]
Desulphurization of calcination flue gas *end-of-pipe*	300 mg/m³	Reduction of SO_2 emissions in the calcination flue gas by approximately 90%, also reduces the dust emissions [Ref. 3, /L32/]

4.2.2 Nitrogen oxides

The main sources of NO_x emissions are:

- Flue gas from refinery furnaces
- Flue gas from catalytic cracking plants

Table 19 Candidates BAT for emission reduction of NO_x

Technique, *Measure*, (Reference Chapt. 3)	**Achieved Values**	**Environmental performance, cross-media aspects, Remarks (Reference)**
Refinery furnaces (Chapt. 3.6.2.1)		
Installation of low NO_x burners, optimized burner-furnace design, optimized air to fuel ratio *process integrated*	100 mg/m³ (new plants)	for gas fuels, with liquid fuels the legislatory requirements cannot be attained with this technique, higher hydrocarbon and dust emissions could arise [/L32/]
Fuel management: operation of mixed furnaces with the use of liquid and gas fuels *Process integrated*	300 mg/m³	[/L32/]
NO_x reduction via SNCR *end-of-pipe*)	150 mg/m³ (gas), 150 – 300 mg/m³ (liquid)	Reduction of NO_x emissions in flue gases up to approximately 60 %, NH_3 emissions can possibly arise, not used in German refineries (in process furnaces) [/L51/, /L32/]
NO_x reduction via SCR *end-of-pipe*	55 mg/m³ (gas) 150 mg/m³ (liquid)	Reduction of NO_x emissions in flue gases up to approximately 95 %, NH_3 emissions can possibly arise, not used in German refineries (in process furnaces) [/L51/, /L32/]

Catalytic cracking plants (Chapt. 3.6.2.3)		
Staged incineration (CO-Boiler),	100 - 250 mg/m³	Reduction of NO_x emissions in regenerator flue gas by approximately 50-80 %, Emissions of SO_3 and NO_x increase in "total combustion mode" [Ref. 10]
Optimized excess air, reduction of promotor	100 - 250 mg/m³	reduction of promotor increases CO emissions [Ref. 10]
NO_x reduction via SNCR *end-of-pipe*	300 mg/m³	Reduction of NO_x emissions in flue gases up to approximately 60 %, NH_3-Emissions can possibly arise [Ref. 10]
NO_x reduction via SCR *end-of-pipe*	120 mg/m³	Reduction of NO_x emissions in flue gases up to approximately 95 %, NH_3-Emissions can possibly arise [/L51/]

4.2.3 Dust and dust components

he main sources of dust emissions are:

- Flue gas from refinery furnaces
- Flue gas from catalytic cracking plants
- Petroleum coke production

The dusts contain, according to feedstock, more or less heavy metals which are mainly nickel and vanadium.

Table 20 Candidates BAT for emission reduction of dust

Technique, *Measure*, (Reference Chapt. 3)	**Achieved Values**	**Environmental performance, cross-media effects, Remarks (Reference)**
Refinery furnaces (Chapt. 3.6.2.1)		
Fuel management: operation of mixed furnaces with the use of liquid and gas fuels *Process integrated*	Gas 5 mg/m³ Liquid 50 mg/m³	[/L32/]
Switch to liquid fuels with low ash proportion *Process integrated*	20 -50 mg/m³	[/L52/]
Catalytic cracking plants (Chapt. 3.6.2.3)		
Dust removal from regenerator flue gases by cyclone and electrostatical separator *end-of-pipe*	20 - 50 mg/m³	Reduction of dust emissions in regenerator flue gas by more than 99,8 %, higher consumption of electrical energy [Ref. 7, 8]
Coke production and Calcination (Chapt. 3.6.2.2)	20 - 50 mg/m³	
Dust removal from calcination flue gases by electrostatical separator *end-of-pipe*	30 mg/m³	Reduction of dust emissions in calcination flue gas [Ref. 9]

4.2.4 Hydrocarbons

The main causes of emissions from hydrocarbons are:

- Storage tanks
- Product supply/transfer, loading
- Diffuse emissions from sealing elements
- Flares

Table 21 Candidates BAT for emission reduction from hydrocarbons

Technique, *Measure*, (Reference Chapt. 3)	**Achieved values**	**Environmental performance, cross-media effects, Remarks (Reference)**
Storage (Chapt. 3.6.2.6)		
Floating-roof tanks with double (primary and secondary) sealings *process integrated*		Reduction of hydrocarbon emissions by up to 95 % as compared to fixed-roof tanks, for products with vapour pressure > 13 hPa/20°C [/L32/]
Fixed-roof tanks with floating covers *process integrated*		Reduction of hydrocarbon emissions by up to 95 % as compared to fixed-roof tanks, for products with vapour pressure > 13 hPa/20°C [/L32/] Technique is used only in special cases, mostly because of product quality reasons
Fixed roof tanks with connection to a gas collection system *end-of-pipe*		Flue gases are either refed or fed to a flue gas purification plant (cf. Chap. 3.6.2.5), Products with vapour pressure > 13 hPa/20°C, [/L32/]
Fixed roof tanks with forced breathing and feeding of the flue gases to an incinerator *end-of-pipe*	10 mg/m³ hydrocarbon (total) 1 mg/m³ benzene	Reduces the hydrocarbon emissions by approximately 99,99 % compared to fixed roof tanks, Products with a high hazard potential, e.g. benzene [Ref. 9]
Fixed-roof tanks with tank coatings which reflect radiation heat to at least 70 % *Process integrated*		Reduction of emissions through tank breathing Emissions from solvents during painting [/L32/]
Fixed-roof tanks with floating covers with overpressure/underpressure valves *Process integrated*		reduces the emissions through tank breathing [/L32/]
Feeding of the flue gases from bitumen tanks to an incinerator *end-of-pipe*	20 mg/m³ hydrocarbons	Eliminates odour intensive flue gases; without additional measures such as, accompanying heating danger of "thickening" of pipes[/L32/]

Loading/unloading, transfer (Chapt. 3.6.2.5)		
Vapour balancing in connection with submerged loading *Process integrated*		Reduction of hydrocarbon emissions by approximately 80 % as compared to free ventilation, for products with vapour pressure > 13 hPa/20°C [/L32/]
Feeding of flue gases to a recovery and/or incineration unit *end-of-pipe*	150 mg/m^3 hydrocarbons (without methane) 1 mg/m^3 benzene	Reduction of hydrocarbon emissions by approximately 99,98 % as compared to free ventilation, Products with a vapour pressure > 13 hPa/20°C [/L32/]
Use of low-emission techniques during tank cleaning *Process integrated/end-of-pipe*		Reduction of hydrocarbon emissions during tank cleaning [/L48/]
Diffuse emissions from sealing elements (Chapt. 3.6.1)		
Pumps, e.g. with multiple mechanical seal with quench or buffer medium or canned motor pumps *Process integrated*		Technically tight, for products with a high hazard potential, e.g. benzene [/L32/]
Compressors with multiple sealing systems *Process integrated*		Technically tight, for gases with a high hazard potential, e.g. ethylene [/L32/], [/L32/]
Shut-off- and control fittings with tightly sealed metal bellows with a downstream safety gland or equivalent sealing system. *Process integrated*	10^{-4} hPa l/(s m) at $T < 250$ °C or 10^{-2} hPa l/(s m) at $T \geq 250$ °C	Technically tight, for products with a high hazard potential, e.g. benzene [/L32/]
Flange connections with metal and welded sealings (with smooth rail) or equivalent through constructive design (e.g. groove and tongue) *Process integrated*	10^{-4} hPa l /(s·m)	Technically tight, for products with a high hazard potential, e.g. benzene [/L32/]
Flares (Chapt. 3.6.2.8)		
Flare gas collection unit *Process integrated*		Gases from pressure release fittings are refed to the refinery heat system by recompression, operation of flares generally only in the case of major malfunctions (e.g. for major accidents and fire) [/L32/]
Optimize burnout via controlled steam injection *Process integrated*		> 99 % burnout attained with respect to total C, via suitable construction of the flare head reduction of noise emissions [/L32/]

4.3 Water Protection

4.3.1 Emissions into waters

The most important waste water flows from a refinery arise during the following processes:

- Atmospheric distillation (desalting) and vacuum distillation
- Catalytic cracking
- Thermal cracking
- Hydrocracking
- Desulphurizing plants
- Alkylation
- Mercaptan conversion (Merox plants)
- Tank cleaning and tank drainage

All waste water flows from the abovementioned processes, some after planned pretreatment by e.g. gravity separation or stripping (physical, chemical, biological stages) are fed to the central waste water treatment.

Substances which cannot be treated in the central waste water treatment plant or only inadequately are to be avoided or are to be pretreated as tributary waste water stream. This holds e.g. for halogen-organic extractives which are used for dewaxing. These extractives are to be substituted either by biologically degradable substances or e.g. by stripping of tributary waste water stream. Also for substances which can be degraded in the central biological treatment plant it can be meaningful to have a decentral pretreatment.

Here the following example:
Depending on the ammonia load in waste water flows and in the entire process waste water, the optimal procedure with respect to reduction of nitrogen lies between pretreatment through NH_3 stripping and nitrification/denitrification in the central waste water treatment plant. Beside minimization of nitrogen into waters, the aim should be the smallest possible salting of the waste waters and the minimization of the energy input in connection with an economic combination of methods.

Fundamental measures for reducing emissions and water consumption have the goal of determining the optimal combination of prevention, pretreatment and posttreatment measures_for minimizing water consumption and emissions according to state of the art. These include:

- Preparation of a water balance (necessary quantity and quality of feedstock, generation of waste water)
- Separate recording of unpolluted rain water, oily rain water, low-polluted processing waste water with a low salt content and condensates as well as from strongly organic-polluted processing waste water
- Determination of characteristics of important tributary waste water streams (atmospheric and vacuum distillation, cracking plants, desulphurization plants, flare system, desalter, alkylation, tank cleaning and drainage)
- Determination of waste water prevention and re-utilization potential and, as the case may be, the necessary treatment measures

Process-integrated and treatment measures for minimizing emissions and water consumption are contained in the following table.

Table 22 Candidates BAT for reducing water consumption and emissions

Technique, Measure, (Chapt. 3.6.3)	Environmental performance, cross-media effects, Achieved Values, Remarks
Process-integrated measures	
Desulphurization with hydrogen instead of sweetening	Reduces water usage, relieves central waste water treatment
Regenerative desulphurization (gas scrubbing, desulphurization, Merox Process)	Reduces water usage, relieves central waste water treatment
Re-utilization or further use of waste water (desalting of crude oil, washing and cleaning water, extinguishing water, cooling water, steam condensate)	Reduces water usage, relieves central waste water treatment
Oil separation in processing plants	Relieves central waste water treatment, re-utilization of oils
Switch from water cooling to air cooling (in new plants and suitable locations of use)	Reduces water usage
Closed cool water recirculation (cooling towers)	Reduces water usage, conditioning of cooling water possibly needed
Closed steam recirculation (condensate recovery)	Reduces water usage, mud water treating needed
Waste water treatment	
Treatment of tributary waste water streams by separation from hydrocarbons via gravity separation, flotation and/or stripping	Relieves central waste water treatment with respect to:
Gravity separation for all oily waste water flows	Hydrocarbons
Stripping the waste water flow from:	
Crude oil distillation, cracking plants, hydroplants	Volatile hydrocarbons (aromatics), sulphide, sulphate, ammonia, phenols, cyanide
Treatment of waste water containing sulphides via pressure oxidation	
Stripping of halogen-organic extractives which are used in dewaxing	AOX, < 0.5 mg/l surely attained
Process waters used often: use of stripping water in desalter	Reduces water usage
Separation of waste water flows in production waste water, non-contaminated surface water, cooling water	Relieves central waste water treatment
Multistage waste water treatment with physical, chemical, biological stages	1 Separation of undissolved hydrocarbons via gravity (API, PPI, skimming in storage tank) 2 Separation of dispersed hydrocarbons and sulphides via flocculation/precipitation and flotation stage for further hydrocarbon separation 3 Elimination of dissolved contents via biological treatment, degradation of carbon compounds and, if necessary, nitrogen compounds through regenerative processes, removal of COD to < 30 - 80 mg/l
Nitrification and denitrification stages	Removal of N_{tot}. up to 10 -40 mg/l
homogenization and treatment of nonusable rain water (oil separation and, if necessary, further treatment)	Relieves central waste water treatment, minimization of pollutant load
Storage tanks	homogenization of crude waste water (quantitatively and qualitatively)
Biological oxidation of sulphides via autotrophic denitrification	Up to 130 mg/l sulphide are directly oxidized biologically, reduces energy consumption, prevents waste production (no need for iron sulphide precipitation)
Further elimination via installed filtration, fixed-bed biology or adsorption of the treated waste water	Reduction of load (suspensa restraint), reduces water usage, further utilization is possible

Special measures for reducing emissions into waters

In the following Section, 3 measures for reduction of emissions into waters which are realized in separate German refineries are described in detail.

Measure A (Refinery 10)

As BAT especially such measures are to be emphasized which effectively reduce all types of emissions.

To reduce nitrogenous emissions into waters, it is recommended to eliminate ammonia via further stripping of tributary waste water streams. The ammonia water collected in this way can be used as a DeNOx agent for reducing NOx-Emissions into the air.

Tributary waste water streams which have sulphide concentrations of 1050 – 3300 mg/l and ammonia concentrations of 730 - 1370 mg/l are fed firstly to a steam stripping column, the H_2S Stripper. The stripped hydrogen sulphide is converted in the Claus Plant to sulphur. In a downstream steam stripping column (NH_3 Stripper) ammonia is expelled under alkaline conditions and concentrated to a 15 % solution. Subsequently, the ammonia water produced is injected in the flue gas stream of the catalytic cracking plant as a DeNOx agent.

In the run-off of the NH_3 Stripper, a sulphide concentration between 2 and 7 mg/l and ammonia concentration between 3 and 9 mg/l are found in the waste water which corresponds to an elimination rate of ammonia nitrogen and hydrogen sulphide from crude waste water of approximately 99 %. The pretreated waste waters are further treated in a central biological waste water treatment plant.

Injection of ammonia water reduces emissions of nitrogen oxides in flue gas of the catalytic cracking plant by 55 %.

A further advantage of the plant described is that wastes to be disposed off are not generated. High investments for denitrification in the central waste water treatment plant can be avoided. By means of the upstream tributary waste water stream treatment of the sour water a considerable reduction in the O_2 demand is achieved. In connection to this advantage, also approximately 10 % less excess sludge is to be disposed off.

The plant described operates successfully since 1997. The investment costs for expansion of existing sour water stripping in the NH_3 Stripper were about 3,3 Mio. Euro. Annual operating costs (steam, energy, cooling water, sulphuric acid, caustic lye, fuel gas) for the entire plant is approximately 425,000.00- Euro. In contrast to the annual operating costs for operation of only the H_2S Strippers (350,000.00- Euro), the annual operating costs are approximately 75,000.00- Euro because of expansion of the NH_3 Stripper.

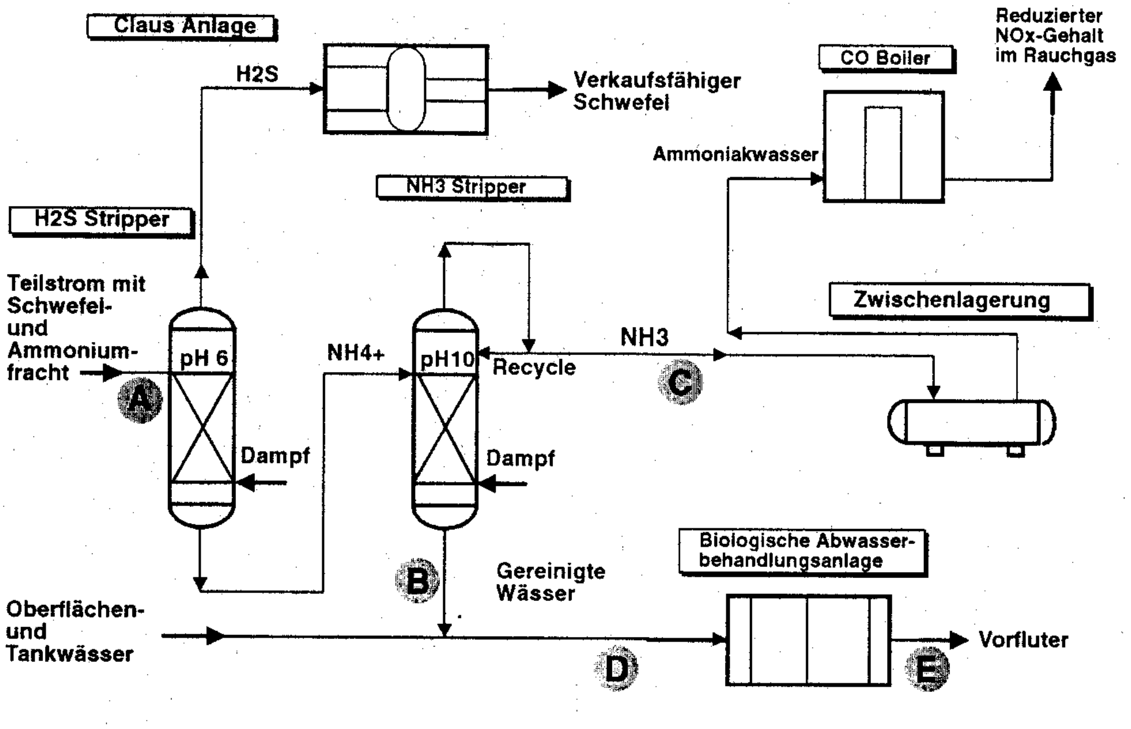

Figure 2 Simplified diagram of combined methods of waste water treatment

Source: C.Stein, J. Elster, I.Heine, J.Sachse, H. Peper „Entfernung von Ammonium-Stickstoff und Schwefelwasserstoff aus Raffinerieabwässern“ Erdöl Erdgas Kohle 114, Heft 10 (Oktober 1998)“

Measure B (Refinery 11)
In a central biological waste water treatment plant the following technique concept was realised which corresponds to the BAT:
Waste waters are collected in separate systems according to the degree of pollution and cleaned biologically. The weakly loaded waste waters such as e.g. rain water in need of treatment from plant sectors are injected before the last biological treatment stage (fixed-bed reactor) and subsequently treated (see in Fig. 3 "Mischabwasser").

The strongly loaded process waste waters are treated in the multi-stage biological waste water treatment plant. In the first activated sludge step, the processes of heterotrophic denitrification and autotrophic sulphide oxidation occur parallel to each other. The chosen processing steps, in the order denitrification/nitrification, allows the use of sulphides as a reduction substance and therefore as additional energy source beside COD in the anaerobic denitrification stage. Precipitation of sulphide with iron salts is therefore not necessary. The following activated sludge step is necessary for the heterotrophic, aerobic COD reduction as well as the nitrification reactions. This activated sludge step is preceded by an additional denitrification. Secondary sedimentation is succeeded by a combination of fixed-bed reactor for remaining nitrification and double-layered filter for suspensa separation.

In the biological waste water treatment plant described, supply concentrations for the parameter COD of approximately 1300 mg/l, for NH_4-N of approximately 550 mg/l and for sulphide up to approximately 130 mg/l are treated. This leads to a reduction in COD of approximately

94 % and a reduction in nitrogen of over 90 %. Sulphide is not found in the purified water run-off.

Special value is placed on process stability. It is designed extensively redundant and possesses an activated sludge reserve in a separate sludge stabilising tank.

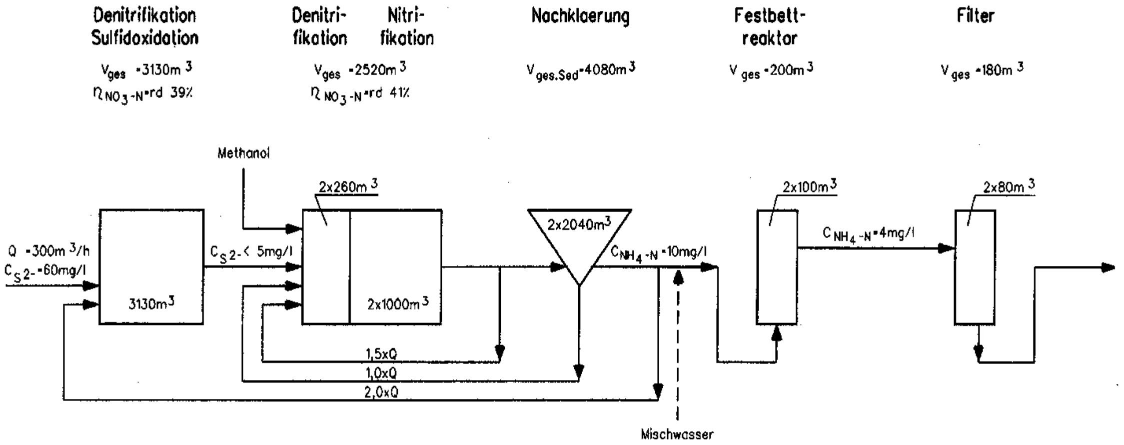

Figure 3 Diagram of the biological treating

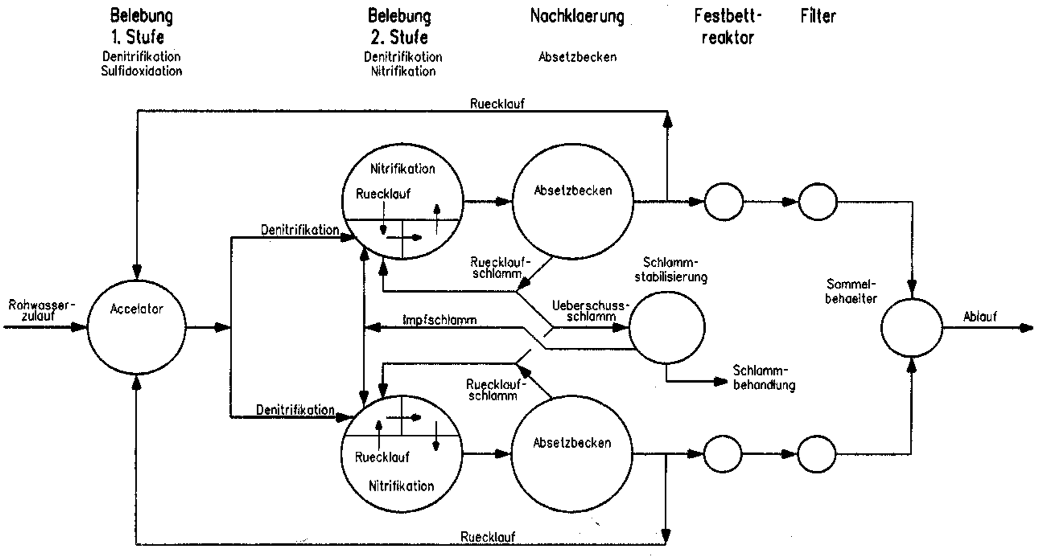

Figure 4 Entire concept of the biological treating

Source: H.A. Joel, Th. Jenke „Entwicklung und Bau einer neuartigen biologischen Reinigungsstufe“ Erdöl Erdgas Kohle 110, Heft 4 (April 1994)“

Measure C (Lubricating oil refinery 6)

During dewaxing, halogen-organic extractives such as dichloromethane and dichloroethane are used which are recovered by stripping. Through optimization of the stripping process and a quasi continuous monitoring automatic, the attainment of run-off values of the stripper of < 0,5 mg/l AOX is guaranteed. During run-off not according to specification an automatic recirculation of waste waters occurs.

4.3.2 Prevention of emissions into soil and ground water

Plants from which substances which pose a hazard to water can enter the soil and ground water are

- Plants for manufacturing, treating and utilizing substances which are hazardous to water (processing plants)
- Plants for storage, filling and transfer of substances which are hazardous to water
- Pipelines for transport of substances which pose a hazard to water

With respect to construction techniques, plants must be permanently sealed and stable. Materials used and type of construction must be adequately resistant against the expected thermal, mechanical and chemical influences. Leakages from plants must be recognized swiftly and reliably. If substances which pose a hazard to water are released they must be recognized quickly and reliably, restrained and utilized or properly disposed off.

Table 23 Candidates BAT for prevention of contamination of soil and ground water by substances which pose a hazard to water

Technique;Measure (See Chap. 35)	**Environmental performance Remarks**
Tight and durable enclosure of substances which pose a hazard to water	Primary safety against release
Production of sealed assembly areas	Quality and certificates correspond to the hazard potential of the plant
Establishment of sealed restraining facilities for liquid substances which pose a hazard to water	Secondary safety for harmless restrainment in the case of leakage
Introduction of infrastructural measures, performance of controls	Measures for swift recognition of leakages in plants and functional units

4.4 Waste

The most important wastes from refineries, according to type and quantity, are:

- oily or oil-polluted waste
- Sludge from waste water purification
- Spent catalysts

Table 24 Candidates BAT for waste reduction and utilization

Technique, Measure, (see Chapt. 3.3.3)	Environmental performance, cross-media effects, Remarks
Separation of different types of wastes	allows planned utilization or elimination
Use possibilities for energetic utilization	Utilization measure
Dewatering or incineration of sludges from waste water purification	Reduction/Utilization
Possibilities for utilization in the construction and cement industries	Utilization
Minimization of waste during tank cleaning by organizational measures and low-waste cleaning stages	Waste reduction
Recycling of catalysts, internal/external	Solid waste reduction, metal recovery
Slop systems with recirculation	Reduction of wastes containing hydrocarbons
Recirculation of oily sludges into production e.g. in coking or desalting	Internal waste prevention

4.5 Utilization of waste heat

Utilization of waste heat is a main factor for efficient energy use. As heat sources primarily refinery furnaces, catalytic cracking and petroleum coke production as well as exothermic processes (Claus process) are considered.

The remaining waste heat emissions are discharged mainly either directly into the atmosphere or indirectly via cooling water into the environment.

Table 25 Candidates BAT for waste heat utilization

Technique, Measure, (Chapt. 3.3.5.1)	Environmental performance, cross-media effects, Remarks
Production of steam, hot water, feeding heat transfer oil systems, in special cases combined with the production of electrical energy	Energy used to warm feedstocks, drive compressors or pumps; emission reduction besides economic aspects, saving of primary energy sources
Optimal design of heat exchanger network, operation with measuring and control facilities	In existing plants sometimes very expensive or not to realize because of space
Heat insulation of functional units and pipelines	Reduction of waste heat

4.6 Organizational Measures

In connection with BAT, organizational measures should not be left unconsidered. Suitable instruments for the support of environmental or integrated management systems are e.g. the relevant systems in conformity with the EMAS Directive /E11/ and the Standards of the Series ISO 14000 /L47/. According to the present status in German refineries, environmental management systems are already implemented or planned.

By careful analysis of the input/output data and regular environmental audits especially the following goals can be achieved:

- Installation of controlling systems
- Definition of responsibility
- Optimization of energy management
- Optimization of waste management
- Optimization of safety management
- Optimization of sulphur management
- Identification of deficiencies and of weakest points
- Increasing plant safety
- Participation of external facilities and the Public
- Improvement of worker’s protection

5 Best Available Techniques

5.1 Preface

The techniques mentioned in Chapter 4 come into consideration for the BAT. The lists presented in Chapter 4 will not be repeated in Chapter 5; they will be summarized and mentioned. Furthermore, where it is necessary, the conditions under which the candidate BAT are or can be used are described further in detail

When judging BAT the economic aspects are to be considered. Data on the cost of each measure are only partly available. They are not informative because they vary greatly according to location and the calculation principles are different. This applies for the investment costs as well as the operating costs. Hence, costs, if at all, are given as a lump-sum.

5.2 BAT for air pollution control

5.2.1 SO_2 Emissions

The candidate BAT with a high environmental protection performance for reducing the SO_2 emissions into the air are mainly the primary measures and suitable management of sulphur:low-sulphur or desulphurized feedstocks, catalytic cracking and during the production of petroleum coke, low-sulphur fuels in refinery furnaces.

The limit values for SO_2 in German refineries are partly attained by blending high- and low-sulphur fuels or feedstocks. It is proceeded similarly with a "bubble concept": By using feedstocks with different sulphur contents in separate plants the limit values of the bubble as an annual mean is attained.

In refinery furnaces within the context of sulphur management gas fuels are preferred to liquid fuels; the refinery gas is desulphurized by regenerative gas scrubbing. The additional use of natural gas comes into consideration as BAT as long as natural gas is available on location considering the economic aspects.

Secondary measures for the reduction of sulphur oxides in the flue gases during catalytic cracking are considered when low-sulphur feedstocks are not available in adequate quantities. In this case, emissions can be reduced by alkaline supplements (DeSOx) to the catalyst. This measure is very expensive at a relatively small level of emission reduction of - after careful estimation - approx. 30%. The use of DeSOx catalysts as BAT is considered only as an exception. The use of flue gas purification plants for process furnaces involves, on one hand, high costs and, on the other hand, mostly decentral spatial organization of furnace plants.

During calcination flue gas scrubbing can serve as a secondary measure to reduce the SO_2 by >90 %. This expensive technique is considered if high-sulphur green cokes is used.

During sulphur recovery the use of candidate BAT in German refineries - 2-staged Claus plants with a further stage - sulphur emission rates of < 0,5% are attained. In lubricating oil refineries H_2S-containing gases from desulphurizing plants or vacuum distillation are not normally treated further as long as less than 2 t/d H_2S at a concentration of <0,4% are produced. The flue gases are incinerated according to the BAT to attain the H_2S concentration in flue gas of < 10 mg/m³.

Because the marketing potential of heavy fuel oil is small and the quality requirements of fuels increase, it is increasingly necessary to refine heavy fractions in refineries. Hydrocrackers give high yields, effectively reduces the sulphur content in the products and results in less emissions compared to catalytic cracking. This measure is very expensive. The available hydrogen in the refineries is possibly not adequate to cover the demands of the hydrocracker. In this case, additional investments are necessary to produce hydrogen in a separate plant.

5.2.2 NO_x Emissions

The most effective Candidate BAT for the reduction of nitrogen oxides from refinery furnaces are, as for SO_2, primary measures, the use of modern burner technology with optimized operation. In new plants, the extra costs for low-NO_x burners is relatively small compared to those of the conventional technique. During the renovation of existing plants it is not possible in some cases, because of the shape of the oven, to optimize the burner-furnace design and therefore to attain concentrations of < 100 mg/m³ as in gas furnaces of new plants.

The NO_x concentration in flue gas from the regenerator of catalytic cracking can be effectively reduced likewise to < 250 mg/m³ by primary measures, staged incineration and optimizing reaction conditions.

As long as the feedstocks in refinery furnaces and catalytic cracking is hydrodesulphurized, the content of bounded nitrogen is reduced since organic nitrogen compounds are converted by hydration to ammonia. A smaller nitrogen content leads to a limited reduction of the NO_x emissions.

During catalytic cracking, among others, SCR and SNCR come in question as secondary measures. Both measures are expensive. With SCR, the NO_x concentration can be reduced by approx. 60 %. These techniques are considered if the primary measures do not effectively reduce the NO_x concentration. These techniques are not used in process furnaces because they are unproportional.

5.2.3 Dust Emissions

In refinery furnaces, the most effective BAT candidate for the reduction of dust emissions is the use of low-ashfuels which allows a dust concentration from 5 to 50 mg/m³.

Dust in flue gases from the regenerator of catalytic cracking and calcination is removed by secondary measures to attain concentrations of <50 mg/m³.

For dust reduction according to the BAT, mechanical, filtering and electrostatical separation as well as scrubbers are available. For catalytic cracking, a two-staged plant with cyclone separator and electrofilter allows the sure attainment of the limit value 50 mg/m³.

5.2.4 Hydrocarbon Emissions

The candidate BAT reduces hydrocarbon emissions mainly during farm tank processes and - for all processing plants - emissions from sealing elements. The measure or combination of measures according to the BAT which is applied depend (s) on the hazard potential of the products i.e. from vapour pressure which determines the emission mass flow, from the toxic characteristic as well as the degradability and accumulability.

According to the BAT, special effective measures are required for products with a vapour pressure of >13 hPa at 20°C, for carcinogenic products (R45, R49 according to Directive

67/548 EWG /E6/) and products with a high acute toxicity (e.g. R23, R26) as well as for products which accumulate and are difficult to degrade.

Hydrocarbon emissions from loading/unloading and from storage are fed to a vapour recovery unit (VRU) and/or a flue gas purification plant in conformity with BAT. In this way, hydrocarbon emissions are reduced by approximately 99.98% as compared to free ventilation (< 150 mg/m³ hydrocarbons; < 1 mg/m³ benzene).

The BAT for the reduction of hydrocarbon emissions (and also SO_2 emissions) from flare operation is based on minimization of operation time, a flare gas recovery plant can reduce operation to a magnitude of 24h/a.

5.3 BAT for water pollution control

The BAT for water pollution control include the measures described in Section 4.3.1. They allow establishment of optimal combination of measures for prevention, pretreatment and posttreatment in order to minimize water consumption and emissions into waters according to the individual situation. The reliable reduction of emissions attained in each location, characterized as “state of the art” in Germany, is defined by means of the water legislatory requirements in Annex 45 of the waste water ordinance (Section 1.5.2).

According to BAT, the small specific quantity of waste water of 0,5 m³/t feedstock (1,3 m³/t in lubricating oil refineries) has the purpose, via highly concentrated polluted streams, to effectively reduce the pollutant load when waste water is treated. Simultaneously, they allow the saving of water.

For candidate BAT for waste water treatment a major aspect is the tributary waste water stream treatment which must be considered in close connection with the central waste water treatment. The higher the treatment performance of the tributary waste water stream treatment the higher the total treatment performance. Sour water strippers which correspond to the BAT remove ammonium nitrogen and hydrogen sulphide up to more than 97%.

In central waste water treatment plants which correspond to the BAT at a corresponding load of the raw waste water the COD is removed to at least 80%, as mean to over 90%. Hydrocarbons, aromatic hydrocarbons, phenols and special organic compounds (Furfurol) can partly be more effectively eliminated (>95->99%). The elimination rate of inorganic nitrogen differs according to which proportion was already eliminated with pretreatment (stripping). Via nitrification/denitrification stages and, if necessary, in combination with autotrophic oxidation of sulphides in biological waste water purification a concentration of <10 to 40 mg/l can be attained.

The BAT for ground water and soil protection include the measures listed in Section 4.3.2. They are applied in new plants independent of location and are used in German refineries. Renovation of existing plants is not completed since measures during long stoppage of operation of tanks put considerable demands on storage operations and also are very expensive.

5.4 BAT for waste management

The Candidate BAT for waste prevention are applicable mainly independent of location and without further conditions. The possibilities for utilization, however, depend on location and the configuration the refinery. Some locations possess an incineration plant in which wastes can be thermally used internally. Waste management in this case can differ widely from that of a refinery without incineration.

5.5 BAT for utilization of waste heat

The Candidate BAT for re-utilization of waste heat are applied mainly general and independent of location. In compactly-built refineries, more possibilities exist to effectively re-utilize waste heat in all plants than in refineries in which the process plants are distributed over a large area.

Heat utilization interfere, as a rule, with process integration i.e. in an existing refinery this is realised only through measures that are very expensive. Since by heat integration fuels are saved which can be additionally marketed, this is realised very extensively in all refineries.

5.6 BAT for organizational measures

The candidate BAT for organizational measures are applied independent of location.

Annexes

0 List of abbreviations

A	
AbwasserV	german ordinance "Abwasserverordnung" (waste water)
AOX	Adsorbable organic halogen
B	
BAT	Best available technique
BImSchG	german act "Bundes-Immissionsschutzgesetz" (immission protection)
BImSchV	ordinances according to "Bundes-Immissionsschutzgesetz"
BOD	Biological Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
C	
COD	Chemical Oxygen Demand
D	
DIN	Deutsche Industrienorm (german industry standard)
DEA	Diethanolamine
DruckbehV	german ordinance "Druckbehälterverordnung" (pressure vessels)
E	
EC	European Council
EN	European Standard
EU	European Union
F	
FCC	Fluid catalytic cracking
H	
HC	Hydrocarbons
HCU	Hydrocracking Unit
I	
IPPC	Integrated Pollution Prevention and Control
ISO	International Organization for Standardization
L	
LPG	Liquified petroleum gas
M	
MWV	german "Mineralölwirtschaftsverband" Hamburg

P	
PAH	Polycyclic aromatic hydrocarbons
S	
StörfallV	german ordinance "Störfall-Verordnung, 12. BImSchV" (major accidents)
SCOT	Shell Claus offgas treating
SRU	Sulfur recovery unit
T	
TA Luft	german direction "Technische Anleitung zur Reinhaltung der Luft" (pollution abatement of the atmosphere)
TNb	total nitrogen (bound)
TRbF	german technical directions "Technische Regeln brennbare Flüssigkeiten" (flammable liquids)
TRGS	german technical directions "Technische Regeln für Gefahrstoffe" (dangerous substances)
TRwS	german technical directions "Technische Regeln für wassergefährdende Stoffe" (substances hazardous to water)
U	
UVV	german rules "Unfallverhütungsvorschriften" (prevention of accidents)
V	
VAwS	german regulation "Verordnung über Anlagen zum Lagern, Abfüllen und Umschlagen wassergefährdender Stoffe" (plants as to handling substances hazardous to water)
VbF	german regulation "Verordnung über brennbare Flüssigkeiten" (flammable liquids)
VDI	Verein Deutscher Ingenieure, association of german engineers
VOC	Volatile organic compounds
VRU	Vapour recovery unit
VVAwS	administration rules according to "VAwS"
VwVwS	german administration rule "Allgemeine Verwaltungsvorschrift zum Wasserhaushaltsgesetz über die Einstufung wassergefährdender Stoffe in Wassergefährdungsklassen" (water hazard classes)
W	
WGK	Wassergefährdungsklasse water hazard class
WHG	german act: Wasserhaushaltsgesetz (federal water act)

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2 Present Consumption / Emission levels

see Questionnaires A and B

Files:

DAT_A.DOC: Complete Refinery

Processing plants:

Datb1.DOC	General information
Datb2.DOC	Air
Datb3.DOC	Water
Datb4.DOC	Waste
Datb5.DOC	Materials and energy
Datb6.DOC	Other data

Table A1: GENERAL INFORMATION TO THE REFINERY

Name and location of refinery:	
Contact person for further inquiry: telephone:	
Capacity - permitted capacity of crude processing (t/yr) - if necessary actual throughput in reference year 19___ - annual working hours in reference year	
Main-products and by-products amount/year, if necessary characteristics *please list, if necessary on separate page*	

Year of erection Type and term of essential changes of the processing structure, which are relevant for the following Data, including the designation please list up, if necessary on separate page	
Short description of the production process (sequence of processes, parts of plant/plant configuration, relevant secondary installations) *please add simple flow sheet!*	

A2: EMISSIONS INTO THE AIR

Crude oil throughput (Mio t/yr)	permitted effective / reference year		/	
Pollutant	**Emissions/reference year (t/yr)**			
Dust				
SO_x as SO_2				
NO_x as NO_2				
Hydrocarbons	**1)**	**2)**	**3)**	**4)**
Benzene				

1)Processing 2)Storage 3)Flare 4) Loading

Remarks
(e.g. for demarcation of the not excluded processing units such as power plant, petrochemical plants)

A3: EMISSIONS INTO THE WATER

Origin of Data:	
Reference year or period of Data	
Applied Emission-reduction-measures:	
– downstreamed waste water cleaning measures (if necessary including reduction performance):	
– production integrated measures for emission reduction: (if necessary including reduction performance):	
– measures to reduce the water consumption:	

☐ Direct discharging
☐ Indirect discharging

Waste water volume flow:

please differentiate according to:

☐ crude production waste water:_____m^3/yr

☐ Treated waste water: _____m^3/yr

☐ Direct cooling water _____m^3/yr

☐ Atmospheric water _____m^3/yr

☐ Ballastwater _____m^3/yr

Table A3: Effluents

	Untreated Water		**Treated Water**		
Parameter	Measured concentration (mg/l)	Discharge kg/t Crude oil throughput	Measured concentration (mg/l)	Discharge kg/t Crude oil throughput	Reduction (%)
COD					
TOC					
BOD_5					
TN_b					
N (tot.-inorganic).					
P (tot.)					
HC (tot.)					
BTEX aromatics					
Phenols					
AOX					
Sulphides/Mercaptanes					
Cyanides					
Luminous bacteria toxicity					
Fish toxicity					
Conductivity					
pH value					
Temperature					

Explanations

1) if no measured values exist: please specify calculated/estimated size and shortly explain calculation at “Notes”

2) if measured values are under proof- or determination limit quote these

Notes:

A4 Waste

Origin of Data (e.g. waste statistics):	
Reference year of data:	
Measures to prevent or reduce waste production and to recover wastes	

Waste types and quantities

Table A4.1: Hazardous waste for recovery - particular supervision required

Designation of waste	Origin (processing unit)	Waste code EWC	Waste quantity absolute (t/yr)	Notes
(listing, compare Page 8)				

Table A4.2 Hazardous waste for disposal – particular supervision required

Designation of waste	Origination (processing unit)	Waste code EWC	Waste quantity absolute (t/yr)	Notes
please check assignment page 7or 8				
tank bottom sludges	storage	05 01 03		
acid alkyl sludges	alkylation	05 01 04		
oil spills		05 01 05		
spent filterclays	product-, waste water-, exhaust gas cleaning	05 04 01		
oil fly ash	furnaces	10 01 04		
oil-/ water separator solids	exhaust gas cleaning	13 05 01		
oil-/water separator sludges	„	13 05 02		
interceptor sludges	„	13 05 03		
desalter sludges or emulsions	desalter	13 05 04		
other emulsions		13 05 05		
oil waste not otherwise specified		13 06 01		
sulphuric acid and sulphurous acid	sulphur recovery unit Claus plant	06 01 01		

A5: CONSUMPTION of material and Energy

- only for processing units

A6 Other Data (complete only if applicable for entire refinery; otherwise only for processing units)

Table A6a: Waste heat emissions

main heat source(s)	
measured amount [GJ/h]	
waste heat transfer medium (water, product, gas)	

Table A6b: Noise

	1	2	3	4
relevant immission point - distance: - classification of area: - standard value immission: sound pressure level L_{Aeq} at immission point sound insulation measures				

Table A6c: Specifications of costs (if known)

- if possible, please assign the costs of the particular used emission reducing techniques-

investment costs for (incl. calculation basics):	
operating costs for (incl. calculation basics):	
reference sizes - reference year - processing capacity	

B1: GENERAL INFORMATION (PLEASE COMPLETE FOR EVERY PROCESSING PLANT)

Name of processing plant:	
Contact person for further inquiry: telephone:	
Type of processing plant	
Capacity - approved capacity (t/yr) - if necessary actual amount of production in reference year 19___ - annual working hours in reference year	
Main-products, if necessary by-products amount/year, if necessary characteristics *please list, if necessary on separate page*	

Year of erection	
Type and term of essential changes of the processing structure, which are relevant for the following data, including the designation please list, if necessary on separate page	
Short description of the production process Sequence of processes, parts of plant /plant configuration, relevant secondary installations *please add simple flow sheet!*	

B2: EMISSIONS INTO THE AIR

B2.1 General Information

Processing plant:	
Origin of data (e.g. declaration of emission):	
Reference year of data:	
Applied emission-reduction-measures:	
– downstreamed exhaust gas reduction measures: (if necessary including reduction performance):	
– production integrated measures for emission reduction: (if necessary including reduction performance):	
– measures for the reduction of diffuse emissions: (if necessary including reduction performance):	

B2.2 Emissions from point sources

Table B2.2.1: Furnaces

Please complete this table for processing plants with modern furnace plants

Furnace for plant: **Fuel** **Thermal output** permitted effective (average in %)	
Exhaust flow rate (m³/h)	
Exhaust gas temperature (°C)	

Pollutant	**achievable levels (continuous operation)**			
	½ h average (mg/m³) 1)	24 h average (mg/m³) 1)	mass flow (kg/h)	remarks
Dust				
As, Pb, Cd, Cr, Co, Ni, Sb, V and their compounds (total)				
SO_x as SO_2				
NO_x as NO_2				
Carbonmonoxide				

1) normal conditions

remarks

Table B.2.2.2:

Processing plant: delayed coking		
Capacity	permitted	
(t/y)	effective /reference year	/
Exhaust flow rate (m³/h)		
Exhaust gas temperature (°C)		

Pollutant	**achievable levels (continuous operation)**			
	½ h average (mg/m³) 1)	24 h average (mg/m³) 1)	mass flow (kg/h)	remarks
Dust				
Ni, V and their compounds (total)				
SO_x as SO_2				
NO_x as NO_2				
Carbonmonoxide				
Organic substances as C				

1) normal conditions

remarks

Table B2.2.3:

Processing plant: FCC	
Capacity permitted **(t/yr)** effective /reference year	/
Exhaust flow rate (m^3/h)	
Exhaust gas temperature (°C)	

Pollutant	**achievable levels(continuous operation)**			
	½ h average (mg/m^3) 1)	24 h average (mg/m^3) 1)	mass flow (kg/h)	remarks
Dust				
Ni, Sb, V and their compounds (total)				
SO_x as SO_2				
NO_x as NO_2				
Carbonmonoxide				

1) normal conditions

remarks

Table B2.2.4:

Sulphur recovery Plant				
Capacity permitted **(t/yr)** effective /reference year				/
Exhaust flow rate (m³/h)				
Exhaust gas temperature (°C)				
Pollutant	**achievable levels (continuous operation)**			
	½ h average (mg/m³) 1)	24 h average (mg/m³) 1)	mass flow (kg/h)	remarks
SO_x as SO_2				
H_2S				
COS				
CS_2				

1) normal conditions

remarks

Table B2.2.5:

Vapour recovery unit				
Type				
Exhaust flow rate (m^3/h)				
Exhaust gas temperature (°C)				
Pollutant	**achievable levels (continuous operation)**			
	½ h average (mg/m^3) 1)	24 h average (mg/m^3) 1)	mass flow (kg/h)	remarks
Hydrocarbons (without methane) as C				
Hydrocarbons (with methane) as C				
Benzene				

1) normal conditions

remarks

Table B2.2.6:

Flare	
Capacity permitted	
(t/yr) effective /reference year	/
Exhaust flow rate (m^3/h)	
Exhaust gas temperature (°C)	

Pollutant	**achievable levels (continuous operation)**			
	½ h average (mg/m^3) 1)	24 h average (mg/m^3) 1)	mass flow (kg/h)	remarks
Dust				
Hydrocarbons as C 2)				
SO_x as SO_2				
NO_x as NO_2				
Carbonmonoxide				

1) normal conditions
2) combustion efficiency of 99%

remarks

B2.3 Planar sources (diffuse emissions)

Table B2.3.1:

Please complete for every relevant processing plant

Processing plant	
Pollutant	**rate in kg/h from type and number of sealing elements 1)**
Hydrocarbons as C	

1) using the emission factors of VDI-guideline 2440 (Draft 1999)

Table B2.3.2:

Sulphur recovery- and Clausanlagen	
Pollutant	**rate in kg/h from type and number of sealing elements 1)**
H_2S	

1) using the emission factors of VDI-guideline 2440 (Draft 1999)

Table B2.3.3:

Storage	
Pollutant	**rate in kg/h for sealing elements and emissions from fixed roof- and floating roof tanks 1)**
Hydrocarbons as C	
Benzene	

1) using the emission factors of VDI-guideline 2440 (Draft 1999) and the formulas of VDI-guideline 3479 (1985)

remarks

Table B2.4: Applied measuring methods

Pollutant	**methods of determination**
Dust	
Arsenic and compounds.	
Lead and compounds	
Cadmium and compounds	
Chromium (ges.) and compounds	
Cobalt and compounds	
Nickel and compounds	
Antimony compounds	
SO_x as SO_2	
NO_x as NO_2	
H_2S	
COS	
CS_2	
Carbonmonoxide	
Hydrocarbons as C (without methane)	
Organic substances as C	
Benzene	

remarks

B3: EMISSIONS INTO THE WATER

General Information

Name of processing plant (e.g. mech.separator, flotation, sour water stripper, processing plant)	
Origin of data:	
Waste water from the following areas:	
Reference year of data:	
Applied emission-reduction-measures	
– downstreamed waste water cleaning measures (if necessary including reduction performance):	
– production integrated measures for emission reduction (if necessary including reduction performance):	
– measures to reduce the water consumption:	

☐ direct discharging
☐ indirect discharging

Table B3.1: Effluents:

(for indirect discharging without consideration of communal treatment)

processing water				**effluent**			
Origin (e.g. steam, process water, treated water)				**Remains** (e.g. biology)			
Input m³ /t crude m³ /t process capacity				**Amount** m³ /t crude m³ /t process capacity			
processing water condition				effluent condition			
Parameter	measured concentration (mg/l)	discharge kg/t crude	discharge kg/t capacity	measured concentration (mg/l)	discharge kg/t crude	discharge kg/t capacity	cleaning capacity (%)
COD							
TOC							
BOD_5							
TN_b							
N (tot.-inorganic)							
P (tot.)							
HC (tot.)							
BTEX							
Phenols							
AOX							
Sulphides/Mercaptanes							
Cyanides							
Luminous bacteria toxicity							
Fish toxicity							
Conductivity							
pH value							
Temperature							

Explanations

1) if the waste water from sampling point is taken from different plants, calculate back on partial stream from in this table described processing parts or production area

2) if no measured values exist: please specify calculated/estimated size and shortly explain calculation at “Notes”

3) if measured values are under proof- or determination limit quote these

4) discharges with reference to the actual processing amount

5) cleaning capacity relevant only for waste water treatment plants

remarks:

e.g.

- breakdown of discharges
  with combined treatment with
  other production waste waters

- if no special measuring available:
  please quote, how data has been derivated

- others

Table B3.2: Sampling and Measuring methods:

Parameter	Type and time of sampling 1)	Measuring method (also: calculation/estimation)	number of measurements per year (official and self controlling)
COD			
TOC			
BOD_5			
TN_b			
N (tot.-anorganic)			
P (tot.)			
HC (tot.)			
BTEX			
Phenols			
AOX			
Sulphides/Mercaptanes			
Cyanides			
Luminous bacteria- toxicity			
Fish toxicity			
Conductivity			
pH value			
Temperature			

1)	- Continuous measuring	KM
	- Sample	S
	- Qualified sample	QS
	- 2-h-composite sample	2M
	- 24-h-composite sample	24M
	- other	(please quote)

remarks:

B4: WASTE

General Information

Name of Processing plant	
Origin of Data (e.g. waste statistic):	
Reference period of Data:	
Applied measures for waste reducing and for recovery	

Table B4.1: Hazardous waste for recovery – particular supervision required

Designation of waste	Origination	Waste code (EWC)	Waste quantity absolute (e.g. t/yr)	Specific waste quantity per product amount (e.g. kg/t)	Characteristic attributes (e.g. calorific value, dry substance, contents of pollutants)	Recovery-treatment 1)	Notes 2)

1) if necessary further explaining
2) e.g. Data according to German Nachweisverordnung

Table B4.2 Hazardous waste for disposal – particular supervision required

Designation of waste	Origination	Waste code (EWC)	Waste quantity absolute (e.g. t/yr)	Specific waste quantity per product amount (e.g. kg/t)	Characteristic attributes (e.g. calorific value, dry substances contents of pollutants)	Disposal mode 1)	Notes 2)

1) further explaining if necessary, note why waste can not be recovered
2) e.g. Data according to German Nachweisverordnung

Table B4.3: Other Waste

(a) waste for disposal, supervision required
(b) waste for recovery, supervision required
(c) waste, no supervision required

Designation of waste (a),(b),(c) please quote	Origination	Waste code (EWC)	Waste quantity absolute (e.g. t/yr)	Specific waste quantity per product amount (e.g. kg/t)	Characteristic attrib-utes (e.g. calorific value, dry substances , contents of pollutants)	Processing or disposal mode 1)	Notes

1) further explaining if necessary, note why waste can not be recovered

Table B4.4: Examples for other waste

Designation of waste	Origination (Processing plant)	Waste code (EWC)
sludges from on-site effluent treatment	effluent treatment	05 01 01
desalter sludges	desalter	05 01 02
sludges from plant, equipment and maintenance operations	all	05 01 06
boiler feedwater sludges	boiler plant	05 02 01
waste from cooling columns		05 02 02
spent catalysts containing precious metals	desulphurisation, FCC, dust filter	05 03 01
other spent catalysts	desulphurisation, FCC, dust filter	05 03 02
waste containing sulphur	desulphurisation, claus plant	05 05 01
calcium based reaction wastes from flue gas desulphurisation in solid form	furnace	10 01 05
other solid wastes from gas treatment	furnace	10 01 06
calcium based reaction wastes from flue gas desulphurisation in sludge form	furnace	10 01 07
other sludges from gas treatment	furnace	10 01 08
spent catalysts e.g. from removal of NOx	furnace	10 01 10
aqueous sludges from boiler cleansing	boiler plant	10 01 11

B5: CONSUMPTION OF MATERIAL AND ENERGY

Processing plant:

	Substance /Energy	Absolute amount	Unit (e.g. t/yr)	Characteristic attributes (e.g. concentration, water content, calorific value etc.)	Notes
Feedstock e.g. Fraction from Distillation Residues					
Process materials e.g. lubricants					
Process materials e.g. Catalysators Waste water treatment chemicals Chemicals for gas scrubbing					

Processing plant:

	Substance/Energy	Absolute amount	Unit (e.g. t/yr)	characteristic attributes (e.g. concentration, water contents, calorific value etc.)	Notes
Energy input Primary energy carrier - natural gas - fuel oil - energetic used residues					
End energy carrier e.g. electric energy					
Collectible energy carrier thermal energy etc.					
Energy generation - internal					

B6: Other data

Processing plant:

Table B6.1: Waste heat emissions

Main heat source (n)	
Measured amount [GJ/h]	
Waste heat transfer medium (water, product, gas)	
Waste heat temperature in straight condition, without cooling air or cooling fluids (fresh water)	
Continuous /discontinuous amount:	continuous • discontinuous

Table B6.2: Noise and concussions

Sources of noise units Relevant immission point - distance: - classification of area: - standard immission value: sound pressure level L_{Aeq} at immission point sound insulation measures	

Table B6.3: Specifications about costs (if known)

- if possible please assign the costs of the particular used emission-reduction-techniques -

Investment costs for (incl. calculation basis):	
Operation costs (incl. calculation basis):	
Reference sizes - reference year - plant capacity:	

3 Current international and national Legislation

3.1 International Directives and Agreements

E1 Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control
Official Journal L 257, 10/10/1996 p. 26 BGBl. I, 1997, S. 542

E2 Directive 88/609/EEC on the limitation of emissions of certain pollutants into the air from large combusting plants, as last amended by Directive 94/66/EC
Official Journal L 336, 07/12/1988 p. 1

E3 Directive 75/442/EEC on waste, as amended by Directive 91/156/EEC
Official Journal L 194, 25/07/1975 p. 39

E4 Directive 91/689/EEC on hazardous waste
Official Journal L 377, 31/12/1991 p. 20

E5 Council Directive 84/360/EEC of 28 June 1984 on the combating of air pollution from industrial plants
Official Journal L 188, 16/07/1984 p. 20

E6 Directive 67/548/EEC on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances of 27 June 1967
Official Journal L 196, 16/08/1967 p. 1

E7 94/904/EC: Council Decision of 22 December 1994 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

E8 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 of 20 December 1994
Official Journal L 365, 31/12/1994 p. 24

E9 Directive 96/82/EC on the control of major-accident hazards involving dangerous substances of 9 December 1996
Official Journal L 10, 14/01/1997 p. 13

E10 Council Directive 1999/13/EC of 11 March 1999 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

E11 COUNCIL REGULATION (EEC) No 1836/93 of 29 June 1993 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

E12 Directive 94/9/EC EC of the European Parliament and the Council of 23 March 1994 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

3.2 National Legislation in Germany

Bundes-Immissionsschutzgesetz - BImSchG /D1/

- Verordnung über genehmigungsbedürftige Anlagen - 4. BImSchV /D2/
- Verordnung über das Genehmigungsverfahren - 9. BImSchV /D35/
- Emissionserklärungsverordnung - 11. BImSchV /D3/
- Störfallverordnung - 12. BImSchV /D4/
- Verordnung zur Begrenzung der Emissionen flüchtiger organischer Verbindungen beim Umfüllen und Lagern von Ottokraftstoffen - 20. BImSchV /D7/
- Verordnung über Großfeuerungsanlagen - 13. BImSchV /D5/
- Verordnung über Verbrennungsanlagen für Abfälle - 17. BImSchV /D36/
- TA Luft /D8/
- TA Lärm /D9/

Wasserhaushaltsgesetz - WHG /D10/

- Abwasserverordnung mit Anhang 45 der AbwasserV, Erdölverarbeitung /D13/
- Abwasserabgabengesetz /D31/
- Wassergesetze der Bundesländer mit Regelung der Genehmigungspflicht für Indirekteinleiter
- Verordnung über Anlagen zum Umgang mit wassergefährdenden Stoffen und über Fachbetriebe - VAwS Verordnungen der Bundesländer /D12/.

Kreislaufwirtschafts- und Abfallgesetz KrW-/AbfG /D21/

- Verordnungen zum KrW-/AbfG /D32,33,34/
- Abfallgesetze der Bundesländer

Gerätesicherheitgesetz GSG /D18/

- Verordnung für brennbare Flüssigkeiten - VbF /D19/
- Druckbehälterverordnung DruckbehV - /D20/
- Dampfkesselverordnung /D28/
- Explosionsschutzverordnung /D29/
- Verordnung über elektrische Anlagen in explosionsgefährdeten Bereichen, ElexV /D27/

D1 Bundes-Immissionsschutzgesetz – BImSchG, BGBl. I, 1990, S. 880, 1193; zuletzt geändert am 19.10.1998 durch BGBl. I, 1998, S. 3178

D2 Verordnung über genehmigungsbedürftige Anlagen 4. BImSchV -Fassung vom 14. März 1997 (BGBl. I 1997 S. 504, S. 548; zuletzt geändert 1998 S. 723)

D3 Elfte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes Emissionserklärungsverordnung - 11. BImSchV, vom 12. Dezember 1991 (BGBl. I S. 2213; 1993 S. 1782, 2949) BGBl. III 2129-8-II-2

D4 Zwölfte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes Störfall-Verordnung - 12. BImSchV In der Fassung der Bekanntmachung vom 20. September 1991 (BGBl. I S. 1891; 1993 S. 1782, 2049; 1998 S. 723)

D5 Dreizehnte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Verordnung über Großfeuerungsanlagen – 13. BImSchV) vom 22.06.1983 (BGBl. I S. 719), geändert am 23.09.90 (BGBl. II S. 885)

D6 Verordnung über Verbrennungsanlagen für Abfälle und ähnliche brennbare Stoffe - 17. BImSchV vom 23. November 1990 (BGBl. I S. 2545, ber. S. 2832)

D7 Verordnung zur Begrenzung der Emissionen flüchtiger organischer Verbindungen beim Umfüllen und Lagern von Ottokraftstoffen - 20. BImSchV vom 27. Mai 1998 (BGBl. I S. 1174)

D8 Erste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft) - TA Luft, GMBl., 1986, S.95, ber. S. 202;

D8a Empfehlungen des Länderausschusses für Immissionsschutz -LAI- zur Konkretisierung von Dynamierungsklauseln der TA Luft; umgesetzt in Verwaltungsvorschriften der Bundesländer, z.B. Sächsisches Amtsblatt Nr. 12, 1993 S.351.

D9 Sechste Allgemeine Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz (Technische Anleitung zum Schutz gegen Lärm - TA-Lärm) vom 26.08.98 (GMBl. S. 503)

D10 Wasserhaushaltsgesetz – WHG, BGBl. I, 1996, S. 1695, zuletzt geändert am 25. August 1998 durch BGBl. I, 1998, S. 2455

D11 Richtlinie zur Bemessung von Löschwasser-Rückhalteanlagen beim Lagern wassergefährdender Stoffe (LöRüRL) RdErl. d. Ministerium für Bauen und Wohnen v. 14.10.1992 (MBl. NW. 1992 S.1719; ber. 1993 S. 879)

D12 Verordnung über Anlagen zum Umgang mit wassergefährdenden Stoffen und über Fachbetriebe, Anlagenverordnung - VAwS für die einzelnen Bundesländer

D13 Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer, Abwasserverordnung – AbwV, in der Fassung vom 9. Februar 1999 (BGBl. I 1999 S. 86)
Anhang 45: Erdölverarbeitung

D13a Erdölverarbeitung: Hinweise und Erläuterungen zu Anhang 45 der Rahmen-AbwasserVwV; Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, Länderarbeitsgemeinschaft Wasser (Hrsg.); Köln, 1995; Bundesanzeiger; ISBN 3-88784-656-7 (zur Zeit in Überarbeitung)

D14 Verwaltungsvorschriften zum Vollzug der Verordnung über Anlagen zum Umgang mit wassergefährdenden Stoffen und über Fachbetriebe, VVAwS für die einzelnen Bundesländer

D15 Grundwasser-Verordnung BGBl. I, 1997, S. 542

D16 Allgemeine Verwaltungsvorschrift zum Wasserhaushaltsgesetz über die Einstufung wassergefährdender Stoffe in Wassergefährdungsklassen - Verwaltungsvorschrift wassergefährdende Stoffe (VwVwS) –BGBl. I vom 17. Mai 1999

D17 Gesetz über Umweltstatistiken (Umweltstatistikgesetz – UStatG) in der Fassung vom 21. September 1994, BGBl. I, 1994, S.2530

D18 Gesetz über technische Arbeitsmittel (Gerätesicherheitsgesetz - GSG) in der Fassung der Bekanntmachung vom 23. Oktober 1992 (BGBl. I S. 1793; .zuletzt geändert 1998 S. 730 BGBl. III 8053-4-10)

D19 Verordnung über brennbare Flüssigkeiten - VbF Fassung vom 13. Dezember 1996 (BGBl. I S 1938, ber. 1997 S. 447)

D20 Verordnung über Druckbehälter, Druckgasbehälter und Füllanlagen (Druckbehälterverordnung - DruckbehV) in der Fassung vom 21. April 1989 (BGBl. I S. 843; zuletzt geändert 1997 S. 1402)

D21 Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der umweltverträglichen Beseitigung von Abfällen (Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG) Vom 27. September 1994 (BGBl. I 1994 S. 2705; zuletzt geändert 1998 S. 2455)

D22 Zweite allgemeine Verwaltungsvorschrift zum Abfallgesetz Teil 1: Technische Anleitung zur Lagerung, chemisch/physikalischen, biologischen Behandlung, Verbrennung und Ablagerung von besonders überwachungsbedürftigen Abfällen TA-Abfall Vom 12.März 1991 (GMBl I S. 139, ber. GMBl S. 467)

D23 Gesetz über das Inverkehrbringen von und den freien Warenverkehr mit Bauprodukten zur Umsetzung der Richtlinie 89/106/EWG des Rates vom 21. Dezember 1988 zur Angleichung der Rechts- und Verwaltungsvorschriften der Mitgliedstaaten über Bauprodukte und anderer Rechtsakte der Europäischen Gemeinschaften (Bauproduktengesetz - BauPG) Neufassung vom 28. April 1998 (BGBl. I. 1998 S. 812)

D24 Baugesetzbuch (BauGB) In der Fassung vom 27. August 1997 (BGBl. I 1997 S. 2141; 2902; ber. 1998 S. 137)

D25 Landesbauordnungen für die einzelnen Bundesländer

D26 Unfallverhütungsvorschriften (UVV): Eine Zusammenstellung der Unfallverhütungsvorschriften ist bei der jeweiligen Berufsgenossenschaft zu erhalten

D27 Verordnung über elektrische Anlagen in explosionsgefährdeten Bereichen (ElexV) Fassung vom 13. Dezember 1996(BGBl. I S. 1932)BGBl. III 7102-41

D28 Verordnung über Dampfkesselanlagen Dampfkesselverordnung - DampfkV Vom 27. Februar 1980(BGBl. I S. 173; ...; 1996 S. 1917)(BGBl. III 7102-38)

D29 Elfte Verordnung zum Gerätesicherheitsgesetz Verordnung über das Inverkehrbringen von Geräten und Schutz-Systemen für explosionsgefährdete Bereiche (Explosionsschutzverordnung - 11. GSGV) Vom 12. Dezember 1996 (BGBl. I 1996 S. 1914)

D30 Beschluß der Umweltminister- und -senatoren-Konferenz am 5. April 1984 zum Thema „Minderung der Stickstoffoxidemission aus Großfeuerungsanlagen“, Umwelt Nr. 102 vom 30. April 1984, S. 27/28

D31 Gesetz über Abgaben für das Einleiten von Abwasser in Gewässer Abwasserabgabengesetz - AbwAG Fassung vom 3. November 1994 (BGBl. I S. 3370, zuletzt geändert 1998 S. 2455)

D32 Bestimmungsverordnung besonders überwachungsbedürftige Abfälle - BestbüAbfV Vom 10. September 1996 (BGBl. I S. 1366, geändert 1998 S. 3956)

D33 Bestimmungsverordnung überwachungsbedürftige Abfälle zur Verwertung - BestüVAbfV, vom 10. September 1996 (BGBl. I S. 1377)

D34 Verordnung über Verwertungs- und Beseitigungsnachweise Nachweisverordnung - NachwV, vom 10. September 1996 (BGBl. I S. 1382, ber. S. 2860)

D35 Neunte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes 9. BImSchV - Verordnung über das Genehmigungsverfahren, in der Fassung vom 29.Mai 1992 (BGBl I S. 1001, zuletzt geändert 1999 S.186)

D36 Siebzehnte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes Verordnung über Verbrennungsanlagen für Abfälle und ähnliche brennbare Stoffe - 17. BImSchV vom 23. November 1990 (BGBl. I S. 2545, ber. S. 2832)

4 Monitoring the level of emissions and safety

4.1 Emissions into the Air

Measurement of emissions is performed in conformity with the TA Luft. In refineries the pollutants SO_2, dust, NO_x and CO are sometimes measured continuously. Otherwise, single measurements are done. The methods for measuring emissions are fixed in the VDI-Directives. The Directives cited can be obtained from the Beuth Verlag Berlin (http://www.beuth.de). Emissions can also be calculated. Methods of calculation are listed in the VDI Directive 2440 /L32/.

The following table shows a selection of methods of measurement which are applied.

Pollutant	**methods of determination**
Dust	Photometry VDI 2066 Sheet 4
Arsenic and compounds	e.g. DIN 38406 Part E22 after disintegration
Lead and compounds	
Cadmium and compounds	
Chromium (tot.) and compounds	
Cobalt and compounds	
Nickel and compounds	
Antimony and compounds	
SO_x as SO_2	IR Absorption VDI 2462 sheet 4, also calculation
NO_x as NO_2	UV Absorption VDI 2456 sheet 4 NDUV-Resonance VDI 2456 sheet 9
H_2S	VDI 3486 sheet 1,2,3
COS	
CS_2	VDI 3487 sheet 1
Carbonmonoxide	IR Spectroscopy, VDI 2459 sheet 6
Hydrocarbons as total-C (without methane) Organic substances as total-C	Chromatography VDI 2457, IR-Absorption VDI 2466 sheet 1, also: VDI 3481 sheet 2,6
Benzene	VDI 2475 sheet 5

4.2 Emissions into the Water

The following list shows a typical example for monitoring waste water in a refinery. The parameters are monitored either continuously, daily, on working days or in larger time intervals. One differentiates between self-monitoring and monitoring by the regulatory authorities. The methods of measurement are fixed in the waste water ordinance.

The German norms cited can be obtained from the Beuth-Verlag Berlin(http://www.beuth.de).

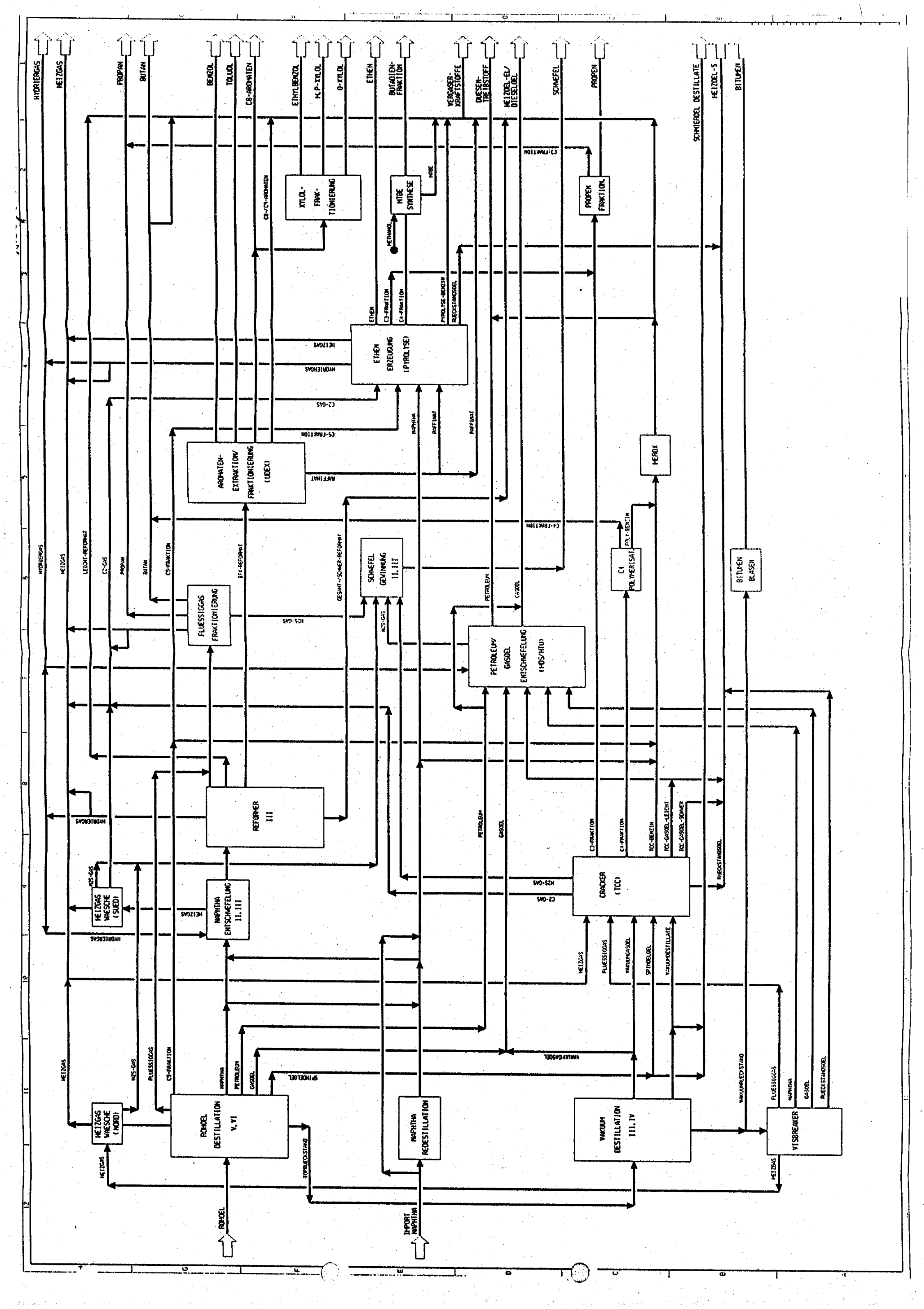
Parameter	Type of sampling	Measuring method	Number of measuring per year (official (=O) and self (=S) controlling)
CSB	qualified random sample	DIN 38409H41	on week-days S appr. 5/a O
TOC	continuously and qualified random sample	DIN 38409H3	Contin. and on week-days S appr. 5 /a O
BSB$_5$	qualified random sample	DIN 38409H51	weekly S appr. 5/a B
TNb	------	-----	------
N (total inorganic)	qualified random sample, NH4-N continuously	NH4-N: DIN 38406E23 NO3-N:DIN 38405D19 DIN-EN-ISO 10304-2 NO2-N: DIN38405D19 EN 26777	NH4-N: continuously and tot. N on week-days S appr. 5/a O
P (total)	qualified random sample	DIN38405D11-4	on week-days S appr. 5/a O
HC (total)	qualified random sample	DIN38409H18	monthly S appr. 5/a O
BTEX	------	------	------
Phenols	qualified random sample	DIN38409H16	monthly S appr. 5/a O
AOX	qualified random sample	DIN38409H14	monthly S appr. 5/a O
Sulphides/ Mercaptanes	qualified random sample	DIN38405D26	weekly S appr. 5/a O
Cyanides	qualified random sample	DIN38405D13-1	weekly S appr. 5/a O
Luminous bacteria-toxicity	-------	DIN 38412	-------
Fish toxicity	-------	DIN 38412	-------
Conductivity	-------	------	-------
pH value	continuously and qualified random sample	DIN38404C5	continuously and weekly S, appr. 5 x/a O
Temperature	continuously		continuously (S) appr. 5 x/a O

4.3 Monitoring the safety of the installation

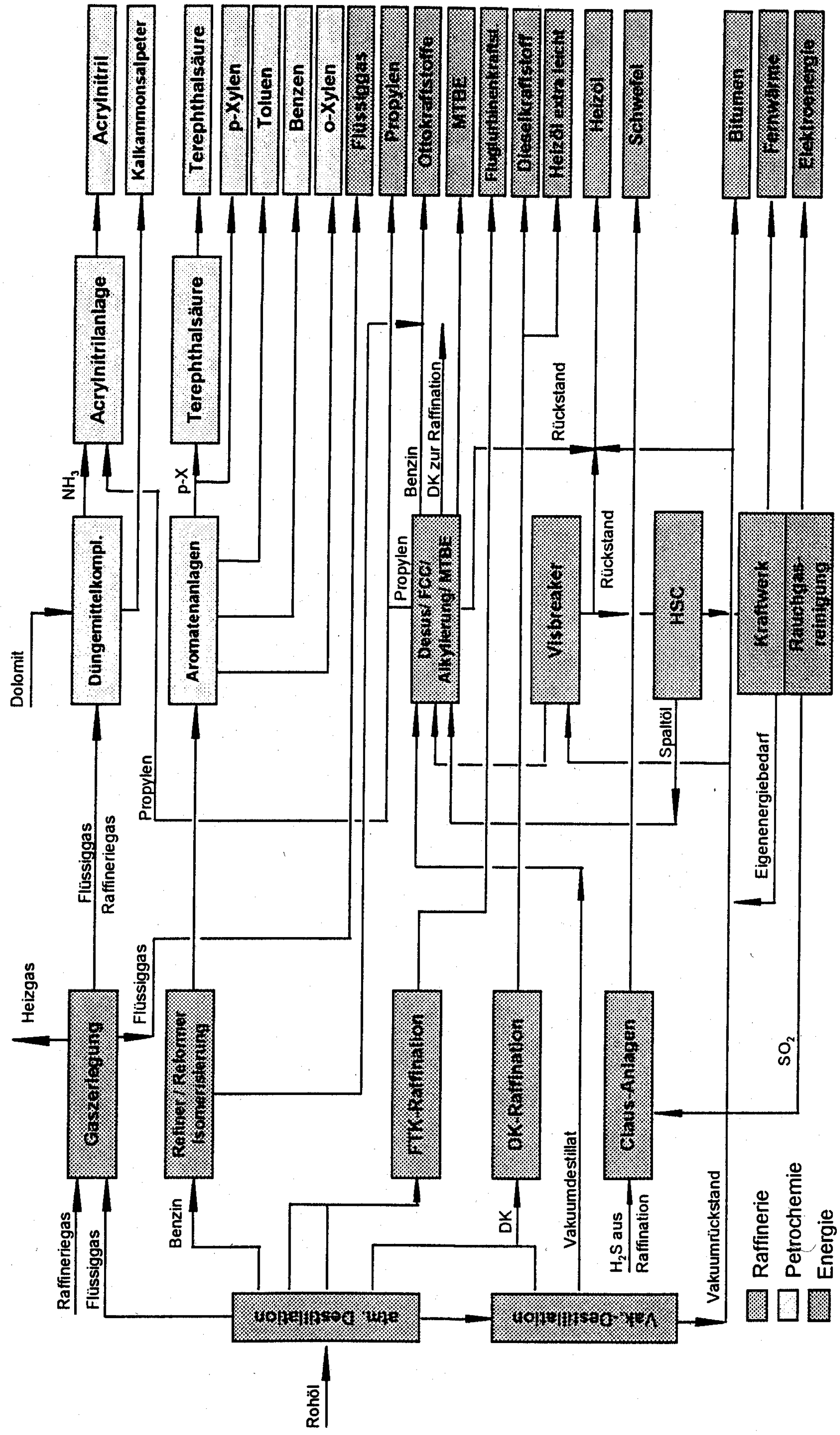
Information on plant safety and monitoring is contained in Chapter 3.4.

5 Flow Sheets of the Refineries

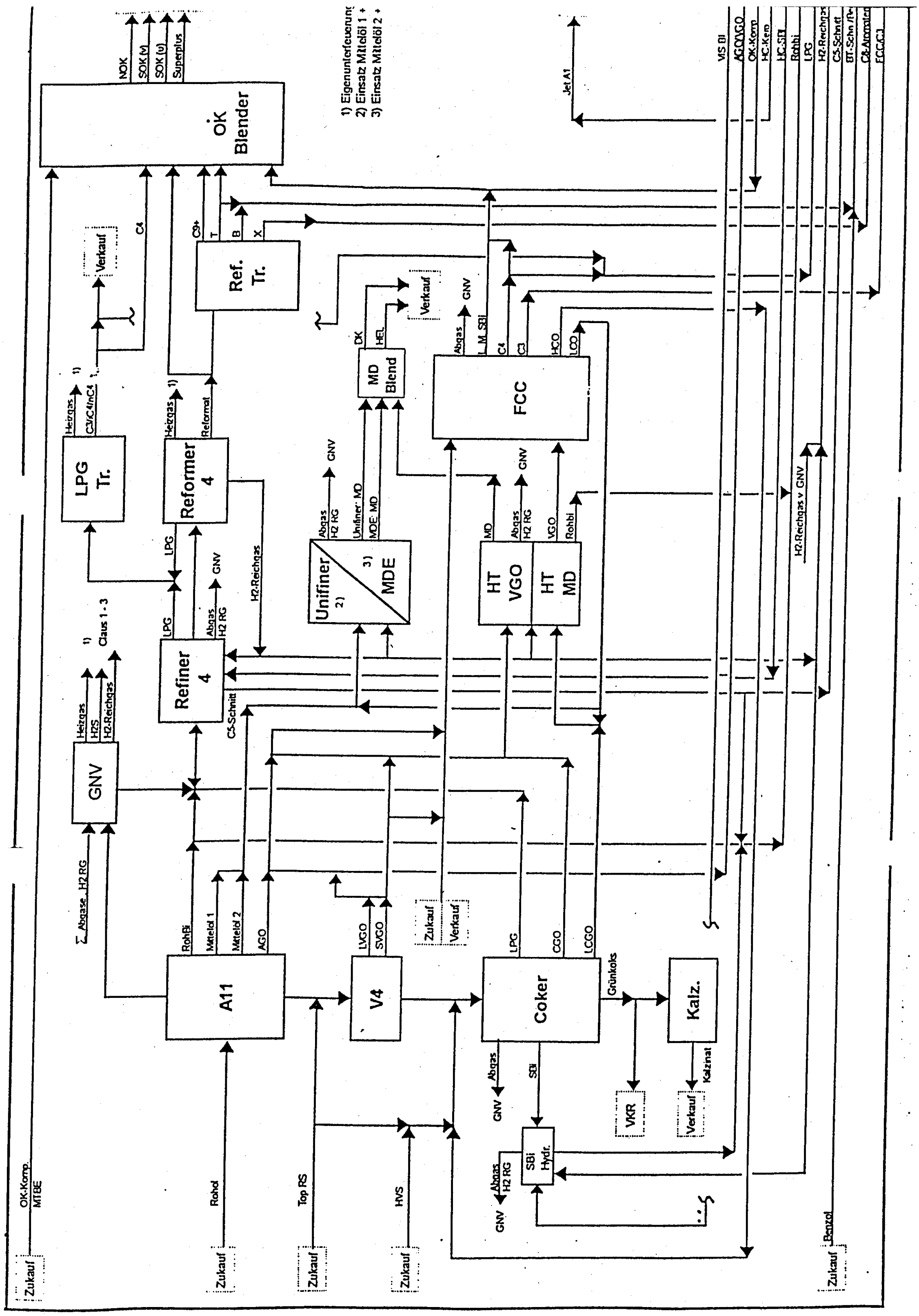
The following flow sheets show the configuration of the refineries in which the data on emissions and consumption were collected. Sometimes the drawings are very simplified.


HYDRIERGAS
HEIZGAS
PROPAN
BUTAN
BENZOL
TOLUOL
C8-AROMATEN
ETHYLBENZOL
M,P-XYLOL
O-XYLOL
ETHEN
BUTADIEN-FRAKTION
VERGASER-KRAFTSTOFFE
DUESEN-TREIBSTOFF
HEIZOEL-EL/DIESELOEL
SCHWEFEL
PROPEN
SCHMIEROEL DESTILLATE
HEIZOEL-S
BITUMEN
C3-FRAKTION
C8-/C9-AROMATEN
XYLOL-FRAK-TIONIERUNG
MTBE SYNTHESE
MTBE
METHANOL
PROPEN FRAKTION
ETHEN
C3-FRAKTION
C4-FRAKTION
PYROLYSE-BENZIN
RUECKSTANDSOEL
HEIZGAS
HYDRIERGAS
ETHEN ERZEUGUNG (PYROLYSE)
C2-GAS
C5-FRAKTION
NAPHTHA
RAFFINAT
RAFFINAT
AROMATEN-EXTRAKTION/ FRAKTIONIERUNG (UDEX)
RAFFINAT
MEROX
C4-FRAKTION
POLY-BENZIN
C4 POLYMERISAT
HYDRIERGAS
HEIZGAS
LEICHT-REFORMAT
C2-GAS
PROPAN
BUTAN
C5-FRAKTION
BTX-REFORMAT
GESAMT-/SCHWER-REFORMAT
SCHWEFEL GEWINNUNG II, III
BITUMEN BLASEN
FLUESSIGGAS FRAKTIONIERUNG
H2S-GAS
H2S-GAS
PETROLEUM
GASOEL
PETROLEUM/ GASOEL ENTSCHWEFELUNG (HDS/HTU)
REFORMER III
HYDRIERGAS
PETROLEUM
GASOEL
C3-FRAKTION
C4-FRAKTION
TCC-BENZIN
TCC-GASOEL-LEICHT
TCC-GASOEL-SCHWER
RUECKSTANDSOEL
H2S-GAS
HEIZGAS WAESCHE (SUED)
NAPHTHA ENTSCHWEFELUNG II, III
HEIZGAS
HYDRIERGAS
H2S-GAS
C2-GAS
CRACKER (TCC)
HEIZGAS
FLUESSIGGAS
VAKUUMGASOEL
SPINDELOEL
VAKUUMDESTILLATE
HEIZGAS
H2S-GAS
FLUESSIGGAS
C5-FRAKTION
NAPHTHA
PETROLEUM
GASOEL
SPINDELOEL
VAKUUMGASOEL
VAKUUMRUECKSTAND
FLUESSIGGAS
NAPHTHA
GASOEL
RUECKSTANDSOEL
HEIZGAS WAESCHE (NORD)
ROHOEL DESTILLATION V, VI
NAPHTHA REDESTILLATION
VAKUUM DESTILLATION III, IV
VISBREAKER
HEIZGAS
TOPRUECKSTAND
HEIZGAS
ROHOEL
IMPORT NAPHTHA
1
2
3
4
5
6
7
8
9
10
11
12
F
G
F
E
D
C
B
A

Refinery 1

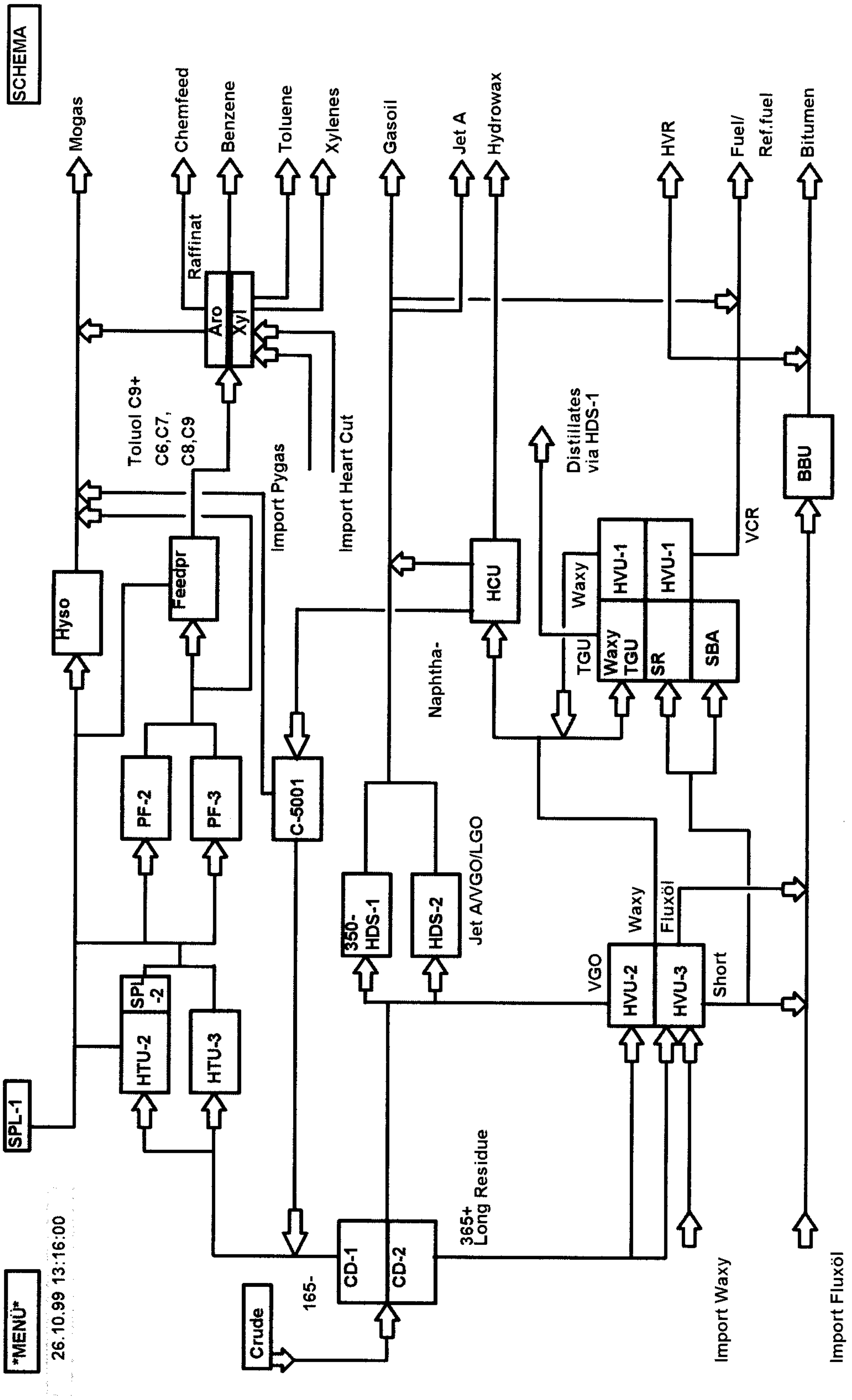

Rohöl
atm. Destillation
Vak.-Destillation
Raffineriegas
Flüssiggas
Gaszerlegung
Heizgas
Flüssiggas
Benzin
Refiner / Reformer Isomerisierung
FTK-Raffination
DK
DK-Raffination
Vakuumdestillat
H_2S aus Raffination
Claus-Anlagen
Vakuumrückstand
SO_2
Flüssiggas
Raffineriegas
Flüssiggas
Propylen
Dolomit
Düngemittelkompl.
NH_3
Acrylnitrilanlage
Aromatenanlagen
p-X
Terephthalsäure
Propylen
Desus/ FCC/ Alkylierung/ MTBE
Benzin
DK zur Raffination
Visbreaker
Rückstand
Rückstand
HSC
Spaltöl
Eigenenergiebedarf
Kraftwerk
Rauchgas-reinigung
Acrylnitril
Kalkammonsalpeter
Terephthalsäure
p-Xylen
Toluen
Benzen
o-Xylen
Flüssiggas
Propylen
Ottokraftstoffe
MTBE
Flugturbinenkraftst.
Dieselkraftstoff
Heizöl extra leicht
Heizöl
Schwefel
Bitumen
Fernwärme
Elektroenergie
▨ Raffinerie
☐ Petrochemie
▨ Energie

Refinery 2


ÖK Blender
NOK
SOK (v)
SOK (u)
Superplus
1) Eigenunterfeuerung
2) Einsatz Mitteldl 1 +
3) Einsatz Mitteldl 2 +
Jet A1
VIS Bl
AGO/VGO
OK-Komp.
HC-Kero
HC-SBI
Rohbi
LPG
H2-Reichgas
C5-Schnitt
BT-Schnitt
C8-Aromaten
FCC C3
Verkauf
C4
C9+
T
B
X
Ref. Tr.
GNV
Abgas
L.M. SBI
C3
HCO
LCO
FCC
MD Blend
DK
HEL
LPG Tr.
Heizgas
C3/C4/nC4
Reformer 4
Reformat
H2-Reichgas
Unifiner
MDE
Unifiner MD
MDE MD
H2 RG
HT VGO
HT MD
MD
VGO
Rohbi
H2-Reichgas v. GNV
Refiner 4
C5-Schnitt
Claus 1-3
H2S
GNV
Σ Abgase H2 RG
A11
Rohbi
Mitteldl 1
Mitteldl 2
AGO
V4
LVGO
SVGO
Zukauf
Verkauf
Coker
CGO
LCGO
Grünkoks
Kalz.
Kalzinat
VKR
SBi
SBi Hydr.
OK-Komp.
MTBE
Rohöl
Top RS
HVS
Benzol

Refinery 3

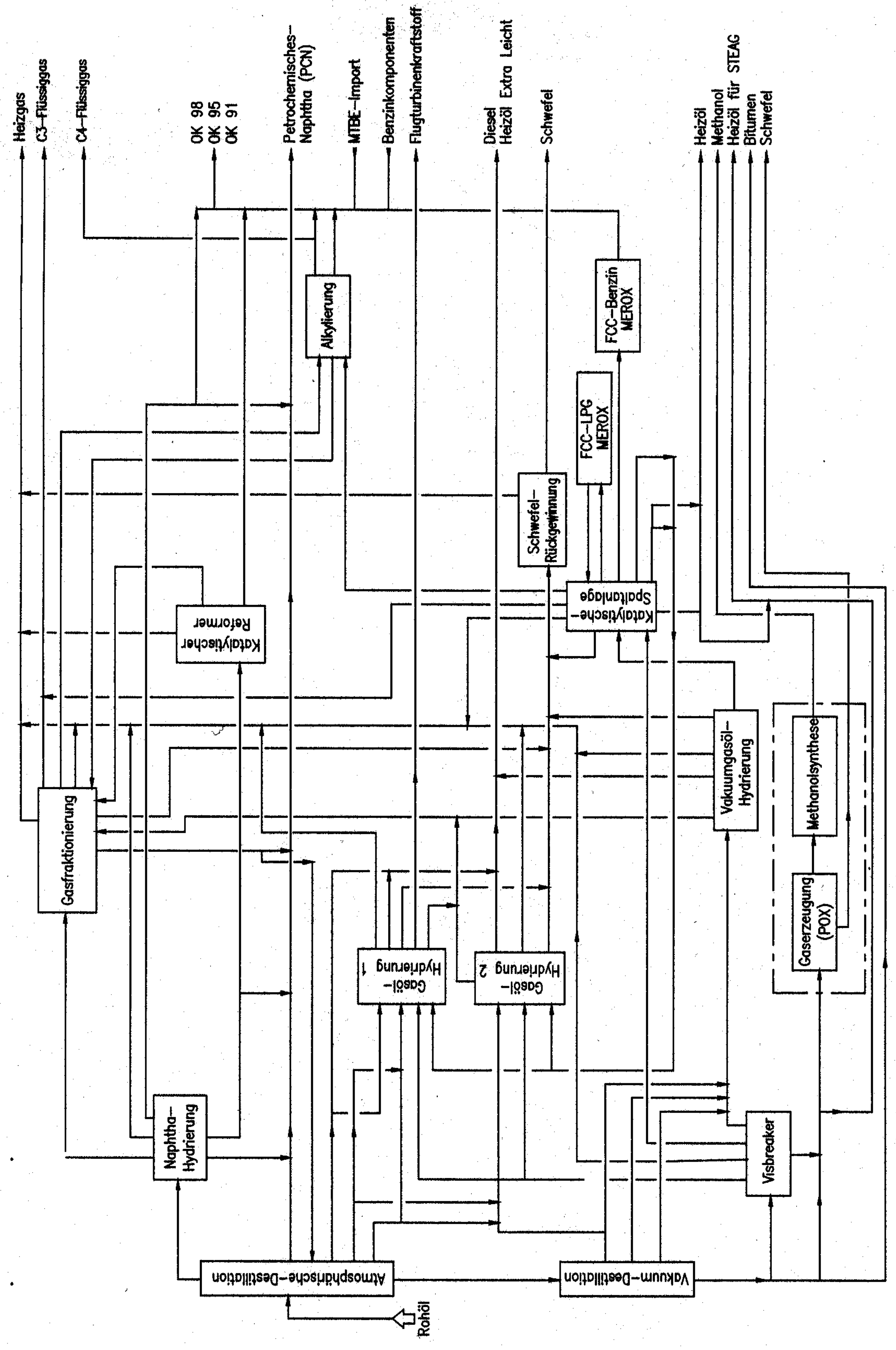
	Key
A11	Atmospheric (Top-) Distillation A11
AGO	Atmospheric Gasoil ex Top-Distillation
B	Benzene
BT-Schn.	Benzene / Toluene - fraction
C3	C3-Hydrocarbons
C4	C4- Hydrocarbons
C8 Aromaten	Ethylbenzene, Xylene
C9+	Heavy components ex reformat-separation; C >= 9
CGO	Coker-Gasoil
DK	Diesel fuel
FCC/C3	C3-Hydrocarbon fraction ex FCC
GNV	Gas treeting
Grünkoks	Feedstock Calzination
H2 RG	Hydrogen -rich gas -
HCO	Heavy Cycle Oil ex FCC
HEL	Fuel oil extra light t
HT MD	medium distillates desulphurisation (Hydrotreating)
HT VGO	Vakuum-Gasoil- desulphurisation (Hydrotreating)
HVS	Fuel oil heavy
Jet A1	Jet fuel
Kalzinat	Product of Calcination
L M SBi	heavy petrol ex FCC
LCGO	Light Coker Gasoil
LCO	Light Cycle Oil (FCC)
LPG	Liquified Petroleum Gas = Flüssiggas
LPG Tr.	LPG -separation
LVGO	Light Vacuum Gasoil
MD	medium distillates
MD Blend	medium distillates - (Blender)
MDE	medium distillates-desulphurisation; Hydrotreater
MDE MD	medium distillates-Fraction ex MDE
Mittelöl 1	medium distillates from Topdistillation A11
Mittelöl 2	medium distillates fraction from Topdistillation A11
MTBE	Methyl-tert.-butyl-ether
NOK	Petrol-normal
OK Blender	Petrol blender
Ok.-Komp	components for petrol
Ref Tr.	Reformat-separation
Roh Bi	crude petrol
SBi	heavy petrol
SOK (u)	Petrol, Super unleaded
SOK (v)	Petrol, Super leaded
SVGO	Heavy vacuum gasoil
T	Toluene (reformat-separation)
Top RS	residue from Topdistillations
Unifiner MD	medium distillate ex Unifiner
V4	Vacuumdistillation A4
VIS Bi	Petrol fractions ex Visbreaker
VGO	Vacuum Gasoil
X	Xylenefraction ex Reformat-separation


SCHEMA
Mogas
Chemfeed
Benzene
Toluene
Xylenes
Gasoil
Jet A
Hydrowax
HVR
Fuel/
Ref.fuel
Bitumen
Raffinat
Aro
Xyl
Toluol C9+
C6,C7,
C8,C9
Import Pygas
Import Heart Cut
Distillates
via HDS-1
BBU
Hyso
Feedpr
HCU
Waxy
HVU-1
HVU-1
TGU
Waxy
TGU
SR
SBA
VCR
Naphtha-
PF-2
PF-3
C-5001
350-
HDS-1
HDS-2
Jet A/VGO/LGO
Waxy
Fluxöl
VGO
HVU-2
HVU-3
Short
SPL-1
HTU-2
SPL
-2
HTU-3
MENÜ
26.10.99 13:16:00
Crude
CD-1
CD-2
165-
365+
Long Residue
Import Waxy
Import Fluxöl

Refinery 4

Key

CD	Crude Destillation
HTU	Hydro Treating Unit
HDS	Hydro Desulphurisation Unit
HVU	High Vakuum Unit
TGU	Thermal Gasoil Unit = thermal Cracker
SBA	special bitumen plant = "Visbreaker"
BBU	blow bitumen unit
PF	Platformer
HCU	Hydrocracking Unit
Feedprep	aromatics, pre-distillation
Aro	aromatics, processing
Xyl	Xylene plant


Heizgas
C3–Flüssiggas
C4–Flüssiggas
OK 98
OK 95
OK 91
Petrochemisches–Naphtha (PCN)
MTBE–Import
Benzinkomponenten
Flugturbinenkraftstoff
Diesel
Heizöl Extra Leicht
Schwefel
Heizöl
Methanol
Heizöl für STEAG
Bitumen
Schwefel
Alkylierung
FCC–Benzin MEROX
FCC–LPG MEROX
Schwefel–Rückgewinnung
Katalytische Spaltanlage
Katalytischer Reformer
Vakuumgasöl–Hydrierung
Methanolsynthese
Gasfraktionierung
Gaserzeugung (POX)
Gasöl–Hydrierung 1
Gasöl–Hydrierung 2
Naphtha–Hydrierung
Visbreaker
Atmosphärische–Destillation
Vakuum–Destillation
Rohöl

Refinery 5