

# **WATER AND WASTEWATER MANAGEMENT IN THE OIL REFINING AND RE-REFINING INDUSTRY**



# **WATER AND WASTEWATER MANAGEMENT IN THE OIL REFINING AND RE-REFINING INDUSTRY**

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Water Research Commission

by

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## EXECUTIVE SUMMARY

South Africa has four oil refineries processing approximately 19 million metric tons of crude oil per year, and two synfuel refineries processing 9 million "equivalent" tons per year. The oil re-refining industry is estimated to process 120 000 tons per year.

Using the year 1995 as a snapshot of the industry, the objectives of this project were to determine in the oil refining and re-refining industry:

- \* the volumes of water intake and discharge
- \* a breakdown of water use
- \* pollutant loads in the effluent generated

Using this data, recommendations were made for water and wastewater management in the oil refining and re-refining industry. The survey covered three crude oil refineries and one synthetic fuel refinery. In addition four re-refineries were surveyed.

Refineries in South Africa have a range of Specific Water Intake (SWI) between 0.51 and 0.67 m<sup>3</sup>/t crude. The synfuel refinery has an average SWI of 2.90 m<sup>3</sup>/t. The re-refineries showed much greater variation and have a range of SWIs between 0.06 and 7.20 m<sup>3</sup>/t. For the crude refineries there is no clear correlation between refinery size and SWI. For the re-refineries the type of process used strongly influences the SWI.

The largest users of water in the oil refining industry are the boilers and cooling water circuits. Water saving measures in these areas will lead to more significant reduction in SWI values as compared to that which would be obtained by reducing the wash water used in the desalter.

It was found that for the crude refining industry the average Specific Effluent Volume (SEV) is 0.26 m<sup>3</sup>/t crude, for the synthetic fuel refinery it is 1.32 m<sup>3</sup>/t feed and for the re-refining industry it ranges between 0.13 and 5.76 m<sup>3</sup>/t feed. For the crude refining industry the waste water discharged is approximately 46% of the water intake, whilst for the re-refining industry this can exceed 100%. The re-refining industry takes in large volumes of water together with their feedstock and this is subsequently discharged in the effluent. The synthetic fuel refinery also discharges 46% of its water intake as effluent.

The Specific Pollutant Load (SPL) for oil ranges between 2.5 and 4.7 g/t for the crude refining industry, 4.5 g/t for the synthetic fuel refinery and 110 g/t for the re-refineries. Despite the synthetic fuel process being inherently water intensive, their SPL for oil is comparable to the crude refining industry.

Recommendations for reducing pollution loads are given. These include aspects in the primary and secondary treatment of the effluent, the segregation of clean and dirty surface run-off, the segregation of different effluent streams, the reduction/limitation of surface water run-off, the reduction in volumes of process water requiring treatment and consideration of clean technologies.

## GLOSSARY

<b>CATALYTIC REFORMER</b>	A catalytic process unit in which alkanes are converted to isomers and cycloalkanes converted to aromatics to increase the octane of the fuel.
<b>CRUDE DISTILLATION UNIT (CDU)</b>	The Crude Distillation Unit (CDU) effects initial separation of the crude into fractions based on boiling point differences.
<b>CRUDE OIL</b>	Crude oil has its source many metres below ground level. Crude oil consists of a complex mixture of chemical compounds. The main constituent is a range of hydrocarbon compounds containing approximately one to twenty carbon atoms. These may be straight chained, branched or in a ring structure. In addition to hydrocarbons, crude oils also contain sulphur and nitrogen (each approximately 0.5-3 % by mass), certain heavy metals and inorganic salts.
<b>DESALTER</b>	Salt and sediment are removed from the crude oil in the desalter. These are removed from the crude oil by mixing the crude with stripped sour water which dissolves the salts.
<b>FISCHER TROPSCH REACTION</b>	The catalytic reaction of hydrogen and carbon monoxide to produce high-molecular weight hydrocarbons.
<b>FLUIDISED CATALYTIC CRACKING UNIT (FCCU)</b>	A process unit which catalytically cracks a heavy gas oil stream into lighter products such as petrol, gas oil (diesel) and fuel oil.
<b>FRACTIONATION</b>	The separation of a mixture into fractions based on differences in relative volatilities (boiling points).
<b>HYDROTREATER</b>	A process unit which removes sulphur compounds from fuel products by reacting these with hydrogen to form hydrogen sulphide.
<b>ISOMERISATION UNIT</b>	A process unit in which alkanes are converted to isomers to increase the octane of the fuel.
<b>SOUR WATER</b>	Water which collects in the overhead products of distillation and stripping operations containing high levels of phenols, sulphides and ammonia. This water originates either directly from the crude or is introduced as a result of steam stripping.
<b>SPECIFIC POLLUTION LOAD</b>	The mass of a given pollutant discharged during a particular period divided by the feedstock mass for the same period.

<b>SPECIFIC EFFLUENT VOLUME</b>	The effluent volume for a particular period divided by the feedstock mass for the same period.
<b>SPECIFIC WATER INTAKE</b>	The volume of water taken in for a particular period divided by the feedstock mass for the same period.
<b>STRIPPED SOUR WATER</b>	The product of sour water stripping in which medium/low pressure steam is used to strip contaminants such as sulphides and ammonia from the sour water.
<b>SWEETENING</b>	A catalytic process of removing sulphur products from a hydrocarbon stream.
<b>SYNFUEL</b>	Synthetic fuel, not derived from crude oil.
<b>SYNTHOL UNIT</b>	The process unit which catalytically converts hydrogen and carbon monoxide to high-molecular weight hydrocarbons.
<b>VACUUM DISTILLATION UNIT (VDU)</b>	A distillation column operating under a vacuum which effects separation into fractions based on boiling point differences.
<b>VACUUM CRACKER</b>	A process unit which operates under a vacuum to thermally crack a heavy residue into lighter products such as petrol, gas oil (diesel) and fuel oil.
<b>VISBREAKER UNIT</b>	A process unit which thermally cracks a heavy residue into lighter products such as petrol, gas oil (diesel) and fuel oil.
<b>WASTE OIL</b>	Contaminated fuel oil originating from ship bunkering or used lubricating oils as well as out of specification oil products from blending plants.



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## 1. INTRODUCTION

South Africa is known for its scarce water resources and its low average rainfall of 500mm per annum (Department of Water Affairs and Forestry, 1991). This, coupled with a rapidly growing population and economic sector, makes the competent management of water imperative. A sustainable and healthy socio-economic development can be ensured by maximizing production per unit volume of water used, and by effectively managing the volumes and quality of the wastewater discharged.

A number of industries in South Africa use significant volumes of water, and hence also discharge significant volumes of wastewater. The water and wastewater management of many of these industries has been surveyed and documented as part of the *Natsurv: Water and Wastewater Management* series as commissioned by the Water Research Commission. This report serves to add the oil refining and re-refining industry to this series.

### 1.1 THE SOUTH AFRICAN OIL REFINING AND RE-REFINING INDUSTRY

#### 1.1.1 Oil refining

About 19 million metric tons of crude oil is imported into South Africa each year. South Africa has four oil refineries and two synfuel refineries (Table 1).

Table 1. Oil and synfuel refineries in South Africa (Paxton, 1997)

Name	Location	Company	Barrels crude processed/day	Tons crude processed/month
<u>Oil refineries:</u>				
Engen	Durban	Engen	105 000	425 000
Sapref	Durban	Shell & BP	165 000	668 000
Natref	Sasolburg	Sasol & Total	85 000	344 000
Caltex	Cape Town	Caltex	110 000	445 000
<b>TOTAL</b>			<b>465 000</b>	<b>1 882 000</b>

**Table 1. (continued) Oil and synfuel refineries in South Africa (Paxton, 1997)**

Name	Location	Company	Barrels crude processed/day	Tons crude processed/month
<u>Synfuel refineries:</u>				
Sasol	Secunda	Sasol	"160 000" equivalent	648 000
Mossgas	Mossel Bay	Central Energy Fund	"35 000" equivalent	142 000
<b>TOTAL</b>			<b>"195 000" equivalent</b>	<b>790 000</b>

In the early years of the decade fuel demand exceeded supply and products had to be imported. In recent years an increase in refinery capacity has meant that South Africa can currently export excess product mainly to East Africa, but also to the Indian and Atlantic markets (Mbendi, 1997). However, it has been predicted that South Africa will soon have insufficient refining capacity as demand increased by as much as 6 % in 1995 and 1996 (SAPIA, 1997).

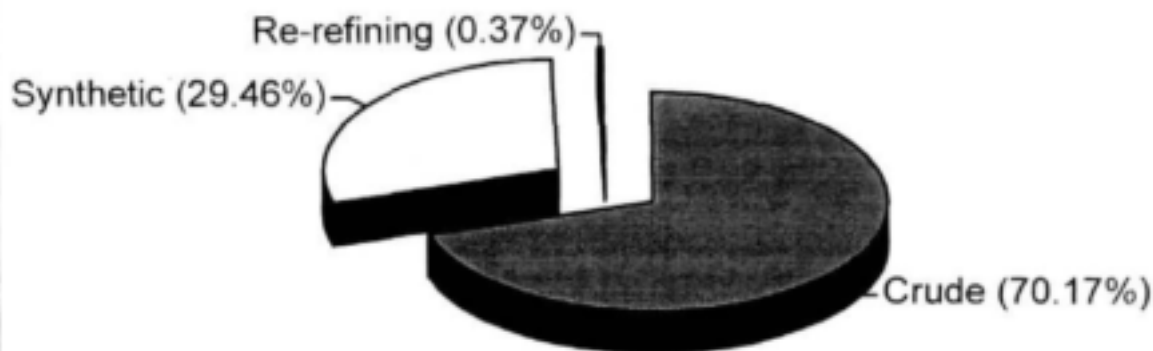
### 1.1.2 Re-refining

Each year about 360 million litres of lubricating oil are sold in South Africa. An estimated 40 million litres or 11 % of what is sold is recovered (Doke, 1996). This creates a potential source of pollution, especially if there is no obvious alternative to dumping old oil by irresponsible end-users. In April 1994 the main lubricant companies launched the Recovery of Oil Saves the Environment (ROSE) Foundation. The ROSE Foundation provides the necessary finance, coordination and management mechanisms to successfully manage the collection, for subsequent re-refining, and disposal of used oils. ROSE currently collects 29 million litres of used oil a year. These volumes are expected to grow substantially in future years (SAPIA, 1997).

Figure 1 indicates the relative sizes of the crude, synthetic and re-refining sectors of the South African oil industry.

# Oil Industry

## Production contribution by sector



**Figure 1: Production contribution of the South African oil industry.**

### 1.2 PROJECT OBJECTIVES

Using the year 1995 as a snapshot of the industry, the objectives of this project were to determine in the oil refining and re-refining industry:

- the volumes of water intake and discharge
- a breakdown of water use
- pollutant loads in the effluent generated

Using this data recommendations were to be made for water and wastewater management in the oil refining and re-refining industry.

### 1.3 PROJECT METHODOLOGY

Potential participating refineries and re-refineries were identified and approached to determine their willingness to participate in the national survey.

Participating refineries and re-refineries were surveyed over a period of 1 - 3 days. The information collected included:

- a brief overview of the entire production process for the compilation of a schematic process flow diagram.
- a brief overview of each logical production stage for the compilation of a schematic process flow diagram showing water consumption and wastewater discharge from each stage.
- representative values for the water consumed, wastewater discharged and quantity of product processed. The production period January to December 1995 was used as a common basis for comparative purposes.
- any effluent analyses of the relevant permitted parameters for all the wastewater streams.
- a brief overview of the effluent treatment process

The information and flow diagrams were used to compile a generic process résumé of the oil refining and re-refining industry, also showing water usage, discharge and treatment. The data was then analysed to calculate Specific Water Intake (SWI), Specific Effluent Volume (SEV) and Specific Pollutant Loads (SPL). Details of how each parameter was calculated are given in Appendix 1.

While it is tempting to compare the results of different refineries and re-refineries, great caution should be used in comparing and correlating water use and discharge data. Significant differences could be a result of the cost and availability of water, underlying raw material considerations, operational philosophies, equipment limitations and the type of wastewater receiving body (e.g. municipal treatment works, sea, river etc.). Furthermore utility operations can have widely differing water requirements. A further factor to take into consideration is that some plants tend to have a greater variety of downstream products which affects water use, effluent volumes and effluent quality.

## **2. PROCESS RÉSUMÉ**

Petroleum refining involves separating and/or transforming the components of crude and waste oil feedstock into a range of products such as petrol, diesel, fuel oils, lubricating oils and asphalts.

### **2.1 CRUDE OIL REFINING INDUSTRY**

After the crude oil is received at the refinery, it is desalted through the removal of salt and sediments. Thereafter, the Crude Distillation Unit effects fractionation into four categories of product, namely petrol or naphtha products, kerosene, diesel or gas oil and residues. These products are either sold as is, or are further treated through removal of sulphur, dehydration, polymerisation or blending with other components prior to being sold. Further details and a process flow diagram are provided in Appendix 2.

### **2.2 SYNTHETIC FUEL REFINERY**

Synthetic fuel refineries obtain their feedstock from gas well fields or from the gasification of coal. The participating refinery's feedstock is a natural gas and condensate stream. Dehydration of these streams takes place on the offshore platform and a dry feedstock is provided to the onshore plant. This survey only reports on the water and wastewater management of the onshore operation.

The Liquid Petroleum Gas (LPG) range is separated from the gas and sold as is. The remainder is processed using the South African developed Synthol process using the Fischer Tropsch reaction to convert  $H_2$  and CO into longer chain hydrocarbons suitable for use as fuel. Further details and a process flow diagram are provided in Appendix 2.

The main products from the refining process are leaded and unleaded petrol, diesel, kerosene for illumination and LPG (propane and butane). A mixed alcohol product is also produced and this is exported as a motor fuel or as a chemical feedstock.

### **2.3 OIL RE-REFINING INDUSTRY**

The re-refining industry in South Africa is characterised by two distinctly different types of processes. The first type uses mass transfer processes similar to the crude refining



industries, namely fractionation, cracking and distillation. The oils that are re-refined in this process are used lubrication oils. The second type uses primarily physical separation processes such as settling and centrifugation, to re-refine marine slops collected from ships. Some used lubricating oils are also re-refined using physical separation processes. As the processes are so different a brief résumé of each type of re-refining industry is given, together with process flow diagrams in Appendix 2. The prime objective of the re-refining process is to separate moisture and solids from the used oil thereby making it suitable for re-use.

The main products of the fractionation based re-refining industry are base oils, spindle oils and diesel fuel. The base and spindle oils are blended with additives and are sold as a range of lubricating products. Subsequent to this study, the plant surveyed has closed.

The main product of the physical separation based re-refining industry is a furnace fuel suitable for use in direct fired kilns. Three re-refineries of this type were surveyed.

### **3. BYPRODUCTS, WASTES AND EFFLUENTS**

The refining process generates large volumes of waste water containing a variety of chemical contaminants. Waste water is generated in almost every refining operation, from primary distillation, to thermal cracking to the cooling water blowdown. Indirect waste water generation includes surface run off water from the refinery. However, the quantity and composition of the waste water will differ according to differences in (Dold, 1989):

- 1) refinery process configuration and operating conditions;
- 2) product lines;
- 3) composition of the feedstock; and
- 4) the site of the refinery i.e. a coastal or inland refinery.

#### **3.1 CRUDE OIL AND SYNTHETIC FUEL REFINING INDUSTRY**

- **Desalter wash-water and sludge**

This wash-water forms the main component of the crude refinery effluent (0.04 to 0.09 m<sup>3</sup> effluent/ton crude intake). The wash water contains elevated levels of phenols,

originating from the stripped sour water used to wash the crude oil. At low pH, phenols in the water are extracted by the crude oil (approx 85% removal). An oily sludge is also generated during desalting due to the presence of sediment in the crude oil.

- **Sour water**

Water, originating from the crude or as a result of steam stripping, collects in the overhead products of distillation and stripping operations and is termed sour water. This sour water contains high levels of phenols, sulphides and ammonia.

- **Reaction water**

This is a large volume stream generated by the Fischer-Tropsch reaction used in the synthetic fuel refinery which has an extremely high Chemical Oxygen Demand (COD) due to the presence of organic acids. The crude oil refineries do not have this effluent stream.

- **Demineralisation plant regeneration waste waters**

This waste water originates from the boiler feed water treatment system comprising of ion exchange.

- **Blowdown water**

The relatively high salinity blowdown water originates from the steam generation plants and the cooling towers. Due to the use of various corrosion and scale inhibitors the need for blowdown is reduced.

- **Process condensates**

This is an effluent originating from the process and due to the high temperature of the condensate streams, quench water is often discharged together with the condensates.

- **Other liquid effluents**

General wash water of the process areas, laboratory and fire school effluents, tank drainage and storm water run-off are further contributors to the waste waters from a refinery. A domestic waste water is also generated by personnel of the production plant.

- **Solid wastes**

Oil recovered from the gravity separation operations is routed to the refinery slop oil system for reprocessing. An oily sludge results from gravity separation of oily water

containing high levels of suspended solids. A further oily sludge is generated during the desalting process.

Solid wastes generated from the synfuel refinery include the spent catalyst from the Synthol process, water treatment sludges from the raw water treatment and softening processes and a biological sludge from the water recovery plant.

### **3.2 OIL RE-REFINING INDUSTRY**

- **Oily water**

Approximately 0.09 m<sup>3</sup> of water/t waste oil in the fractionating process and between 0.14 and 0.17 m<sup>3</sup> of water/ t waste oil in the physical separation process is removed from the feedstock and discharged as effluent.

- **Process condensate**

The condensate originates from the steam ejectors used to draw a vacuum on cracking and distillation columns, as well as the top products of the fractionating columns and the dehydrator. The condensate contains some lighter hydrocarbon compounds. Quench water can be discharged with the condensates to the effluent system.

- **Demineralisation plant regeneration waste waters**

This waste water originates from the boiler feed water treatment system comprised of ion exchange.

- **Blowdown water**

The relatively high salinity blowdown water originates from the steam generation plants. Due to the use of various corrosion and scale inhibitors the need for blowdown is reduced.

- **Other liquid effluents**

General wash water of the process areas and storm water run-off are further contributors to the waste waters from a re-refinery. Due to the inherently messy nature of re-refining, blockages and spillages can occur and these are all washed into the effluent system.

## 4. ANALYSES AND DISCUSSION OF WATER AND EFFLUENT MANAGEMENT DATA

All results are based on data obtained for the calendar year 1995.

### 4.1 CRUDE OIL AND SYNTHETIC FUEL REFINING INDUSTRY

#### 4.1.1 Water Intake

A comparison between the water intake and the specific water intake (SWI) for each of the refineries is given in Table 2.

**Table 2. Comparison of water intake and Specific Water Intake (SWI) for each refinery.**

Refinery	Average monthly feedstock intake (t/month)	Average monthly water intake (m <sup>3</sup> /month)	SWI (m <sup>3</sup> /t)		
			Minimum monthly	Maximum monthly	Average
1 (synthetic)	192 033	557 117	2.32	4.61	2.9
2 (crude)	294 463	175 943	0.52	0.68	0.6
3 (crude)	615 000	313 483	0.42	0.73	0.51
4 (crude)	329 626	220 003	0.58	0.78	0.67
* Industry average	413 030	236 476	---	---	0.57
* (Crude industry - refineries 2,3 & 4)					

Due to the different process, the synthetic fuel refinery (Refinery 1) uses significantly more water than a crude oil refinery, and therefore the SWI values cannot be compared. The synfuel plant consumes larger volumes of water than the other refineries would use on average. This highlights the water intensity of producing fuel catalytically. Between the crude oil refineries surveyed a close correlation of SWIs is noted. Contrary to what was expected the inland refinery did not have the lowest average SWI. There is no correlation between the production capacity and the SWI, in that the smallest refinery is not the least water efficient.

When compared to a study undertaken of Texan refineries (Appendix 3), South African crude refineries use up to 5 times less water per ton of crude intake.

#### 4.1.2 Breakdown of water use

An estimate of the breakdown of the different uses of the water over the entire refining process is given in Table 3.

**Table 3. Breakdown of water use**

Use of water	Percent of total intake			
	Refinery 1	Refinery 2	Refinery 3	Refinery 4
Boilers (steam generation)	41.4	50.8	54.7	50.4
Cooling	47.2	29.4	32.8	33.8
Wash water & other	10.2	19.6	11.9	5.3
Domestic	1.2	0.2	0.6	10.5

Steam generation (boiler) make-up water is the largest consumer in the crude refining industry, and this together with cooling water make up constitutes in excess of 80% of the total refinery water consumption. A significant quantity of water is saved if condensate recycling is implemented and the water re-used for steam generation. Whilst recycling treated effluent is not widely implemented, this practice could lead to further reductions of water consumption.

Open cooling water systems lose water by evaporation, and make-up water consumption therefore varies seasonally and due to climatic differences between the refineries. The degree of air cooling practised on the refinery also effects the quantity of water used in the cooling systems. No South African refinery practises once-through cooling and this reduces the amount of water required by the refinery when compared to some overseas refineries (Appendix 3). The synfuel process has a significantly higher cooling water requirement in comparison to the crude refineries. This is due to the nature of the production process. The high apparent domestic consumption in Refinery 4 is possibly due to a portion of this water also being used for processing purposes.

Process and wash water consumption varies with plant operating practices.

#### 4.1.3 Effluent generated

A comparison between the volumes of effluent discharged and specific effluent volume (SEV) for each of the crude and synthetic refineries surveyed, based on monthly average data, is given in Table 4.

**Table 4. Comparison of Specific Effluent Volume (SEV) for each refinery**

Refinery	Average monthly feedstock intake (t/month)	Average monthly effluent discharged (m <sup>3</sup> /month)	SEV (m <sup>3</sup> /t)		
			Minimum monthly	Maximum monthly	Average
1 (synthetic)	192 033	254 032	0.57	2.34	1.32
2 (crude)	294 463	95 423	0.27	0.41	0.32
3 (crude)	615 000	127 418	0.17	0.27	0.21
4 (crude)	329 626	104 829	0.26	0.38	0.32
* Industry average	413 030	109 223	---	---	0.26
* (Crude industry - refineries 2,3 & 4)					

On average 46% of the fresh water taken into a crude refinery or the synthetic fuel plant is discharged as effluent. This includes rainfall runoff from the oily processing areas and crude tank water drainage (which enters with the crude) as well as process effluent. The balance of the water is lost due to evaporation primarily from cooling systems.

The Specific Effluent Volume (SEV), based on the volume of water discharged per mass of crude processed, varies from 0.26 m<sup>3</sup>/t crude in the crude refining sector to 1.32 m<sup>3</sup>/t intake for the synthetic fuel plant. Once again, caution should be exercised in comparing the synthetic fuel refinery data to the crude oil refinery data. It is interesting to note that a coastal refinery has the lowest SEV of the crude oil refineries.

#### 4.1.4 Specific pollutant load

The main contaminants analysed for in the effluent water resulting from the crude oil and synthetic refining process are oil, phenols, sulphides and ammonia, resulting from contact with the hydrocarbon product processed. In addition to the above parameters,

pH and organic content (measured as chemical oxygen demand (COD) or oxygen absorbed (OA)) are also monitored. Table 5 gives an indication of the South African refining industry's effluent quality. It should be borne in mind that only primary treatment has been used on the effluent.

**Table 5. Refining industry effluent quality**

Contaminant	Concentration (mg/l)		
	Minimum monthly average	Maximum monthly average	Industry average
Oil	3.6	27	11.6
Sulphide	0.1	8.8	3.2
Phenol	3	8	4
COD	179	837	384
OA	93	117	104
Ammonia	1.2	24	10.2
pH	7.2	9.2	8.1

The large difference between the COD and oil concentration could be an indication of a high concentration of other soluble, polar organics in the effluent. Large differences in concentrations of the various parameters are observed and this indicates process irregularities within the refinery.

The above concentrations are representative of effluent quality after primary treatment. The oil concentration is higher than that reported in overseas literature (Appendix 3) after secondary treatment. The ammonia concentration, however, is very similar to that reported by overseas refineries.

Specific Pollutant Loads (SPL) for the refining industry, based on monthly averages are tabulated in Table 6.

**Table 6. Specific pollutant loads (SPL) for refining industry**

Pollutant	SPL (g/t processed)			
	Refinery 1	Refinery 2	Refinery 3	Refinery 4
Oil	4.5	2.5	4.7	n.d
Sulphide	n.d	0.1	1.2	1.1
Phenol	n.d	1.8	0.9	1.9
COD	449.9	95.9	n.d	121.9
OA	n.d	n.d	21.8	n.d
Ammonia	10.5	2.2	n.d	4
n.d= not determined				

The oil SPL of refinery 2 is approximately half that of refinery 3, which indicates the positive effect of the induced air flotation treatment which refinery 2 uses after the API separator. Also noteworthy is that the sulphide SPL of refinery 2 is an order of magnitude lower than refinery 3 and 4.

Due to there being no sulphur in the feedstock to the synfuel refinery, sulphides are not monitored in their effluent.

## **4.2 OIL RE-REFINING INDUSTRY**

### **4.2.1 Water Intake**

A comparison between the water intake and the specific water intake (SWI) for the re-refining industry based on monthly average data is given in Table 7.



**Table 7. Comparison of water intake and Specific Water Intake (SWI) for each re-refinery.**

Re-refinery	Average monthly feedstock intake (t/month)	Average monthly water intake (m <sup>3</sup> /month)	SWI (m <sup>3</sup> /t)		
			Minimum monthly	Maximum monthly	Average
1	1 317	9 478	5.27	10.25	7.2
2	3 686	235	0.04	0.1	0.06
3	3 109	2 078	0.59	0.7	0.67
4	729	823	0.14	2.51	1.13
Average	2 210	3 154	---	---	1.43

The volumes of water used in the re-refining industry are approximately one hundredth of that used in the crude oil and synfuel refineries. Within the re-refining industry, the range in SWI indicates that the different processes used have a marked impact on the volume of water consumed per ton of product processed. The fractionation-based re-refinery (Refinery 1) uses an order of magnitude more water than the other re-refineries. This is due to the relatively more complex processing that is undertaken. It is significant to note that this re-refinery is significantly less water efficient than the large crude refineries.

Re-refineries 2, 3 and 4 have essentially the same process, but are very different in their water efficiencies. The variation between the minimum and maximum values is larger than in the crude refining sector.

#### **4.2.2 Breakdown of water use**

An estimate of the breakdown of the different uses of the water over the entire re-refining process is given in Table 8.

**Table 8. Breakdown of water use**

Use of water	Percent of total intake			
	Re-refinery 1	Re-refinery 2	Re-refinery 3	Re-refinery 4
Boilers (steam generation)	n.a.	25.5	43.5	21.4
Cooling	n.a.	21.3	21.7	0
Wash water & other	n.a	31.9	27.6	64.7
Domestic	5	21.3	7.2	13.9
n.a. = not available				

Process and wash water consumption varies with plant operating practices, and in the re-refining industry is the largest water consumer. This is due to the inherently messy operation of having to handle the feedstock in smaller containers (drums) and the associated cleaning and washing. On average 41% of the water intake is used for washing operations in the re-refining industry.

The next largest water user is steam generation make up which constitutes on average 30% of the total water consumption in the re-refining industry. This is less than in the crude refining industry. A significant quantity of this water could be saved if condensate recycling was implemented and re-used for steam generation. Not all of the re-refineries in this survey practise condensate recycling, and those that do, only have a limited amount of condensate recycling.

Little water is used in cooling systems in the re-refining industry, and one of the plants surveyed has no cooling water system.

#### **4.2.3 Effluent generated**

A comparison between the effluent generated and the specific effluent volume (SEV) for each of the re-refineries based on monthly average data is given in Table 9.

**Table 9. Comparison of effluent generated and Specific Effluent Volume (SEV) for each re-refinery.**

Re-refinery	Average monthly feedstock intake (t/month)	Average monthly effluent discharged (m <sup>3</sup> /month)	SEV (m <sup>3</sup> /t)		
			Minimum monthly	Maximum monthly	Average
1	1 317	7 582	4.21	8.2	5.76
2	3 686	473	0.02	0.22	0.13
3	3 109	2 159	0.6	0.74	0.69
4	729	842	0.79	13.37	1.16
Average	2 210	2 764	---	---	1.25

The Specific Effluent Volume (SEV) varies from 0.13 m<sup>3</sup>/t oil to 5.76 m<sup>3</sup>/t oil. This large variation is due to the vastly different types of waste oil processed as well as the different processes used. Another contributing factor is the relatively low priority given to water conservation measures in the re-refining sector.

In most of the re-refineries more water is discharged as effluent than is taken in as fresh water. This is due to the large volume of water mixed with the used oil which is removed and discharged during the re-refining process.

#### **4.2.4 Specific pollutant load**

The main contaminants in effluent water resulting from the oil re-refining process are oil, phenols, sulphides and ammonia, resulting from contact with the hydrocarbon product processed.

A characteristic of the re-refining industry is that they typically discharge their effluent to municipal sewage works where the effluent is treated further. As the re-refineries surveyed were all in different municipal areas, their effluent discharge was subject to different controls. Effluent contaminant data is only available for the parameters required by the municipality and as a result it is not possible to provide specific pollutant load data for the industry as a whole. Table 10 gives an indication of the re-refining industry's

effluent quality based on the limited data obtained from a few of the re-refiners' effluent quality.

**Table 10. Re-refining industry effluent quality**

Contaminant	Concentration (mg/l) (typical values)
Oil	124 to 171
Sulphide	not reported
Phenol	not reported
COD	2036 to 7052
Ammonia	303 to 834
pH	4.2 to 9.1

Table 11 gives an indication of the re-refining industry's specific pollutant loads based on the limited data obtained from a few of the re-refiners' effluent quality.

**Table 11. Specific pollutant loads (SPL) for re-refining industry**

Pollutant	Specific pollutant load (g/t processed) Typical value
Oil	110
Sulphide	not reported
Phenol	not reported
COD	46 700
Ammonia	10 100

The SPLs of the re-refining industry are orders greater than those in the crude and synthetic refineries which indicates that the re-refineries surveyed could improve on their effluent management. However, as the total production from this sector of the industry is small the impact of these high SPLs is less severe than the values suggest.

## **5. WATER AND EFFLUENT MANAGEMENT**

### **5.1 CRUDE OIL REFINING INDUSTRY**

The effluent management is shown schematically in Figure 2. In general, the refineries have a dual sewer system, whereby relatively uncontaminated rainwater runoff is kept separate from the process effluent and rainwater runoff from potentially contaminating areas. The relatively uncontaminated runoff is routed to the clean water sewer while the oil contaminated water is routed to the oily water sewer for treatment prior to discharge.

In crude oil refining four effluent streams can be identified (Figure 2). These are the sour water effluent, the clean water sewer effluent, the oily water sewer effluent and the saline effluent requiring neutralization. Oily sludge is an inevitable part of the refining process and also requires attention.

#### **Sour water effluent**

The sour water is routed to sour water strippers where medium/low pressure steam is used to strip contaminants such as sulphides and ammonia. This process can be highly efficient, resulting in up to 98 %  $H_2S$  removal and 95% ammonia removal. The stripper overheads are routed to furnaces or sulphur recovery units. Stripped sour water (stripper bottoms) is used as desalter make-up water.

#### **Clean water sewer effluent**

The relatively uncontaminated runoff is routed to the clean water sewer from where it is discharged directly or passes through a gravity separator where free oil is separated from the water. The quality of this water is monitored and if it meets the General Standard it is disposed of to the environment. At some refineries boiler blowdown is also discharged into this system.

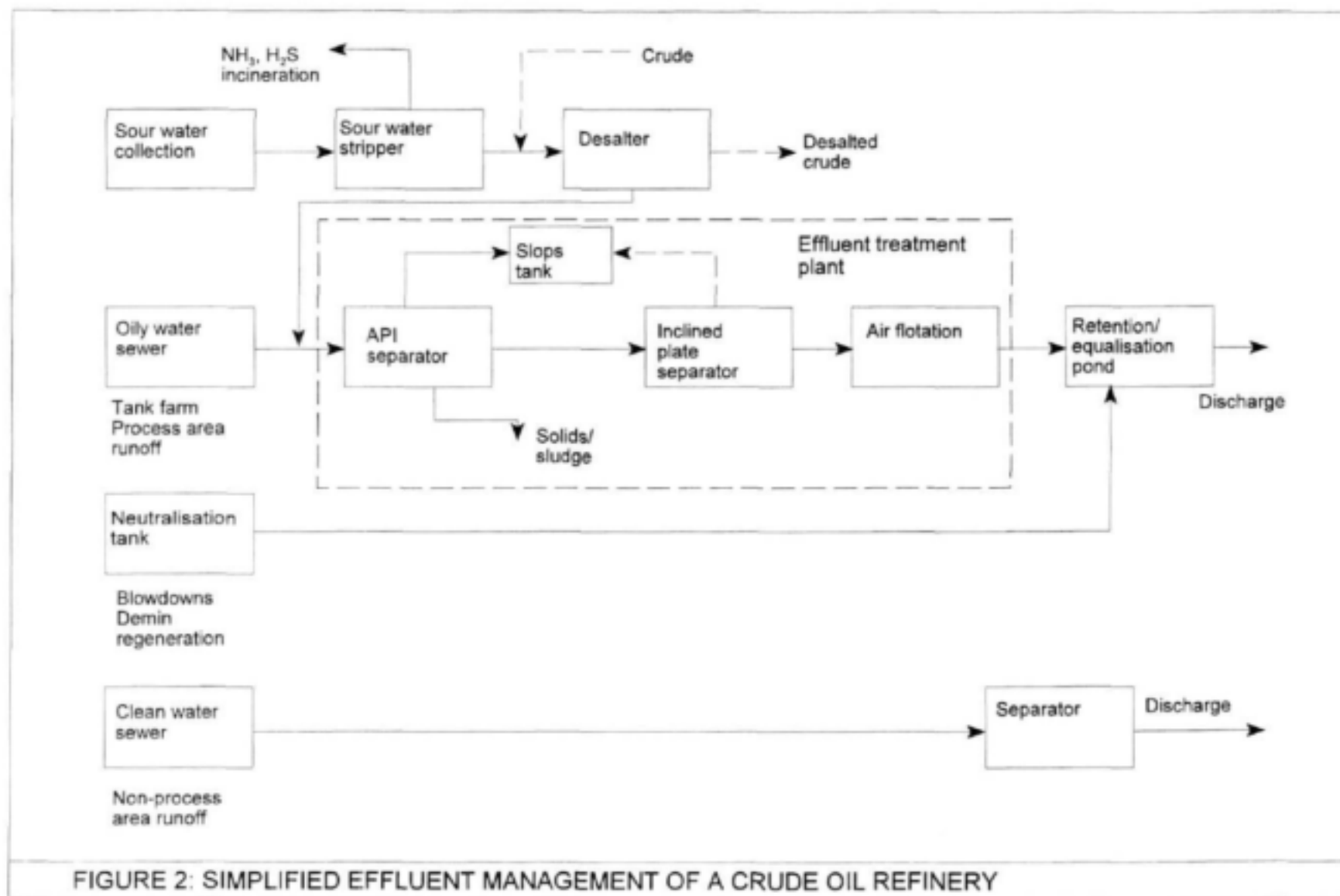


FIGURE 2: SIMPLIFIED EFFLUENT MANAGEMENT OF A CRUDE OIL REFINERY

### **Oily water sewer effluent**

Refinery effluent water is treated in an effluent treatment plant . The effluent treatment plant consists of one or more of the following processes; gravity separation, induced and dissolved air flotation (see Table 12 and Figure 2). Effluent routed to the oily water sewer includes desalter wash water, cooling water blowdown, laboratory effluent, tank bottoms, tank farm and process area runoff.

The inland refinery practises pre-treatment of the desalter effluent prior to combining this with the remaining oily water effluents. This pretreatment consists of dissolved air flotation (DAF) and the objective is to reduce oil and phenol concentration in the desalter effluent.

The combined oily water streams are routed to an oil separation stage for oil-water separation by gravity settling. The most commonly used systems are American Petroleum Institute (API) separators or inclined plate separators. The inclined plate separators have inclined corrugated plates which aid the separation of free oil from the water. Skimmed oil from these unit operations is routed to slop tanks prior to reprocessing. The water fraction is either routed to the sour water stripper or the oily water sewer depending on whether it contains sulphur. Effluent water may then be further treated in an induced air flotation (IAF) unit for removal of residual free oil and suspended solids, but at most refineries passes directly to a Retention or Equalisation Pond for equalisation prior to discharge. The two coastal refineries discharge to sea via a sea outfall and diffuser system. The inland refinery discharges to an off-site biological plant for further treatment. Table 12 gives a summary of the effluent treatment practices for the various refineries and the ultimate fate of the effluent.

**Table 12. Effluent treatment practices of the crude oil refineries**

Refinery	Type of Treatment	Permit conditions	Ultimate fate of effluent
2	API separator, induced air flotation	"Old" Water Act with exemptions	Sea discharge (Self operated)
3	API separator, inclined plate separator	Municipal by-laws	Sea discharge (Local authority operated)
4	DAF, API separator, inclined plate separator	Biological plant acceptance standards	River discharge after subsequent biological treatment (operated by other)

### **Saline effluent**

Effluent from the laboratories, boiler water blowdown and the demineralisation regeneration effluents and rinse waters may be contained in an isolated sewer system. This stream is routed to a neutralisation tank where it is neutralised using caustic or mineral acid prior to discharge to the Retention Pond. At the inland refinery this effluent is evaporated in solar evaporation ponds and the residue is disposed of to landfill. This is due to the high salinity of this effluent and the threat this would pose to salination of the fresh water environment if this was discharged together with the other effluent as at the coastal refineries.

### **Oily sludge**

The oily sludge generated during desalting due to the presence of sediment in the crude oil can be utilised as a feed product in the re-refining industry or is disposed of. The oil recovered from the gravity separation operations is routed to the refinery slop oil system for reprocessing. Sludge removed from these separators is either taken off-site for disposal in a classified disposal site or is treated on-site.



remove free oil. Following this stage the effluent passes through inclined plate oil separators. These separators have inclined corrugated plates which aid the separation of free oil from the effluent. The oil that is recovered is collected and is reworked through the process or is disposed of to landfill. After passing through the separators the effluent stream is dosed with de-emulsification chemicals before being passed through a number of dispersed air flotation units. This stage removes the emulsified fraction of the oil in the effluent. The treated effluent is then held in retention tanks prior to being discharged via the sea outfall. The effluent quality is measured in the tanks and is redirected back to the inlet of the effluent plant if it does not meet the discharge specification.

### **Saline effluent**

The spent regeneration solutions from the demineralisers and the blowdown streams comprise the saline effluents and these are collected separately and do not pass through the oil separation stages of the effluent plant. The pH of this effluent is adjusted to near neutral by means of acid or caustic addition. Once this effluent is neutralised it is discharged together with the other effluents via the ocean outfall.

### **Reaction water effluent**

A large volume of high COD effluent is generated in the Synthol process. This reaction water stream contains primarily acetic acid and other organic acids and is collected in an equalization basin from where it passes into the water recovery plant. The effluent is dosed with microbiological nutrients (nitrogen, phosphorus and potassium) and lime and then flows into anaerobic reactors. These reactors are of the immobilised biomass configuration. By means of the anaerobic reactions the acids are converted into methane and carbon dioxide. The biogas formed during the anaerobic reaction is flared off. Following anaerobic treatment the effluent passes into aeration basins where the remaining organic matter is degraded. The water is then dosed with lime and ferric chloride and is clarified and filtered. This filtered water is then softened in a cation exchange bed and recycled back into the cooling water circuit as make-up water.

## Sludges

The sludges generated from the raw water treatment clarification and the treated reaction water clarification as well as the excess biosolids from the biological processes are thickened together in a large gravity thickener. The thickened sludge is dewatered on a belt press prior to disposal in the landfill. The supernatant from the dewatering operations is returned to the reaction water recovery plant.

Oily sludges are dewatered and disposed of to the landfill.

Table 13 gives a summary of the effluent treatment practice for this refinery.

**Table 13. Effluent treatment practice of the synthetic fuel refinery**

Type of Treatment	Permit conditions	Ultimate fate of effluent
Oil-water separator, dispersed air flotation	Water Act with exemptions	Sea discharge (Self operated)

### 5.3 OIL RE-REFINING INDUSTRY

One re-refinery has a complete dual sewer system whereby the contaminated rainwater runoff is kept separate from the process effluent. The rainwater runoff is collected in two large rectangular tanks where, through gravity separation, free oil is separated from the water fraction. After passing through the separation tanks, the effluent then passes through a coalescer and inclined plate separator before being discharged into the municipal sewer. The collection sump of this system is designed to capture the first ten minutes of runoff from a 1 in 50 year storm. Any water in excess of this, is discharged untreated into the environment.

One other re-refinery has a partial separate sewer system whereby the contaminated rainwater runoff from part of the site is directed to a different system to the process effluent. This rainwater runoff which is collected from within the bunded areas around storage tanks and off-loading areas passes through a three chamber "over-under" static oil separator. This separator achieves the separation of free oil from the water. The oil that is recovered is collected and reworked through the process. After passing through this separator the water is discharged to the municipal sewer.

The remaining two re-refineries have a combined sewer system whereby the contaminated rainwater runoff from the site is directed to the same effluent system as the process effluent.

The treatment undertaken at the different re-refineries is based essentially on free oil separation, but each refinery has its own adaptations to comply with their specific treatment requirements. In general, the process effluent from the different production areas is collected in a sump and then passes through an inclined plate oil separator. This separator has inclined corrugated plates which aid the separation of free oil from the effluent. The oil that is recovered is collected and reworked through the process.

After passing through the separator, the pH of the effluent stream is usually adjusted by the addition of lime or caustic lye. At one re-refinery the effluent then cascades through aerated tanks, which operate in series. The aeration is used to strip ammonia from the effluent. At another re-refinery the neutralised effluent then is further treated in a dissolved air flotation (DAF) unit where further oil separation is achieved.

One re-refinery undertakes extreme treatment of its effluent so as to have a zero liquid effluent operation. This is as a result of not being able to meet the local authorities discharge requirements. At this refinery the water and solids separated from the used oil, as well as from contaminated run-off from unbunded areas, are all treated together in a common "sludge" handling system. In addition, the boiler blowdown is also treated in this system. The contaminated water and solids are collected and pumped into a heated tank. The water fraction is driven off in this tank due to heating, and the remaining sludge residue is disposed of to a hazardous waste disposal site.

Table 14 gives a summary of the effluent treatment practices for the various re-refineries.

**Table 14. Effluent treatment practices of the re-refineries**

Refinery	Type of Treatment	Permit conditions	Ultimate fate of effluent
1	Inclined plate separator, neutralisation, ammonia stripping by aeration	Municipal by-laws	After municipal treatment river discharge
2	"Over-under" separator	None	Co-disposal on landfill site as dust suppression water
3	Inclined plate separator, neutralisation, DAF	Municipal by-laws	Sea discharge (Local authority operated)
4	Run-off by means of "Over-under" separator	Municipal by-laws	Municipal sewer
	Effluent by means of evaporation	None	Evaporation

## 6. CONCLUSIONS AND RECOMMENDATIONS

### 6.1 WATER INTAKE

Crude oil refineries in South Africa have a range of SWI between 0.51 and 0.67 m<sup>3</sup>/t crude. The synfuel refinery has an average SWI of 2.90 m<sup>3</sup>/t. The re-refineries show much greater variation and have a range of SWIs between 0.06 and 7.20 m<sup>3</sup>/t. For the crude refineries there is no clear correlation between refinery size and SWI. For the re-refineries the type of process used strongly influences the SWI.

### 6.2 RECOMMENDATIONS FOR REDUCING SWI

The largest consumers of water in the oil refining and re-refining industry are the boiler make up and cooling water circuits. Water saving measures in these areas will lead to more significant reduction in SWI values as compared to that which would be obtained by reducing wash water for example. However, it is recognized that it is not always feasible to retrofit water saving measures, but that these could be considered in new designs for expansions or new plants.

Measures of reducing water intake could include:

- Condensate recovery in steam circuits. This will not only reduce boiler feed water intake but will also eliminate the need for quench water.
- Increased use of air cooling as opposed to water cooling.
- The use of vacuum pumps rather than steam ejectors for drawing vacuum could be investigated.
- Leaking steam traps should be immediately repaired after becoming faulty.
- Treated waste water can be upgraded for use as cooling water make-up, as is practised at the synthetic fuel refinery in South Africa.

### **6.3 WASTE WATER**

It was found that for the crude refining industry the average SEV is 0.26 m<sup>3</sup>/t, for the synthetic fuel refinery it is 1.32 m<sup>3</sup>/t and for the re-refining industry it ranges between 0.13 and 5.76 m<sup>3</sup>/t. For the crude and synthetic refineries surveyed the waste water discharged is approximately 46% of the water intake. For the re-refining industry the waste water discharged can exceed the water intake. The re-refining industry takes in large volumes of water together with their feedstock and this has to then be discharged as effluent.

The SPL for oil ranges between 2.5 and 4.7 g/t for the crude refining industry, 4.5 g/t for the synthetic fuel refinery and 110 g/t for the re-refineries. Despite the synthetic fuel process being inherently water intensive, the SPL is comparable to that found in the crude refining industry.

### **6.4 RECOMMENDATIONS FOR REDUCING POLLUTION LOADS**

Once again it is noted that it is not always feasible to retrofit pollution reducing measures, however, these can be considered during expansion or in new designs. Options for improving effluent quality could include:

#### **6.4.1 Primary treatment**

It should be checked that oil separators are not only efficient during dry weather flows. When rainfall produces significantly increased flow rates, oil which has been retained by the separator prior to skimming may suddenly be carried through, overloading the downstream units. Should this be the case the oil separator size should be increased.

High efficiency separators, such as the tilted plate separators, can replace the API type separator. An existing API separator can be upgraded by installing the tilted plates within the separator. The separator can also be designed in such a way that once the oil has been separated it cannot then be carried through the separator even during periods of high flow rate. Build up of oil is avoided through the design.

In the past, the most commonly used skimming device was the rotating slotted pipe, due to its robust construction and simplicity of operation. However, the method of operation is labourious and frequent manpower attention is required for it to be effective. Poor operation results in large quantities of water being skimmed at the same time as the oil or ineffective skimming with the danger of oil carry-through.

A range of more efficient skimming devices are now available, which work on different principles e.g. oil adheres better to plastic or metal than water. This has led to the belt skimmers, oil mops etc..

DAF units require regular maintenance including cleaning, replacement of worn scraper blades and diffusers.

#### **6.4.2 Secondary treatment**

Secondary treatment is not usually practised in the South African oil refining and re-refining industries, but should be considered when an improvement in the quality of effluent is required.

#### **6.4.3 Segregation of clean and dirty surface run-off**

Contaminated run-off should be kept separate from relatively clean run-off. The introduction of dirty water at clean water outfalls will lead to the requirement of additional

treatment facilities. It is usually more economical to restrict treatment to that portion of the flow that is unavoidably contaminated. This volume can be kept low through the use of kerbing, drains and weirs, and by adjusting drainage slopes to segregate the flow.

#### **6.4.4 Segregation of different effluent streams**

Where possible, different effluent streams not requiring the same treatment should be kept separate to prevent having to provide oversized treatment units and also to prevent hydraulic overloading of the units.

#### **6.4.5 Reduction/limitation of volume of surface water run-off**

The quantity of surface water entering the drainage system is dependent on three aspects: 1) rainfall; 2) the run-off co-efficient of the ground surface and 3) the size of the catchment area draining into the system. Rainfall is fixed, however, the run-off coefficient and the catchment area may be reduced by selecting a permeable surface covering, such as grass and gravel rather than tarmac and concrete. In this way percolation rather run-off to the drainage system is encouraged. This is only applicable for clean areas.

#### **6.4.6 Reduction in volumes of process water requiring treatment**

This can be achieved by controlling the processes in a refinery including such measures as containing areas of frequent spillage, preventing the product released from entering the drainage system, management of water drawn off from slop tanks and recycling process water wherever possible. The use of cleaning agents should be controlled, as they create problems at the effluent treatment stage. Emulsified oil is far more difficult to treat than free oil as gravity separation becomes less effective.

#### **6.4.7 Cleaner technology**

Improvements in the water and waste water management within the oil industry as a whole have been evident. Although the focus in South Africa is still mainly on "end-of-pipe" treatments, the world wide trend is shifting towards "clean technologies", and this philosophy should be pursued wherever possible.

## 7. REFERENCES

Department of Water Affairs and Forestry , (1991). Water Quality and Management Policies and Strategies in the RSA. Pretoria.

Doke, L. (1996). Rosy future ahead for used oils. *Safety Management*, January, 21 - 23.

Dold, P.L. (1989). Current practice for treatment of petroleum refinery wastewater and toxics removal. *Water Poll. Res. J. Canada*, **24** (3), 363 -390.

Mbendi, 1997. Oil refineries in South Africa. Mbendi Information Services. Internet site: <http://mbendi.co.za>.

Paxton, B. (1997). Southern African fuel supply and demand outlook. UNCTAD Oil Conference, Harare, 14 April, 1997.

SAPIA, (1997). **South African Petroleum Industry Association: Second Annual Report.** August 1997.



## APPENDIX 1 CALCULATIONS OF VALUES

The manner in which the different values reported were calculated is presented below.

For each refinery and re-refinery the following calculations were performed:

### Data

	Jan	Feb	Mar	.....	Dec
Feedstock intake (tons)	$F_{Jan}$	$F_{Feb}$	$F_{Mar}$	.....	$F_{Dec}$
Water intake ( $m^3$ )	$W_{Jan}$	$W_{Feb}$	$W_{Mar}$	.....	$W_{Dec}$
Effluent discharged ( $m^3$ )	$E_{Jan}$	$E_{Feb}$	$E_{Mar}$	.....	$E_{Dec}$
SWI ( $m^3/t$ )	$W_{Jan}/F_{Jan}$	$W_{Feb}/F_{Feb}$	$W_{Mar}/F_{Mar}$	.....	$W_{Dec}/F_{Dec}$
SEV ( $m^3/t$ )	$E_{Jan}/F_{Jan}$	$E_{Feb}/F_{Feb}$	$E_{Mar}/F_{Mar}$	.....	$E_{Dec}/F_{Dec}$

For refineries that had scheduled maintenance shutdowns, the months in which the shutdowns occurred were excluded from the calculations.

### Calculations

$$Average\ Monthly\ Feedstock\ intake_{Refinery\ j} = \frac{\sum_{i=Jan}^{Dec} F_i}{12}$$

$$Average\ Monthly\ Water\ intake_{Refinery\ j} = \frac{\sum_{i=Jan}^{Dec} W_i}{12}$$

$$Average\ Monthly\ Effluent\ discharge_{Refinery\ j} = \frac{\sum_{i=Jan}^{Dec} E_i}{12}$$

$$Average\ SWI_{Refinery\ j} = \frac{Average\ Monthly\ Water\ intake_{Refinery\ j}}{Average\ Monthly\ Feedstock\ intake_{Refinery\ j}}$$

$$Average\ SEV_{Refinery\ j} = \frac{Average\ Monthly\ Effluent\ discharged_{Refinery\ j}}{Average\ Monthly\ Feedstock\ intake_{Refinery\ j}}$$

$$Minimum\ Monthly\ SWI = \min_{i = Jan}^{Dec}(SWI_i)$$

$$Maximum\ Monthly\ SWI = \max_{i = Jan}^{Dec}(SWI_i)$$

$$Maximum\ Monthly\ SEV = \max_{i = Jan}^{Dec}(SEV_i)$$

$$Industry\ average\ Monthly\ Feedstock\ intake = \frac{\sum_{j = Refinery\ 1}^{Refinery\ n} Average\ Monthly\ Feedstock\ intake_{Refinery\ j}}{n}$$

$$Industry\ average\ Monthly\ Water\ intake = \frac{\sum_{j = Refinery\ 1}^{Refinery\ n} Average\ Monthly\ Water\ intake_{Refinery\ j}}{n}$$

$$Industry\ average\ Monthly\ Effluent\ discharge = \frac{\sum_{j = Refinery\ 1}^{Refinery\ n} Average\ Monthly\ Effluent\ discharge_{Refinery\ j}}{n}$$

$$Industry\ Average\ SWI = \frac{Industry\ Average\ Monthly\ Water\ intake}{Industry\ Average\ Monthly\ Feedstock\ intake}$$

$$Industry\ Average\ SEV = \frac{Industry\ Average\ Monthly\ Effluent\ discharge}{Industry\ Average\ Monthly\ Feedstock\ intake}$$

## APPENDIX 2

### PROCESS RÉSUMÉ

#### 1. CRUDE OIL REFINING INDUSTRY

##### 1.1 Background

The refineries are designed to process Arabian/Iranian crude oil, although a wide variety of crude types can be processed by the different refineries. Crude oil arrives by tanker in Saldanha Bay, Cape Town and Durban. From the tankers the oil is usually off-loaded at an offshore mooring buoy and is transferred by subsea or underground pipelines to the respective refinery's storage facilities or the Strategic Fuel Fund Tank Farm. The inland refinery receives its crude by means of an underground pipeline from the coastal tank farms.

The main products from these refineries are petrol, gas oil (diesel), illuminating kerosene and jet fuel. Lighter products such as Liquefied Petroleum Gas (LPG), butane, sales gas and by-products such as sulphur and heavier products, including fuel oil and bitumen, are also produced.

##### 1.2 Crude Oil Processing

The generic production process is shown schematically in Figure 2.1.

###### 1.2.1 Pretreatment

Before distillation of crude oil, salt and sediment are removed in the desalter. This stage reduces fouling and corrosion in the subsequent units. Salt is removed from the crude oil by mixing the crude with stripped sour water that dissolves the salts. The subsequent separation of the water from the crude is enhanced by a strong electric field in the desalter. This stage occurs at elevated temperatures and pressures.

###### 1.2.2 Refining Process

The Crude Distillation Unit (CDU) effects initial separation into fractions based on boiling point differences. The CDU fractionates crude into four categories of products, namely: petrol or naphtha products, kerosene, gas oil (diesel) and residues.

###### *Petrol products*

Lower boiling point fractions are removed from the top of the column, with sour gas ( $H_2S$ ). Products containing sulphur compounds are "sweetened" by a process of hydrodesulphurisation. This is a catalytic process that uses hydrogen to convert sulphur to hydrogen sulphide ( $H_2S$ ). The naphtha fraction is therefore desulphurised, forming  $H_2S$ , and split into light naphtha and heavy naphtha.

Light naphtha is routed to an isomerisation process to produce a high-octane number blending component. Heavy naphtha is routed to a catalytic reforming process to produce a high-aromatic content blending component. The latter process generates hydrogen which is used for hydrodesulphurisation. The  $H_2S$ -rich gas is treated with amine, and the  $H_2S$ , which is subsequently stripped from the amine, is routed to the Sulphur Recovery Unit for conversion to elemental sulphur, which is sold as a by-product.

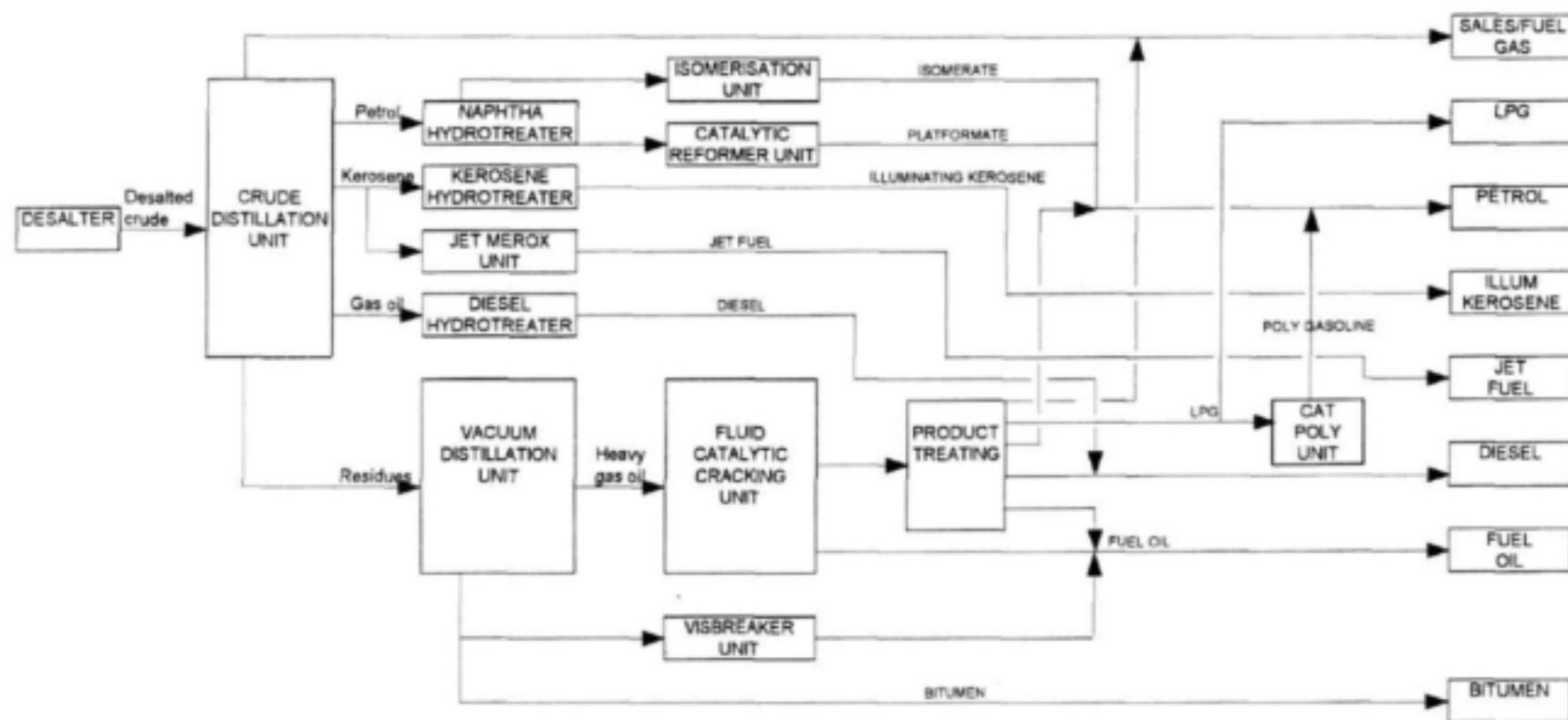


FIGURE 2.1: SIMPLIFIED FLOW DIAGRAM OF A CRUDE OIL REFINERY

### *Kerosene*

Kerosene, which is commercially known as "paraffin", is sold as illuminating kerosene (for household fuel) or as jet (aviation) fuel. Crude kerosene from the CDU is desulphurised (through hydro-desulphurisation) to meet the specification for illuminating kerosene. Jet fuel is produced from crude kerosene by oxidising mercaptans catalytically to meet the specification for jet fuel. Kerosene products are "dried" in filters for water removal.

### *Gas oil (diesel)*

Light diesel is used for blending directly from the CDU, and the heavy diesel fraction, which contains more sulphur, is desulphurised before blending.

### *Residues*

The bottoms fraction (high boiling point) from the CDU is heated and further distilled under vacuum in the Vacuum Distillation Unit (VDU). Light gas oil, which falls within the diesel boiling range, is desulphurised with the diesel. Heavy gas oil is routed to a fluidised catalytic cracking unit (FCCU) for conversion to petrol, gas oil fractions and fuel oil. The LPG fraction from the FCCU is catalytically polymerised to produce a high-octane blending component. The bottoms fraction from the VDU is used as a fuel oil or thermally cracked in the Visbreaker Unit to produce petrol, gas oil (diesel) and fuel oil.

## **2. SYNTHETIC FUEL REFINERY**

### **2.1 Background**

Synthetic fuel refineries obtain their feedstock from gas well fields or from the gasification of coal. The origin of the feedstock for the refinery surveyed is from well fields situated some 85 km offshore. A production platform is situated at the well field site and the feedstock is piped 91 km to the onshore refinery. The feedstock is a natural gas and a condensate stream. Dehydration of these streams takes place at the offshore platform and a dry feedstock is provided to the onshore plant. This survey only reports on the water and wastewater management of the onshore operation.

The main products from the refining process are leaded and unleaded petrol, diesel, kerosene for illumination and liquid petroleum gas (propane and butane). A mixed alcohol product is also produced and this is exported as a motor fuel or as a chemical feedstock.

### **2.2 Processing**

#### **2.2.1 Pretreatment**

The natural gas and condensate are pumped ashore and stored separately at the onshore plant for use in the process. The LPG range (propane, butane and heavier) is separated from the gas and these are marketed as is with no further processing. No further pretreatment of the gas and condensate takes place onshore and the water removed from the feedstock is disposed of at sea and does not form part of the onshore plant's effluent.

#### **2.2.2 Petrochemical Production Process**

The production process is shown schematically in Figure 2.2.

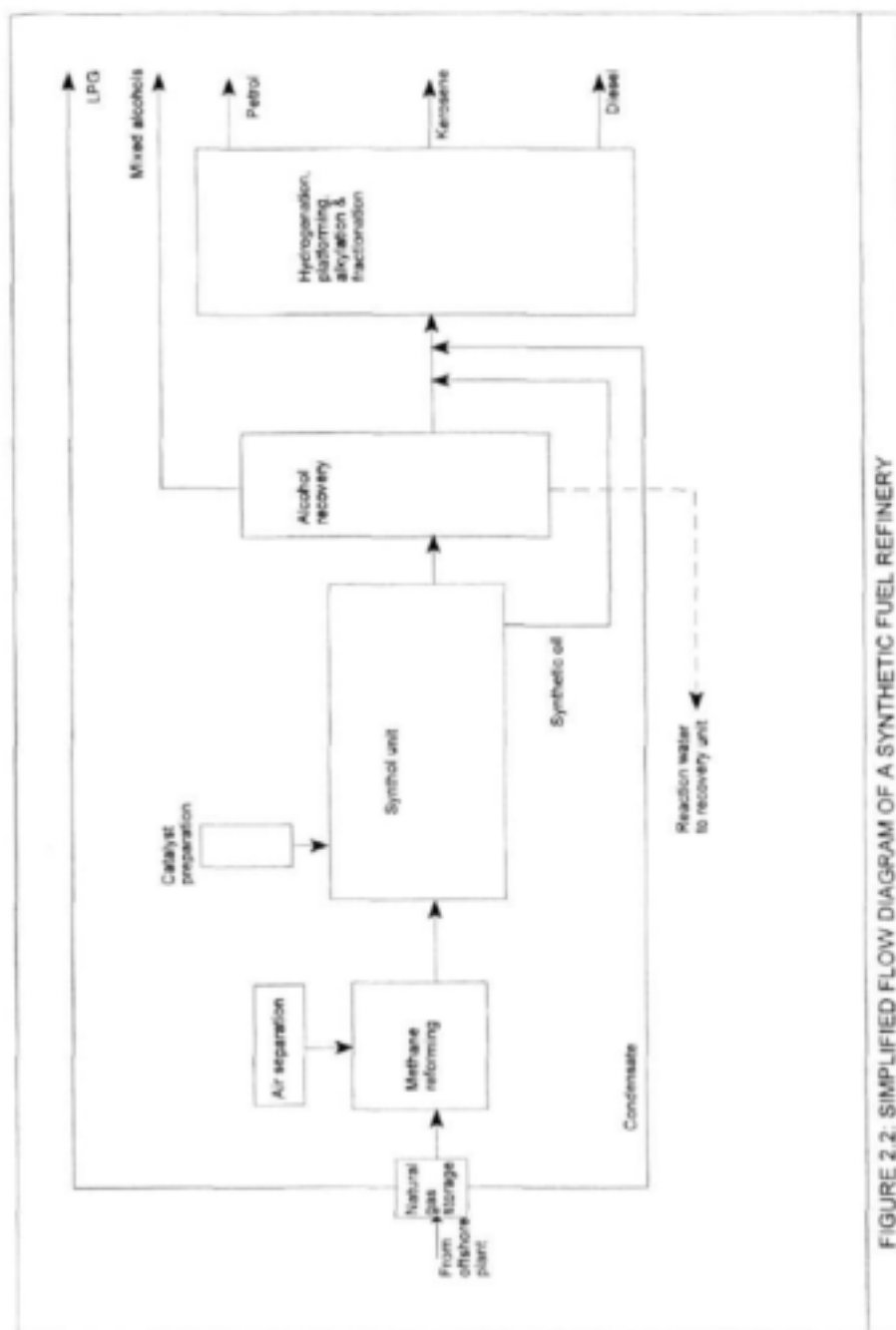


FIGURE 2.2: SIMPLIFIED FLOW DIAGRAM OF A SYNTHETIC FUEL REFINERY

### Syngas production (Methane reforming)

The first stage in the production process is the conversion of the natural gas to the synthesis gas (Syngas) required in the fuel production process. Formation of the Syngas takes place in the presence of high pressure steam and oxygen and is composed primarily of  $H_2$  and  $CO$ . The oxygen required for this reforming reaction is obtained from an air separation plant, which separates the oxygen and nitrogen fractions in air.

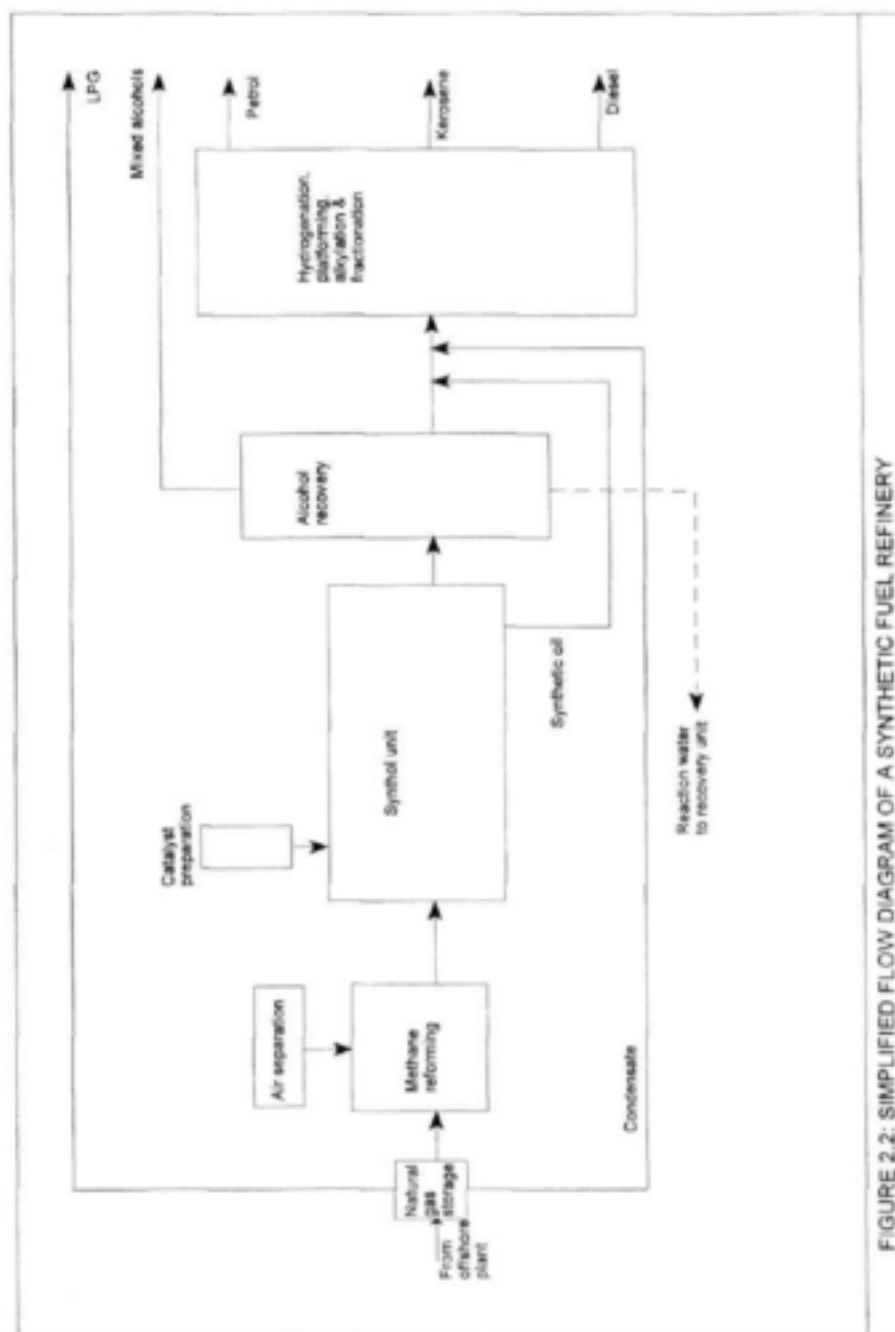


FIGURE 2.2: SIMPLIFIED FLOW DIAGRAM OF A SYNTHETIC FUEL REFINERY

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#### *Synthesis process (Synthol unit)*

The heart of the synthetic fuel production process is the South African developed Synthol process. This process uses the Fischer-Tropsch reaction to convert  $H_2$  and CO into longer chain hydrocarbons suitable for use as fuel. The process requires a catalyst, and uses a circulating fluidised bed reactor.

Products from this process are a synthetic oil stream and a mixed alcohol stream. The synthetic oil stream is combined with the offshore condensate for further processing by means of conventional refining processes.

#### *Alcohol recovery*

Besides the synthetic oil produced by the Synthol unit, a mixed alcohol stream is also produced. In the alcohol recovery unit, these alcohols are recovered as fuel grade alcohols for subsequent blending into petrol or it is sold as is. An acetic acid rich aqueous stream remains after the alcohol recovery.

#### *Light oil refining*

The synthetic oil and offshore condensate are passed through a variety of hydrogenation, platforming and alkylation processes. Vacuum fractionation is also performed on the process streams to produce the required hydrocarbon fractions for blending into petrol, diesel and kerosene.

### **3. OIL RE-REFINING INDUSTRY**

#### **3.1 Fractionation based re-refining**

This process is schematically depicted in Figure 2.3.

##### **3.1.1 Background**

The oil that is re-refined is used lubrication oils collected through the ROSE foundation. This used oil is transported to the site by bulk tanker trucks.

Main products from the re-refining of the used oil are Base oils, Spindle oils and a diesel fuel. Base oil and Spindle oil are blended with additives in a blending plant to produce a range of lubricating products. The diesel fuel is sold directly for use as an energy source.

##### **3.1.2 Used Oil Processing**

The used oil delivered for processing has a high moisture content and this water has to be removed before the subsequent processing. On receipt the waste oils are stored in large used oil receiving tanks. In these tanks the free water phase separates from the oil and is drained from the bottom of these tanks.

The oil fraction is fed into a dehydration unit that operates at 130°C. This unit is heated by a synthetic oil circuit which is recirculated in a closed circuit. By heating the used oil the remaining water is driven off in the vapour phase. Any lighter fractions in the used oil are also driven off and these are separated from the water in a separation vessel. The light ends recovered are used as fuel for heating purposes on the plant.



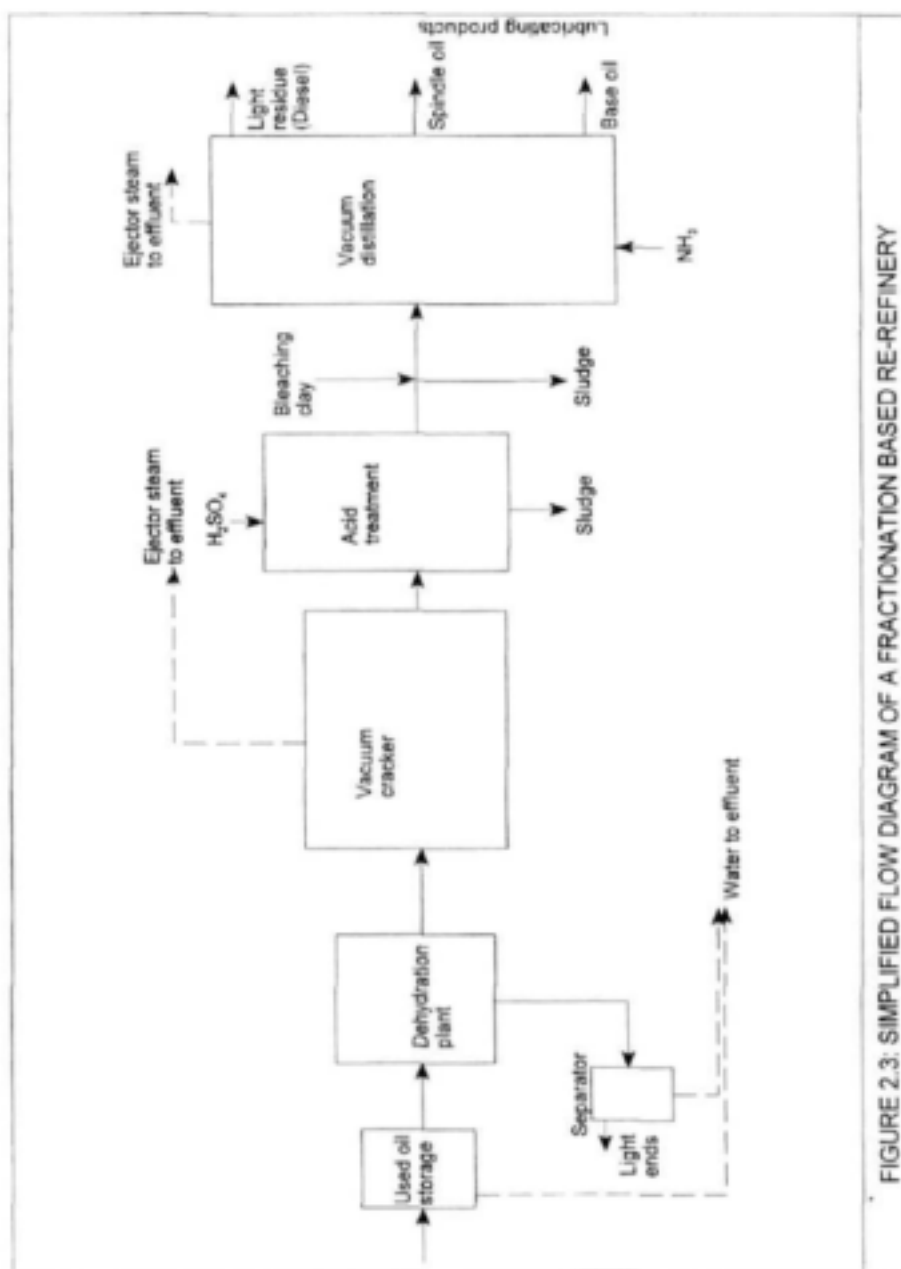


FIGURE 2.3: SIMPLIFIED FLOW DIAGRAM OF A FRACTIONATION BASED RE-REFINERY

After all the water is removed from the used oil, it is then processed further in the refining section of the plant.

The first stage is a vacuum cracker, which operates at 300°C under a vacuum. This unit is used to break down any of the additives that may have been added to the oil.

Following the cracker unit are the acid treatment and bleaching system. Concentrated sulphuric acid is added to the used oil stream and the mixture is allowed to settle for six hours. After the acid treatment, bleaching clay is added to the oil and this is then removed from the oil by means of a filter press, prior to the oil being processed in the distillation unit.

The distillation unit is operated under vacuum. The processed oil is fractionated into three fractions. The heaviest fraction is the base oil fraction which is used for engine oils. The middle fraction is the spindle oil fraction which is used as hydraulic oils. The lightest fraction is a diesel fraction and this is sold as a heating source. Ammonia is added into the distillation column to neutralise acidity in the light fraction.

### 3.2 Physical separation based re-refining

This process is shown schematically in Figure 2.4.

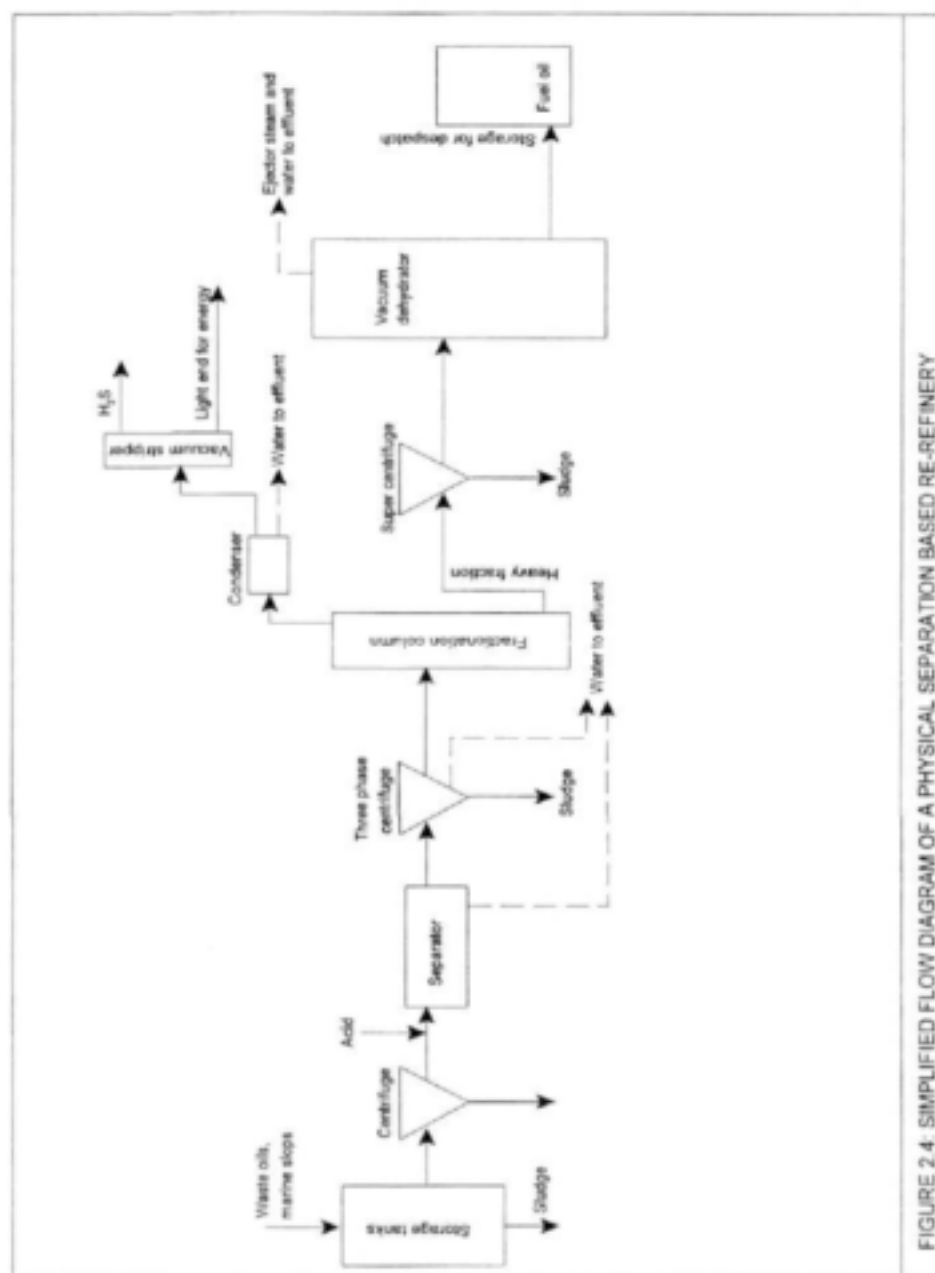


FIGURE 2.4: SIMPLIFIED FLOW DIAGRAM OF A PHYSICAL SEPARATION BASED RE-REFINERY

### **3.2.1 Background**

The oils that are re-refined are primarily marine slops collected during bunkering operations when ships call into port. South Africa is a signatory to the Marpol agreement, which makes provision for ships to discharge their marine slops when calling on South African ports. This contaminated fuel oil is transported to the re-refinery by bulk tanker trucks.

Another source of feedstock is used lubricating oils from garages and large organisations and also out of specification oil products from blending plants.

The main product from the re-refining of the marine slops and used oil is a furnace fuel. This fuel is suitable for use in direct fired kilns. As the fuel is processed from a waste product, it does not have the same specifications as heavy fuel oil obtained from crude oil refining.

### **3.2.2 Used oil processing**

The oil delivered for processing has a high moisture content and this water has to be removed before the further processing. Besides the moisture present solids can also be contaminating the oil. On receipt, the waste oils are temporarily stored from where it is sampled.

The first stage of the process removes any sludge present in the oil. The settled sludge is removed from the bottom of the storage tanks. The oil is then heated and processed in a rough cut centrifuge, which removes further solid matter from the oil.

After the rough cut centrifuge, the oil is dosed with acid to break any water emulsion in the product. A static separator followed by a three-phase centrifuge removes the water and remaining solid matter present in the oil.

After all the solid contamination has been removed from the waste oil, it is then processed further in the refining section of the plant.

The first stage is a fractionating column, where the light hydrocarbon fraction and remaining water are recovered from the heavier hydrocarbon fraction. The light fraction is condensed and passes through a vacuum stripping column to remove any sulphur present in the oil. The removed  $H_2S$  is flared off. The sweetened product is either used as an energy source on the plant or distributed as a light fuel oil.

Following the fractionating column is the super centrifuge section. This centrifuge operates at forces of 15 000 G and removes further sludge from the oil fraction.

The final stage in the processing is the final drying of the fuel oil in a vacuum dehydrator. From here the fuel oil is stored and then despatched for sale as a fuel oil.

## APPENDIX 3 INTERNATIONAL PERSPECTIVES

The aim of this literature survey was, as far as possible, to determine water usage (volumes and distribution), and also waste water discharge volumes, the pollutant load and waste water treatment methodologies in refineries outside South Africa. As there has been a shift in the last few years to enhanced methods of wastewater and waste management, the literature survey is structured to include an overview of any methodologies which may assist both refiners and re-refiners.

### 1. WATER INTAKE

The Specific Water intake in Texan refineries in the USA is given in Table 3.1 using data from the Texas Water Development Board (TWDB)(1993). The data, collected during 1991/1992, is an average of a number of refineries (indicated in the table).

**Table 3.1. Specific water intake from Texan refineries (adapted from TWDB, 1993)**

Region	Area	Number of refineries included	SWI m <sup>3</sup> /t
Beaumont	Coastal	4	2.69
Houston	Coastal	9	2.55
Corpus Christi	Coastal	7	0.98
All other	Inland	8	1.37

The water intake is higher in Beaumont and Houston as these areas have more abundant and less costly water. Furthermore they produce petrochemical derivatives as part of the operation, whereas the inland refineries concentrated on fuel products only. Further factors contributing to the spread of SWI values included that the refineries in the different regions may have different raw materials, different operational philosophies and equipment limitations, hence different utilities which have different water requirements. The report commented that oil refiners operating large materials-processing installations felt that water usage would be proportional to production, for a given feedstock and technology - rather than a decreased unit consumption of water with an increment in production. After analyses of the data there was no correlation of water usage with plant size i.e. a larger refinery would not necessarily use less water per barrel of crude capacity than a smaller refinery.

From data presented in Lemlin (1981) an Esso refinery in Fawley had, at that time, an SWI of approximately 6 m<sup>3</sup>/t of crude. This is exceptionally high, but is explained by their usage of a once through cooling system.

The more recent data obtained from the TWDB indicates that South African refineries use far less water per ton of crude intake than the Texan refineries.

### 2. WATER USE

The Esso refinery in Fawley, UK, reported a refining capacity of 1 600 000 tons/month in 1981 and at that time was one of the largest and most complex refineries in Europe (Lemlin, 1981). The Fawley refinery used a once-through cooling system. Water consumption was compared to the Milford refinery, which had a capacity of 725000 tons/month and used an air cooled system. Water usage of the Fawley and Milford Haven refineries is given in the Table 3.2 below. No rain water run off has been included as this is highly variable.

**Table 3.2. Comparison of water consumption (Lemlin, 1981).**

Component	Fawley (m <sup>3</sup> /h)	Milford Haven (m <sup>3</sup> /h)
Cooling water	18600 (once-through)	2 (air-cooled)
Process water	2800	100
Ballast water	100	150
<b>Total effluent</b>	<b>21500</b>	<b>252</b>

The above table shows the tremendous difference in water usage between a once through and an air-cooled system. The percentage of cooling water used agrees with Dold (1989) who reported that a major component of water (80 - 90 %) is used as once through cooling water.

Water blowdown discharge volumes are given in a comparative study undertaken by Bloemkolk and van der Schaaf (1996) on design alternatives for the use of cooling water, while taking into account the impact on the environment (Table 3.3). It is evident that substantial water savings can be effected through use of alternative systems.

**Table 3.3. Comparative values for the blowdown volume utilized for 3 different cooling water options**

Option	Cooling water blowdown discharge (m <sup>3</sup> /h)
Once-through cooling	26 000
Cooling tower	156
Air cooled	0

In South Africa no refinery practices a once-through cooling system. In the refineries surveyed there are a number of examples where air-cooling is practised together with other cooling practices.

### **3. WASTE WATER POLLUTANTS**

As far back as 1981 it was recognized that measuring the gross hydrocarbon content and traditional parameters of refinery effluent may not be the correct ones (Lemlin, 1981). It was suggested that research needed to establish a better understanding of the relationship between effluent composition and the acute and chronic effects on receiving waters to determine whether there is a real or perceived need for reduction of specific pollutants. Pollutant levels should be reduced to those which are consistent with the natural assimilative capacity of the receiving waters (e.g. sea, river, lake) which are each different. This still holds true today.

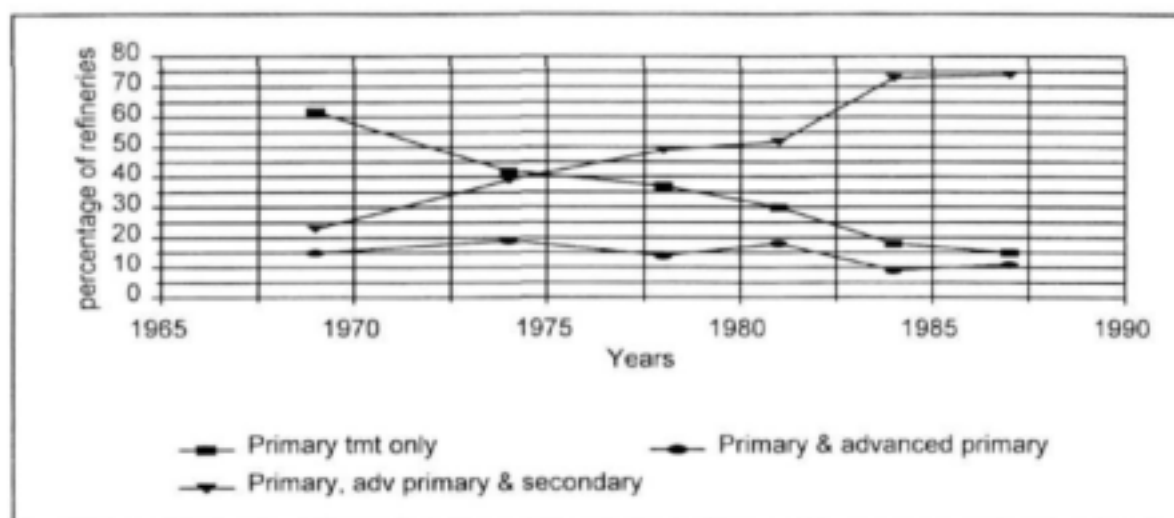
Although the majority of refineries of the USA and Europe have shown huge reductions in oil pollutants in the last 24 years (of 80 % and greater), they generally show higher concentrations of organic matter other than oil, in the effluents (Siljeholm, 1993). Emissions are now characterized by compounds with greater water solubility and a lower vapour pressure. Emissions of highly water soluble (polar) components to the environment from the effluent represent more than half of all the organic components emitted. Many of these are components of water soluble chemicals added in the refinery process. The difference between the COD and oil concentration in the South African industry averages, may be due to soluble organics not individually analysed for.

This may also imply an increase in the discharge of water soluble organic material in future effluents, when components such as methyl-tertiary-butyl-ether (MTBE) and light weight alcohols

are added to petrol. Siljeholm suggests that attention should be given to more accurate and focussed analytical techniques to measure components in the emissions, and to changing inputs of certain water soluble chemicals to the primary waste stream. This implies changing some reactor designs and modifying the operations of specific processes, such as desalters and desulphurization units, as well as instituting more closed loop operations. These changes would all be steps towards the concept of pollution prevention and clean technology, however they would obviously carry with them initial cost implications, which may not be acceptable to the refineries.

#### 4. WASTE WATER TREATMENT

The emphasis from primary (gravity separation) towards advanced primary (flocculation, DAF, filtration), secondary (biological) and tertiary treatment has changed significantly over the last years. This is reflected in Figure 3.1.



**Figure 3.1. Changes in waste water treatment systems in oil refineries in western Europe from 1969 to 1987 (from data in Siljeholm, 1993).**

Refineries situated inland have stricter control measures than those at the coast and have generally shown greater compliance. Siljeholm (1993) stated that in 1984, 17 out of 18 inland Western European refineries had discharge levels of oil lower than 5 ppm, while less than 31 out of 67 coastal refineries had reached this standard.

In 1989, some refineries were already practising tertiary treatment, although Canadian refineries, during this time (Dold, 1989) were using primary and secondary treatment only.

##### 4.1 Primary treatment

Primary treatment is generally seen to be the physical separation of pollutants from the wastewater stream.

A Croatian oil refiner utilizes a dissolved air floatation (DAF) unit which combines flocculation, flotation and multi layer filtration with hydro anthracite and fine sand to produce a high quality effluent (Meier and Nikolic, 1995). Prior to the unit, the oily waste water flowed into the API unit with a concentration of hydrocarbons of  $\geq 1000$  mg/l and emerged with a decreased concentration of 10-60 mg/l. Influent and effluent quality is given in Table 3.4. This effluent is further treated in the DAF unit, which reduces the hydrocarbon concentration to 0.3 - 0.8 mg/l.

**Table 3.4. Influent and effluent quality using API separation and DAF unit (Meier and Nikolic, 1995).**

	Influent API separator	Effluent API separator	Effluent of unit after UV disinfection
Flow m <sup>3</sup> /d	200-250	200-250	200-250
Temperature °C	35	30	28-30
Suspended solids mg/l	10-20	10-20	not measurable
COD mg/l	450	160	100
BOD <sub>5</sub> mg/l	300	80	40
KMnO <sub>4</sub> mg/l	NA	NA	15
Total organic carbon, mg/l	250	45	20
Total dissolved solids, mg/l	450	450	450
Turbidity, NTU	120	40-60	0.3-0.8
Colour, TCU	420	240	40-70
Total hydrocarbons, mg/l	1000 (1-2%)	10-60	0.3-0.8
Total bacteria count / 100 ml	10 <sup>5</sup> - 10 <sup>6</sup>	10 <sup>5</sup> - 10 <sup>6</sup>	10 <sup>2</sup>

This effluent is then recycled. Options for use are for fire protection, the facilities hydrant system or it can be pumped into their underground wells. Although the quality is high enough to be used in the cooling system, the temperature is too high. This system, which has a comparable cost to alternative treatment systems, is used at the refinery due to the limited space requirements of the unit (30 x 15 m) and other manufacturers of DAF equipment would not guarantee less than 5 mg/l of residual oil in the effluent after filtration.

If a comparison is made of the industry average of the South African refineries of effluent quality after API separation with the results above, it is evident that the South African COD average is much higher (384 mg/l compared to 160 mg/l). However, if the oil and grease concentration is compared to the total hydrocarbon concentration given by Meier and Nikolic, it appears that the South African industry average is on the low side of the range given in the table.

Although not yet required in South Africa, many refineries in other countries are required to remove volatile organic compounds (VOCs) from their waste waters. Research done on a pilot scale found that up to 20 % of the VOC concentration is lost by volatilization at an air water ratio of 0.5 in a DAF system. Adsorption by granular activated carbon reduced the VOC concentration in the off-gases by 99 % (Al-Muzaini *et al.*, 1994).

## 4.2 Secondary treatment

In biological treatment the principal mode of pollutant removal is through biological degradation, however, the stripping of volatile materials, biosorption, bioaccumulation and heavy metal precipitation may also occur (Dold, 1989). Biological treatment is accepted as an effective means of removing a substantial portion of the dissolved and suspended organic material in primary treated effluent. Biological treatment, although not commonly used in South Africa to treat refinery waste waters, has been widely adopted in Europe, Israel (Galil and Rebhun, 1992a&b, Rebhun and Galil, 1994) the United States of America and Canada (Dold, 1989). Even as far back as 1981, Lemlin (1981) reports that Europe was using biological treatment, albeit without further tertiary treatment.

Table 3.5 illustrates the comparative composition of the influent of an activated sludge treatment system and the treated effluent. In the table Dold (1989) compares the values as given by Rebhun and Galil (1987, as reported by Dold, 1989) to those found in other literature sources.

**Table 3.5. Concentration of pollutants before and after activated sludge treatment (Dold, 1989).**

Component (mg/l except for pH)	Influent		Effluent	
	R & G*	Literature	R & G*	Literature
pH	8.14	6.2 - 10.6	7.85	6.7 - 7.9
Total suspended solids	98	15 - 85	47	6 - 112
Volatile suspended solids	65		26	
COD - total	625	140 - 3 340	230	80 - 300
COD - soluble	443		165	
BOD - total	268	7 - 230	19	4 - 100
BOD - soluble	143		7	
Hydrocarbons	40	23 - 200	4.8	0.5 - 9.0
Ammonia (as N)	21	0 - 120	13	0 - 43
Chlorides		19 - 1 080		
Sulphides		0 - 38		
* Rebhun and Galil (1987) as reported by Dold, 1989.				

The wide range is indicative of the range of crude oil feedstock, as well as different processing procedures in the refineries. The insoluble portion of the COD (Total - soluble) comprises mainly of the free and emulsified oil not removed in the primary treatment. The soluble COD comprises mainly of phenolics, short-chain carboxylic acids, naphthenic acids and substituted aromatics.

Again it is only possible to compare the above results with that achieved after primary treatment in South African refineries. If the above hydrocarbon concentrations (0.5 - 9 mg/l) are compared to the oil concentrations obtained in South African refinery effluents after primary treatment (average of 11.6 mg/l), it appears that biological sludge treatment is effective for hydrocarbon degradation. However, ammonia concentrations appear to be very similar, average of 13 mg/l after biological treatment compared to a South African industry average of 10.2 mg/l after primary treatment.

Rebhun and Galil (1994) compared three biological treatment modes, viz. activated sludge, rotating biological contactor (RBC) and aerated ponds. Although RBC was indicated to produce a better quality water, the refinery in Haifa (with an effluent volume of approximately 238 000 m<sup>3</sup> /month) opted to use aerated ponds as part of a combined biotreatment process to save costs. This biotreatment consisted of the aerated ponds as a partial primary stage, followed by an existing lime clarification stage to remove solids and then the bio-oxidative capacity of the recirculated cooling system is used to complete the treatment, simultaneously using the clarified effluent as make-up water. The performance of this system is shown in Table 3.6. Figure 3.2 shows the overall performance of the effluent treatment system.



Table 3.6. Performance of Biotreatment System (Rebhun and Galil, 1994).

Component	DAF effluent (mg/l)	Combined Biotreatment (mg/l)		
		Aerated Ponds	Lime Treatment	Water Cooling System
Suspended solids	69	123	49	48
COD Total	486	272	88	80
Soluble	392	118	79	71
Phenols	11	0.1	0.1	<0.1
Ammonia	16	10	8.3	0.9
Oil Total	48	26	3.6	2.8
Soluble	39	4.7	3.3	2.4

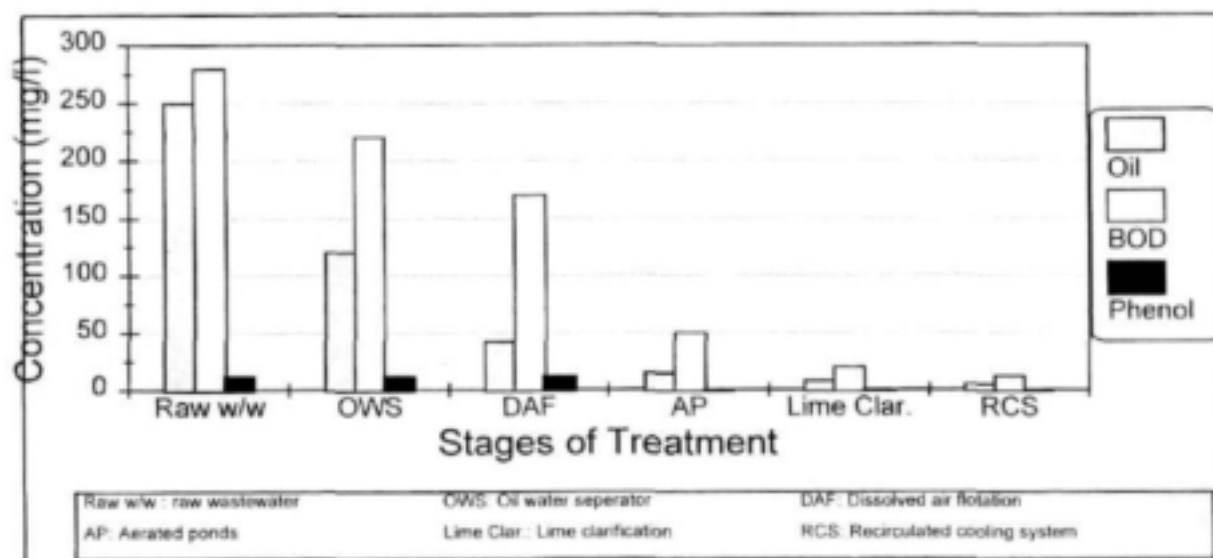


Figure 3.2. Removal of pollutants at various treatment stages at Haifa Refinery, Israel (Rebhun and Galil, 1994).

A refinery in South East Asia uses API separation, followed by DAF, after coagulation and flocculation, and an aerated lagoon system (Chin, 1994). The results are given in Table 3.7. The refinery found these results not up to standard and major upgrading was considered to be needed.

**Table 3.7. Wastewater pollutant concentrations through treatment process (Chin, 1994).**

Process	Parameter	Influent (mg/l)		Effluent (mg/l)	
		Range	Mean	Range	Mean
API	Oil & Grease	12 830 - 840	7220	680 - 104	550
DAF	Oil & Grease	680 - 75	550	228 - 26	145
	COD	2580 - 75	1460	1288 - 731	970
	BOD	695 - 48	549	511 - 24	338
	Sulfide	18 - 6	8	16 - 1.3	2.72
	TKN	42 - 18	22	22 - 3.2	8.21
	TP	11 - 5	7	2 - 0.4	0.96
	Cd	Not determined		0.06 - ND*	0.01
	Cr	Not determined		0.08 - ND	0.03
	Cu	Not determined		0.12 - 0.01	0.08
	Fe	Not determined		8.34 - 1.83	2.81
	Ni	Not determined		1.87 - 1.28	0.93
	Pb	Not determined		0.62 - ND	0.23
Aerated Lagoon (30 day HRT**)	COD		970		177
	BOD		336		19
	Oil & Grease		145		16
	Sulfide		2.72		0.43
ND = not detectable HRT = hydraulic retention time					

The large difference between the COD and BOD in the final effluent is indicative of the large concentration of refractory organics.

The above results show that the effluent quality after DAF treatment (Rebhun and Galil, 1994) appear to be very similar or worse than achieved in South Africa after only API separation. This is corroborated with the results after DAF treatment reported by Chin (1994).

Certain problems have been noted with biological treatment. These include inhibition of biological degradation due to toxic materials, shock loadings after accidental spillages and poor sludge settleability. The operator of the system needs to be aware of these aspects and have an appropriate management plan in place. One aspect of a management plan is to have protective strategies in place for the biological treatment system.

Rebhun and Galil (1994) suggest a system where biological treatment is protected by preliminary wastewater flow regulation, thereby controlling both pollutant and hydraulic loads. Further protection of the biological system is given by improving the quality of the primary treated effluent. This was achieved by treating the effluent of the oil water separation by means of DAF after chemical flocculation.

#### 4.3 Tertiary treatment

Oil refinery waste waters can still contain up to 20 mg/l hydrocarbons and 30 mg/l suspended solids after biological treatment. The new European standards will require less than 5 mg/l hydrocarbons and less than 10 mg/l suspended solids. An effluent free of hydrocarbons and suspended solids was obtained using an ultrafiltration experimental unit as described by Elmaleh and Ghaffor (1996).

Reports of a membrane biological filter have been given by Knoblock *et al.* (1994) and Sutton *et al.* (1994). This system consists of a suspended growth biological reactor combined with a membrane filtration unit. The system met or exceeded performance expectations.

#### **4.4 Sludge treatment**

The Valero Refining Company in Corpus Christi, Texas, USA uses a bioslurry process, comprising of centrifugation, biological slurry treatment and dewatering, such that it can overcome the restrictions on land disposal of oil refinery wastes (Oolman *et al.*, 1996). Despite some operating challenges to overcome foaming problems, the treated residues now meet the Universal Treatment Standards of the Resource Conservation and Recovery Act of the USA.

Further reviews of refinery sludge treatment using a combination of dehydration and solvent extraction treatment (Trowbridge & Holcombe, 1995) and for a heavy-oil-gasification combined cycle power plant (Holopainen, 1993) have been published.

#### **5. WASTE MINIMIZATION**

The waste minimization process, including preventing hydrocarbon loss and decreasing expenses associated with waste disposal, should be seen as increasing operating efficiency, lowering expenses and decreasing liability (Spearman and Zagula, 1992).

This is the view taken by Amoco Oil Company, one of the largest in the USA. In 1989, the Amoco Corporation and the United States Environmental Protection Agency began a voluntary joint project to study pollution prevention opportunities (Schmitt & Podar, 1994).

The essential elements for waste minimization at the Amoco Oil refinery are identified to be (Spearman and Zagula, 1992):

- a corporate environmental policy supportive of waste minimization
- the allocation of dedicated resources and support of senior management
- an organised system for recording waste generation and associated costs
- a means of tracing waste minimization project progress, barriers and successes
- a training programme for operators and personnel and
- participation in trade association efforts in waste minimization

As 1 kg of soil entering the sewer after contact with oil and water results in 3 - 10 kg of listed hazardous sludge, one of the initial projects included the minimization of sewer solids by developing a sewer catch basin and sweeping refinery streets fortnightly. A further project involves chemical reuse and waste reduction, specifically of mono-ethanol amine through better operation of amine contactors, and through better maintenance of sumps and skimmers for recovery purposes.

#### **6. RE-REFINING OF WASTE OIL**

A commercial prototype utilizing a new process (Rhodes, 1994) has recently been tested at full scale at a Gulf Coast refinery. The process uses chemically assisted, thermal flashing to break difficult emulsions and recover the oil for reprocessing. High recoveries ( $\geq 97.9 - 99.5\%$ ) of high purity oils ( $\geq 99\%$ ) were found.

In California, used oil is regulated as a hazardous waste and residues derived from used oil are presumed to be hazardous wastes. The definition of used oil was revised in January 1995, and used oil re-refining distillation bottoms (also known as asphalt flux) recycled into asphalt products were excluded from the definition of used oil, but were not excluded from classification as hazardous waste. The proposed exemption is based on a preliminary investigation which showed that the above-mentioned wastes recycled into asphalt products substitute for virgin asphalt in asphalt production, add desired properties to the paving materials and, in the case

of distillation bottoms, are typically purchased by asphalt producers at the prices near those of non-waste counterparts.

Although US EPA needed more time to complete its study on such recycling operations, it concludes that the incorporation of these materials into asphalt was a legitimate recycling process and not disposal.

A different process to those used in South Africa is used by one company in American. After the waste oil feed is preheated and mixed with propane, the mixture is extracted in a patented process where the water and insolubles in the oil are separated from the propane/base oil mixture. The solvent is recovered and the treated oil is sent to a VDU. The bottoms of the VDU are used as an asphalt modifier. After a clay finishing step, the main product of the process is a base oil (Saunders, 1996).

Despite a drive to the contrary, it appears that there is still resistance to using a re-recycled lubricating oil in the USA on the basis that it may void automobile manufacturers' engine warranties (Internet site 1). There now exists an API certification program for petrol engine motor oils. API's certification program was developed in conjunction with the American Automobile Manufacturers' Association, whose members include Chrysler Corporation, Ford, and General Motors (GM). API's certification program identifies virgin or re-refined motor oils meeting minimum standards established by automobile manufacturers to maintain vehicle performance.

## 7. REFERENCES

- Al-Muzaini, S., Khordagui, H. and M. F. Hamouda, (1994). Removal of VOCs from refinery and petrochemical wastewaters using dissolved air flotation. *Water Science and Technology*, **30** (3), 79 - 90.
- Bloemkolk, J. W. and R J van der Schaaf (1996). Design alternatives for the use of cooling water in the process industry: minimization of environmental impact from cooling systems. *Journal of Cleaner Production*, **4**(1), 21 -27.
- Chin, Kee Kean (1994). Evaluation of treatment efficiency of processes for petroleum refinery wastewater. *Water Science and Technology*, **29** (8), 47 - 50.
- Dold, P.L. (1989). Current practice for treatment of petroleum refinery wastewater and toxics removal. *Water Poll. Res. J. Canada*, **24** (3), 363 -390.
- Elmaleh, S. and N. Ghaffor, (1996). Upgrading oil refinery effluents by cross-flow ultrafiltration. *Water Science and Technology*, **34** (9), 231 -238.
- Galil, N. and M. Rebhun (1992a). Multiple technological barriers combined with recycling of water and oil in wastewater treatment of a coastal petrochemical complex. *Water Science and Technology*, **25** (12), 277 -282.
- Galil, N. and M. Rebhun (1992b). Waste management solutions at an integrated oil refinery based on recycling of water, oil and sludge. *Water Science and Technology*, **25** (3), 101 - 106.
- Holopainen, O. (1993). IGCC Plant employing heavy-petroleum residues. *Bioresource Technology*, **46**, 125 - 128.
- Internet site 1, (1997). Federal Environmental Executive Tackles Tough Issues. <http://www.ornl.gov/ornlp2/fcart.htm>
- Knoblock, M.D., Sutton, P.M., Mishra, P.N., Gupta, K. and A. Janson, (1994). Membrane biological

reactor system for treatment of oily wastewaters. *Water Environment Research*, **66** (2), 133 - 139.

Lemlin, J.S. (1981). The value of ecological monitoring in the management of the petroleum industry effluent discharges: Experience in Esso Petroleum Company in UK Refineries. *Water Science and Technology*, **13**, 437 - 464.

Meier, A.L. and O. Nikolic (1995). Croatian refinery meets waste water treatment standards, reduces fines. *Oil & Gas Journal*, Nov. 27, 70 - 72.

Oolman, T., Baker, R.R., Renfro, N.L. and G.E. Marshall (1996). Refinery uses bioslurry process to treat RCRA wastes. *Hydrocarbon Processing*, April, 71 - 76.

Rebhun, M. and N. Galil (1994). Technological strategies for protecting and improving the biological treatment of wastewater from a petrochemical complex. *Water Science and Technology*, **29** (9), 133 - 141.

Rhodes, A. (1994). New process effectively recovers oil from refinery waste streams. *Oil & Gas Journal*, Aug 15, 92 - 94.

Saunders, J. (1996). Used oil refining revolution? *Lubricants World*, September 1996.

Schmitt, R.E. and M. K. Podar, (1994). Pollution prevention planning in refineries: setting priorities based on risk. *Waste Management*, **14** (3-4), 289 - 298.

Siljeholm, J. (1993). An assessment of water pollution from refineries in the USA and western Europe. *Hazardous Waste & Hazardous Materials*, **10** (3), 365 -376.

Spearman, M.K. and S. J. Zagula (1992). The development of a waste minimization program at Amoco Oil Company. *Water Science and Technology*, **25** (3), 107 - 116.

Sutton, P.M., Mishra, P.N. and P. M. Crawford, (1994). Combining biological and physical processes for complete treatment of oily wastewaters. *International Biodeterioration & Biodegradation*, **33**, 3 - 21.

Texas Water Development Board (1993). **Industrial Water Use Efficiency Study**. Published by Pequod Associates, Inc., California, USA.

Trowbridge, T.D. and T.C. Holcombe, (1995). Refinery sludge treatment/hazardous waste minimization via dehydration and solvent extraction. *Journal of the Air & Waste Management Association*, **45**, 782 -788.



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