Chapter 14

Oil Refining

14.1 Introduction

The oil refining industry is the cornerstone of a modern economy. All countries are subject to the vagaries of global oil prices, which have significant influence on local economies. Current global oil refining capacity is in excess of 11 million metric tons per day (82.5 million barrels/day) [1]. Figure 14.1 shows the world's refining capacity, as well as other major refining processes by continent. Nearly 90% of this is located in non-OPEC (Organisation of Petroleum Exporting Countries) countries [2]. The United States is the world's largest oil refiner with 149 of the world's 691 refineries and a crude oil refining capacity of about 2.3 million metric tons/day (16.9 million barrels/day) followed by Russia's – 0.73 million metric tons/day (5.4 million barrels/day), Japan – 0.65 million metric tons/day (4.7 million barrels/day) and China – 0.62 million metric tons/day (4.6 million barrels/day) [2].

There are major challenges facing the refining industry in the 21st century. The industry is unique in that both the processes used to refine petroleum as well as the products generated, are subject to government regulation. Some of these challenges are:

- Addressing the long term decline of easily accessible resources
- Demand for more energy
- Decrease in crude quality (heavier, higher sulphur and metal concentrations more prevalent)
- Climate change and pressure from government and environmental groups to reduce CO_2 emissions and Nitrogen oxides
- Meet new emission standards for diesel and gasoline
- Low refinery margins (until recently) and over capacity
- Competition from newly developing countries (China and India)

The positive aspect of these challenges has been to shut inefficient refineries, grow through consolidation or acquisition of more efficient refineries and invest in new environmentally benign processes. The downside is that some of these processes use more water.

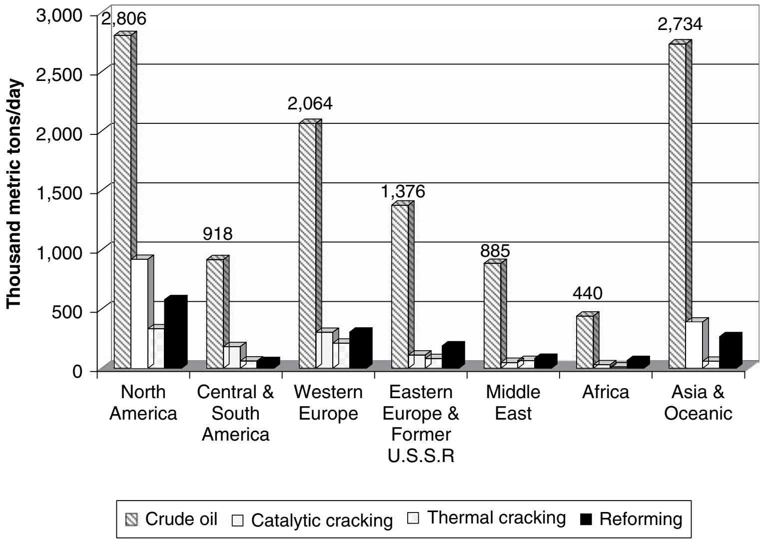

Figure 14.1 World refining capacity in 2004 [1]

(1 Metric ton of crude oil = 7.33 barrels)
Adapted from Energy Information Administration.

For example, in the U.S. between 1981 and 2003, from just over 300 refineries only 149 are now operating [1–3]. In Europe, between 1991 to 2000 only two refineries have been built. While the number of refineries declined, the overall crude processing capacity has increased by between 1 and 2%, due to existing refineries modifying their processes. Figure 14.2 shows the distribution of refineries by continent [1].

The energy industry is dominated by a few large integrated oil companies able to withstand the political and cyclical nature of the business. ExxonMobil is the largest and revenue for the year 2006 was reported at

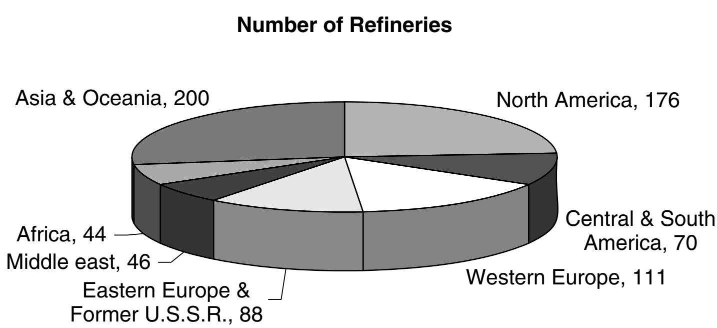

Figure 14.2 Distribution of refineries by continent (2004)

Adapted from Energy Information Administration.

US$ 39 billion which is greater than the combined economies of most developing countries. Other oil majors are Royal Dutch Shell, BP, Chevron and Total.

14.2 Oil Refining Processes

Crude oil is essentially a mixture of hydrocarbons – aliphatic and aromatic hydrocarbons. It also contains many impurities, such as organic sulphur, nitrogen, heavy metals, salt and sediment. Crude oil therefore needs to be washed to remove the salt and sediment and then separated into their fractions in the crude distillation tower. The products are liquefied petroleum gas (essentially propane gas and butane), naptha (which is then processed into gasoline), kerosene/aviation turbine fuel, diesel oil and residual fuel oil. These products are further processed in thermal and catalytic cracking units (alkylation and reforming processes) to produce higher quality and stable products. The degree of refining complexity will dictate how many of the secondary processes are present. The simplest refineries (topping refineries) use distillation to separate gasoline or lube oil fractions from crude, leaving further refining of their residuum to other refineries or for use in asphalt. More sophisticated refineries will have thermal and/or catalytic cracking capabilities, allowing them to extract a greater fraction of gasoline blending stocks from their crude. The largest refineries are often integrated with chemical plants, and utilise the full range of catalytic cracking, hydroprocessing, alkylation and thermal processes to optimise crude utilisation. These processes are discussed briefly below.

14.2.1 Desalting, Crude Distillation and Vacuum Distillation

The first step in refining is to rid the crude oil of salt and sediment. This is done in a desalter. Next step is to separate the hydrocarbon fractions according to their boiling points. This is done by preheating the desalted crude and then separating them first in the atmospheric distillation unit. This separates the light fractions such as propane and gasoline from the heavier fractions such as heavy gas oil and heavy crude residue. The vacuum distillation unit takes the heavy crude residue and then distils them again under vacuum to prevent the decomposition of heavier hydrocarbons. The gas oil is sent to the cracker. The heavy distillates are converted to lubricating oils and asphalt.

14.2.2 Thermal and Catalytic Cracking

Some of the fractions from the crude distillation unit undergo further processing in thermal and catalytic cracking units where larger hydrocarbon molecules from the middle distillate and gas oil are broken into smaller molecules either thermally or catalytically. Catalytic cracking is one of the most widely used refining processes. It produces large amounts of sour water which contains BOD, ammonia, phenols, cyanides and sulphides. Hydrocracking (Isomax) is cracking in the presence of hydrogen. The end products are jet fuel and gasoline.

14.2.3 Hydrotreating

Sulphur, heavy metals, oxygen, halogens and nitrogen are impurities found in crude oil. These need to be removed because they poison or deactivate catalysts as well as cause emission problems. Hydrotreating converts unsaturated hydrocarbons (such as ethylene) into saturated hydrocarbons (such as ethane). Hydrogenation converts organic sulphur into hydrogen sulphide and is then recovered as elemental sulphur. Nitrogen is converted into ammonia and can be recovered as fertilizer feed.

14.2.4 Reforming

Crude distillation unit fractions have very low octane rating. The reforming process boosts the octane rating of hydrocarbons by rearranging the molecules. In the reformer, the same number of carbon atoms is kept but the process rearranges them into a different molecule. For example, cyclic hydrocarbon is reformed into aromatic hydrocarbons which have a higher octane rating. The reforming process uses catalysts such as Rhenium and Platinum and generates hydrogen gas.

14.2.5 Alkylation and Polymerisation

Smaller hydrocarbon molecules are combined into larger high octane gasoline feedstock. Catalysts are hydrofluoric and sulphuric acid.

14.2.6 Coking

Coking is a process that produces useful forms of coke from heavy residue products that are generated from other refining processes, such as vacuum distillation. The different coking processes include delayed coking, fluid coking and Flexicoking (a proprietary process developed by Exxon Research and Engineering).

14.2.7 Blending

This is the last phase where various feedstock are blended to achieve the desired end product characteristics.

Other processes are Lube oil production and asphalting.

A flow chart of a complex refinery is shown in Figure 14.3.

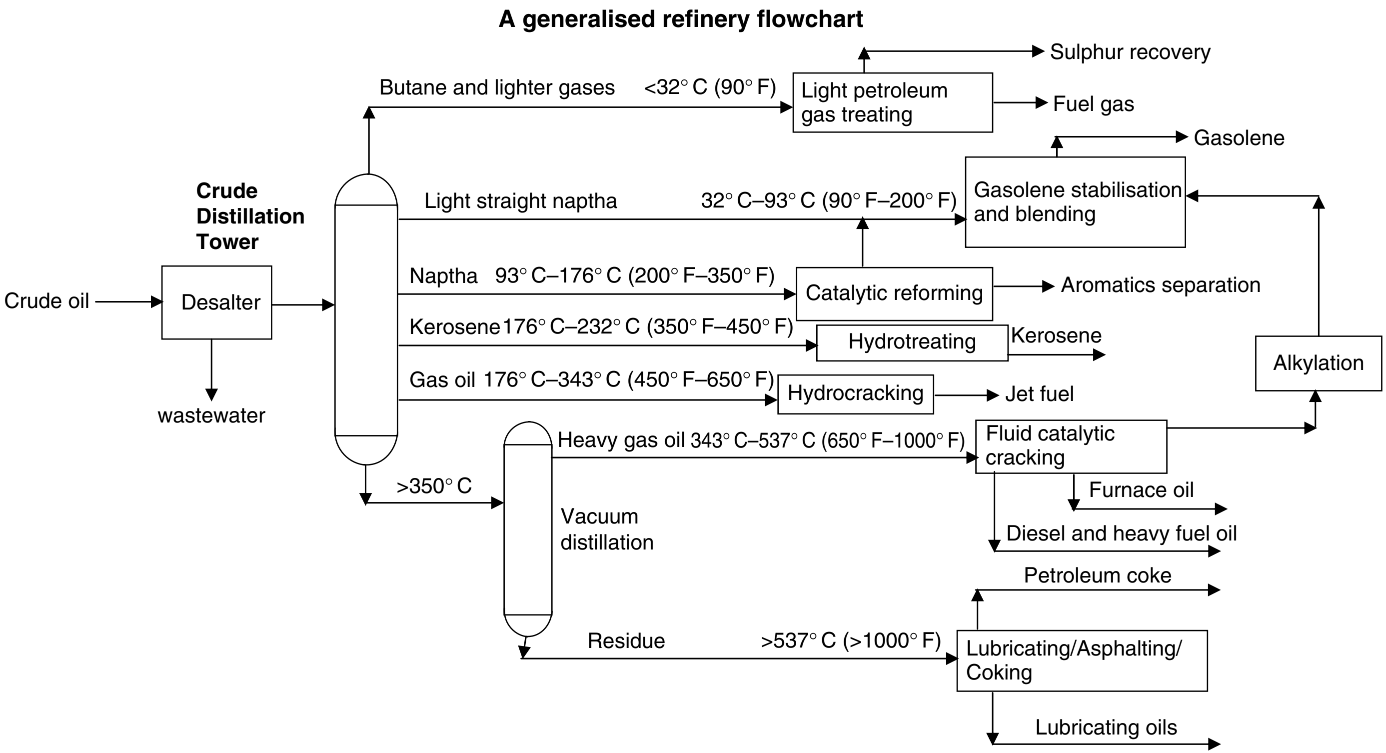

Figure 14.3 Flowchart of a complex refinery

14.3 Water Usage

The main purpose of water use in refineries is to transfer heat. Boiler feed-water makeup and cooling water account for 40–45% of water usage in refineries [4]. Other uses of water are as desalter wash water, quench water, drinking, sanitary and fire water. A hypothetical refinery's water balance is shown in Figure 14.4.

European Union benchmarks for total water usage is given as 0.1–4.5 m^3/ton of crude oil (3.6–162 US gal./barrel) and freshwater usage is given as 0.01–0.62 m^3/ton of crude oil (0.36–22.3 US gal./barrel)[5]. In the US oil refining industry the water usage ratios quoted by one source is 1.8–2.5 m^3/ton of crude oil (65–90 US gal./barrel)[4].

How much water is used in the oil refining industry?

From a water usage point of view, if roughly 2 m^3 of water is used to process one ton of oil and 0.3 m^3 of wastewater per ton of crude is generated then this equates to 25.8 million m^3 (3.5 billion U.S.gallons) of water is used each day by the whole refining industry to process crude oil and in the process generates 3.5 million m^3 of wastewater.

14.3.1 Cooling Water Systems

Evaporative losses account for the bulk of water and energy losses in oil refineries. Cooling water systems play a very important role in rejecting heat from process streams. A cooling water system may consist of once-through (sea water), tempered closed loop cooling and open recirculating systems. In oil refineries air fin coolers are used upstream of water cooled heat exchangers since the process temperatures are higher than atmospheric dry bulb temperatures. Cooling water normally does not come into direct contact with process fluids and therefore is relatively clean. However heat exchanger leaks can dump oil to the cooling water system resulting in increased blowdown and generation of wastewater. Given the large cooling water requirements, it is a natural target for substitution of potable water. Chapters 5 and 6 provides more details on cooling water systems.

14.3.2 Steam Systems

The primary source of steam in the oil refining industry is utility boilers and heat recovery steam generators (waste heat boilers) and lately cogeneration plants. Around one-third of the steam is generated from waste heat boilers.

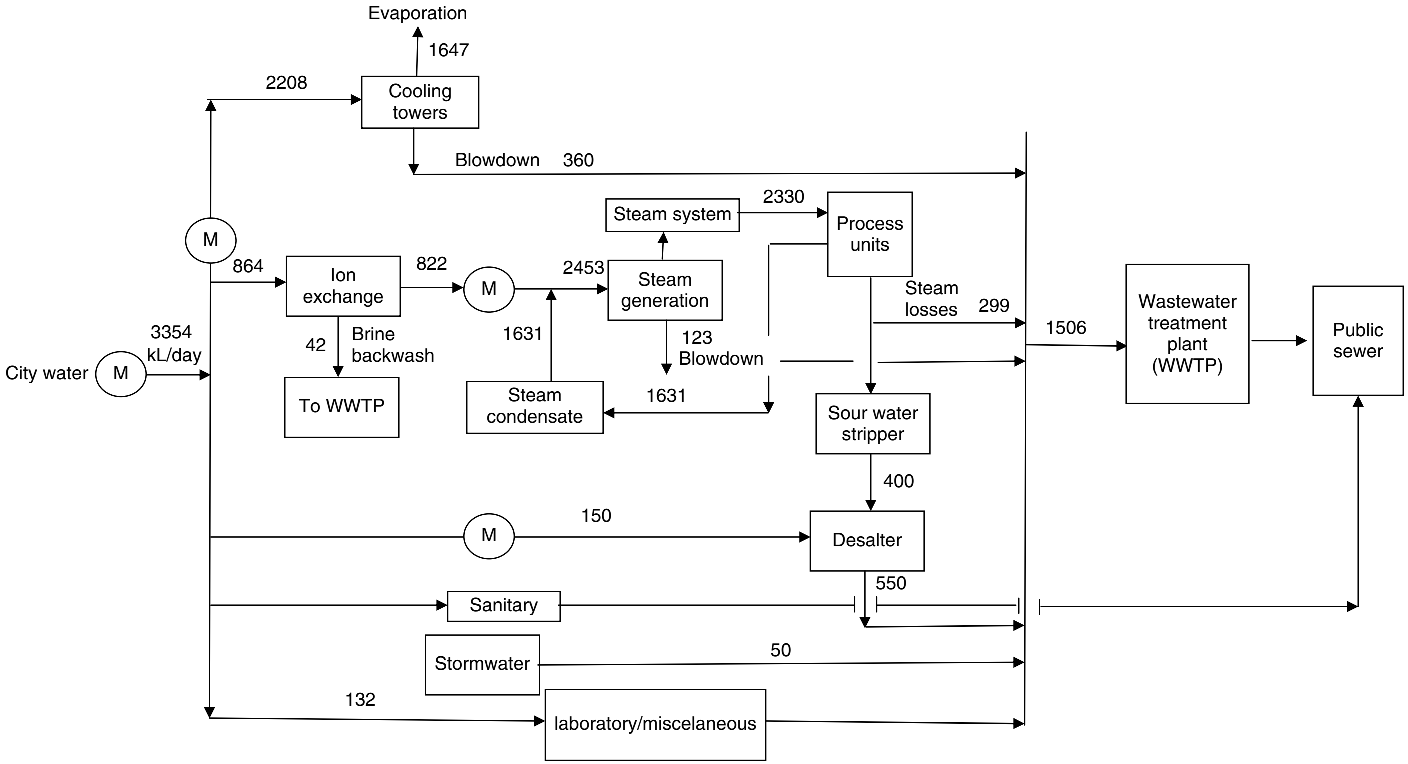

Figure 14.4 A water balance of a hypothetical refinery

The bulk of the steam is used in processes such as

- atmospheric distillation
- vacuum distillation
- catalytic hydrotreating
- reforming
- alkylation
- driving steam turbines.

In the process, large amounts of steam condensate is generated. Steam pressures are generally around 4020 kPa (600 psi) or less. In the US refining industry, 62% of industry's total capacity is less than 2027 kPa (300 psi) pressure [6].

Out of a refinery's total steam use about 40–60% is used directly in the refining process and therefore not available as returned condensate. Steam condensate recovery varies from 30% in older refineries to 70% in well maintained and in newer refineries. Water is lost through

- steam and condensate leakage
- dumping of oil-contaminated steam condensate
- non-recovery of condensate from tank farm areas due to low flows and long distances
- poor steam trap maintenance
- poor blowdown control
- venting to remove non-condensable gases from steam systems.

A total energy balance using energy pinch analysis is one way of identifying and rationalising energy and steam demands. Known as *Pinch Analysis* these are now used by oil refineries to optimise water and energy demands. Steam systems are covered in Chapter 7.

14.3.3 Wastewater Systems

As mentioned earlier wastewater generated per ton of crude ranges from 0.01 to 0.62 m^3/ton of crude (0.36–22.3 U.S. gal /barrel). Wastewater is generated from a number of process units. The process units that contribute the most wastewater are crude distillation, fluid catalytic cracking and catalytic reforming. A well designed and operated refinery could generate only 0.4 m^3/ton [7].

Refineries produce four types of wastewater. These are:

- Process water (desalter wash water, sour water)
- Surface water runoff (storm water)
- Cooling water, boiler water blowdown and pretreatment of ion exchange units
- Sanitary wastewater

A typical breakdown of wastewater sources is given in Table 14.1. Table 14.2 shows the contaminants in refinery wastewater.

The wastewater is treated in API gravity separation, dissolved air flotation units, biological treatment and clarification before discharged to the public sewers, to other receiving waters or preferably reused. Figure 14.5 shows a schematic of a typical wastewater treatment layout.

14.3.4 Energy Usage

The petroleum industry is a very large energy user. Energy usage is a function of type of crude processed, the complexity of the refinery as well as

Table 14.1 Refinery wastewater sources

Source	% of Total effluent
Cooling tower blowdown	20–35
Lost condensate	15–30
Desalter water	12–20
Excess sour water	10–20
Contaminated rain water	6–8
Boiler blowdown	4–8
Pretreatment	2–5

Table 14.2 Typical refinery wastewater quality and effluent limits

Water pollutant	Wastewater after pretreatment [4, 5]	Effluent limits maximum value [5]
pH	7–10	6–9
Biochemical oxygen demand (BOD)	150–400	30
Chemical oxygen demand (COD)	300–700	150
Total Suspended Solids (TSS)	2–80	30
Phenol	20–200	0.5
Oil	100–300*	
	5000**	10
Sulphide	5–15	1
Total Nitrogen	25–50	10
Benzene	1–100	0.05
Benzo (a) pyrene	<1–100	0.05
Total Chromium	0.1–100	0.5
Lead	0.2–10	0.1

All Units expressed as mg/L except pH.
* in desalter water
** in tank bottoms

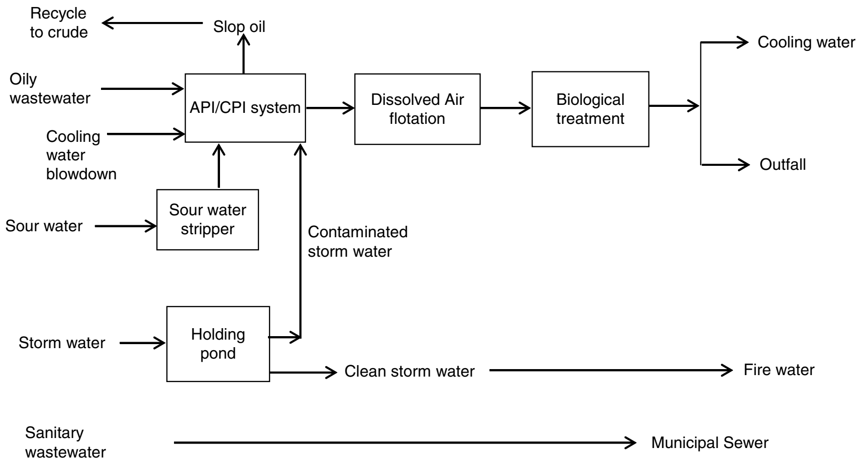

Figure 14.5 Refinery wastewater treatment flow schematic

other factors such as capacity utilisation, age of the refinery and operation and maintenance practices. The largest energy users in a refinery are the crude distillation unit, hydrotreater, reforming and vacuum distillation processes.

A refinery can purchase electricity or produce on site from cogeneration plants. Fuels used are usually by-products of the refining processes such as refinery gas and coke. Natural gas is purchased.

Given that utilities such as steam and cooling water systems play a major role in the refining processes, water conservation and reuse is closely linked to reducing utility costs.

Total energy consumption benchmark can vary from 470 to 1500 kWh per ton of crude oil [5].

14.4 Water Conservation Opportunities

Water conservation opportunities in oil refineries are not dissimilar to other manufacturing plants. In assessing the reuse options it would be helpful to be mindful of water-quality criteria and develop a matrix as shown in Table 14.3

Some options for water conservation are given below:

- substitute sewage treatment plant effluent as cooling water make-up
- reuse stripped sour water as desalter washwater
- investigate reuse of process water as cooling water make-up
- investigate recycle water as cooling tower make-up
- install cooling tower automatic blowdown control system
- improve recovery of steam condensate
- minimise boiler blowdown

Table 14.3 Water-quality matrix

Effluent Source	Type of pollutant and degree of contamination			
	High TDS	Low TDS	TSS	Oil
Cooling water				
Controlled blowdown		X	X	
Other uses and losses		X	X	X
Utilities effluents				
Softener/DI plant	X			
Boiler blowdown		X		
Condensate				
Stripped sour condensate		X		X
Other process condensate		X		X
Other non-process condensate		X		
Process water				
Desalter water	X			X
Other process water		X	X	X
Sanitary wastewater after treatment		X		
Ballast water				
Salt water	X		X	X
Storm water				
Process area		X	X	X
Other areas		X	X	X

- install boiler blowdown control systems
- use boiler blowdown as cooling water make-up
- retrofit amenities blocks
- establish leak detection and repair programme
- prevent solids and oily waste from entering the drainage system
- institute dry sweeping instead of washdown to reduce wastewater volumes.

Case Study: BP Refinery, Kwinana, Western Australia – Water Efficiency Initiatives

Openeed in 1955 BP Refinery Kwinana is Australia's largest oil refinery processing 19 100 metric tons (140 000 barrels/day) of crude oil. In 1997 it initiated a water reuse and minimisation programme with three main objectives:

- to minimise water use
- to maximise water reuse in refinery processes, either after or before treatment;
- to use low quality water (bore water) in place of potable water where practical.

The approach adopted involved four main steps:

Step 1 – Carry out a detailed analysis of the costs of wastewater treatment at the wastewater treatment plant.

Step 2 – Develop a detailed water balance.

Step 3 – Set targets for potable water usage, bore water usage, total water usage, flow to the wastewater treatment plant, water efficiency and percentage of condensate returned to the Refinery systems.

Step 4 – Examine all areas in the Refinery to determine where low quality water could be substituted for high quality water, and identifying areas where process usage could be reduced and returns increased.

An innovative aspect of the programme was approaching water management with a whole refinery perspective. All areas were targeted in order to save as much water as possible. All employees were encouraged to discuss and put forward ideas on water conservation, recycling or reuse. Monthly meetings were held within the refinery to discuss water minimisation. The initiatives are shown in Table 14.4.

14.4.1 Reduction in water consumption

The water reuse and minimisation programme results are given in Table 14.5.

Table 14.4 BP Refinery Kwinana water minimisation initiatives

Initiative	Water saving
Recyle process water in residue cracker unit	200–300 m^3/day.
Steam system – steam trap maintenance program	Improve condesate recovery through reducing leaks in steam condensate system.
Alky cooling tower make up	Replace with process water
In crease process water return	50% increase in process water return
Modifications to operating procedures	Reduce process water use.
Fire water system	Improved maintenace practices
Lube oil refinery	Increased condensate recovery
Reduce hydrocarbon spillage	Reduced process water usage
Stripped sour water	Reuse stripped sour water in desalters

Table 14.5 Water reuse and minisation programme results

Metric	Baseline year		% reduction
	1996	2003	
Total water use m^3/day	7250	4686	35%
Scheme water use (potable water use) m^3/day	6152	2006	67%
Wastewater flow, m^3/day	5258	3386	36%
Condnesate return	32%	49.9%	17.9%

Adapted from Department of Environment and Heritage Canberra – *BP Refinery Kwinana – Cleaner production Initiative* and BP Refinery Water use and minimisation, Kwinana, Western Australia, 2003

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