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Chapter (I)

Introduction to the Design Project

1.1 Introduction

The engineering design of Crude Oil Refinery to process 300000 bbl per day of Brent Crude Oil into a range of valuable petroleum products. The process plant design included separation processes, conversion processes such as catalytic processes, and gas processing units. Service plant was included in the design for onsite utilities supply for different process unit in the oil refinery as well as tank farms for crude oil storage and final products storage before delivery to end user. The refinery was designed to minimise waste production and environmental impact as well as a safe operation and emergency plans for failure of any operation. The plant was designed to operate on-line for 320 days a year.

1.1.1 Safety and Environmental Impact

Safety is an important aspect of the design of the oil refinery plant. Safety measures are discussed for every process in oil refinery plant and emergency processes were designed such as flare stack system for gas emissions in case of an emergency. The plant was designed with minimum environmental impact by selecting the right processes for the purpose and recycling and reusing intermediate products from different processes as well as further treatments to products that may have an impact on the environment.

1.1.2 Objective

The objective of the project was to design a crude oil refinery to transform crude oil into valuable products through conversion and separation processes.

1.2 Site Location

A current Brown Field Site was selected, as planning permission for a Green Field Site would not be given.

With this in mind the sites to be considered were:

- Grangemouth
- Firth of Forth
- Milford Haven
- Chester
- Stanlow
- Preston Island (Forth Estuary)
- Thames Estuary
- Humber Estuary

1.2.1 Feedstock Delivery

Crude oil feedstock has to be delivered to the refinery in Crude Carriers shown in figure 1.1. The largest of which can carry over 400,000 dead weight tonnage (DWT) of crude oil. In this case it is assumed that these large carriers or Ultra Large Crude Carriers will deliver the crude oil in as direct a manner as possible. This is a problem as these ships have average dimensions of:

Length (m)	Draft (m)	Beam (m)
415	35	63

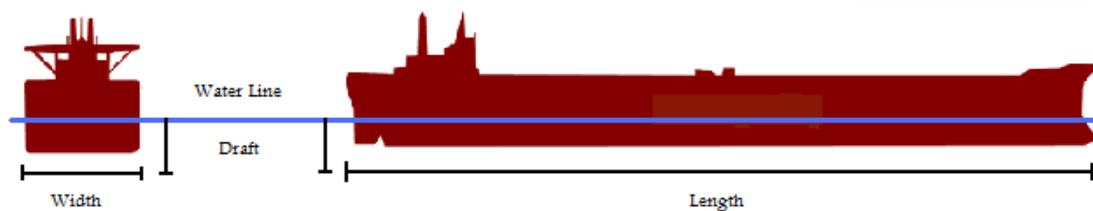


Figure 1.1: Crude Carriers.

Due to the size of these ships a coastal site or large estuary site was needed. This limits the sites that can be chosen for a refinery site for direct crude delivery. Other methods can be used but the cost and benefits had to be assessed. Offshore unloading points could be used but the cost is substantial. It is often more useful to dredge

riverbeds periodically to ensure that tankers can access estuary refineries. This removes some of the sites from above, as they are only accessible by coastal tankers, which are much smaller than the large or ultra large crude carriers.

1.2.2 Site Size

The recently decommissioned Shell Haven site on the Thames Estuary was approximately 0.5km² and was capable of processing 250,000 bbl of crude oil per day. Therefore the proposed site needs to be big enough to accommodate a refinery capable of processing another 50,000 bbl per day and any other units needed for further product processing. The Shell Haven site was ideal, however it has already been set for another project. In the same area of the Thames is another site which was suitable for a slightly larger site that will take advantage of the development taking place at the Shell Haven site. The shell haven site was approximately 4km². Therefore the new site of over 5km² would be suitable for the refinery, storage and downstream processing units.

1.2.3 Thames Estuary

Using these initial parameters it has been decided that a Thames Estuary site would be most suitable. A site on the Thames estuary has been chosen for the proposed Crude Oil Refinery. Figure 1.2 shows the Thames estuary and the surrounding area. The area indicated by the red outline includes the site of the recently decommissioned Shell Haven site. It is clear from figure 1.3 that road access to take products out by road is good, and the M25 motorway is only 10 miles away. Products can leave easily by sea due to the new London Gateway deepwater port. Unfortunately the site is in close proximity to the town of East Tilbury, however the site should be of sufficient size to avoid any construction too close to the town. The area directly around the town could be left clear apart from pipes to a storage area in the lower part of the available site south east of the town. This leaves the larger part of the available site north east of the town for the major site construction. London Gateway is a new port under construction by DP world at the shell haven site. This deepwater port will be big enough to accommodate crude carriers capable of carrying the 400,000 DWT (Dead weight tonnage) of crude oil as set out in the design brief. The site has been chosen

partly because of this development. Although shipping traffic will increase in the Thames estuary it would be advantageous to be near this port as it could be used as a delivery point even if the crude has to be pumped from the new port to storage on the refinery site. If this is not possible then

at least access for the crude tankers is available to within 2km of the new site, and the river would only have to be dredged a relatively short distance to allow tanker access right up to the new site for direct delivery. DP world are encouraging link services between sites on the Thames. Temp figure 1.4 shows the proposed site, the London Gateway and the proposed rail link to the port which runs across the top of the proposed site. A conceptual image of London gateway port is shown in figure 1.5.

1.2.4 Site Maps



Figure 1.2: Sit Map I



Figure 1.3: Site Map II



Figure 1.4: Sit Map III



Figure 1.5: Site Map IV

1.3 Crude Oil

Crude oil has many types depending on the American Petroleum Institute gravity (API gravity) the most common types are shown in table 1.1 Brent Blend, West Texas Intermediate (WTI) and Russian Export Blend are the most common ones used in the industry. Each type of crude oil produce different products yields. Brent Blend was chosen as the crude oil which was the feed to the oil refinery because Brent Blend contains 0.37% sulphur, classifying it as sweet crude oil, and an API gravity of 38. Brent Blend is ideal for producing gasoline, fuel oil and middle distillate. Brent Blend crude oil properties are shown in table 1.2 and the yields for the possible products are shown in table 1.3. Brent Blend is extracted in the North Sea.

Table 1.1: Types of Crude oil.

Types of Crude Oil	API Gravity	Sulphur content (%)
Brent Blend	38	0.4
Russian Export Blend	32	1.2
West Texas Intermediate	40	0.3

Table 1.2: Brent Blend Crude Oil Properties.

Property	Measured
API gravity	38
Gravity SG	0.8333
Sulphur (wt%)	0.37
Acid Number (mg KOH/g)	0.07
Pour Point (⁰ C)	7
Viscosity (cSt) at 40 ⁰ C	3.87
Viscosity (cSt) at 50 ⁰ C	3.25

Table 1.3: Brent Blend Possible products yields.

Possible Product	Yield (% per bbl)
Petroleum gases	6.7
Gasoline/naphtha	45
Middle distillate	33.9
Fuel oil	13.4

1.4 Site Services

Most of the required Site Services are generated on the Crude Oil Refinery Site. For example, the Boiler Feed Water is used to generate steam on-site. The steam was then supplied as Dry saturated steam at the specified quality. The site location permits an abundant source of water nearby to produce steam and used as Cooling Water and Process Water. Furthermore, to produce Demineralized Water it was required that it was physically processed to remove impurities through deionization. One important aspect when operating the Oil Refinery is to supply Electrical Power to the Site. The steam generated on-site was used to generate Electrical Power to the Oil Refinery, and there was also the option of selling surplus Electrical Power to a National Grid. Other services such as Compressed Air and Vacuum Services were generated from the Electrical Power produced. Some Site Services had to be purchased – Oxygen Free Nitrogen (OFN) for instance had to be purchased off-site from another distributor. On the other hand, Carbon Dioxide was obtained from the combustion of the hydrocarbon fuel in the Steam Boiler. Note that it was important to have a Flare Stack System to vent emissions of Hydrocarbons, Vapours and Gases to atmosphere.

1.4.1 Steam and Electricity

The main services needed to operate the plant are steam and electricity, which were done using Cogeneration – the use of a heat engine to simultaneously generate both electricity and steam. Steam from the boiler is first fed to the steam turbine, generating electrical power, and then the same steam is fed to the process plant at a required pressure. The figure below shows the steam turbine cogeneration scheme used on site:

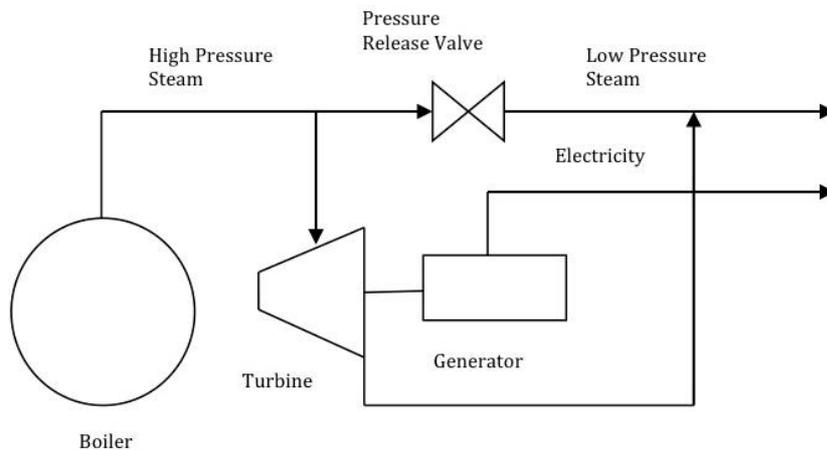


Figure 1.6: Steam Turbine Cogeneration Scheme

Most thermal power plants and heat engines do not convert all of their thermal energy into electrical energy. More than half of the energy is lost to the atmosphere in the form of heat, and hence increases electrical costs to operate plant and has a negative effect on the environment by contributing to global warming. It is therefore, one of the most cost efficient methods to of reducing carbon emissions. By capturing excess heat, cogeneration uses heat that would be wasted in a conventional power plant, potentially reaching an efficiency of 89%, compared with 55% of most conventional plants. Meaning less fuel is consumed to produce the same amount of useful energy on site. The cost of generating power using cogeneration is very cheap since the steam is used twice, first to generate power and then to meet the thermal demand of the process plant.

1.4.2 Boiler

A boiler is a closed vessel where water is heated. Upon heating, steam exits the boiler to be used in the steam turbine to generate electricity and to be used in other processes on site. The source of heat for a boiler is combustion of fuels such as natural gas.

The boiler used in the refinery was a water-tube boiler. Water-tube boilers differ from shell type boilers in that the water is circulated inside the tubes, with the heat source surrounding them. Tube diameter is much smaller than other boilers, which allow much higher pressures. It can produce a high steam output of up to 500 kg/s; a high

pressure steam up to 160 bar; and superheated steam up to 550 °C. The figure below illustrates a water-tube boiler:

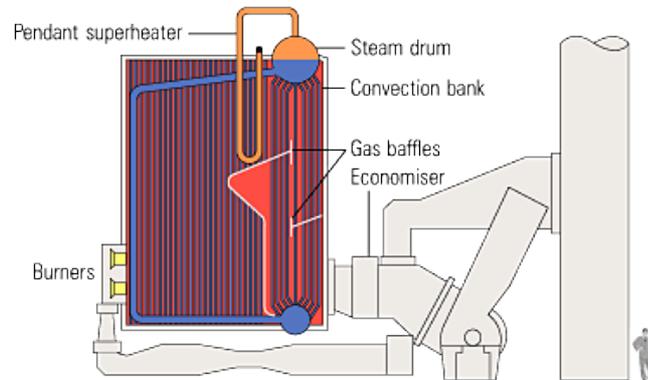


Figure 1.7: Water-tube Boiler.

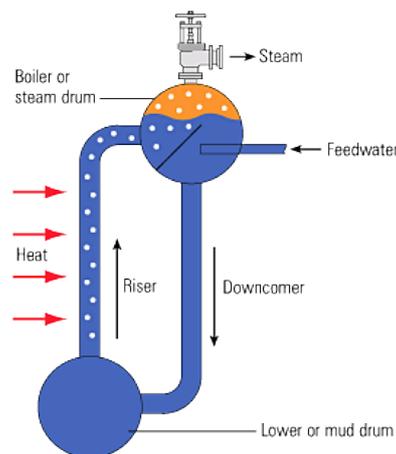


Figure 1.8: Principle of Natural Water Circulation.

Water-tube boilers operate on the principle of natural water circulation. The above diagram helps to explain the principle.

Cooler feed water is introduced into the steam drum behind a baffle where, because the density of the cold water is greater, it descends in the 'down comer' towards the lower or 'mud' drum, displacing the warmer water up into the front tubes. Continued heating creates steam bubbles in the front tubes, which are naturally separated from the hot water in the steam drum, and are taken off. However, when the pressure in the

water-tube boiler is increased, the difference between the densities of the water and saturated steam falls, consequently less circulation occurs. To keep the same level of steam output at higher design pressures, the distance between the lower drum and the steam drum must be increased, or some means of forced circulation must be introduced.

The advantages of water-tube boilers are that they have small water content, and therefore respond rapidly to load change and heat input. Furthermore, small diameter tubes and steam drum mean that much higher steam pressures can be tolerated, and up to 160 bar may be used in power stations. Just as important, is the fact that design may include many burners in any of the walls, which is important if the boiler has an integral super heater, and the temperature of the superheated steam needs to be controlled.

The disadvantages of water-tube boilers are that they are not as simple to make in the packaged form as shell boilers, which means that more work is required on site. Also, the option of multiple burners may give flexibility, but the 30 or more burners used in power stations means that complex control systems are necessary.

1.4.3 Steam Turbine

A steam turbine is a mechanical device that extracts thermal energy from a pressurized steam and converts it into rotary motion. The steam energy converts mechanical work by expansion through the turbine. The expansion takes place through a series of fixed blades (nozzles) and moving blades. Each row of moving blades and fixed blades is called a stage. The steam turbine has a much better thermodynamic efficiency because of use of multiple stages in the expansion of steam. This results in a closer approach to the ideal reversible process. These stages are characterized by how the energy is extracted from them and are known as either impulse or reaction turbines. Most steam turbines use mixture of the reaction and impulse designs; each stage behaves as either one or the other, but the overall turbine uses both. Typically, higher-pressure sections are impulsive type and lower pressure sections are reaction type. The following figure shows a schematic diagram outlining the difference between an impulse and a reaction turbine:

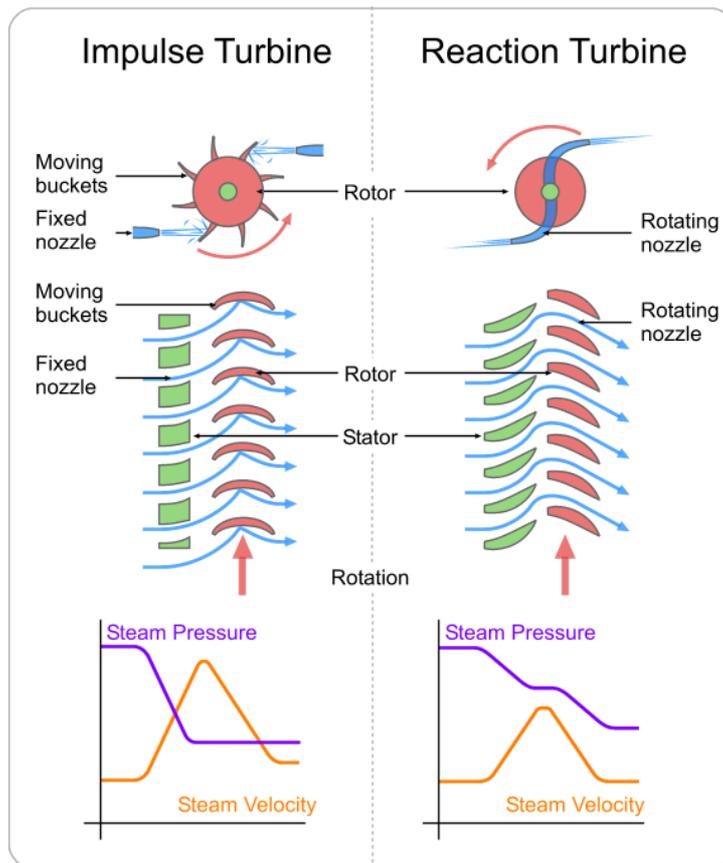


Figure 1.9: Difference between an impulse and a reaction turbine.

An impulse turbine has fixed nozzles that orient the steam into high-speed jets. These jets contain significant kinetic energy, which the rotor blades, shaped like buckets, convert into shaft rotation as the steam jet changes direction. As the steam flows through the nozzle its pressure falls from inlet pressure to the exit pressure. Due to this higher ratio of expansion of steam in the nozzle the steam leaves the nozzle with a very high velocity. On the other hand, a reaction turbine's rotor blades are arranged to form convergent nozzles.

This type of turbine makes use of the reaction force produced as the steam accelerates through the nozzles formed by the rotor. A pressure drop occurs across both the stator and the rotor, with steam accelerating through the stator and decelerating through the rotor, with no net change in steam velocity across the stage but with a decrease in both pressure and temperature, reflecting the work performed in the driving of the rotor. Turbine speed also adds to efficiency of turbine. Higher turbine speeds theoretically give a better efficiency since they are expected to lower certain turbine losses. However, if the operating speed of turbine is beyond the first critical speed of

the turbine, the machine will experience violent vibrations every time it passes the critical speed at startup. Hence, a turbine which operates below the first critical speed is always preferred. Generally, turbines with operating speeds of up to 6000 rpm provide good efficiency as well as trouble free operations. It is therefore preferable to install a medium speed turbine with good efficiency that can operate longer without breaking down, than a high-speed turbine, which is more efficient but possesses more risk of breakdowns.

1.4.4 Boiler Feed Water

Water absorbs more heat for a given temperature rise than any other common inorganic substance. It expands 1600 times as it evaporates to form steam at atmospheric pressure. These unique properties of water make it an ideal raw material for heating and power generating processes. All natural waters contain varying amounts of dissolved and suspended matter and dissolved gases. The amount of minerals dissolved in water varies from 30 g/l in seawater to anything from 0.005 to 1500 mg/l in fresh water supplies. Since water impurities cause boiler problems, careful consideration must be given to the quality of the water used for generating steam.

Feed water purity is a matter both of quantity of impurities and nature of impurities: some impurities such as hardness, iron and silica are more of concern than sodium salts. The purity requirements for any feed-water depend on how much feed water is used as well as what particular boiler design (pressure, heat transfer rate...) can tolerate. As steam is produced, dissolved solids become concentrated and form deposits inside the boiler. This leads to poor heat transfer and reduces the efficiency of the boiler. Dissolved gasses such as oxygen and carbon dioxide will react with the metals in the boiler system and lead to boiler corrosion.

In order to protect the boiler from these contaminants, they should be controlled or removed, through external or internal treatment.

1.4.5 Cooling Water

Cooling Water is used as a cooling agent on site, due to the fact that water is cheap to obtain, easy to move around, highly efficient, recycled cooled and used again, and easy to dispose by just pouring down the drain. The water is treated at the wastewater treatment plant and then cooled. The following table shows the qualities water used on site has:

Table 1.4: Quality of Water used in an Oil Refinery.

Suspended solids	None
Conductivity	50-600 uS/cm
Hardness	8° dH max
pH	7.8
CO2 aggressive	None
Iron	< 0.3 mg/L
Manganese	< 0.05 mg/L
Sulfate	< 250 mg/L
Chloride	< 250 mg/L
COD	< 40 mg/L
Bacteria	< 1000 CFU/ml

1.4.6 Demineralized Water

Demineralized water is water from any source that is physically processed to remove impurities, which can be achieved through deionization. Deionized water is water that has had its mineral ions removed, such as cations from sodium, calcium, iron, copper and anions such as chloride and bromide. Deionization is a physical process, which uses specially manufactured ion exchange resins, which bind to and filter out the mineral salts from water. Because the majority of water impurities are dissolved salts, deionization produces a high purity water that is generally similar to distilled water, and this process is quick and without scale buildup.

However, deionization does not significantly remove uncharged organic molecules, viruses or bacteria, except by incidental trapping in the resin. Deionization can be done continuously and inexpensively using electrodeionization. Deionization does not

remove the hydroxide or hydronium ions from water. These are the products of the self-ionization of water to equilibrium and therefore are impossible to remove.

Deionization entails removal of electrically charged (ionised) dissolved substances by binding them to positively or negatively charged sites on a resin as the water passes through a column packed with this resin. This process is called ion exchange is used on site ways to produce deionized water:

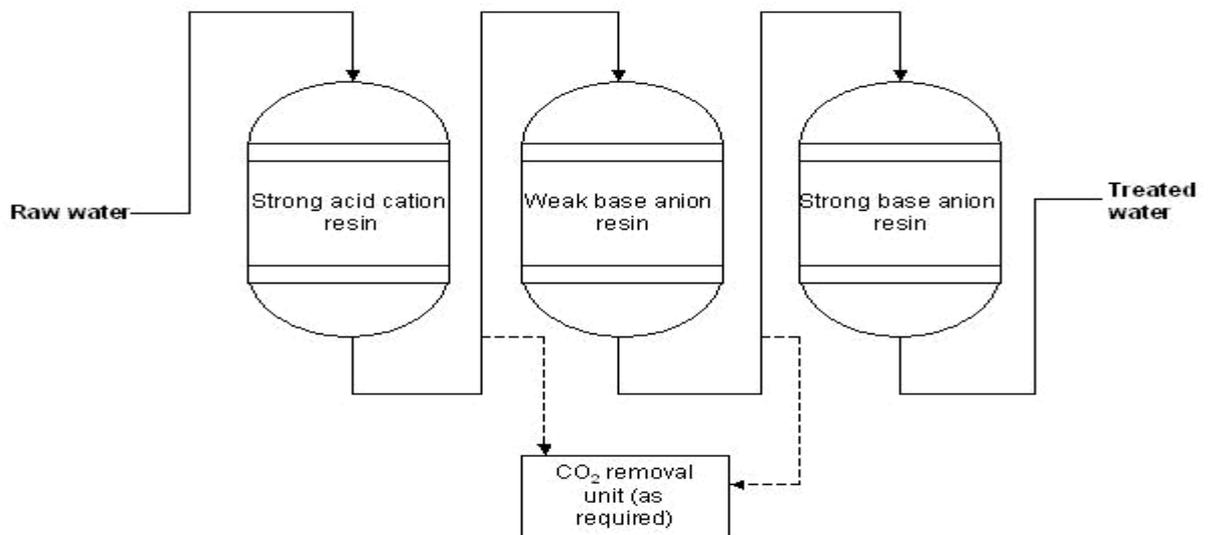


Figure 1.10: Ion Exchange Process.

The system contains three vessels. One contains a cation-exchange resin in the hydrogen (H⁺) form and the other two containing an anion resin in the hydroxyl (OH⁻) form. Water flows through the cation column, whereupon all the cations are exchanged for hydrogen ions. The decationized water then flows through the anion column.

Then all the negatively charged ions are exchanged for hydroxide ions which then combine with the hydrogen ions to form water (H₂O). The flux of ions passed to the anion columns is reduced through the CO₂ removal unit between the ion exchange vessels. This reduces the CO₂ content to a few mg/l and brings about a reduction of the following strong base anion resin volume and in the regeneration reagent requirements. The regeneration of the anion exchangers takes place with caustic soda (NaOH) solution first passing through the strong base resin and then through the weak

base resin. This method requires less caustic soda because the remaining regeneration solution after the strong base anion exchanger is usually sufficient to regenerate the weak base resin completely.

1.4.7 Flare Stack System

A flare stack is an elevated vertical conveyance used to eliminate waste gas, which is otherwise not feasible to use or transport. They also act as safety systems for non-waste gas and released via pressure relief valve when needed to ease the strain on equipment. They protect gas-processing equipments from being over pressured. Also in case of an emergency situation, the flare system helps burn out the total reserve gas.

Whenever plant equipment items are over-pressured, the pressure relief valves on the equipment automatically release gases (and sometimes liquids as well), which are routed through large piping runs called flare headers to the flare stacks. The released gases and/or liquids are burned as they exit the flare stacks. The size and brightness of the resulting flame depends upon how much flammable material was released. Steam is injected into the flame to reduce the formation of black smoke. The injected steam does however make the burning of gas sound louder, which can cause complaints from nearby residents.

Compared to the emission of black smoke, it can be seen as a valid trade off. In more advanced flare tip designs, if the steam used is too wet it can freeze just below the tip, disrupting operations and causing the formation of large icicles. In order to keep the flare system functional, a small amount of gas is continuously burned, like a pilot light, so that the system is always ready for its primary purpose as an over-pressure safety system. The continuous gas source also helps diluted mixtures achieve complete combustion. Enclosed ground flares are engineered to eliminate smoke, and contain the flame within the stack.

1.5 Process Description

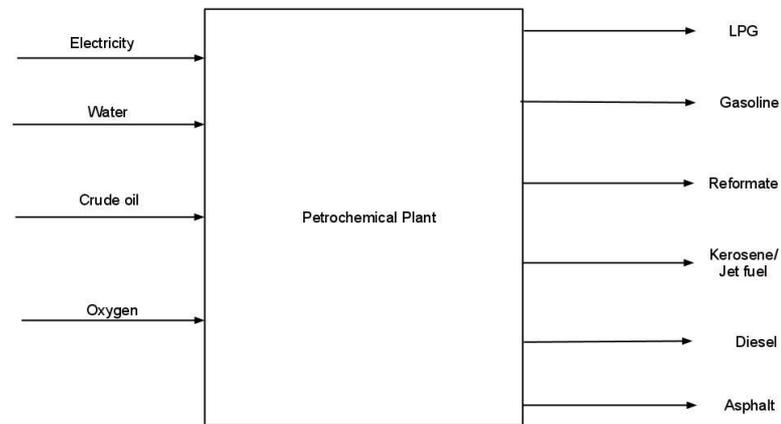


Figure 1.11: Process input/output stream.

Crude oil is the feed to the petrochemical plant where crude oil is transformed, through different chemical processing units, to more valuable products which are liquefied petroleum gas, gasoline, reformate, Kerosene and jet fuel, diesel, and asphalt. The petrochemical plant consists of storage tanks farm for the crude oil and the products, desalting unit, oil refinery for crude oil processing, wastewater treatment plant, electric generation plant, and flaring station for normal and emergency emission of gases.

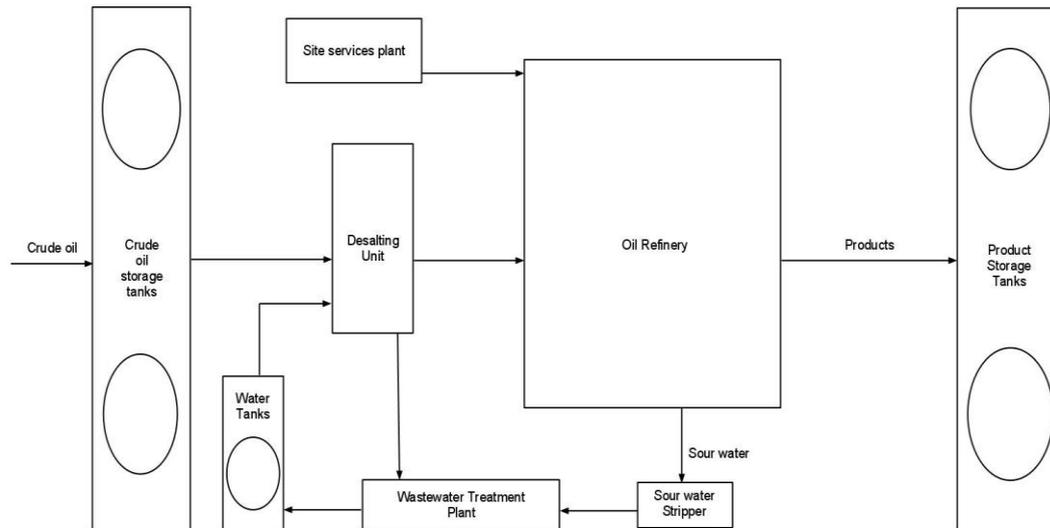


Figure 1.12: Process Description PFD I

First crude oil is settled into the crude oil storage tanks. Then the crude oil is past to a desalting unit where the crude oil is washed of out the salts present in the crude oil. The desalted crude is passed to the oil refinery where crude oil undergoes a series of separation and conversion processes. These separation and conversion processes produce a large amount of water alongside their intended products. The products of the oil refinery are sent to the product storage tanks and the water produced from the oil refinery processes was passed to the sour water stripper where the hydrogen sulphide and ammonia are separated. The sour water stripper output is then passed to the wastewater treatment plant where the wastewater is treated and purified. The treated water is then sent to the water tanks for supplying different processes in the petrochemical plant.

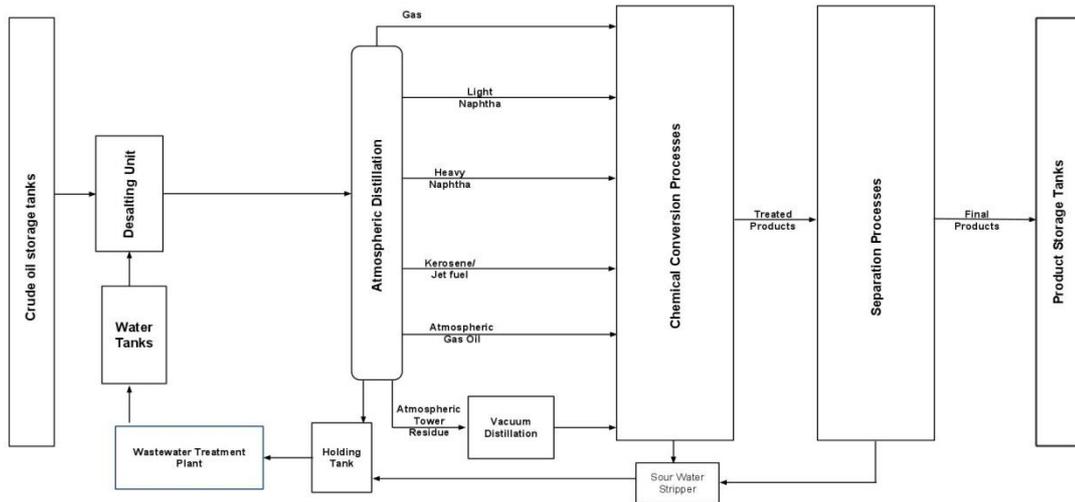


Figure 1.13: Process Description PFD II

The desalted crude is passed to the atmospheric distillation column (ADC) where the crude oil is separated to 7 products. ADC outputs are then passed into chemical conversion processes where ADC products are treated and converted into more valuable products. The chemical conversion processes units consist of desulfurization process, catalytic reformer, mercox treatment, fluid catalytic cracking and a catalytic hydrocracking process. The products from the chemical conversion process units are then passed to a series of separation processes, which are mainly fractionation columns. The final products are passed to the product storage tanks. The water from the atmospheric distillation column, conversion processes and separation processes is passed to the sour water stripper then to the wastewater treatment plant where the water is purified and treated.

Crude oil from a storage tank goes to desalting unit to wash out salt from the crude oil before entering the atmospheric distillation unit where crude oil is distilled into fractions. Atmospheric distillation products are grouped into three categories: light distillates (LPG, gasoline and naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, asphalt). The gases from the top of the atmospheric distillation column is sent to the gas processing units which consisted of amine process, clause unit which produced liquefied petroleum gases (LPG) and a fractionation train to purify and further treat the LPG produced. The light naphtha was passed to a desulfurization unit which used hydrogen to desulfurize naphtha and produce gasoline. The heavy naphtha is sent to a Catalytic Reformer unit which was used to convert the naphtha-boiling range molecules into higher octane reformat (reformer product). The Reformat has higher content of aromatics and cyclic hydrocarbons. An important by-product of a reformer is hydrogen released during the catalyst reaction. The hydrogen was used in the hydrocracking process. Atmospheric gas oil was sent to a Fluid catalytic cracker (FCC) unit which upgraded heavier fractions into lighter, more valuable gasoline and gases which were recycled to the gas processing units.

The Vacuum distillation unit further distilled residual bottoms into asphalt which was sent to the storage tank and the other product from the vacuum distillation is sent to a catalytic hydrocracking unit which produced diesel which is sent to the storage tanks and the catalytic hydrocracking produced gases which is recycled to the gas treatment plant. Merox unit treated kerosene and jet fuel by oxidizing mercaptans to organic disulfides.

1.5.1 Desalting unit

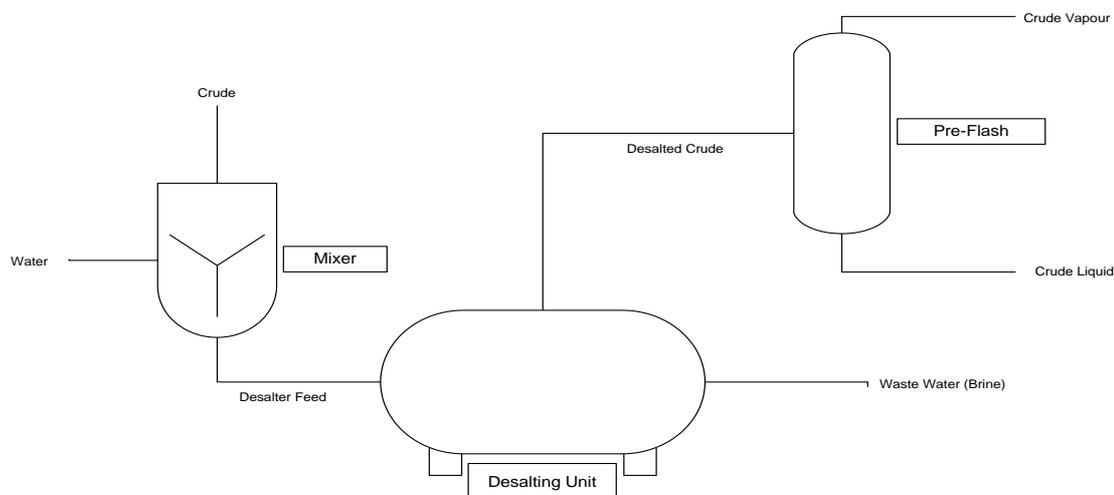


Figure 1.15: Desalting unit and Pre-flash Unit.

Salts, mainly NaCl , MgCl_2 and CaCl_2 , in crude oil can cause severe problems in refinery processes. These problems include:

- ❖ Corrosion induced by the acids formed by chloride salt decomposition.
- ❖ Fouling of heat exchangers and other units by salt deposition.
- ❖ The poisoning of catalysts in downstream processing units.

Therefore it is important that the Crude is desalted before being charged to the distillation unit.

The salt in the crude oil is picked up from the reservoirs or during transportation. The crude may also contain other suspended solids such as sand, clay, iron oxide particles and trace elements. (In Brent crude these trace metallic elements are Vanadium and Nickel.)

From the assay of Brent crude oil the content of salt and trace metal elements is given as:

Table 1.5: Salt and Metal trace elements in Brent Crude.

Component	mg/kg	kg/m ³
NaCl	5	3.66
Vanadium	1	0.73
Nickel	1	0.73

A well designed and operated desalter can achieve between 85 and 99% removal of inorganic salts from the crude oil feed and the water content of the desalted crude will be less than 0.2 volume % of the desalted crude.

The most common setups for desalting units for crude oil are:

- ❖ Two desalters in series, where the brine from the second unit can be treated and used as wash water for the first unit.
- ❖ Two desalters in series with no recycle of brine from the second stage.
- ❖ Using multiple electrostatic fields, within a single vessel, to create the same effect as two or three stages of desalting in one unit. A cross section of an electrostatic crude oil desalter is shown below in Figure 1.16.

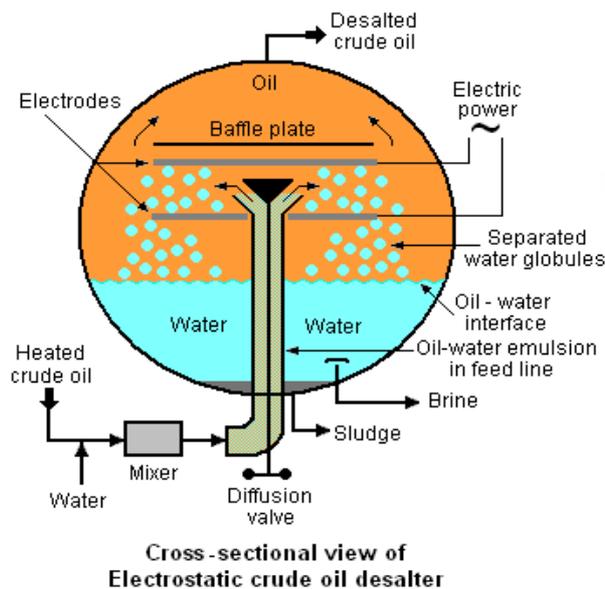


Figure: 1.16: A cross section of an electrostatic crude oil desalter.

A typical electrostatic desalter is a horizontal, cylindrical vessel. The oil-water emulsion that enters from the bottom of the desalter through the feed line is a thorough mixture of two non-miscible liquids consisting of a continuous phase and dispersed phase water in the form of very small droplets. Asphaltenes and finely divided sediment solids are adsorbed on the oil-water interface and stabilize the emulsion. Thus the degree of difficulty involved in coalescing the droplets into larger droplets which can be settled and removed is related to the presence of asphaltenes, sediments and other water-insoluble contaminants.

An electrical system connected to electrodes within the desalter generates an electrostatic field that induce dipole forces between neighbouring droplets of water. Therefore the electrostatic field results in each droplet having a positive charge and a negative charge which caused the droplets to coalesce because of the attractive force generated by the opposite charges on neighbouring droplets. The resulting larger water droplets, along with water-insoluble solids, then settle to the bottom of the desalter. The settled water was continuously withdrawn from the desalter from a point above the desalter bottom and is referred to as brine because it contained the inorganic salts that originally entered the desalter with the water in the crude oil. The settled sediment at the bottom of desalter was withdrawn as sludge at intermittent intervals as needed to prevent solids from entering the settled water outlet.

As shown in Fig1.15, the desalted crude was then fed to a pre-flash unit. This flash unit split the vapour and liquid phases of the crude oil to make the heating of the liquid phase in the furnace more efficient.

1.5.2 Atmospheric Distillation

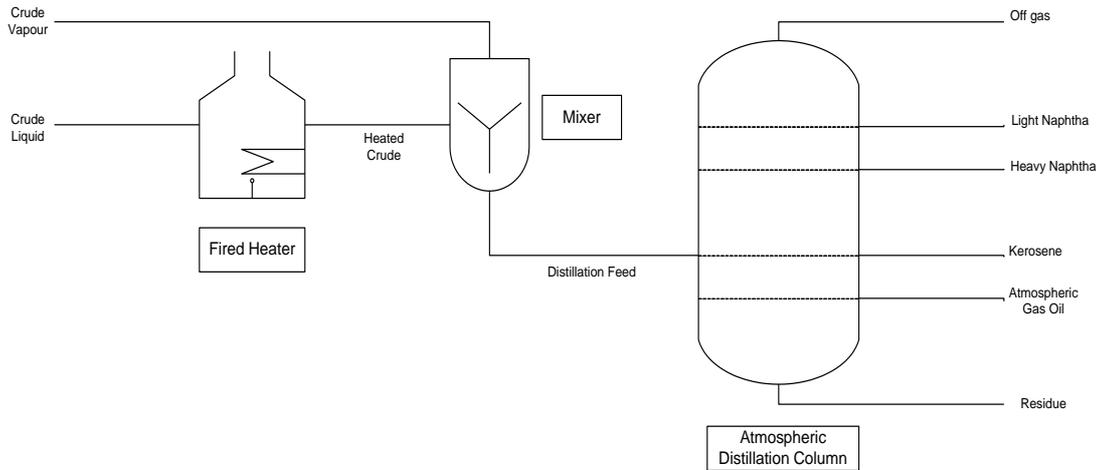


Figure 1.17: Atmospheric Distillation.

In the atmospheric distillation column the crude oil is separated into products component fractions, to be processed downstream into specific products. The crude oil liquid from the pre-flash unit is heated in the furnace (fired heater). The liquid is then mixed with the crude oil vapour from the flash unit (shown in figure 1.15). The crude oil feed to the atmospheric distillation column is approximately 300-400°C. The distillation column operates at a pressure approaching atmospheric at the top. The crude oil is split into the following components from (top to bottom of the column):

- ❖ Off gas
- ❖ Light Naphtha
- ❖ Heavy Naphtha
- ❖ Kerosene
- ❖ Atmospheric gas oil
- ❖ Residue

The temperature is highest at the bottom of the column, which is constantly fed with heat from the bottoms reboiler. The reboiler vaporised part of the bottom outlet from the column and this vapour is recycled back to the distillation column and travels to the top stage absorbing lighter hydrocarbons from the counter current crude oil flow. The temperature at the top of the column is the lowest as

the heat at this stage of the column was absorbed by a condenser which condensed a fraction of the vapours from column overhead. The condensed hydrocarbon liquid was recycled back to the column. This condensed liquid flew down through the series of column trays, flowing counter current to the hot vapours coming from bottom and condensing some of those vapours along the way. The reboiler and condenser created pressure and temperature gradients along the stages of the column, so the fractions listed above could be removed at the correct stages.

1.5.3 Vacuum Distillation Column

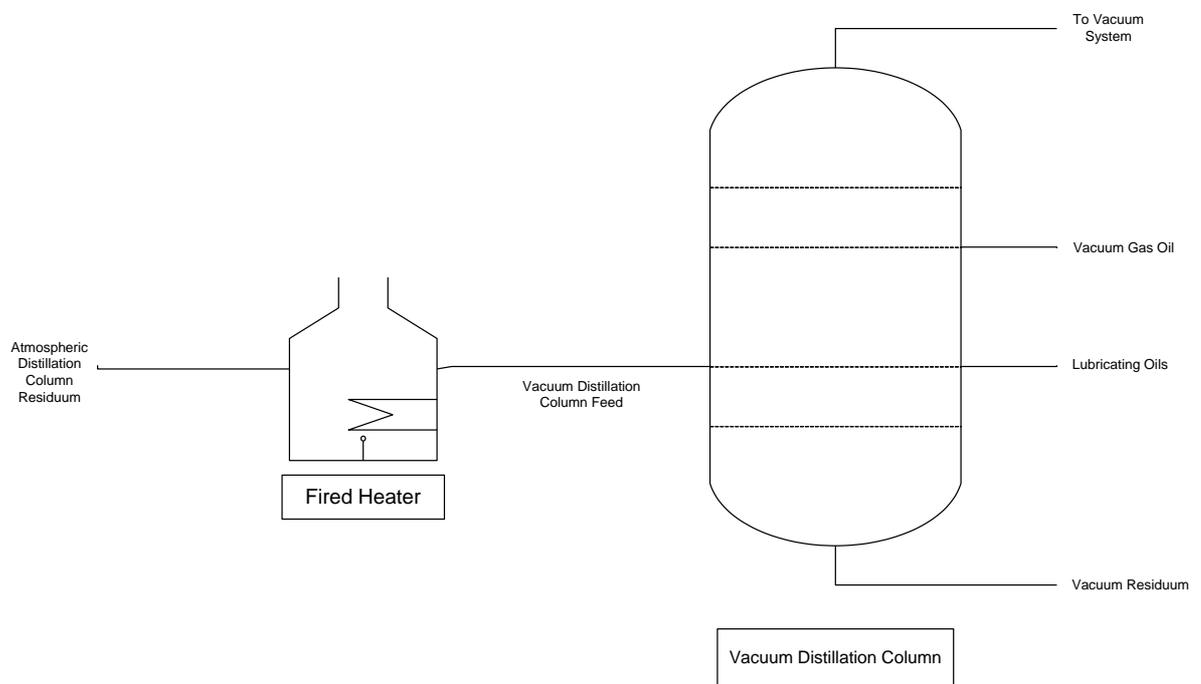


Figure 1.18: Vacuum Distillation Column.

Further distillation of the residuum from the base of the atmospheric distillation column was required. For this a Vacuum distillation column was needed which operates at lower pressures and higher temperatures to the atmospheric distillation column. The lower pressure was required to prevent thermal cracking of the components in the residue. Larger diameter towers are used to keep velocities lower. A typical first-phase vacuum tower may produce gas oils, lubricating oil base stocks and heavy residual for propane deasphalting. A second-phase tower, operating at a lower vacuum, distills surplus residuum from the atmospheric tower which is not used

for lube stock processing, and surplus residuum from the first vacuum tower not used for deasphalting.

1.5.4 Catalytic Reforming Unit

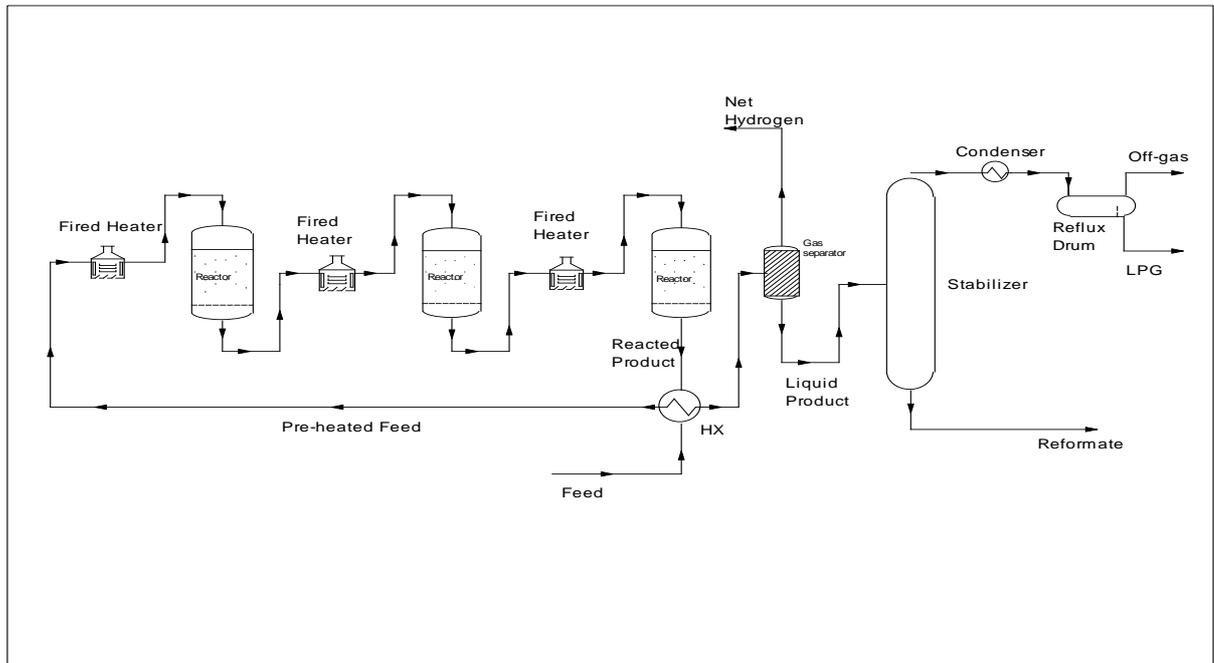


Figure 1.19: Catalytic reforming unit.

The Heavy naphtha from the atmospheric distillation is preheated by flowing through a heat exchanger. The preheated feed is then totally vaporized and heated to the reaction temperature in the first fired heater before entering the first reactor. As the vaporized reactants flow through the fixed bed of the zeolite catalyst in the reactor, the major reaction is dehydrogenation which was highly endothermic and resulted in a large temperature decrease between the inlet and outlet of the reactor. The vaporized product stream from the first reactor is reheated in the second fired heater before flowing through the second reactor to maintain the required reaction temperature and the rate of reaction. The temperature again decreases across the second reactor and the vaporized product stream of the second reactor is again reheated in the third fired heater before flowing through the third reactor. The hot reaction product from the third reactor is cooled by flowing through the heat exchanger, where the feed to the first reactor was preheated, before flowing into the gas separator. As the vaporized

stream proceeds through the three reactors, the reaction rates decreases and the reactors therefore became larger. At the same time, the amount of reheat required between the reactors was smaller.

The hydrogen-rich gas from the gas separator vessel was exported for use in the other refinery processes that consumed hydrogen such as the hydrodesulphurisation units and the hydrocracking unit.

The liquid product from the gas separator vessel is routed into a stabilizer. The overhead off-gas product from the stabilizer contained the by-products such as methane, ethane, propane and butane gases as well as some small amount of hydrogen produced by the hydrocracking reactions. That off gas was routed to the refinery's gas processing plant. The overhead liquid product is LPG and is sent to the LPG storage tanks.

The bottoms product from the stabilizer was the high-octane liquid reformates which was the product of the catalytic reforming unit.

In the catalytic reforming unit many reactions take place in each reactor but the major reactions are shown in the table below:

Table 1.6: Reaction in the Catalytic Reforming Unit.

Reactor	Reaction
1	Dehydrogenation
2	Aromatisation
3	Hydrocracking

1.5.5 Fluid Catalytic Cracking

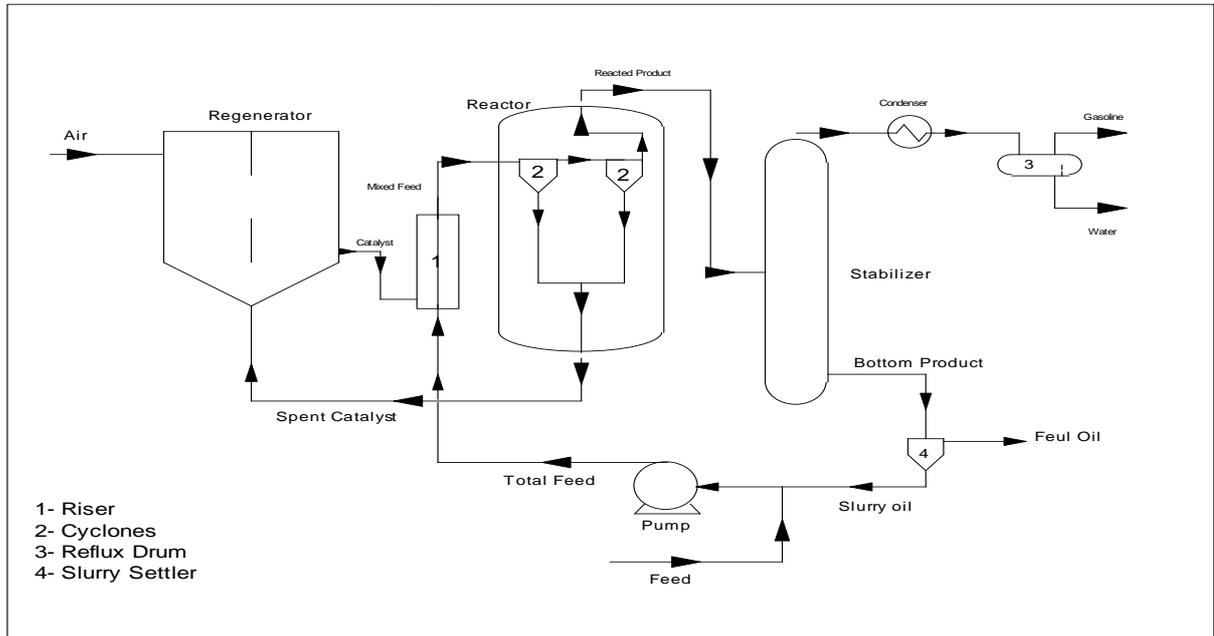


Figure 1.20: Fluid catalytic cracking.

Atmospheric Gas Oil (AGO) from the Atmospheric Distillation Column (ADC) is the feed for the fluid catalytic cracking (FCC). The side-by-side configuration type of FCC was chosen. The feed enters the catalyst riser where the feed mixed and reacted with the catalyst which was produced in the regenerator. The vaporised mixed feed flows upwards to the reactor where the spent catalysts are separated from the hydrocarbon feed by two cyclones. The spent catalysts are recycled to the regenerator. The hydrocarbon product from the reactor is fed to a distillation column where the reactor product is separated into a gasoline product and a gas product at the top of the column and fuel oil product at the bottom of the column. The catalyst is regenerated by burning off the deposited coke with air blown into the regenerator. The regenerator operated at a temperature of 715°C and a pressure of about 3 bars. The combustion of the coke is exothermic and produces a large amount of heat that was partially absorbed by the regenerated catalyst and provided the heat required for the vaporization of the feedstock and the endothermic cracking reactions that takes place in the catalyst riser. Number of reaction take place in the fluid catalytic cracking unit but the important reactions, which take place simultaneously, are the cracking reactions and the isomerisation reactions.

1.5.7 The Gas Plant

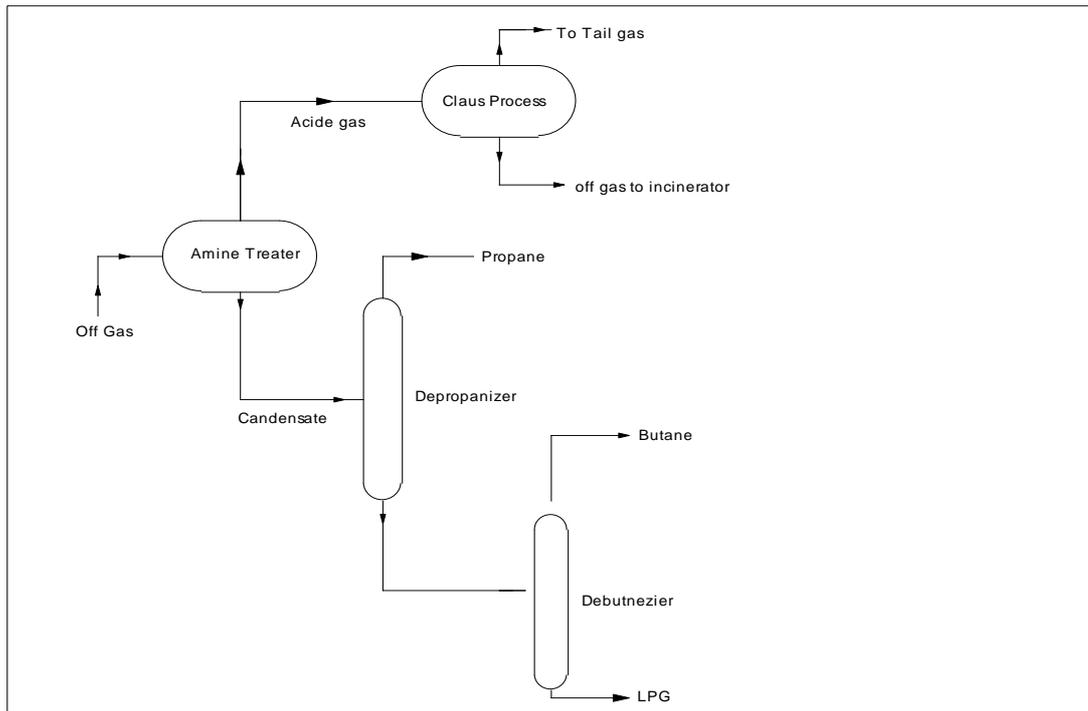


Figure1.22: The Gas Plant.

The off gas entered the gas processing plant and first was fed to the amine treater. Then the H₂S rich vapor product was then fed to Claus process to remove the sulfur. The Tail gas produced by the cluse process was fed to the tail gas-processing unit for treatment of the gas. The liquid product from the Amine Treater was condensated and sent to the Fractionation Train, which contained Deproponizer and Debutanizer.

1.5.8 Amine Gas Treating

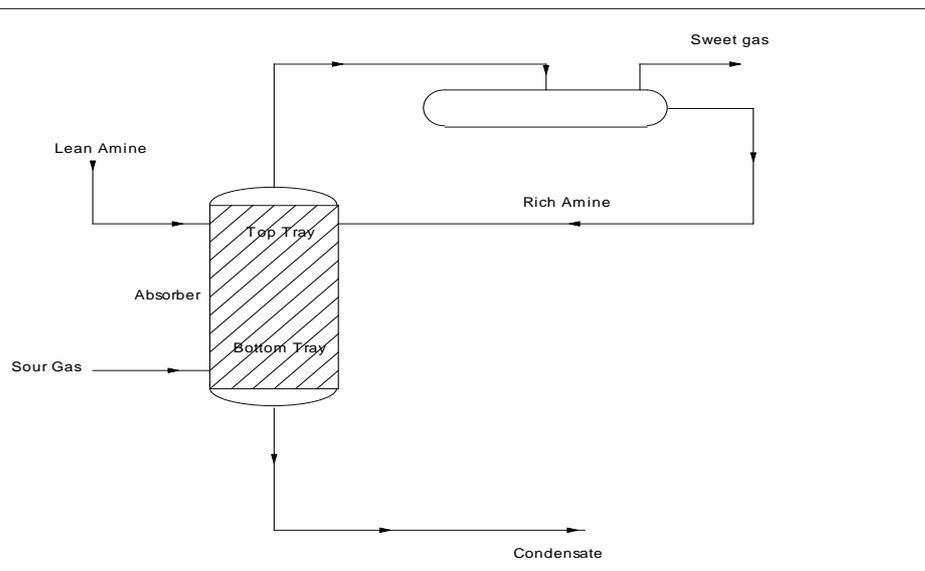


Figure1.23: Amine Treating Process.

The amine gas treating process (as shown in the flow diagram) included an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the down flowing MEA absorbed H_2S from the up flowing sour gas and produced a sweetened gas stream (i.e., an H_2S -free gas) as the product LPG and the amine solution rich in the absorbed acid gases. The "lean" amine that was recycled for reuse in the absorber. This H_2S -rich acid gas stream was then routed into the Claus process. The bottom product from the absorber was the feed for the depropanizer.

1.5.9 Claus process

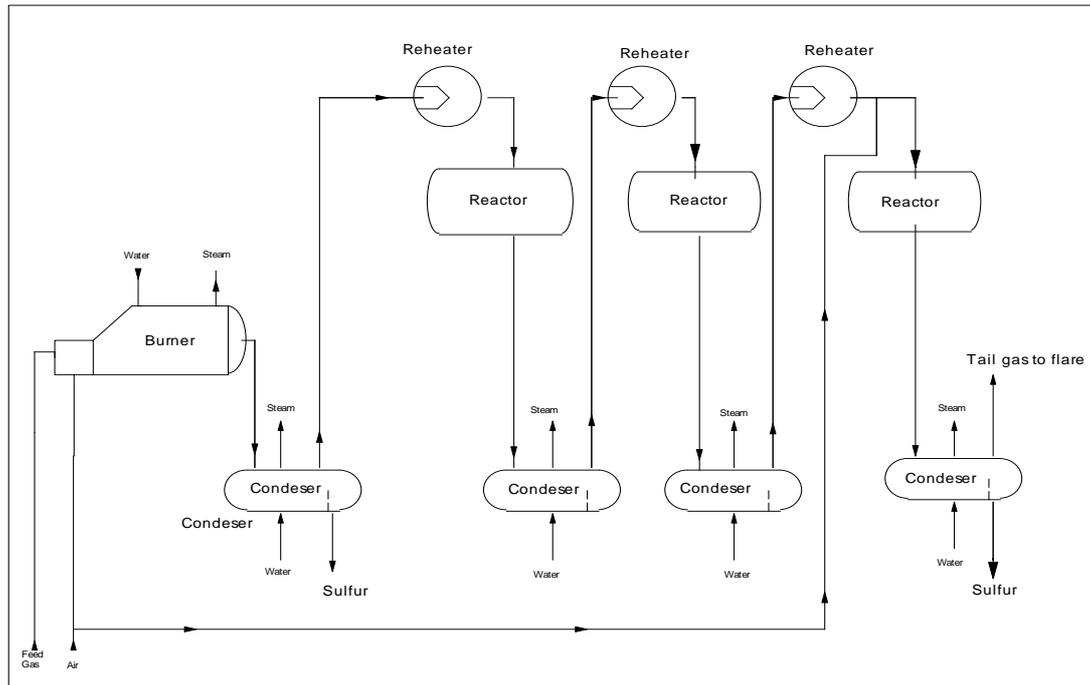


Figure1.24: Claus sulphur recovery unit.

As shown in the schematic diagram, the feed gas to the Claus process unit is burned in a reaction furnace using sufficient combustion air to burn only one-third of the H_2S it contains. That is accomplished by using a control valve (called a *flow ratio controller*) to provide the required ratio of combustion air to feed gas.

The reaction furnace pressure and temperature is maintained. Then the Claus reaction occurred thermally in the reaction furnace (i.e., without requiring any catalyst). About 70% of the H_2S in the feed gas is thermally converted into elemental sulfur in the reaction furnace.

The hot reaction product gas, containing gaseous sulfur, was used to produce steam in a boiler (called a waste heat boiler), which resulted in cooling the gases. The gas was then further cooled and condensed in a heat exchanger while producing additional steam. The condensed liquid sulfur was separated from the remaining unreacted gas in the outlet end of the condenser and sent to product storage.

The separated gas was then reheated and entered the first catalytic reactor maintained where about 20% of the H₂S in the feed gas was thermally converted into elemental sulfur. The outlet product gas from the first reactor was cooled in another condenser while also producing steam. Again, the condensed liquid sulfur was separated from the remaining unreacted gas in the outlet end of the condenser and sent to product storage. The separated gas from the second condenser was sent to another reheater and the sequence of gas reheat, catalytic reaction, condensation and separation of liquid sulfur from unreacted gas was repeated for the second and third reactors at successively lower reactor temperatures. About 5% and 3% of the H₂S in the feed gas is thermally converted into elemental sulfur in the second reactor and third reactors, respectively. For a well-designed and operated Claus sulfur recovery plant having three catalytic reactors (as shown in the diagram above), an overall conversion of at least 98% could be achieved. In fact, the latest modern designs can achieve up to 99.8% conversion of hydrogen sulfide into product sulfur that is 99+% saleable bright yellow sulfur. The remaining gas separated from the last condenser was referred to as *tail gas* and is sent to the flare stack system.

1.5.10 Fractionation Train

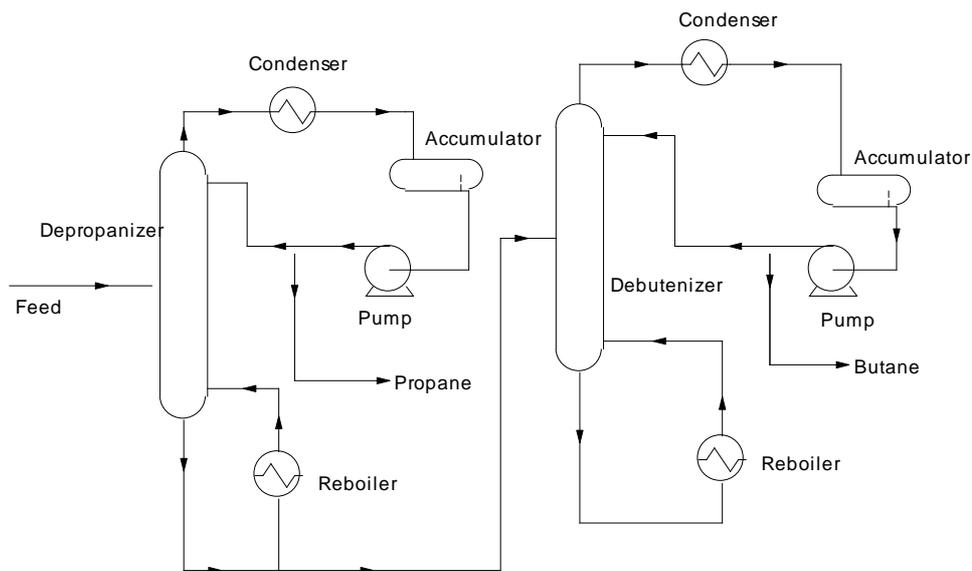


Figure1.25: Fractionation train

Depropanization Process

A depropanizer is trayed tower that includes a reboiler, an overhead condenser, and a reflux accumulator and pump. The propane product was drawn from the reflux accumulator as the liquid product. A water cooler was used as the overhead condenser. The propane product contained small amounts of ethane, butane and heavier components.

Debutanization Process

A debutanizer is trayed tower that included an overhead condenser, and a reflux accumulator and pump. The butane product was drawn from the reflux accumulator as the liquid product. A water cooler was used as the overhead condenser.

The bottoms product from a debutanizer was C5+ LNG. The C5+ LNG stream from the debutanizer bottom was cooled before being sent to the storage tanks

1.5.11 Desulphurisation

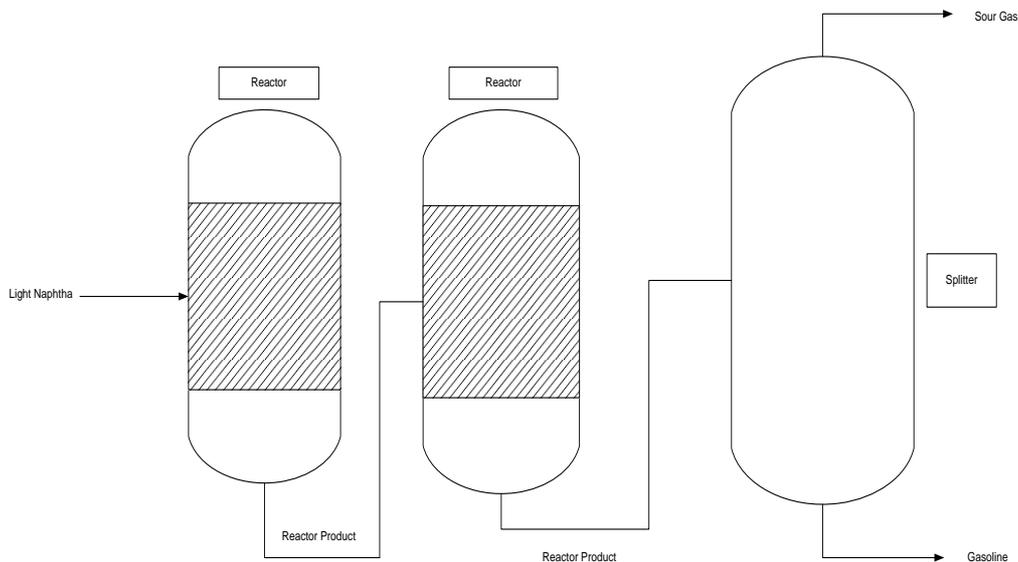


Figure 1.26: Desulphurisation

The purpose of the Desulphurisation unit is to reduce the hydrogen sulfide (H_2S). The Light Naphtha enters the first reactor where olefins are converted to more paraffin. The reactor product then enters the second reactor where the naphthenes react to produce more aromatics compounds. The mixture then enters a splitter which removes all the hydrogen sulphide from the mixture and routes the Sour Gas to the Amine Gas Treating unit. The bottom product is the Gasoline.

1.5.12 Merox Treatment

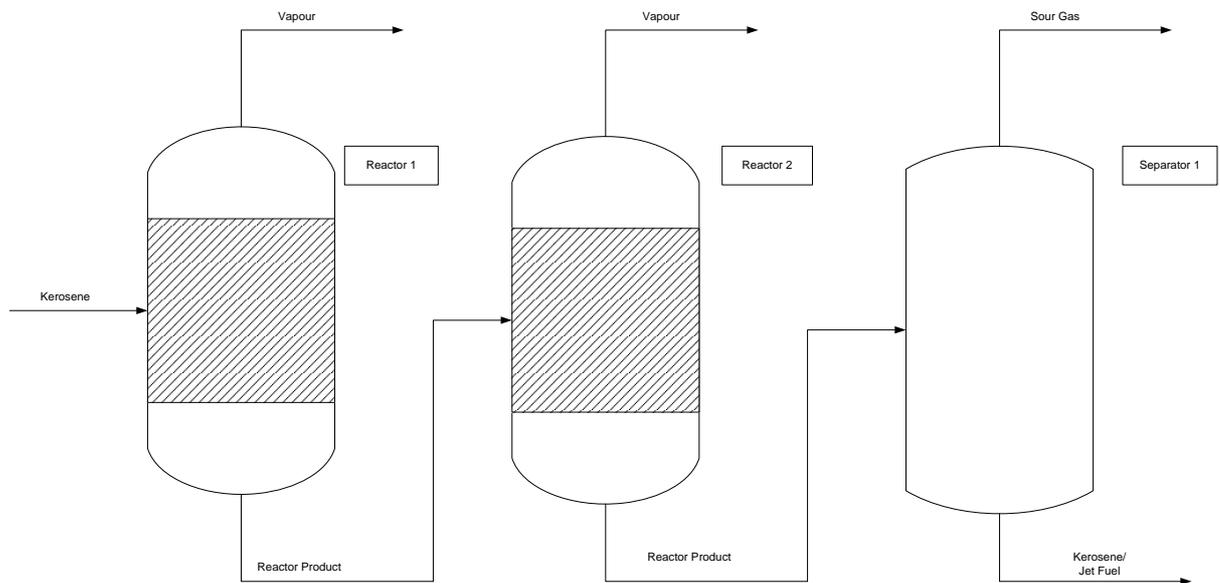


Figure 1.27: Merox Treatment.

The Merox process for kerosene/jet fuel involves removing mercaptans. The process is referred to as a sweetening process.

The Kerosene enters the first Reactor where the aromatic compounds react to produce cyclanes. Furthermore, the Reactor product enters the second Reactor and more cyclanes are produced from the conversion of alkanes. The mixture enters the Separator, and all the mercaptans are separated from the mixture and are routed as Sour Gas to the Amine Gas Treating unit. The bottom product is the resultant sweetened Kerosene/Jet Fuel.

1.5.13 Wastewater Treatment

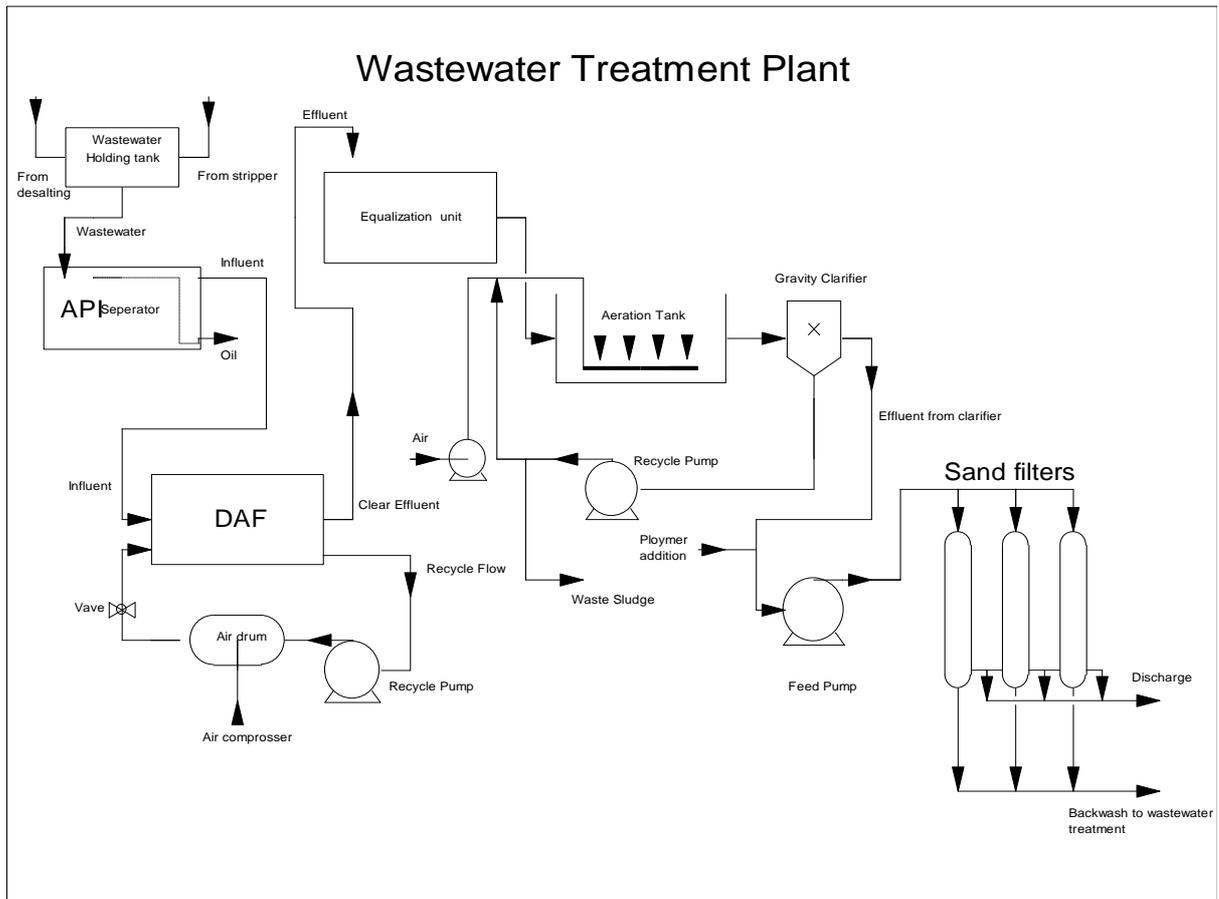


Figure 1.28: Wastewater Treatment Plant.

In a refinery wastewater treatment system, two steps of oil removal were used to achieve the necessary removal of free oil from the collected wastewater prior to feeding it to a biological system. This oil removal was achieved by using an API separator followed by a dissolved air flotation (DAF). The wastewater from the secondary oil/water separation unit was sent to the equalization system that was used to dampen out variations in flow and concentration in the refinery wastewater. The wastewater is then routed to the aeration tank/clarifier that constitutes the biological system. The effluent from the clarifier was then sent to tertiary treatment prior to discharge.

API Separator Unit

First unit used for the wastewater treatment plant was the API separator. It uses the difference in specific gravity to allow heavier material to settle below lighter liquids. Wastewater is first collected in a pre-treatment section that allows sludge removal. A

diffusion barrier slowly allows the wastewater to flow down the separator towards the outlet while the lighter oil fractions skimmed off. Underflow baffle plates used to prevent oil from escaping into the outlet section.

DAF Unit

The first step applied in a dissolved air flotation (DAF) system was coagulation/flocculation to remove colloidal particles from suspension. These processes were done in sequence. Chemicals were mixed with wastewater to promote the aggregation of the suspended solids into particles large enough to settle or be removed. Part of the effluent is recycled, pressurized, saturated with air and mixed with the incoming feed. The recycle stream was depressurized to release the air bubbles, which attached themselves to any free oil/solids, contained in the feed and floated them to the surface of the vessel. The floated material was skimmed off and sent to refinery slops after further dewatering. Some solids settled to the bottom of the DAF where they scraped off and removed periodically.

Equalization Unit

The equalization system was used to minimize and reduce the fluctuations caused due to the sudden changes of parameters in the wastewater treatment plant. Among the different types of equalization processes, the intermittent flow diversion was selected because toxic and difficult-to-treat flows are occasionally expected. The basin's contents were sampled before discharged to determine the rate at which the basin can be emptied into the main process stream without harmful effects.

Activated Sludge Unit

The wastewater entered an aeration tank where the microorganisms were brought in contact with organic contaminants of the wastewater. Air was continuously injected into the system to keep the sludge aerobic and to maintain the solids in suspension. The effluent from the aeration tank was sent to the clarifier. The organic contaminant in the wastewater converted into the biomass and separated later in the clarifier. A portion of the concentrated sludge, referred to as 'return activated sludge' (RAS), from the clarifier was recycled back and mixed with incoming wastewater, and the remainder of the sludge was discharged as 'waste activated sludge' (WAS).

Sand Filtration Unit

This process involves passing the wastewater through a filter bed comprised of a filter media. Dual media filters comprise a layer of anthracite over sand. The anthracite traps the larger particles and the finer solids were held up in the sand. Periodically, the forward flow was stopped and the filter was backwashed to remove the trapped solids.

Chapter (II)

Mass and Energy Balances

2.1 Introduction

Having looked through the Crude Oil Refining process, explaining each process and highlighting the importance of each process in chapter 1. This chapter is presenting a mass balance for each process and overall energy consumption for the oil refinery using UniSem simulation Programme. The diagram bellow shows the BFD of the refinery that is considered in this chapter.

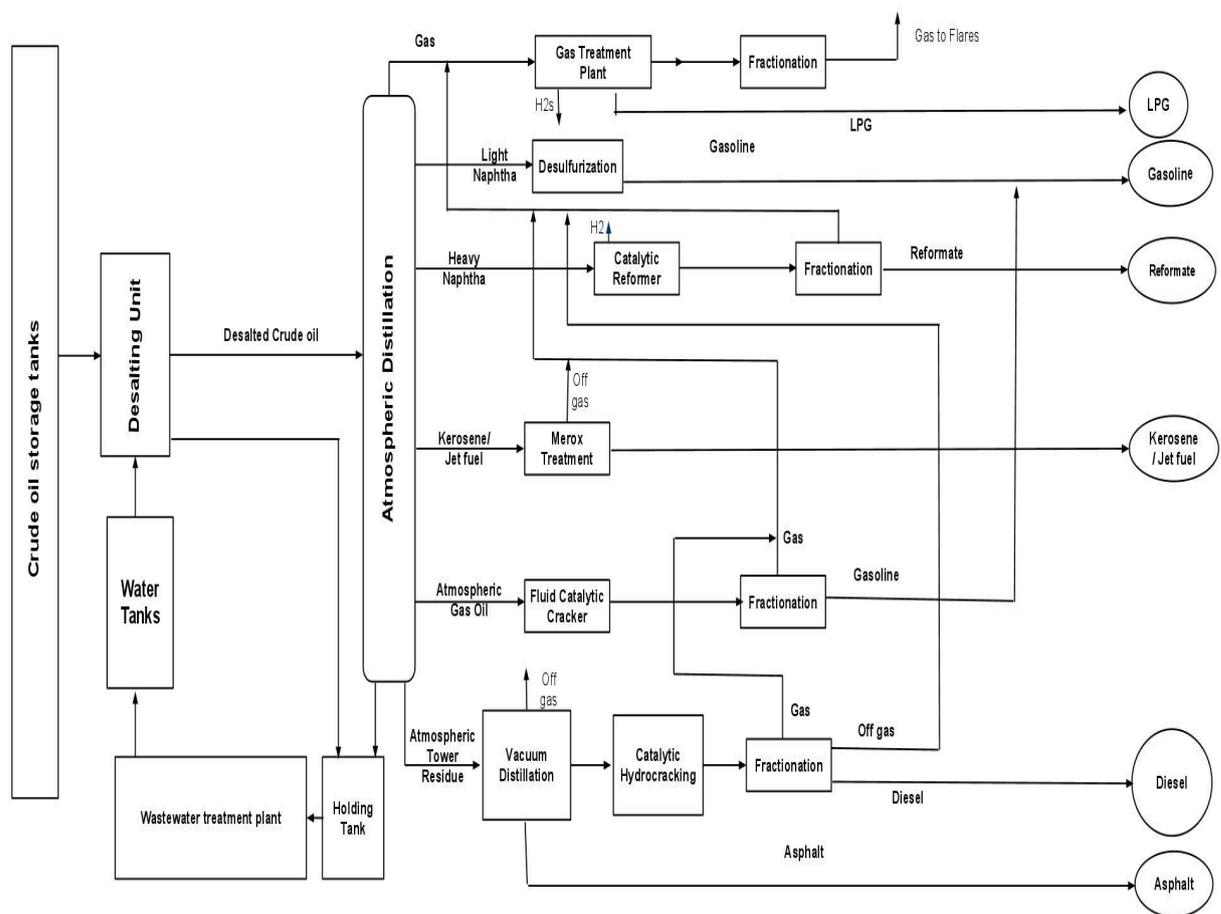


Figure 2.1: The Blok Flow Diagram of the refinery

2.2 Desalting Unit

Table 2.1: Desalting Unit.

MIX-101		
Conditions		
Temperature	(°C)	147
Pressure	(kPa)	517.1
Stream	IN (kgmole/day)	OUT(kgmole/day)
Crude Oil	135144	0
Water	263952	0
Desalter Feed	0	399096

Table 2.2: Desalting Unit Conditions.

Desalter		
Conditions		
Temperature	(°C)	244.2
Pressure	(kPa)	517
Stream	IN (kgmole/day)	OUT(kgmole/day)
Desalter Feed	399096	0
Desalted Crude	0	132480
Waste Water	0	266616

2.3 Atmospheric Distillation Column

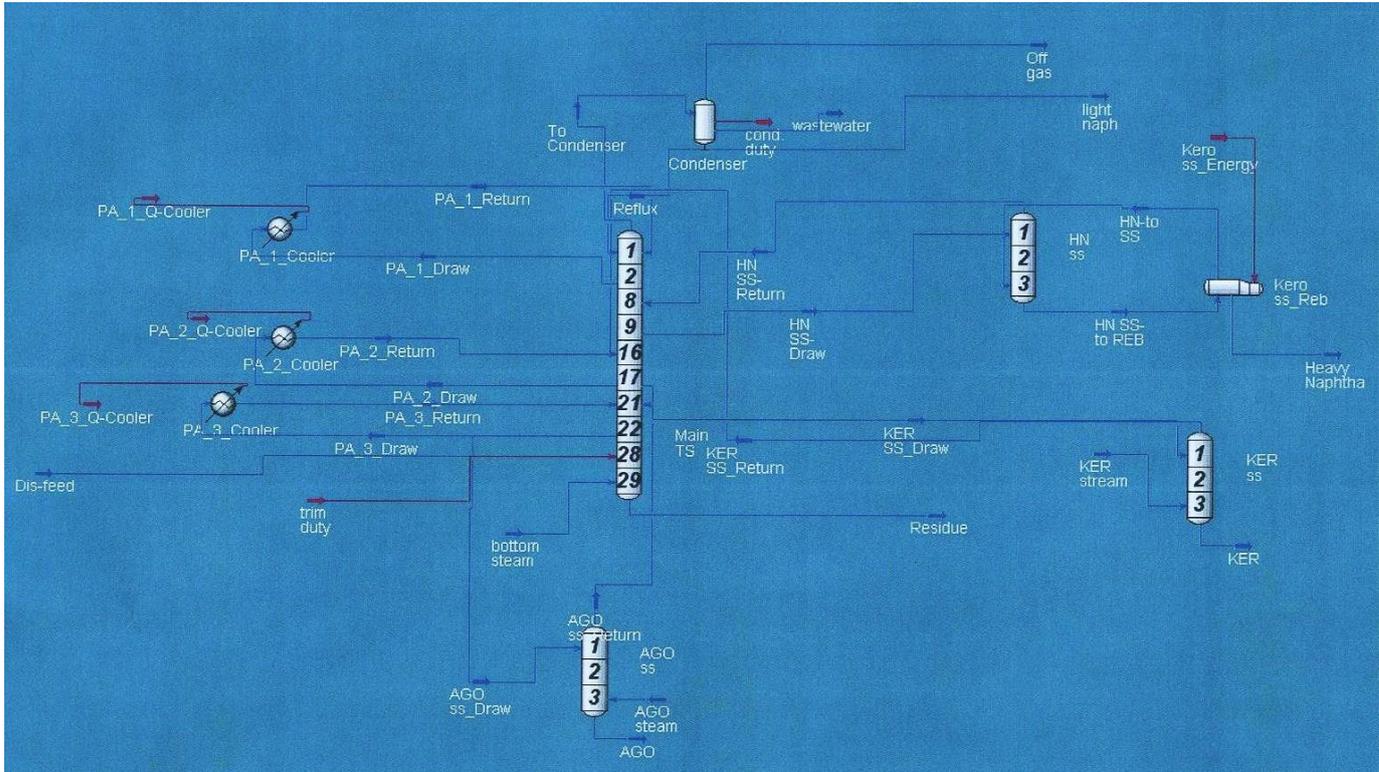


Figure 2.2: Atmospheric Distillation Column.

Table 2.3: Atmospheric Distillation Column.

Stream	IN(kgmole/hr)	OUT(kgmole/hr)
Dis-feed	132480.000	0.000
Off Gas	0.000	5000.005
Wastewater	0.000	21852.800
Light Naphtha	0.000	52186.400
Heavy Naphtha	0.000	21284.000
Kerosene	0.000	21514.400
AGO	0.000	5026.320
Residue	0.000	29168.000
Steam Streams	23551.925	0.000
Total	156031.925	156031.925

2.4 Desulfurization Unit

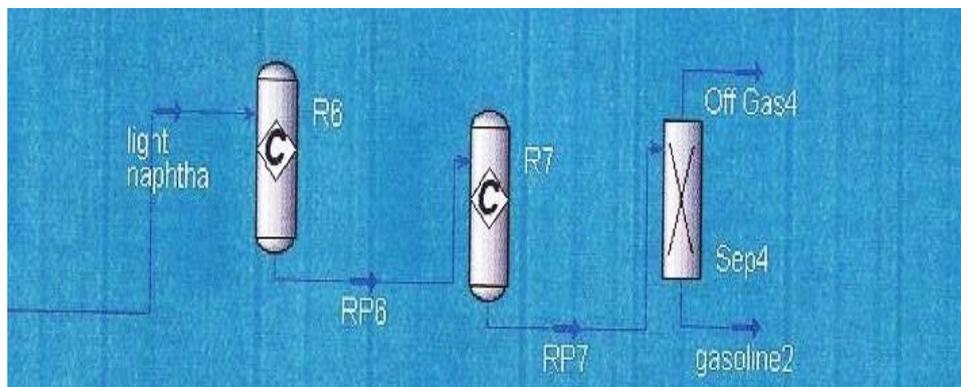


Figure 2.3: Desulfurization Unit.

Table 2.4: Desulfurization Unit.

Components	Composition (mol%)		
	Inlet	Outlet	Off gas
Paraffins	15	38	2
Olefins	23	9	10
Naphtha	20	17	13
Aromatics	18	25	18
Water	2	1	9
Impurities	12	1	8
Pentane	3	1	3
Hydrogen	4	7	31
Butane	3	1	6
Total	100	100	100

Table 2.5: Desulfurization Unit conditions

Conditions	Inlet	Outlet	Off gas
Temperature (°C)	74.46	150	150
Pressure (kPa)	135.8	131	1017
Molar Flow (kgmole/day)	53186.4	10382.4	39470.4

2.6 Merox Treating Unit

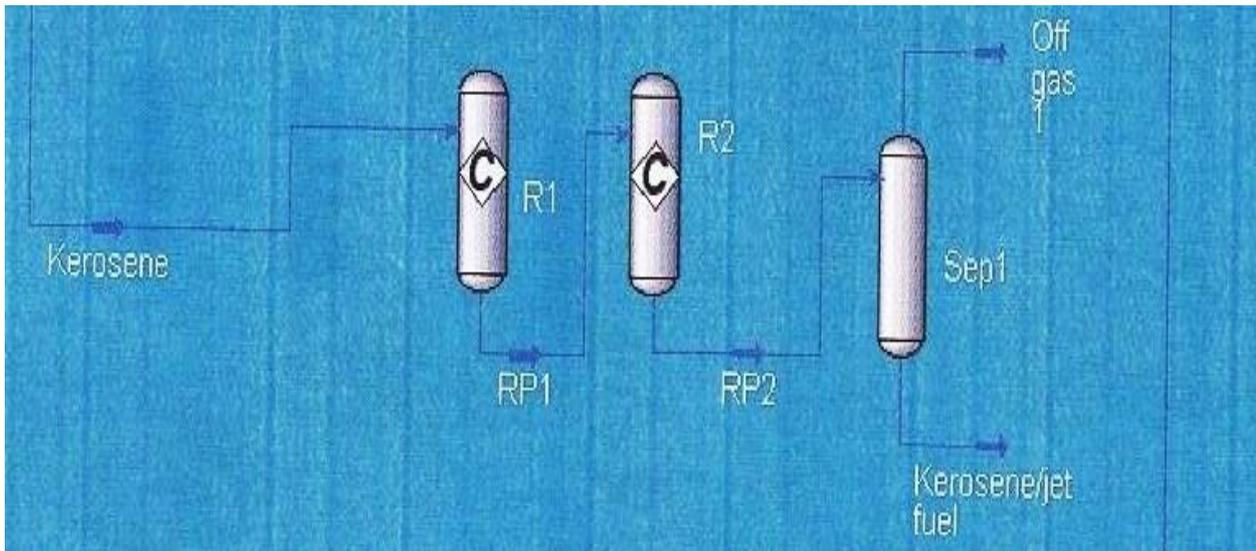


Figure 2.5: Merox Treating Unit

Table 2.8: Merox Treating Unit

Components	Composition (mol%)		
	Inlet	Outlet	Off gas
Aromatics	40	14	25
Olefins	30	62	10
Paraffins	23	18	4
Impurities	5	1	16
Hydrogen	2	5	45
Total	100	100	100

Table 2.9: Merox Treating Unit Conditions

Conditions	Inlet	Outlet	Off gas
Temperature (°C)	232	212	212.4
Pressure (kPa)	312.7	205.7	205.7
Molar Flow (kgmole/day)	22514.4	16912.8	5601.6

2.7 Fluid Catalytic Cracking Unit

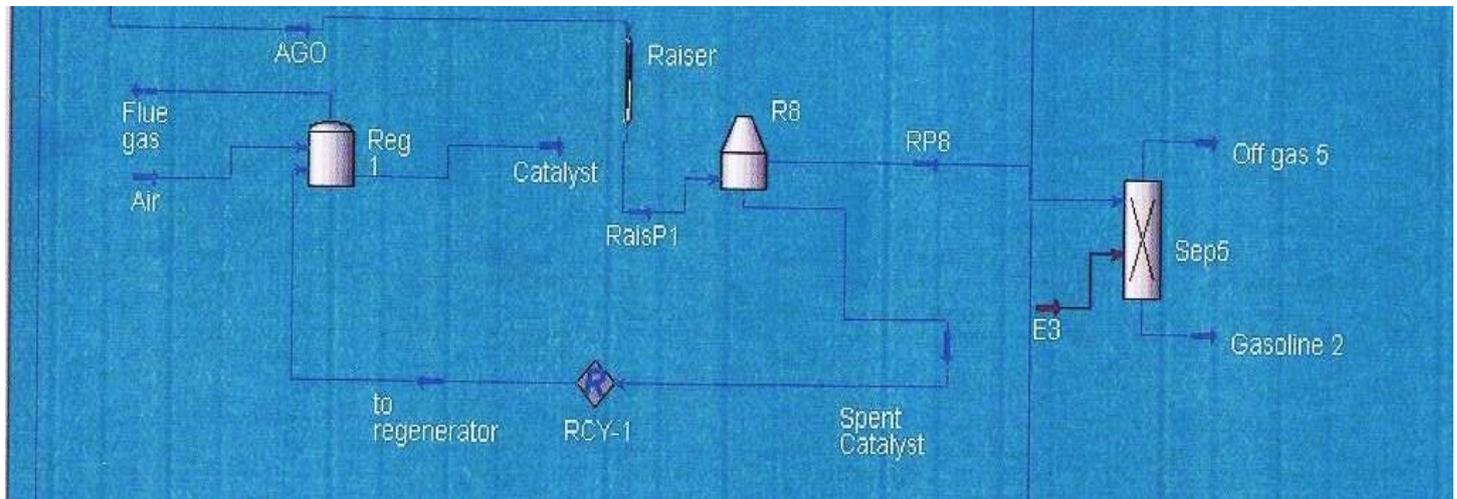


Figure 2.6: Fluid Catalytic Cracking Unit

Table 2.10: Fluid Catalytic Cracking Unit

Components	Compositions (mol%)		
	Inlet	Diesel	Off gas
Paraffins	28.6	4	13
Olefins	15.3	55	2
Naphtha	24.8	5	16
Aromatics	16.3	25	5
Water	3	1	12
Impurities	3	1	10
Pentane	2	1	5
Hydrogen	5	7	30
Butane	2	1	7
Total	100	100	100

Table 2.11: Fluid Catalytic Cracking Unit Conditions

Conditions	Inlet	Diesel	Off gas
Temperature (°C)	298	343.6	384.5
Pressure (kPa)	218.6	100	100
Molar Flow (kgmol/day)	5026.32	3395.52	1889.28

2.8 Vacuum Distillation Column

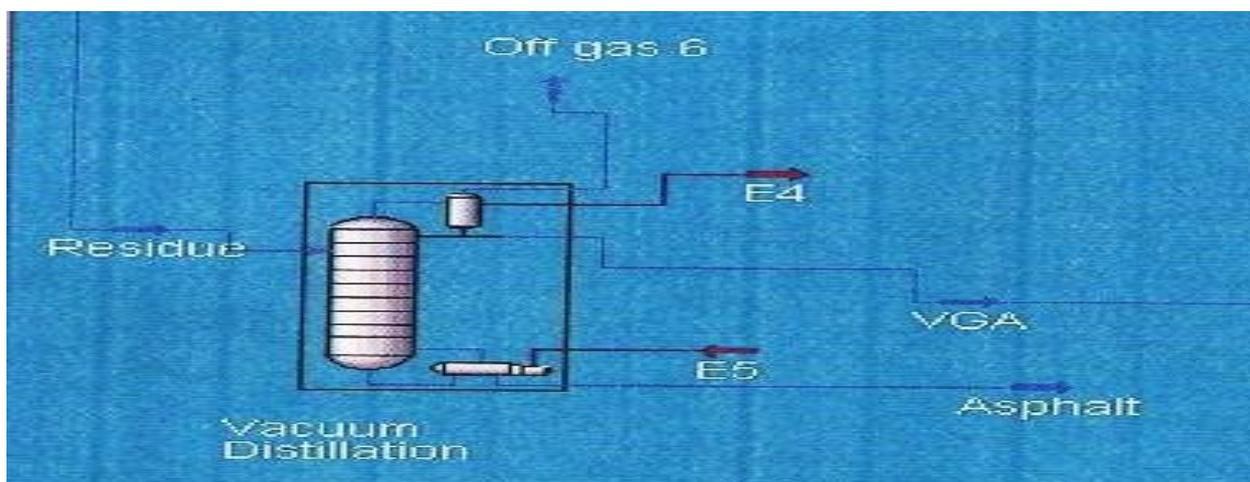


Figure 2.7: Vacuum Distillation Column

Table 2.12: Vacuum Distillation Column

Components	Off Gas
Propane	0.0000
i-Butane	0.0039
n-Butane	0.0026
i-Pentane	0.0012
n-Pentane	0.0016
Paraffins	21.6820
Aromatics	40.3640
Olefins	28.0824
Naphthenes	5.4670
H ₂ O	4.4205

Table 2.13: Vacuum Distillation Column Conditions

Conditions	Inlet	Outlet
Temperature (°C)	348.8	632.5
Pressure (kPa)	225.5	210
Molar Flow (kgmole/day)	30168	15768

2.9 Catalytic Hydrocracking

Figure 2.8: Catalytic Hydrocracking

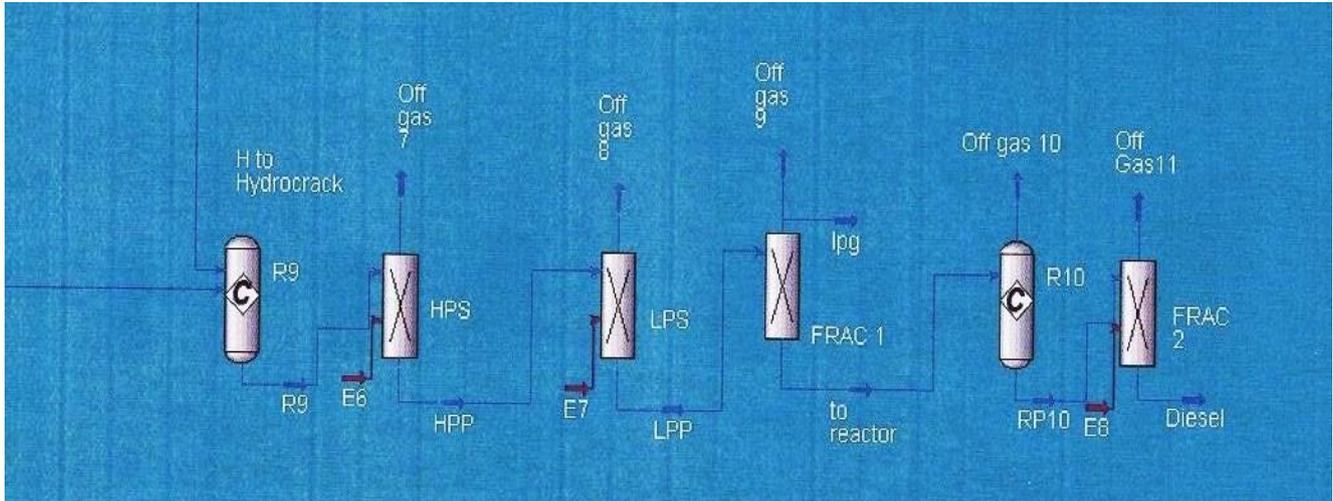


Table 2.14: Catalytic Hydrocracking

Components	Inlet (mol %)	Outlet (mol%)
Paraffins	20.10	63.40
Olefins	22.05	0.00
Aromatics	36.50	0.00
Naphthenes	18.84	36.60
Impurities	2.50	0.00
H2O	0.01	0.00
Total	100.00	100.00

Table 2.15: Catalytic Hydrocracking Conditions.

Conditions	Inlet	Outlet
Temperature (°C)	370	429.3
Pressure (kPa)	50	50
Molar Flow (kgmole/day)	7198.56	2332.08

2.10 Gas Plant

2.10.1 Amine Process

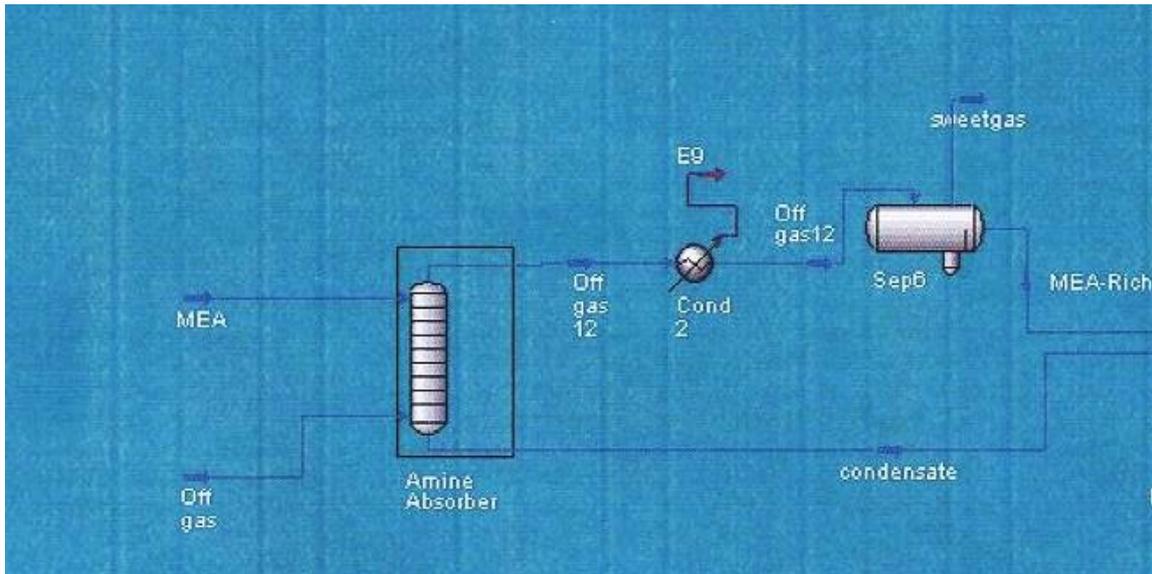


Figure 2.9: Amine Process

Table 2.16: Amine Process

Component (Mol %)	Composition					
	Off gas	MEA	Off gas 12	Condensate	Sweet gas	MEA-Rich
Methane	10	0	18	3	65	3
Ethane	5	0	12	1	15	5
Propane	2	0	5	1	2	9
Butane	11	0	4	8	3	10
Pentane	7	0	6	11	5	8
H2O	10	0	7	13	3	13
H2S	23	0	27	30	2	15
CO2	32	0	18	20	2	10
MEA	0	100	3	13	3	27
Total	100	100	100	100	100	100

Table 2.17: Amine Process Conditions

Stream	Temperature (°C)	Pressure (kPa)	Flow (kgmole/day)
Off Gas	100	500	119448
sweetgas	-150	100	105984
MEA	229.7	506.6	7920
Condensate	90.95	600	2936.16

2.10.2 Claus Process

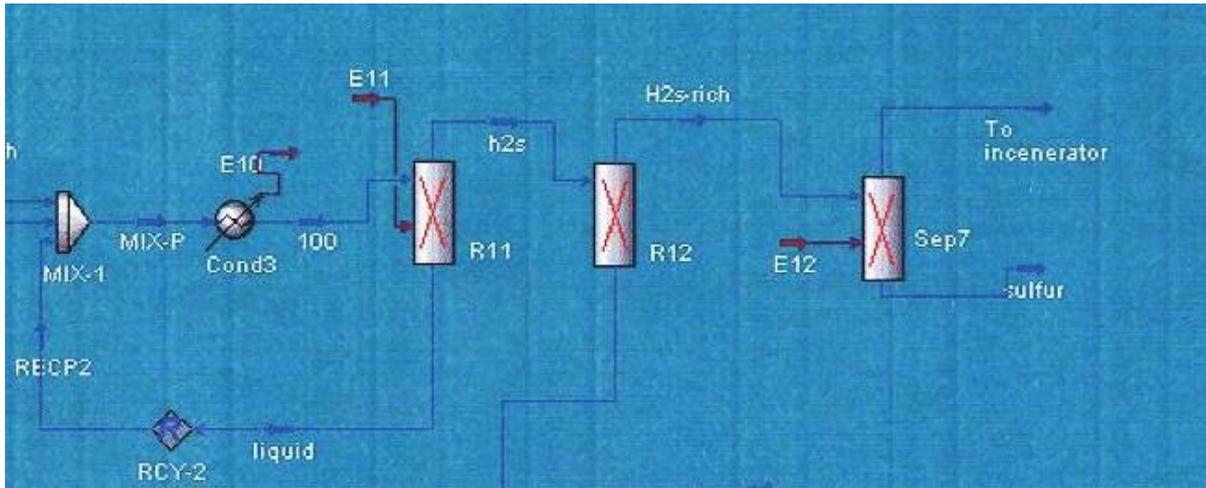


Figure 2.10: Claus Process

Table 2.18: Claus Process

Component (Mol %)	Composition			
	Mix-P	Sulfur	To Incinerator	LPG
Methane	1	0.2	2	3
Ethane	1	0.5	4	5
Propane	1	0.3	3	32
Butane	5	2	5	28
Pentane	7	3	6	22
H2O	13	12	3	5
H2S	34	60	14	1
CO2	24	12	39	1
MEA	14	10	24	3
Total	100	100	100	100

Table 2.19: Claus Process Conditions

Stream	Temperature (°C)	Pressure (kPa)	Flow (kgmole/day)
100	100	50	801360
h2s	-31.87	100	13471.2
liquid	170	100	79992
H2s-rich	-95.96	100	3867.84
To incenerator	-90.54	100	2300.4
Sulfur	-105.3	100	1567.44
LPG	-80.05	100	9604.8

2.11 Fractionation Train

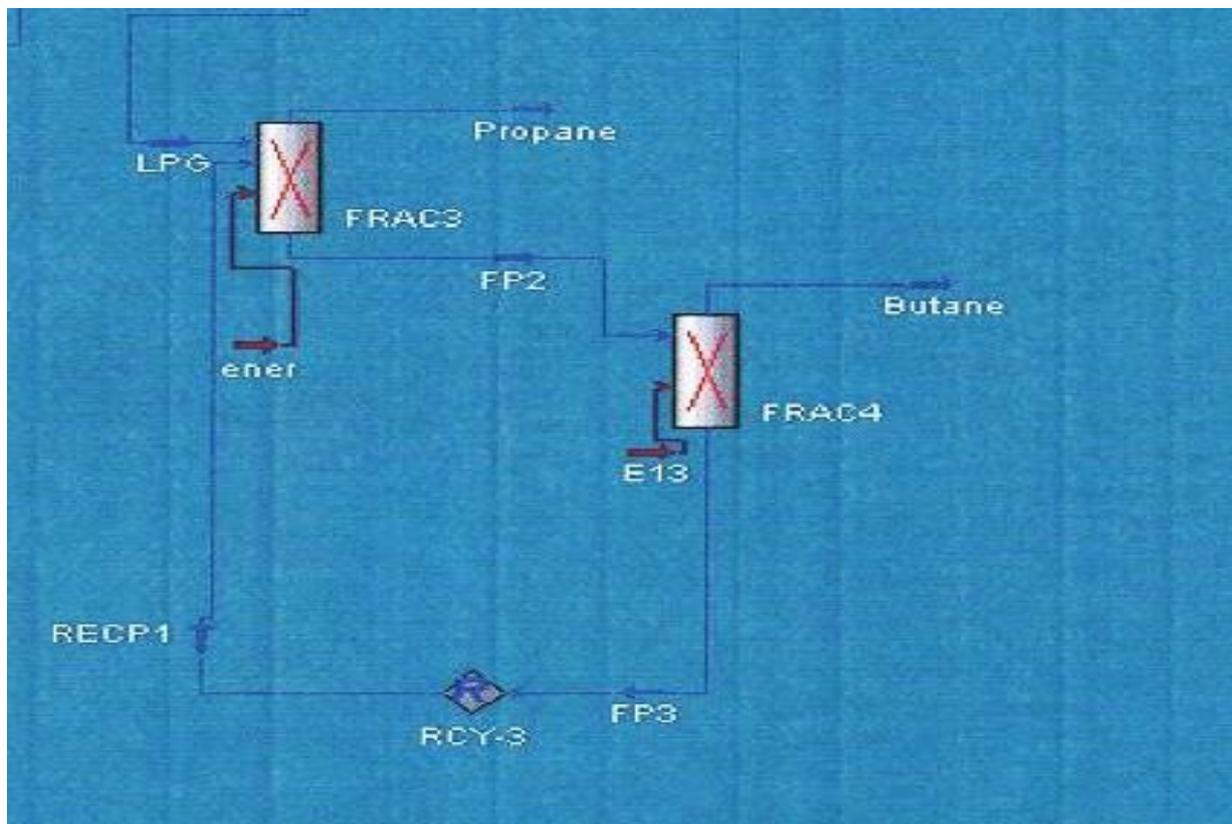


Figure 2.11: Fractionation Train

2.11.1 Depropanizer

Table 2.20: Depropanizer composition

Component (Mol %)	Composition	
	Propane	Fp2
Methane	2	8
Ethane	3	5
Propane	75	3
Butane	7	52
Pentane	2	10
H2O	4	10
H2S	5	6
CO2	1	5
MEA	1	1
Total	100	100

2.11.2 Debutanizer

Table 2.21: Debutanizer composition

Component (Mol %)	Composition	
	Butane	Fp3
Methane	2	5
Ethane	1	7
Propane	1	20
Butane	73	6
Pentane	3	5
H2O	5	10
H2S	4	20
CO2	7	22
MEA	5	5
Total	100	100

Table 2.22: Fractionation train Conditions

Stream	Temperature (°C)	Pressure (kPa)	Flow (kgmole/day)
Propane	-44.2	100	5806.8
Butane	-9.461	100	3591.36

2.12 Wastewater Treatment Plant

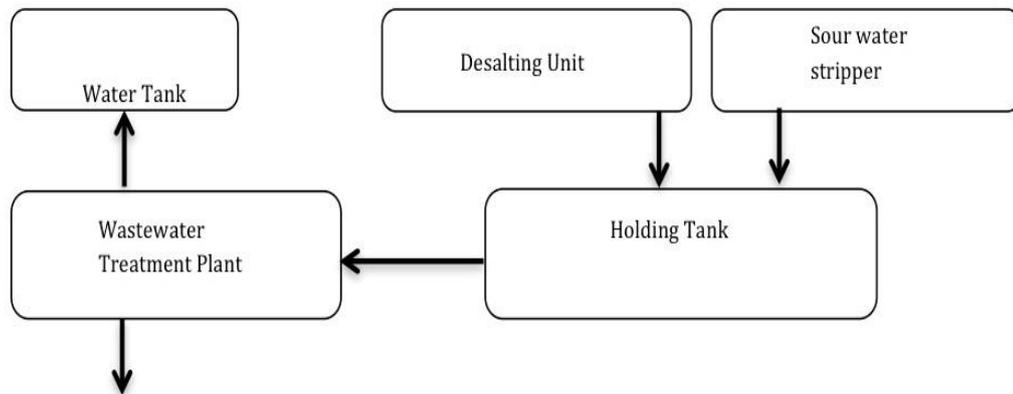


Figure 2.12: Wastewater Treatment Plant

Assumptions

- 1- No chemical Reaction.
- 2- Atmospheric Pressure.
- 3- Temperature was 45 °C.
- 4- 90% of wastewater feed goes to the water thank.
- 5- Basis of 0.5-liter of solution.

Table 2.23: Wastewater output from desalter unit.

Component	mg/l (standard)	Xmol	(kgmole/day)
O ₂	800	0.0005	120.189
Hydrocarbons	1000	6 x10 ⁻⁵	16.025
Solids	500	0.0002	40.010
Phenols	50	1 x10 ⁻⁵	2.557
Benzene	10	2 x10 ⁻⁶	0.616
Sulphate	100	2 x10 ⁻⁵	5.004
Ammonia	100	0.0001	28.280
Water	-	0.9992	266403.318
Total	-	1	266616

Table 2.24: Wastewater output from sour water stripper unit.

Component	mg/l (standard)	Xmol	kgmole/day
O ₂	1000	0.0006	295.184
Hydrocarbons	10	6×10^{-7}	0.315
Solids	10	3×10^{-6}	1.572
Phenols	200	4×10^{-5}	20.098
Sulphate	10	2×10^{-6}	0.983
Ammonia	100	0.0001	55.564
H ₂ S	1	1×10^{-6}	0.673
Water	-	0.9993	524073.610
Total	-	1	524448

Table 2.25: Wastewater total feed.

Component	Xmol	Kgmole/day
O ₂	0.0005	415.373
Hydrocarbons	2×10^{-5}	16.340
Solids	5×10^{-5}	41.582
Phenols	3×10^{-5}	22.655
Benzene	8×10^{-7}	0.616
Sulphate	8×10^{-6}	5.987
Ammonia	0.0001	83.844
H ₂ S	9×10^{-7}	0.673
Water	0.9993	790476.9286
Total	1	791064

Table 2.26: Treated water.

Component	mg/l (standard)	Xmol	kgmol/day
O ₂	200	0.0001	80.106
Hydrocarbons	10	6×10^{-7}	0.427
Solids	45	1×10^{-5}	9.600
Phenols	1	2×10^{-7}	0.136
Benzene	0	0	0
Sulphate	0.5	9×10^{-8}	0.067
Ammonia	10	1×10^{-5}	7.539
H ₂ S	0.185	2×10^{-7}	0.169
Water	-	0.9999	711859.556
Total	-	1	711957.6

Table 2.27: Contaminated water.

Component	mg/l	Xmol	kgmol/day
O ₂	720	0.0454	3589.517
Hydrocarbons	496	0.0033	263.763
Solids	214.5	0.0072	569.575
Phenols	124.1	0.0027	210.619
Benzene	5	0.0001	10.227
Sulphate	54.55	0.0011	90.586
Ammonia	91	0.0108	853.977
H ₂ S	0.33	5×10^{-5}	3.790
Water	-	0.9293	73514.346
Total	-	1	79106.4

2.13 Overall energy consumption

Table 2.27: Overall Energy Consumption

Stream Name	Heat Flow (kJ/h)	Power (kW)
Ene-1	1.94E+08	5.40E+04
trim duty	4.07E+07	1.13E+04
cond. duty	7.17E+07	1.99E+04
E1	1.64E+07	4.54E+03
E2	2.33E+07	6.47E+03
E3	6.78E+06	1.88E+03
E4	5.17E+06	1.44E+04
E5	2.47E+08	6.85E+04
E6	3.75E+06	1.04E+03
E7	1.05E+06	2.91E+02
E8	9.55E+06	2.65E+03
Total	6.19E+08	1.85E+05