REFINING CRUDE OIL

New Zealand buys crude oil from overseas, as well as drilling for some oil locally. This oil is a mixture of many hydrocarbons that has to be refined before it can be used for fuel. All crude oil in New Zealand is refined by The New Zealand Refining Company at their Marsden Point refinery where it is converted to petrol, diesel, kerosene, aviation fuel, bitumen, refinery gas (which fuels the refinery) and sulfur.

The refining process depends on the chemical processes of distillation (separating liquids by their different boiling points) and catalysis (which speeds up reaction rates), and uses the principles of chemical equilibria. Chemical equilibrium exists when the reactants in a reaction are producing products, but those products are being recombined again into reactants. By altering the reaction conditions the amount of either products or reactants can be increased.

Refining is carried out in three main steps.

Step 1 - Separation
The oil is separated into its constituents by distillation, and some of these components (such as the refinery gas) are further separated with chemical reactions and by using solvents which dissolve one component of a mixture significantly better than another.

Step 2 - Conversion
The various hydrocarbons produced are then chemically altered to make them more suitable for their intended purpose. For example, naphthas are "reformed" from paraffins and naphthenes into aromatics. These reactions often use catalysis, and so sulfur is removed from the hydrocarbons before they are reacted, as it would 'poison' the catalysts used. The chemical equilibria are also manipulated to ensure a maximum yield of the desired product.

Step3 - Purification
The hydrogen sulfide gas which was extracted from the refinery gas in **Step 1** is converted to sulfur, which is sold in liquid form to fertiliser manufacturers.

The plant at Marsden Point also manufactures its own hydrogen and purifies its own effluent water. This water purification, along with gas 'scrubbing' to remove undesirable compounds from the gases to be discharged into the atmosphere, ensures that the refinery has minimal environmental impact.

INTRODUCTION

Our modern technological society relies very heavily on fossil fuels as an important source of energy. Crude oil as it comes from the ground is of little use and must undergo a series of refining processes which converts it into a variety of products - petrol for cars, fuel oil for heating, diesel fuels for heavy transport, bitumen for roads.

The NZ Refining Company, situated 40 km from Whangarei at Marsden Point, processes about 4 500 000 tonnes of oil per year. About 90% of the feedstock comes from overseas, and about 10% is the local crude obtained as a byproduct from the production of natural gas at Kapuni. The sources of oil used are given in **Table 1**.

In this chapter we will describe the physical and chemical processes by which New Zealand's refinery converts crude oil into the variety of useful products required to meet New Zealand's needs.

Table 1 - Feedstocks used at the Marsden Point refinery (1992 figures)

Origin	Quantity / kT	% Wt.
Indigenous feedstock	888	19.8
Foreign crudes	2464	55.2
Synthetic gasoline	419	9.4
Other	700	15.6
Total	**4471**	**100**

Uses of refined oil

The refinery produces a range of petroleum products. These are listed on the simplified flow scheme of the refinery in **Figure 1**, and the relative quantities made are given in **Table 2**.

Table 2 - Products (1994 figures)

Type	Quantity / kT	% Wt
Super or Premium petrol	732	15.0
Regular petrol	640	14.6
Jet/DPK	669	15.2
Diesel oil	1482	31.0
Fuel oils	478	10.0
Bitumen	144	3.0
Sulfur	23	1.0
Exports	143	3.0
Refinery fuel and loss	317	7.0
Total	**4716**	**100**

Petrol

Petrol (motor gasoline) is made of cyclic compounds known as naphthas. It is made in two grades: Regular (91 octane) and Super or Premium (96 octane), both for spark ignition engines. These are later blended with other additives by the respective petrol companies.

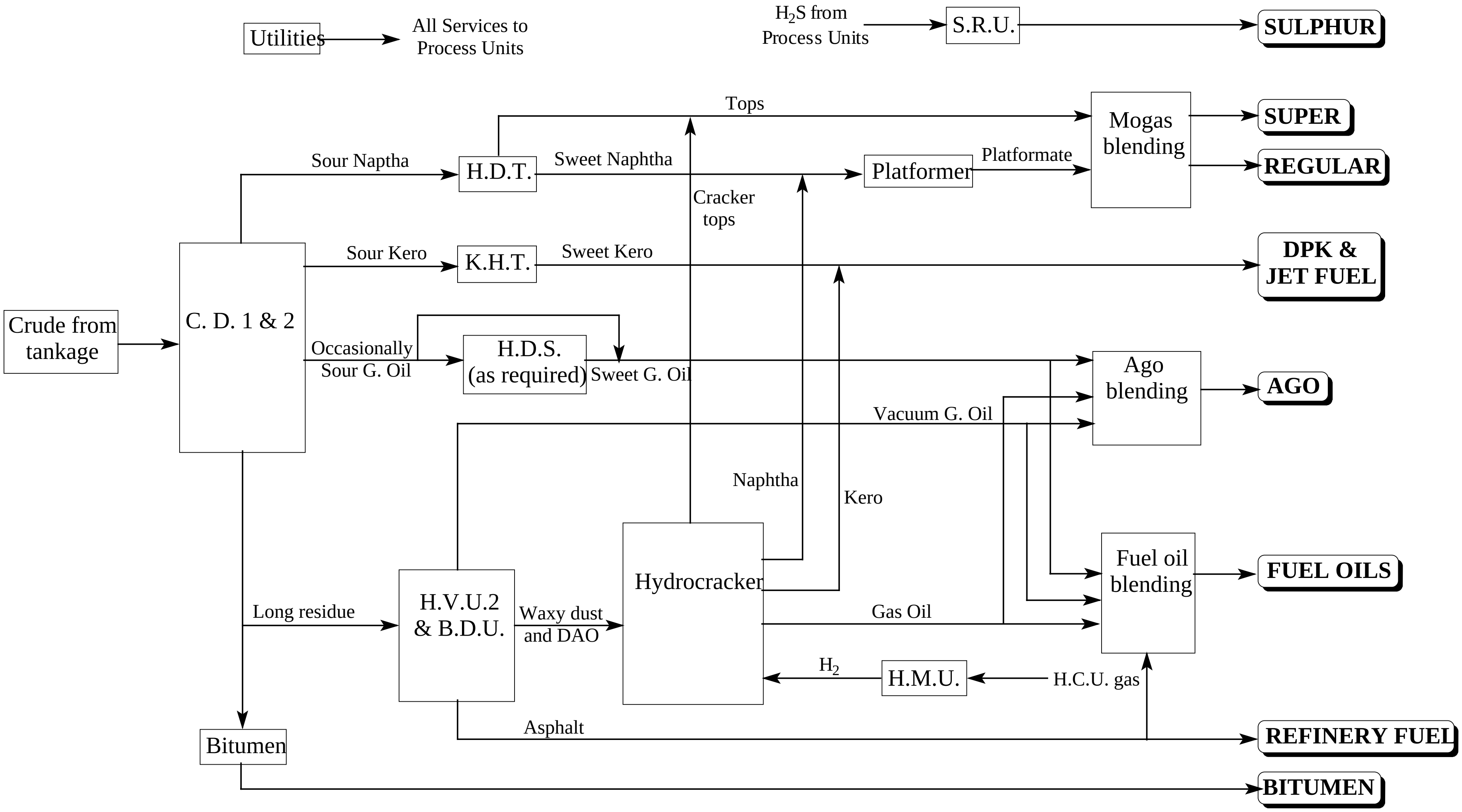


Figure 1 - Schematic representation of the Marsden Point Refinery

AGO = Automotive Gas Oil
B.D.U. = Butane deasphalting unit
C.D.1 & 2 = Crude distillation units
D.A.O. = Deasphalted oil

H.C.U. = Hydrocracking unit
H.D.S. =
H.D.T. =
H.M.U. = Hydrogen manufacturing unit

H.V.U.2 = High vacuumdistillation unit
K.H.T. =
S.R.U. = Sulfur recovery unit

Jet fuel/Dual purpose kerosene
The bulk of the refinery produced kerosene is high quality aviation turbine fuel (Avtur) used by the jet engines of the domestic and international airlines. Some kerosene is used for heating and cooking.

Diesel Oil
This is less volatile than gasoline and is used mainly in compression ignition engines, in road vehicles, agricultural tractors, locomotives, small boats and stationary engines. Some diesel oil (also known as gas oil) is used for domestic heating.

Fuel Oils
A number of grades of fuel oil are produced from blending. Lighter grades are used for the larger, lower speed compression engines (marine types) and heavier grades are for boilers and as power station fuel.

Bitumen
This is best known as a covering on roads and airfield runways, but is also used in industry as a waterproofing material.

Sulfur
Sulfur is removed from the crude during processing and used in liquid form in the manufacture of fertilisers (see article).

THE REFINING PROCESS

The Marsden Point refinery takes crude oil and refines it by first separating it into its various constituents, then converting the undesirable elements to desirable ones before purifying them to make the final products. These processes are based on some chemical principles which are outlined below.

Chemical principles

The processes used to refine oil are based on the chemical principles which govern distillation, and require an understanding of chemical equilibria and the effect on reaction rates of catalysts. The theory behind these is outlined below.

Fractional distillation
When a mixture of two liquids of different boiling points is heated to its boiling point, the vapour contains a higher mole fraction of the liquid with the lower boiling point than the original liquid; i.e. the vapour is enriched in the more volatile component. If this vapour is now condensed, the resultant liquid has also been enriched in the more volatile component. For example, if a 1:1 molar mixture of benzene (b.p. 80.1^{o}C) and toluene (b.p. 110.6^{o}C) is heated it boils at a temperature of 92.2^{o}C and the composition of the vapour (and hence its condensate) is 71.3 : 28.7 benzene:toluene. If this vapour is condensed and then brought to its boiling point its vapour has a mole ration of 86.4 : 13.6. A third cycle produces a condensate of 94.4 : 5.6 benzene:toluene. This is the principle of batch fractional distillation, and in a distillation column many, many such cycles are performed continuously, allowing almost complete separation of liquid components. In this process the more volatile components are drawn from the top of the column and the the least volatile ones concentrate in the lower part. In practice, the distillation is carried out continuously. A generalised distillation column is shown in **Figures 2** and **3**.

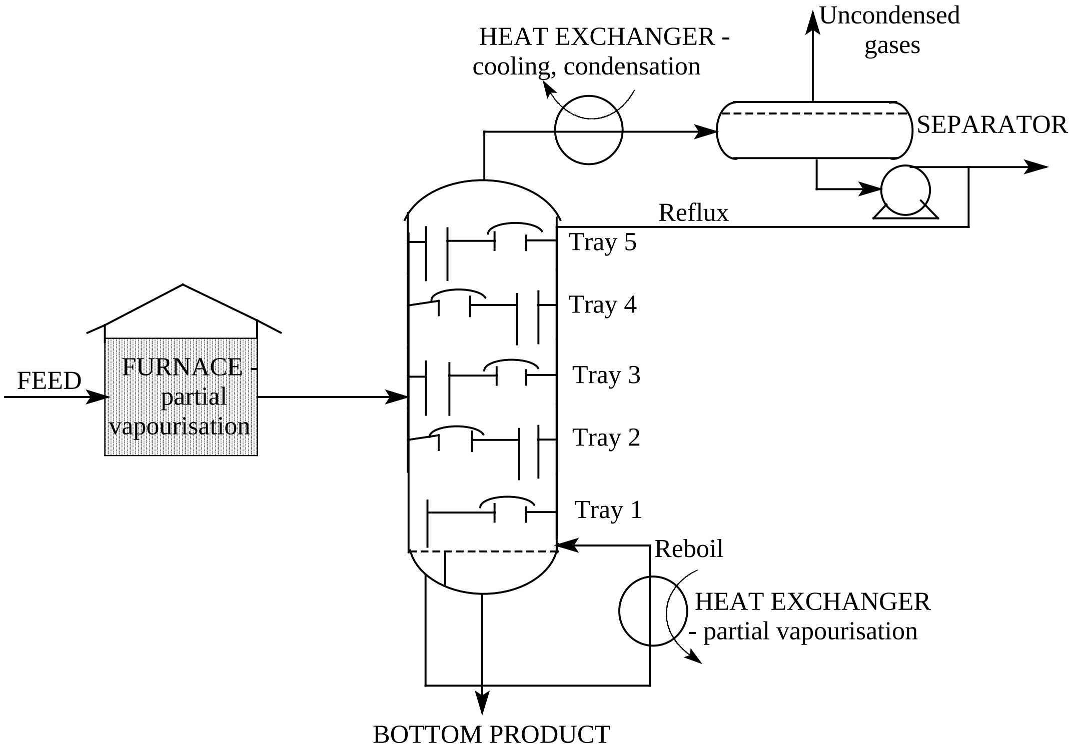


Figure 2 - Fractional distillation

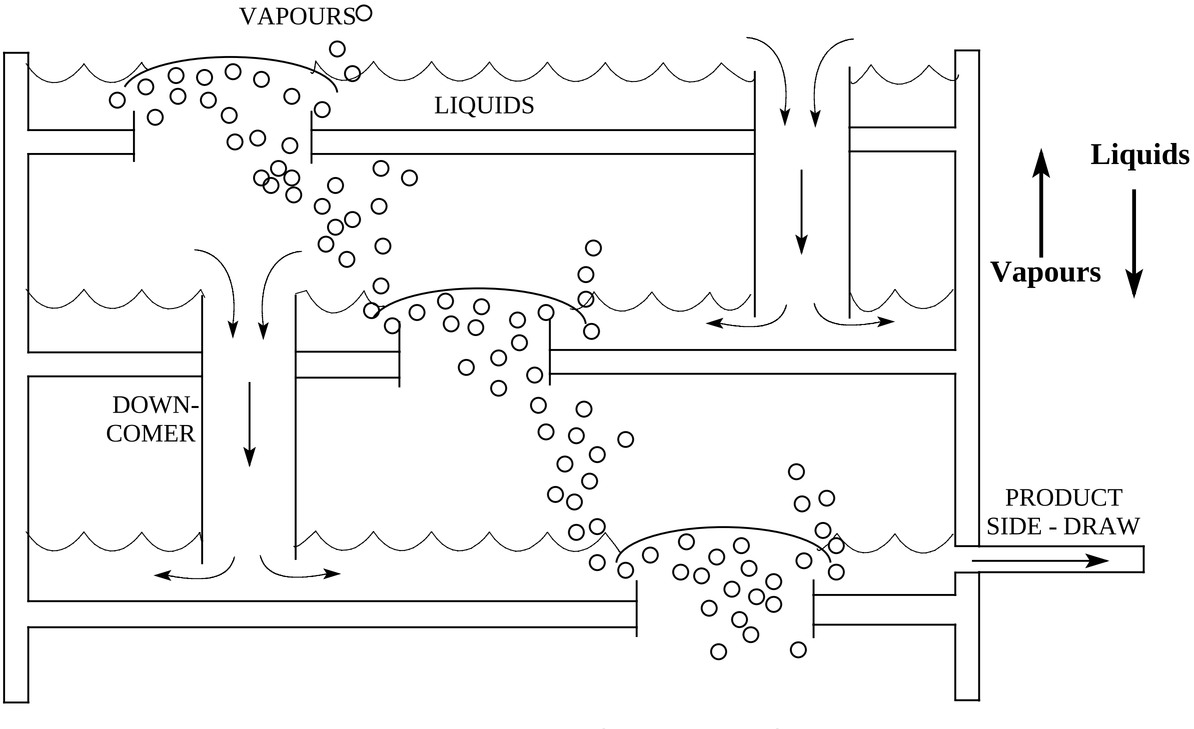


Figure 3 - Schematic representation of the inside of the distillation column

When two species A and B (A more volatile than B) are fed into the distillation column and heated partial vapourisation occurs. The vapour, richer in A, rises from the feed tray (tray 3) through the bubble caps, bubbling through the liquid on tray 4, setting up a vapour/liquid equilibrium. Tray 4 is cooler than tray 3, so some of component B will condense, leaving the vapour rising from tray 4 richer in A. The same process is repeated on tray 5, and we are left with a vapour leaving tray 5 very much richer in component A than was the original feed. To keep a temperature differential between the trays, the top vapour leaving tray 5 is condensed by cooling it, and some is fed back to the top of the column, the remainder leaving as the top product.

The liquid portion of the feed entering the column falls from tray 3 to tray 2, which is hotter than the feed tray 3. On tray 2, because of the increase in temperature, the vapour is richer in A than the liquid, so the composition of the liquid on tray 2 is richer in component B than the original feed. This liquid falls to tray 1, where the process is repeated. To ensure that the temperature falls from tray to tray going up the column, some of the bottom product (rich in B) is heated and fed back to the bottom tray. The remainder leaves as bottom product rich in B.

Thus, by the use of cooled top product (reflux) and heated bottom product (reboil) the temperature difference between trays is maintained, and fractional distillation occurs. It can also be seen that liquid drawn from any of the trays will contain varying concentrations of A and B, changing from a mixture rich in B at the bottom tray, to a mixture rich in A at the top tray.

In distilling petroleum we are considering not just 2 components, but many components. However, the same principles apply and by feeding heated oil to a fractional distillation column, we can, by withdrawing liquid from various trays, separate the oil into varying fractions. However, when withdrawing liquid from intermediate trays, some of the light product that bubbles through the liquid on each tray is present. This can be removed by passing steam through the withdrawn fraction in a small distillation column (called a stripper). The mixture of steam and light material obtained as a top product from the stripper is returned to the main distillation column.

Figure 2 shows only 5 trays with 1 bubble cap per tray. In practice, several tens of trays are used, with of the order of 100 caps per tray.

Chemical equilibrium

Many chemical reactions are reversible, i.e. the products react to reform the reactants. When the reactants are mixed products start to form. As the reactant concentrations decrease and the product concentrations increase, the rate of the forward reaction decreases and the rate of the back reaction increases, reforming the reactants. In a closed system where neither products nor reactants can escape, a state of dynamic chemical equilibrium is eventually reached where the rates of the forward and back reactions are equal (thus meaning that the quantities of reactants and products remain the same) and no apparent change is occurring. For the reaction:

$$aA + bB \leftrightarrows cC + dD$$

where A and B are reactants, C and D are products and a, b, c, d are the stoichiometric coefficients (i.e. the numbers in the chemical equation), the concentrations of reactants and products existing at equilibrium are related by the equation:

$$K = \frac{[C\,]^c\,[D\,]^d}{[A\,]^a\,[B\,]^b}$$

where K is called the equilibrium constant. The value of K is extremely important to the chemist since it shows the extent to which the reactants can be converted into products under a given set of conditions.

Since chemical reactions are employed generally to convert reactants into desirable products, chemists try to convert as much of the reactants as possible into products. Alteration of the conditions of a system is one method whereby the yield of desirable products may be increased. The effect of changes to the system can be predicted by Le Chatelier's principle which states: "If a change is made to a system in equilibrium, the system will adjust itself so as to overcome the effects of the change."

In practice this means that if, for example, reaction products are removed from the system, the reaction can proceed to completion, i.e. all of A and B can be reacted to produce C and D. Also alterating the pressure of a gaseous reaction mixture, where the total number of moles of reactants differ from the total number of moles of products, causes the concentrations at equilibrium to change. If the total number of moles of products is less than the total number of moles of reactants, an increase in pressure will cause the reaction to move to the right. Temperature also affects equilibrium concentrations. The value of the equilibrium constant K changes with temperature. Using Le Chatelier's principle we can see that increase in temperature will cause the reaction to shift to the right if the forward reaction is endothermic (i.e. heat is 'used up' in the reaction).

Reaction Rates and Catalysts

Knowledge of the value of the equilibrium constant K at different temperatures is important to the chemist as it enables prediction of equilibrium concentrations to be made. However, such knowledge does not enable predictions to be made as to the rate at which equilibrium is attained. In industrial processes it is not unusual for equilibrium never to be attained, as the reaction rates are low.

We may consider a reaction taking place *via* the formation of an activated complex which decomposes into the reaction products. Formation of the activated complex requires rearrangement of the molecular structure of the reactants, which requires additional energy, called the activation energy of the reaction. The further rearrangement of the molecular structure of the activated complex to form products also has an associated energy change.

Assuming that the decomposition of the activated complex is fast, the rate at which the activated complex is formed will govern the overall reaction rate. Thus, if a different activated complex can be formed, a different reaction rate will result. A catalyst is a substance that enables a different, easier-to-form activated complex to be formed, and thus increases the overall reaction rate. Put another way a new faster chemical pathway (or mechanism) from reactants to products is possible. The activated complex can be thought of as a combination of A, B and catalyst.

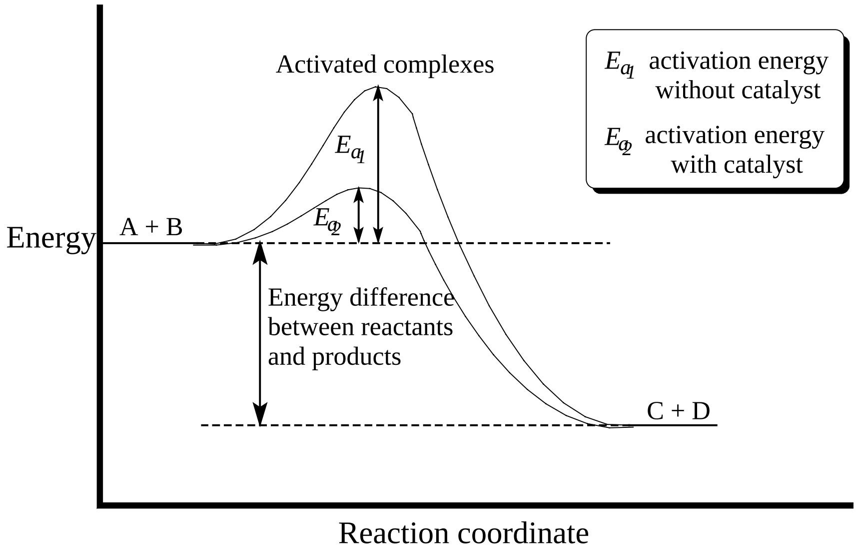


Figure 4 - Reaction pathways with and without a catalyst

The rate of formation of the activated complex with catalyst is faster than the rate of formation of the complex without catalyst. Thus by finding a suitable catalyst, the overall reaction rate can be speeded up. The search for suitable catalysts for various reactions is an important part of industrial research. (**Figure 4** just shows the reaction as one step for simplicity. In fact both catalysed and uncatalysed reactions probably occur in a series of steps, with the activation energy being the difference between the energy of the reactants and the highest barrier.)

In general all reactions go faster at higher temperature, and the rate of increase with temperature is greater the higher the activation energy. Thus many reactions which are too slow at room temperature go at an appreciable rate at elevated temperatures.

Step 1 - Separation

The oil is separated by boiling points into six main grades of hydrocarbons: refinery gas (used for refinery fuel), gasoline (naphthas), kerosene, light and heavy gas oils and long residue. This initial separation is done by distillation. The long residue is further separated in the butane desaphalting unit, and the refinery gas is separated into hydrogen sulfide in the Shell ADIP process.

Distillation

The first step in the refining of crude oil, whether in a simple or a complex refinery, is the separation of the crude oil into fractions (fractionation or distillation). These fractions are mixtures containing hydrocarbon compounds whose boiling points lie within a specified range. A continuous flow of crude oil passes from the storage tanks through a heating coil inside a furnace, where it is heated to a predetermined temperature. The heated oil then enters the fractionating column (**Figures 2 and 3**), which is a tall cylindrical tower containing trays suitably spaced and fitted with vapour inlets and liquid outlets.

Upon entering the column, the liquid/vapour mixture separates - the vapour passing upwards through the column, the liquid portion flowing to the bottom from where it is drawn off as "long residue". The vapours rise through the tray inlets, become cooler as they rise, and partially condense to a liquid which collect on each tray. Excess liquid overflows and passes through the liquid outlets onto the next lower tray. The bottom of the column is kept very hot but temperatures gradually reduce towards the top so that each tray is a little cooler than the one below it.

Ascending hot vapours and descending cooler liquids mix on each tray and establish a temperature gradient throughout the length of the column. When a fraction reaches a tray where the temperature corresponds to its own particular boiling range, it condesnses and changes into liquid. In this way the different fractions are separated from each other on the trays of the fractionating column and are drawn off for further treatment and blending.

The fractions that rise highest in the column before condensing are called light fractions, and those that condense on the lowest trays are called heavy fractions. The very lightest fraction is refinery gas, which is used as a fuel in the refinery furnaces. Next in order of volatility comes gasoline (used for making petrol), kerosene, light and heavy gasoils and finally long residue.

High vacuum distillation unit

This works on the principle that lowring the pressure lowers the boiling point of the compounds concerned. This is used to separate gasoline into gasoline (which boils under these conditions) and short residue (a mixture of asphaltic compounds and oil which does not).

The butane deasphalting unit (BDU)

The BDU uses a solvent extraction process to separate the gasoline and asphaltic compounds in the short residue. The short residue from the high vacuum distillation unit is mixed with liquid butane (a 2:1 mixture of *n*-butane and *iso*-butane) at a specified temperature and pressure close to the critical point of butane. Two liquid phases are formed, one rich in butane containing the extracted oil (Deasphalted Oil - DAO), the other of asphaltic compounds with low butane and oil content (ASPHALT).

The extraction column operates isothermally (without change in temperature) and has a continuous butane rich phase with droplets of the asphaltic phase mixed into it. The density difference between phases drives the dispersed phase downwards in countercurrent flow to the continuous phase which is being forced upwards. This makes an interface level form in the bottom where the two phases are forced past each other. The extractor has perforated trays to enhance the contacting of the two liquid phases, and the butane solvent is recovered from the two phases (DAO and ASPHALT) by flashing and stripping to be recycled for reuse. A diagram of the BDU is given in **Figure 5**.

Butane has been selected as the optimum solvent because it provides the highest deasphalted oil yield with good selectabilily at low solvent-to-feed ratios. The butane easily dissolves the lower boiling hydrocarbons, but its solvent power is limited with respect to the higher boiling hydrocarbons, especially aromatic and asphaltic compounds.

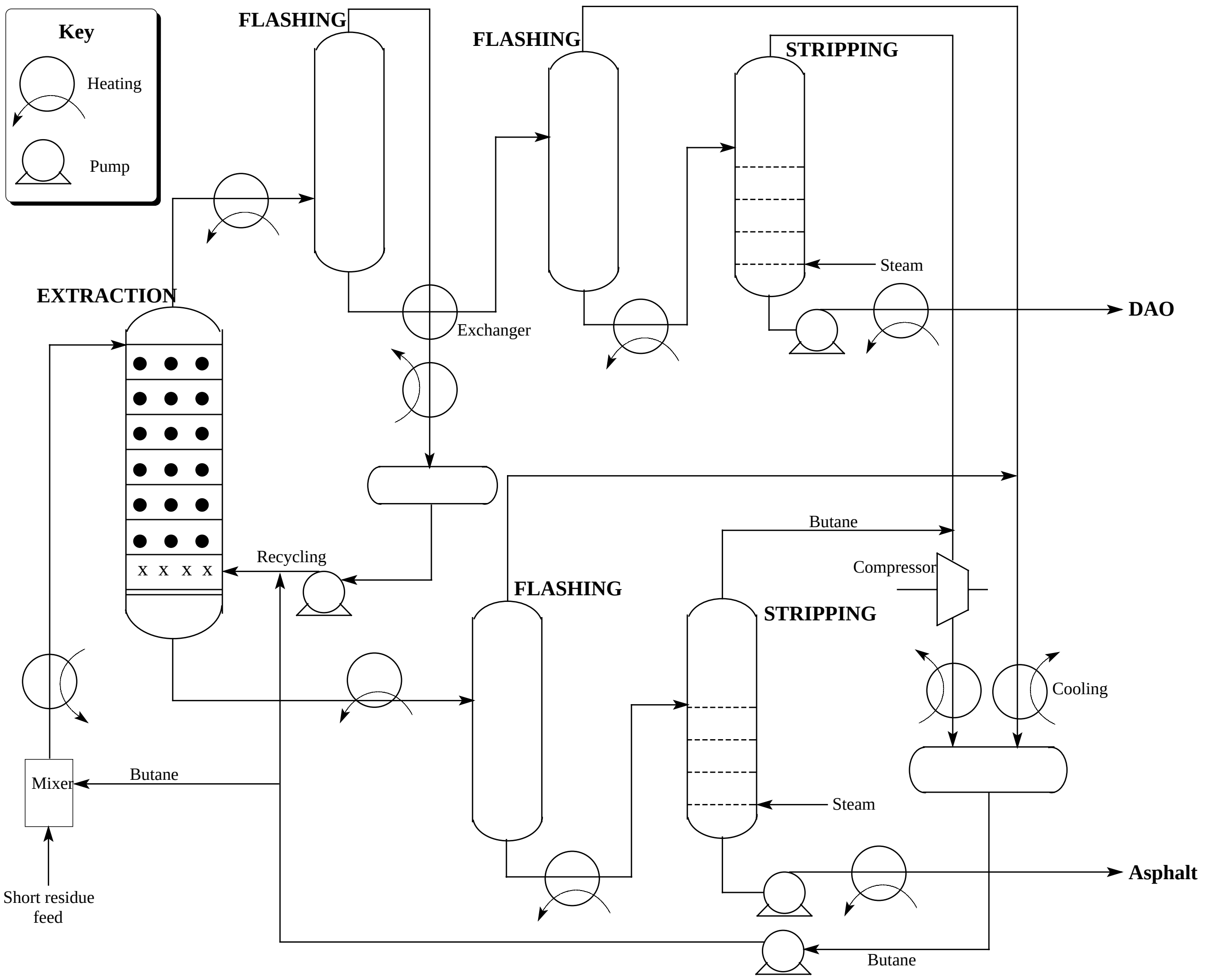
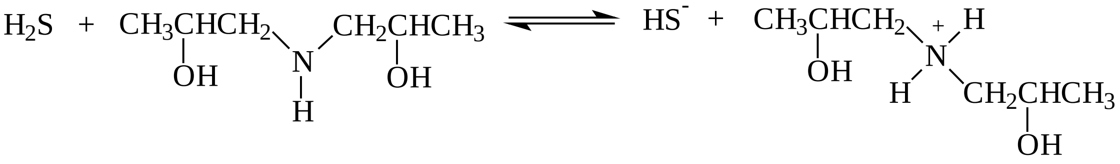


Figure 5 - The Butane Deasphalting unit

Shell ADIP process

The refinery fuel gas contains H_2S, and this must be removed from the gas stream before the gas is burnt as fuel to prevent excessive SO_2 emissions. This is done by reacting the H_2S with a solution of diisopropanol amine (DIPA, a base) known as ADIP. This is called the Shell ADIP process, and it is a regenerable absorption process, meaning that the ADIP is regenerated for further use. The overall reaction can be represented as follows:



$$H_2S + CH_3\underset{OH}{CH}CH_2\underset{H}{N}CH_2\underset{OH}{CH}CH_3 \rightleftharpoons HS^- + CH_3\underset{OH}{CH}CH_2\overset{+}{N}H_2CH_2\underset{OH}{CH}CH_3$$

The solution is used to absorb H_2S at higher pressures and lower temperatures, during which time the equilibrium lies to the right (Le Chatelier's principle). The solution is then regenerated, releasing H_2S, by using higher temperatures and lower pressures. **Figure 6** outlines the ADIP process of absorption and regeneration. The DIPA is dissolved in water at a concentration of 4 mol L^{-1}, and the H_2S concentration of the lean ADIP (the ADIP which is fed into the absorber) is typically 80 ppm wt.

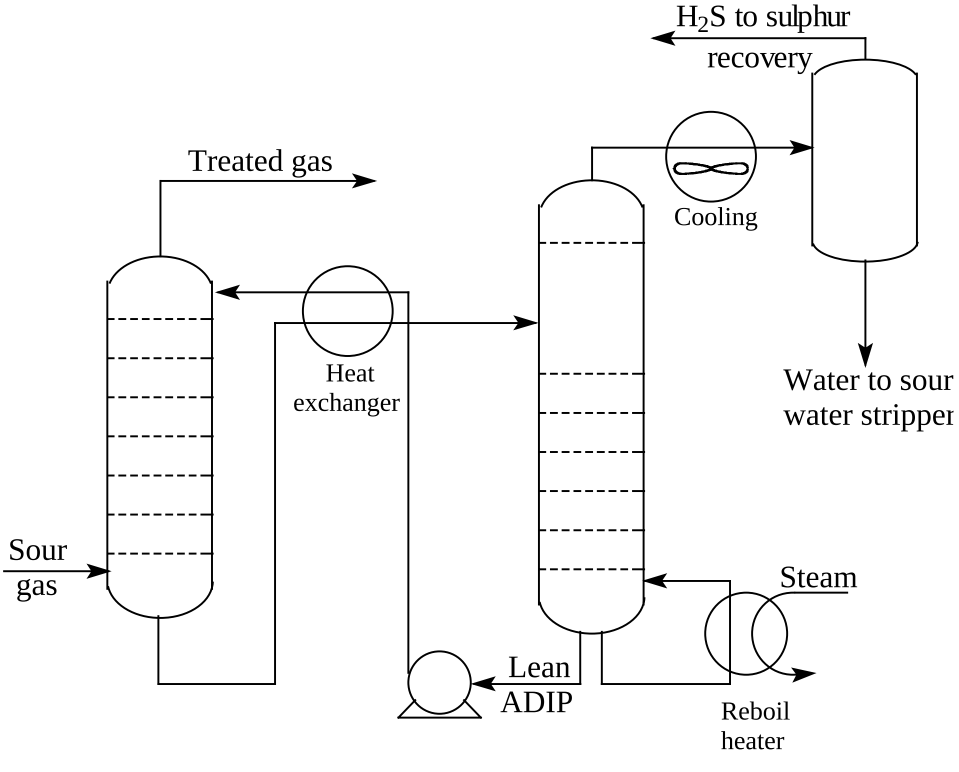


Figure 6 - ADIP process

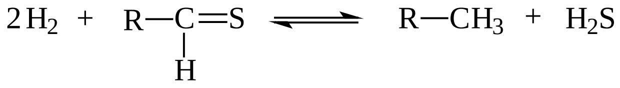
Step 2 - Conversion

Of the oils separated out from the original crude (refinery gas, gasoline, kerosene, light and heavy gasoils and asphalt), only refinery gas can be used as is, and even this is usually ADIP treated. All the others require some further treatment before they can be made into the final product. This firstly involves the removal of sulfur (as it interferes with the success of some later later processes) and then the chemical conversion of the oils into more desirable compounds.

Desulfurisation

The oil products all naturally contain some sulfur compounds. These must be removed from gasoline, kerosene and diesel oils before catalytic reforming (the next conversion process) as otherwise the sulfur poisons the catalyst used. The sulfur is removed by reacting the sulfur compounds with hydrogen, forming hydrogen sulfide, which can be removed as a gas from the cooled liquid oil. The process is carried out over a catalyst at a pressure of about 20 atmospheres and a temperature of about 350 C. Under these conditions the oils are gaseous.

The reactions occurring can be simplified to:



$$2H_2 + R-\underset{\displaystyle H}{\underset{|}{C}}=S \rightleftharpoons R-CH_3 + H_2S$$

(where R is an alkene), and thiol degradation:

$$H_3C-CH_2-CH_2-CH_2-SH + H_2 \rightleftharpoons CH_3-CH_2-CH_2-CH_3 + H_2S$$

Unfortunately, at the temperatures required to cause the reaction to go to the right at a fast rate (see previous section on equilibrium) the hydrocarbons decompose to lighter hydrocarbons and finally to carbon. However, from Le Chatelier's principle we can see that there is another way to force the reaction to the right. The left side of the reaction contains three gaseous moles (the hydrocarbons are gaseous) whereas the right hand side only contains two. By increasing the pressure, the reaction is forced to the right. In addition, if the hydrogen is kept in excess, the reaction is also forced to the right. Thus having an excess of hydrogen and keeping the mixture at high pressure prevents the need to use a high temperature. The rate of conversion of sulfur compounds to H_2S is improved, and the formation of carbon is inhibited. After a period of some months the catalyst does become deactivated by laydown of carbon, and regeneration is carried out by passing a mixture of air and steam at high temperature through the catalyst, thereby burning off the carbon. A mixture of air and steam is necessary, as use of pure air would result in uncontrolled combustion, and the resulting high temperature would adversely affect the catalyst.

Catalytic reforming

This is used to increase the octane ratings of the oil concerned. Octane number is a measure of the 'knock' or 'pinking' that occurs in an internal combustion engine when an unsuitable (too low octane) fuel is used. The octane number is defined by an arbitrary scale which allocates zero octane number to *n*-heptane and 100 to2,2,4-trimethyl pentane (*iso*-octane). The octane number of a fuel is defined as the percentage by volume of *iso*-octane in a mixture with *n*-heptane that gives the same degree of knocking as the fuel in a special test engine.

In proper operation of an internal combustion engine, combustion is initiated by the spark produced by the spark plug at the correct time in the cycle. A flame front then passes through the cylinder at the relatively slow rate of about 100 km/hr, the increase in pressure providing the motive power. Considering, for example, combustion of pentane, we have:

$$\begin{array}{ccccccccc} CH_3CH_2CH_2CH_2CH_3 & + & 8O_2 & \rightarrow & 5CO_2 & + & 6H_2O \\ & \text{9 volumes} & & & & \text{11 volumes} & \end{array}$$

As the reaction produces 11 volumes of product from 9 volumes of reactants but the volume is kept constant, the pressure increases, and the rising temperature also caused by the combustion causes an even greater temperature increase. This increase in pressure provides the motive power. As the pressure increases on ignition, the pressure in the fuel/air mixture in the cylinder not as yet traversed by the flame front rises, with a consequent increase in temperature ($PV = n RT$). If the fuel has too low an octane number, this increase in temperature causes the remaining fuel/air mixture to ignite before the flame front passes through. This ignition is explosive, and causes great impact force to be transmitted by the piston to the bearings. Continual operation of an engine in which such knocking is occurring causes rapid destruction of bearings. Octane numbers of hydrocarbons vary with their oxidation stability. Straight chain paraffins have the lowest octane numbers (e.g. *n*-butane has an octane number of 25) with branched chain paraffins being higher (2 methyl pentane has an octane number of 70) followed by naphthenes (C_6H_{12} = 83) and then aromatics (benzene = 100).

The desired reactions (ring forming and aromatising) are endothermic so, to ensure that the reactions take place at an acceptable rate, a temperature of about 500^{o}C is used. At this temperature all the hydrocarbons considered are gaseous. A pressure of about 25 atmospheres is also used and the process is carried out using a platinum catalyst (platinum dispersed through 1mm spheres of alumina). The process is also sometimes called platforming, because of the use of a platinum catalyst.

Because the reactions are endothermic, 3 furnaces and reactors in series are used. **Figure 7** outlines the process.

As the desirable reactions are endothermic, high temperature favours the forward reaction (Le Chatalier's principle), which leads to the formation of the desired aromatics. The high temperature also ensures that the reactions occur at a reasonably fast rate, but in addition favours the undesirable cracking reaction (see *desulfurisation* above), which gives lay-down of carbon on the catalyst. To suppress coking a high hydrogen pressure is used by recycling some of the light gases (about 70% vol. of hydrogen) from the separator even though this inhibits the formation of the desirable aromatic products to some extent.

As in many industrial processes, this is a compromise. At the previously stated conditions of 500 C and 25 atmospheres, conversion of alkylhexanes into alkylbenzenes is fast. Paraffins (long-chain alkanes of more than twenty carbon atoms) are thus driven to be converted to alkylhexanes as the reaction product is removed almost as soon as it is formed. Also, isomerisation reactions that give molecules capable of forming alkyl hexanes are helped, as again the reaction product is removed.

After a period of several months, deactivation of the catalyst by coke lay-down becomes so pronounced that removal of the coke is necessary. This is achieved by passing a mixture of air and nitrogen through the catalyst, thus burning off the coke. The nitrogen is necessary to control the rate of burn off, as if pure air was used the efficiency of the catalyst would be destroyed by the resulting high temperature. (Steam is not used as in the regeneration of the desulfurising catalyst, as water adversely affects the platinum catalyst.) It is interesting to note that during the lifetime of the catalyst each platinum atom leads to the reaction of about 20 000 000 molecules of gasoline, a truly catalytic act.

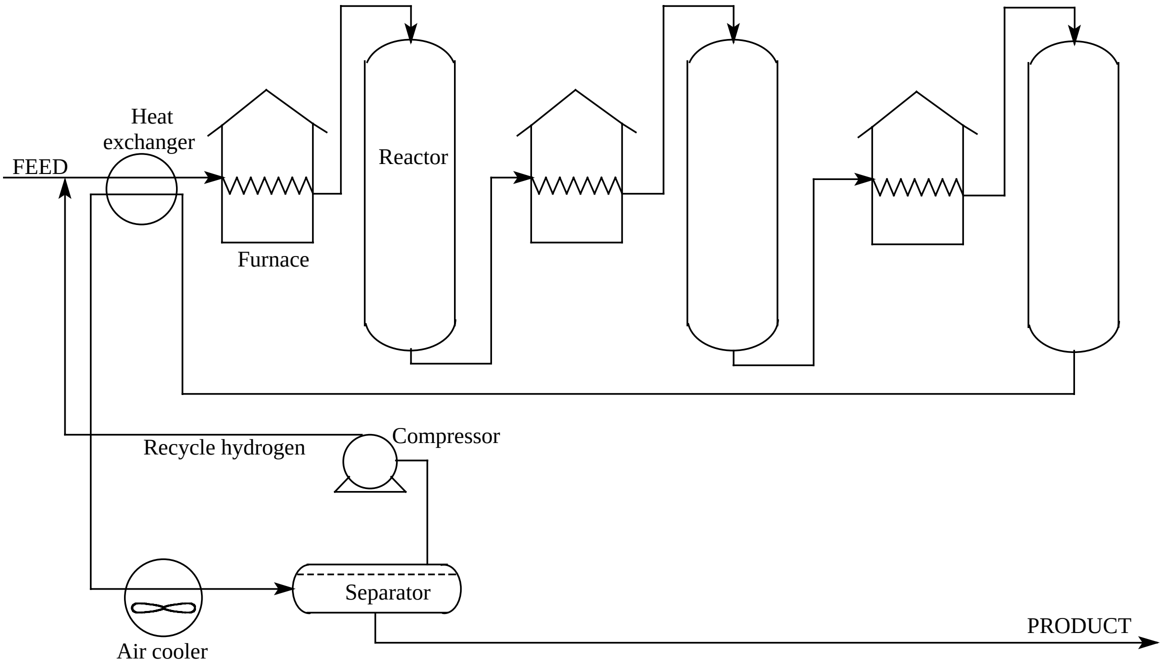
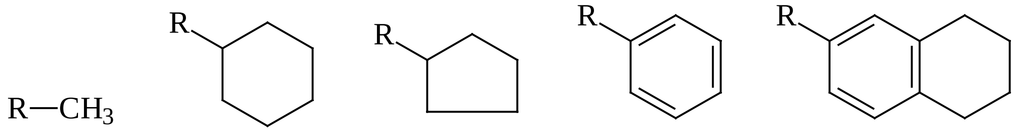


Figure 7 - Catalytic Reforming Unit

A typical reformer feed (bottom product in **Figure 2**) derived from Middle East crude contains about 65% wt. paraffins, 20% wt. naphthenes and 15% wt. aromatics. After processing, the analysis is about 45% wt. paraffins[1], virtually no naphthenes and 55% wt. aromatics. The octane number of the reformer feed is about 50, while the octane number of the product is about 100. The product from the separator contains light gases from partial cracking, and these are removed by fractional distillation.



Paraffins Naphthenes Aromatics

(R consists of branched or unbranched alkane chains)

Bitumen manufacture

Bitumen used to be made by a process that combined distillation and oxidation. Currently it is made simply by mixing some of the short residue from the high vacuum unit with asphalt from the BDU.

Hydrocracking

The hydrocracking process is used to convert waxy distillate and deasphalted oil (DAO) into kerosine and gasoil by breaking down some of their constiuents. The process is carried out in two stages, the first to reduce the amount of nitrogen, sulfur and oxygen impurities that may reach the second stage catalyst, and the second to continue the process of cracking, hydrogenating and isomerising the compounds in the oil. The reactions occuring are denitrogenation, desulfurisation, deoxygenation, hydrogenation, hydrocracking and

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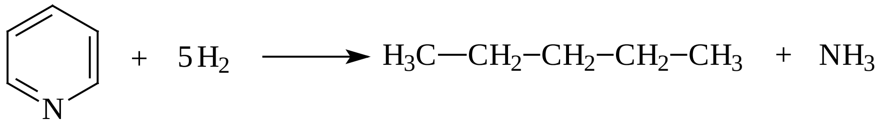
[1] Long-chain alkanes of more than twenty carbon atoms.

isomerisation, all of which are exothermic and all of which, except for isomerisation, consume hydrogen. The heat released is absorbed by injecting cold hydrogen quench gas between the catalyst beds. Without the quench the heat released would generate high temperatures and rapid reactions leading to greater heat release and an eventual runaway. All of the reactions, except for denitrogenation, desulfurisation and deoxygenation which only occur in the first stage, happen in both stages.

Denitrogenation

Carbon-nitrogen bonds are ruptured with the formation of ammonia.



Pyridine *n*-pentane ammonia

Desulfurisation

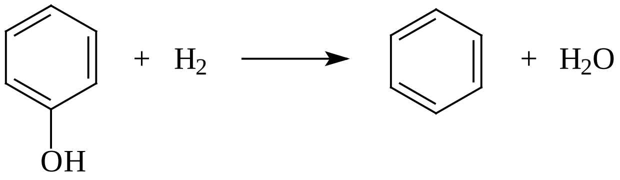
Carbon-sulfur bonds are ruptured with the formation of hydrogen sulfide.

$$H_3C-CH_2-CH_2-CH_2-SH + H_2 \longrightarrow CH_3-CH_2-CH_2-CH_3 + H_2S$$

Butyl mercaptan *n*-butane hydrogen sulfide

Deoxygenation

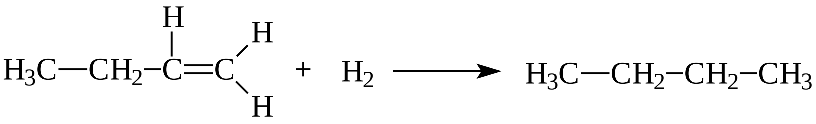
Carbon-oxygen bonds are ruptured with the formation of water.



phenol benzene

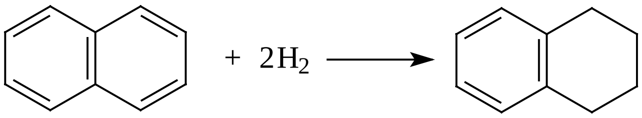
Hydrogenation

The saturation of carbon-carbon double bonds of the olefins or aromatics.



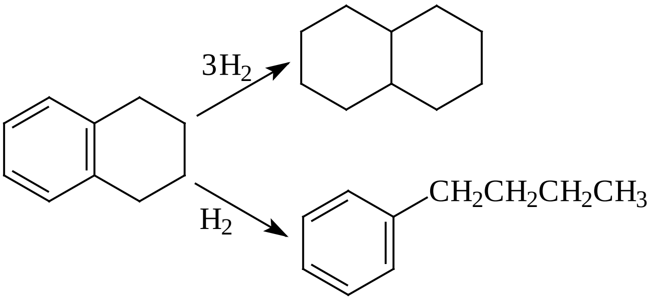
$$H_3C-CH_2-\overset{\overset{H}{|}}{C}=C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} + H_2 \longrightarrow H_3C-CH_2-CH_2-CH_3$$

butylene *n*-butane



naphthalene tetralin

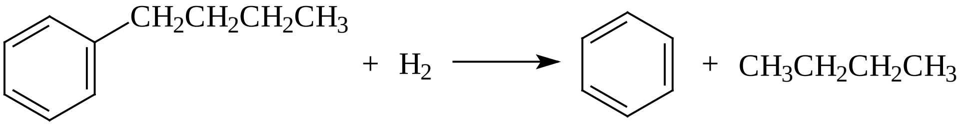
decalin



tetralin butyl benzene

<u>Hydrocracking</u>

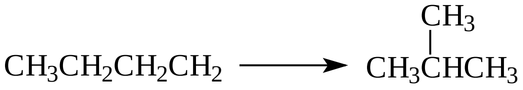
The splitting or breaking of straight or cyclic hydrocarbons and hydrogenation of the ruptured bonds.



butyl benzene benzene *n*-butane

<u>Isomerisation</u>

The change of one compound into another by rearrangement of its atoms.

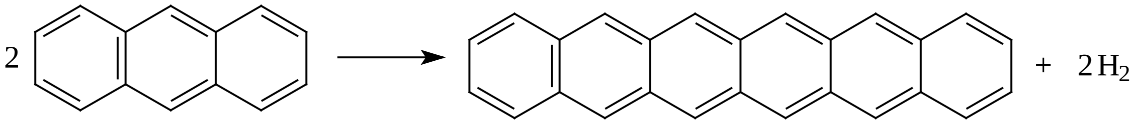


$$CH_3CH_2CH_2CH_2 \longrightarrow CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$$

n-butane *iso*-butane

<u>Condensation</u>

All the previous reactions yield more or less useful products. A less desirable but important reaction is the condensation of aromatics to produce large unsaturated polyaromatics which deposit on the catalyst to form coke. Polyaromatics are much more susceptible to this reaction than monoaromatics. Hence rapid catalyst deactivation due to coke laydown will occur if the feedstock contains a high amount of polyaromatic asphaltenes.



anthracene hexacene

An outline of the hydrocracking unit is given in **Figure 8**.

Step 3 - Purification

The crude oil has now been separated into refinery gas, hydrogen sulfide, naphtha, kerosene, gas oil, asphalt and bitumen. Two more processes have to be carried out, on the naphtha and the hydrogen sulfide respectively, before the hydrocarbons are ready for blending into saleable products.

Sulfur recovery

Crude oil as received for refining contains sulfur in levels up to a few tenths of a percent weight. It is removed from oil products mainly by the desulfurisation process described above which results in the formation of hydrogen sulfide, and further H_2S is separated out of the refinery gas. This H_2S is converted to sulfur in a two step process. Firstly, the "Claus" process of partial combustion of H_2S is used to form SO_2 and this SO_2 is then reacted with the remaining H_2S to produce sulfur. This sulfur recovery process takes place in one thermal and two catalytic stages and recovers 95% of the sulfur. The final 1 or 2 % volume of H_2S in the "tail gas" from the last catalylic reactor is burnt in a separate incinerator so that the effluent gas finally discharged to the atmosphere has an environmentally acceptable H_2S content of less than 5 ppm by volume.

The overall reaction occuring is as follows:

$$H_2S + \tfrac{1}{2}O_2 \rightleftarrows S + H_2O \qquad (l)$$

This overall reaction (1) is the sum of two exothermic reactions, the oxidation of H_2S to SO_2 (2) and the subsequent reaction between H_2S and SO_2 to form sulfur and water (3):

$$H_2S + 1\tfrac{1}{2}O_2 \rightleftarrows SO_2 + H_2O \qquad (2)$$

$$2H_2S + SO_2 \rightleftarrows 3S + 2H_2O \qquad (3)$$

In the first stage of the process (the 'thermal stage'), enough air is supplied to convert one third of the H_2S in the acid feed gases to SO_2 and H_2O according to equation (2). In addition to this, any hydrocarbons and NH_3 in the feed gases are completely combusted:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (4)$$

$$NH_3 + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + 1\tfrac{1}{2}H_2O \qquad (5)$$

In the second and the third stage of the "Claus" process more H_2S is converted to sulfur according to equation (3). To shift the equilibrium of this reaction as far as possible to the right side lower reaction temperatures are applied to these stages. To assure sufficient high reaction rates, the reactions take place in the presence of a catalyst.

Finally, the SRU tail gas (which contains less than 5% sulfur) is oxidised in a catalytic incinerator at a temperature of approximately 400^{o}C. At this temperature, achieved by burning fuel gas in addition to the process gases, the H_2S and sulfur vapour/mist are practically completely oxidised in the presence of a catalyst according to the reactions:

$$H_2S + 1\tfrac{1}{2}O_2 \rightarrow H_2O + SO_2$$

$$S + O_2 \rightarrow SO_2$$

The sulfur is produced in liquid form and heated handling/loading facilities provide sulfur storage before loading into road tankers for delivery to fertiliser works. **Figure 9** gives an outline of the SRU process of the refinery.

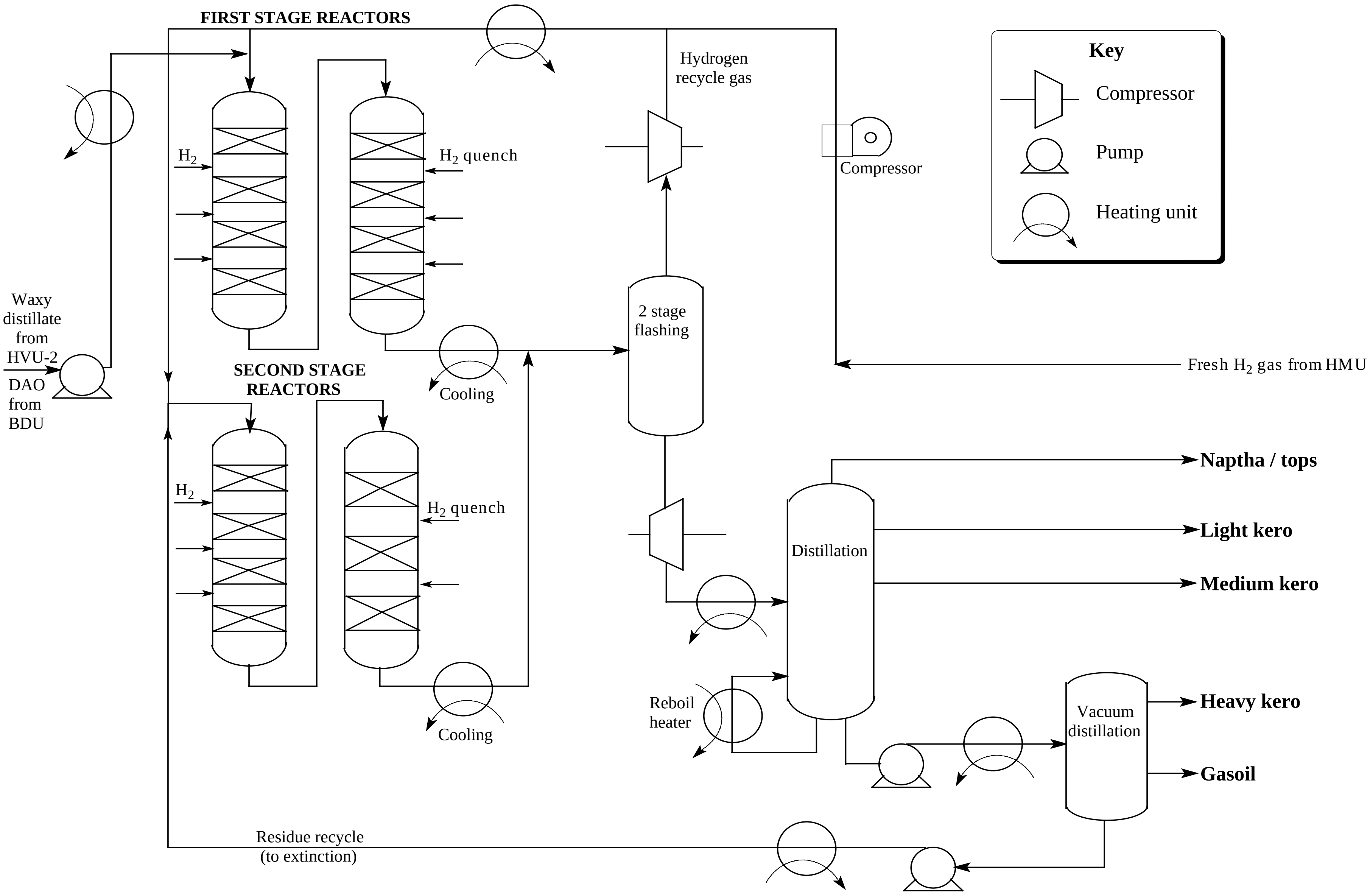


Figure 8 - The two-stage hydrocracking process

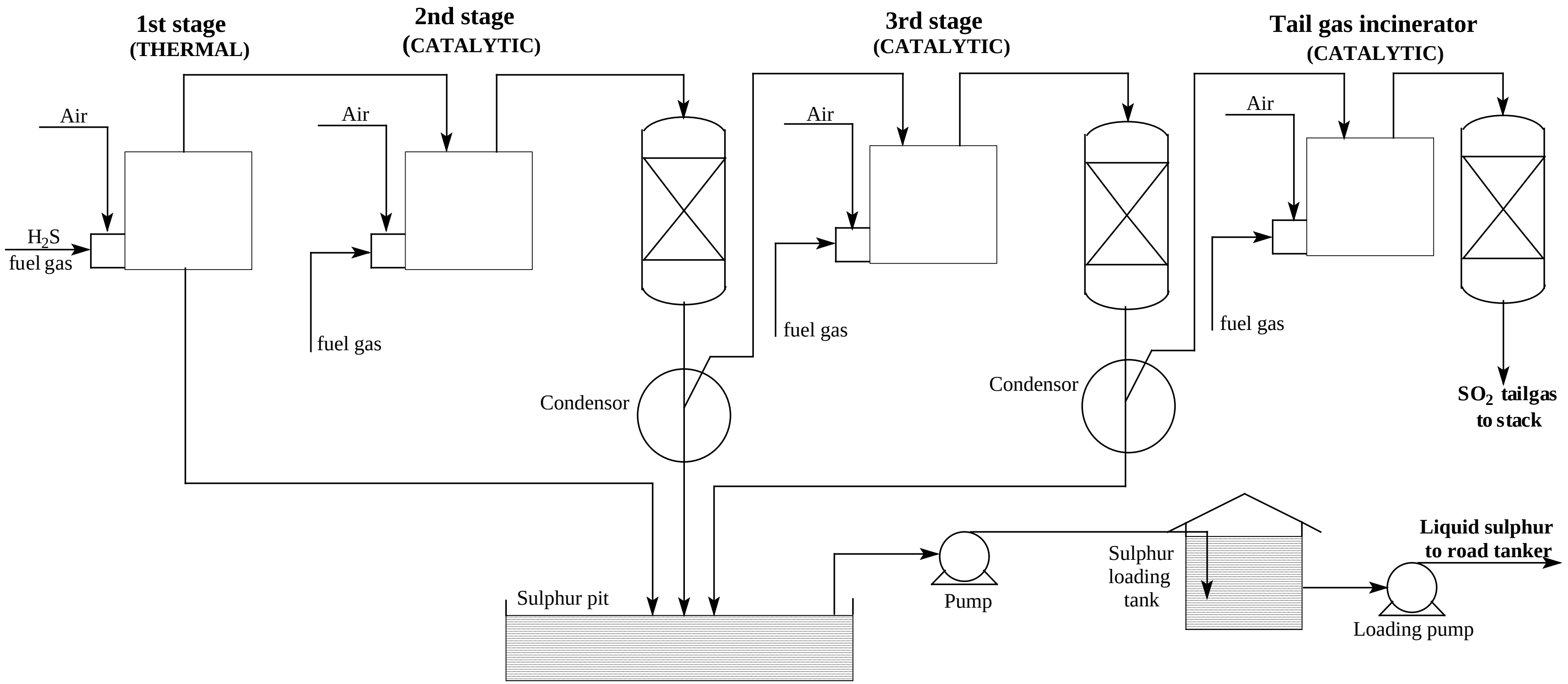


Figure 9 - The sulfur recovery unit

ANCILLARY PROCESSES

Hydrogen manufacture

The large consumption of hydrogen, particularly in the hydrocracker, has meant that the Marsden Point refinery has its own hydrogen manufacturing unit (**Figure 10**). The hydrogen is produced by converting hydrocarbons and steam into hydrogen, and produces CO and CO_2 as byproducts. The hydrocarbons (preferably light hydrocarbons and butane) are desulfurised and then undergo the steam reforming reaction over a nickel catalyst. The reactions which occur during reforming are complex but can be simplified to the following equations:

$$C_nH_m + nH_2O \rightarrow nCO + ((2n + m)/2)H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

The second reaction is commonly known as the water gas shift reaction.

The process of reforming can be split into three phases of preheating, reaction and superheating. The overall reaction is strongly endothermic and the design of the HMU reformer is a careful optimisation between catalyst volume, furnace heat transfer surface and pressure drop.

In the preheating zone the steam/gas mixture is heated to the reaction temperature. It is at the end of this zone that the highest temperatures are encountered. The reforming reaction then starts at a temperature of about 700°C and, being endothermic, cools the process. The final phase of the process, superheating and equilibrium adjustment, takes place in the region where the tube wall temperature rises again.

The CO_2 in the hydrogen produced by reforming is removed by absorption (see *purification* below), but trace quantities of both CO and CO_2 do remain. These are converted to methane (CH_4) by passing the hydrogen stream through a methanator. The reactions are highly exothermic and take place as follows:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Finally, all produced hydrogen is cooled and sent to the Hydrocracker.

In contrast to the desulfurisation process described earlier, the HMU is an example of a non-reversible absorption process applied to protect a valuable catalyst. In this case, desulfurisation is by absorption of H_2S in zinc oxide, according to the equation:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The reaction is non-reversible and consequently the saturated absorbent must be discharged and replaced.

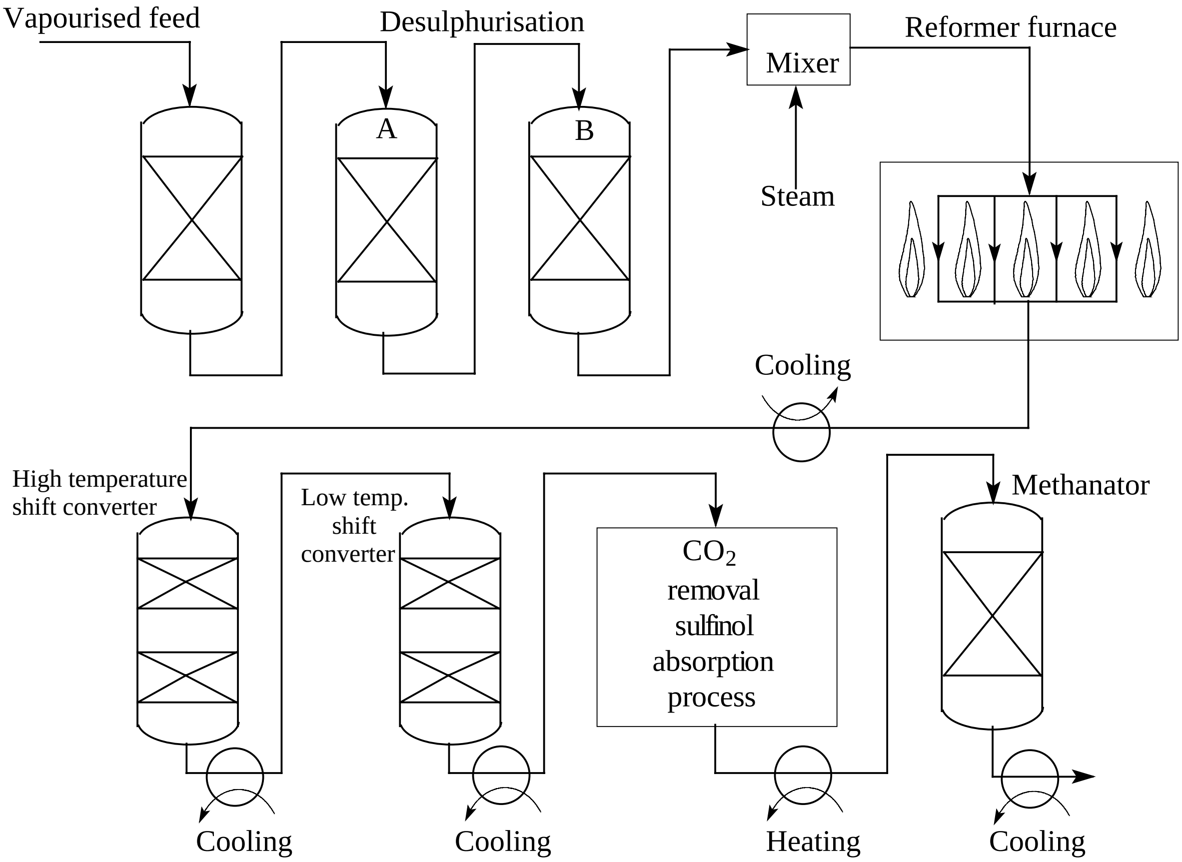
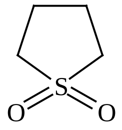


Figure 10 - The hydrogen manufacturing unit

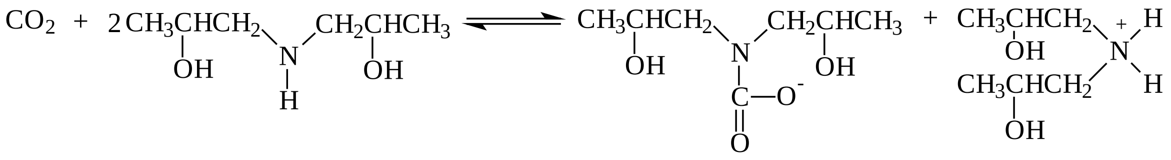
Purification

The hydrogen produced must be purified (to remove the carbon oxides) before it can be usd in the hydrocracker. A regenerable absorption process is applied by circulating a "Sulfinol" solution. This is a mixed solvent, consisting of 50% DIPA, 25% water and 25% tetraydrothiophenedi-oxide (sulfolane).



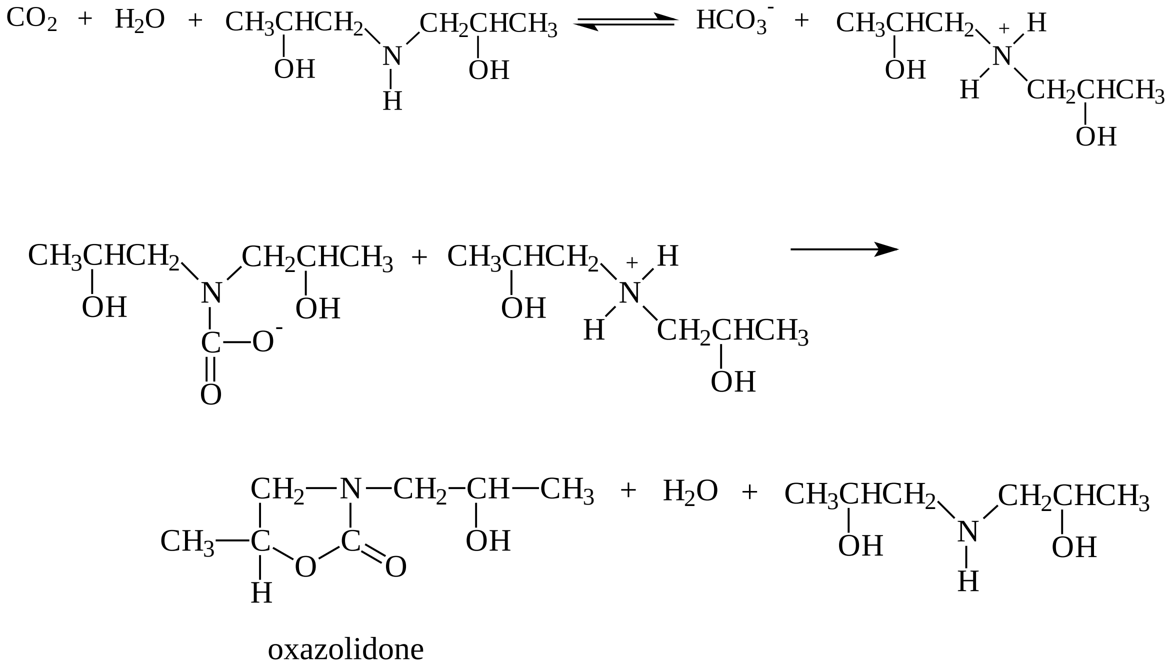
sulfolane

CO_2 is removed by absorption in the sulfinol at low temperatures and high pressure. Subsequently, the "fat" sulfinol solution is regenerated by removal of CO_2 at high temperature and low pressure. The CO_2 is further purified by chilling to give food grade product. The chemistry of the process is as follows:



$$CO_2 + 2\,CH_3CH(OH)CH_2NHCH_2CH(OH)CH_3 \rightleftharpoons (CH_3CH(OH)CH_2)_2N{-}C(=O){-}O^- + (CH_3CH(OH)CH_2)_2NH_2^+$$

DIPA



The water treatment plant

A major ancillary facility of the expanded refinery is the effluent water treatment plant. Extensive facilities, costing $50 million (1985), ensure the continued protection of the marine environment of Whangarei Harbour. The effluent water discharge is continuously monitored for oil content and other contaminants, according to the comprehensive requirements of the discharge permit issued by the Northland Regional Council. **Figure 11** is a simplified block flowscheme of the effluent water treating facilities.

There are two types of water to be dealt with:

- Water which has been, or is likely to have been, in contact with oil. This water must pass through gravity separators to remove the oil and may require other treatment. Such water comes from the refining processes or ballast discharged by coastal tankers.
- Water which has only accidentally been in contact with oil. This water passes through oil traps before being routed to the holding basin and final buffer basin. Such water comes from the boiler plant and collected rainwater.

The treatment of effluent water is as follows. Process water is deodorised in sour-water strippers where the gas (H_2S and NH_3) is stripped off. The stripped water has oil removed in the gravity separators and then, together with some rainwater, is homogenised in a buffer tank. From this tank, the effluent water is piped to a flocculation/flotation unit where air and polyelectrolytes are injected in small concentrations to make the suspended oil and solids separate from the water. The latter are skimmed off and piped to a separate sludge handling/disposal unit. The remaining watery effluent from the flotation unit is passed to adjoining biotreater where the last of the dissolved organic impurities are removed by the action of micro-organisms in the presence of oxygen (biodegradation). On a continual basis, sludge containg micro-organisms is removed to the sludge handling/disposal unit, while the treated effluent water is held first in the retention basin and finally discharged into Whangarei Harbour.

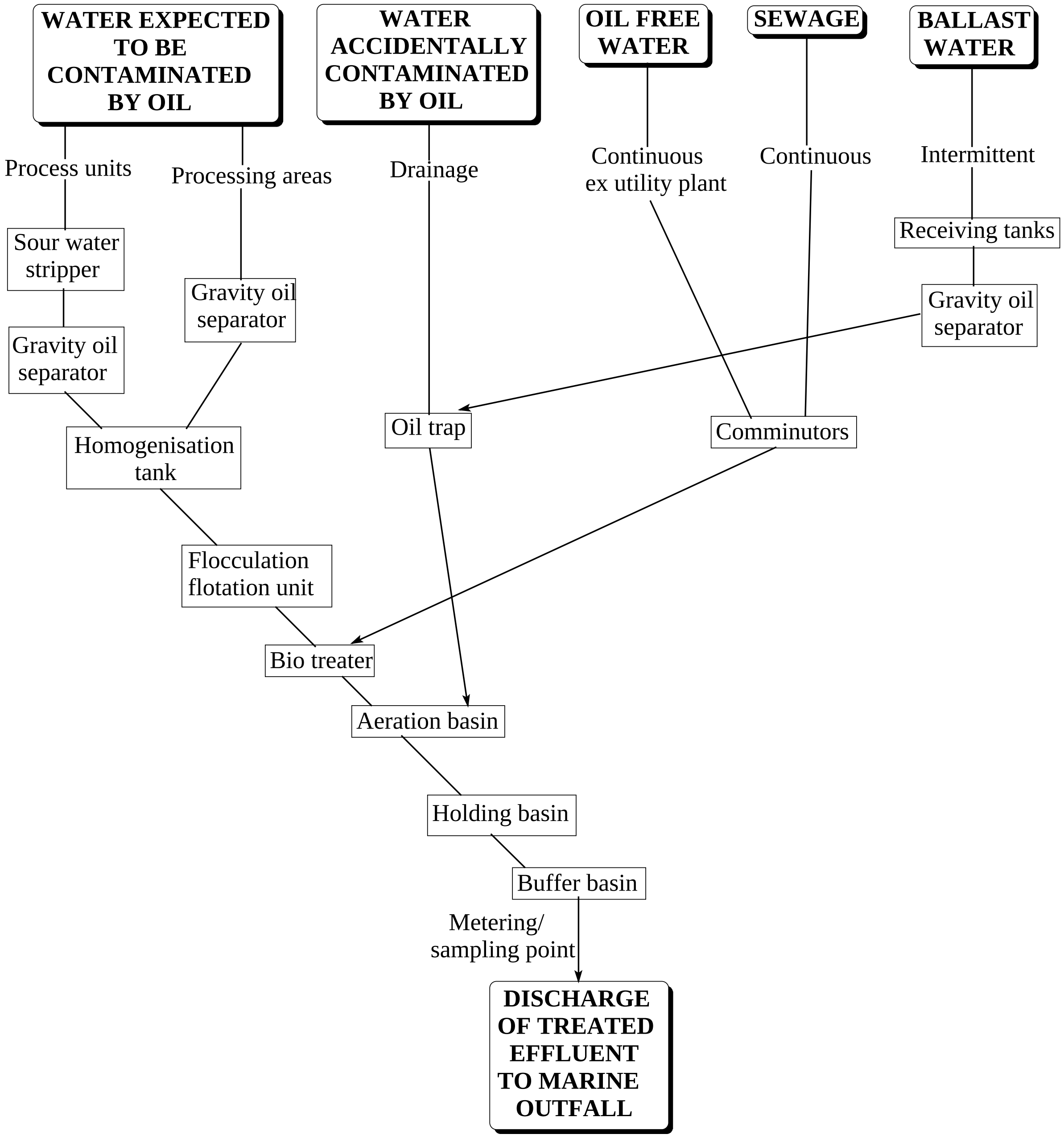


Figure 11 - The water treatment plant

The discharge is through a continuous flow meter and sampling system and terminates at twin diffusers located in deep water where tidal currents ensure the rapid and extensive dilution of the treated effluent water.

A comprehensive system of waste management has also been established at the refinery. This is based on internationally accepted concepts of waste minimisaiton, such as reduction, reuse and recycling. The disposal of any remaining residual waste follows strictly controlled procedures.

ENVIRONMENTAL IMPLICATIONS

The refinery operates under an air discharge permit, monitored by the Northland Regional Council (NRC), since the enactment of the Resource Management Act (RMA). The current permit requires monthly reports to be prepared for the NRC, relating to sulfur dioxide (SO_2) emissions, ground level measurement of SO_2, smoke from chimneys, from flaring and from fire fighting training.

The permit also required that the quantity of SO_2 emitted should be significantly reduced in three steps between 1992 and 1996. Capital costs to achieve these reductions were in the region of $30 million. In addition, operating costs of several million per annum were incurred. The SO_2 limit is now amongst the lowest of any similar refinery in the world.

In addition, the water treatment plant described above ensures that minimal quantites of oil and other effluent are discharged with the water into the Whangarei Harbour.

Article written by Heather Wansbrough, combining the articles from volumes one and two of edition one and information brochures supplied by Tony Mullinger (The New Zealand Refining Company Ltd). Edited by John Packer and John Robertson.