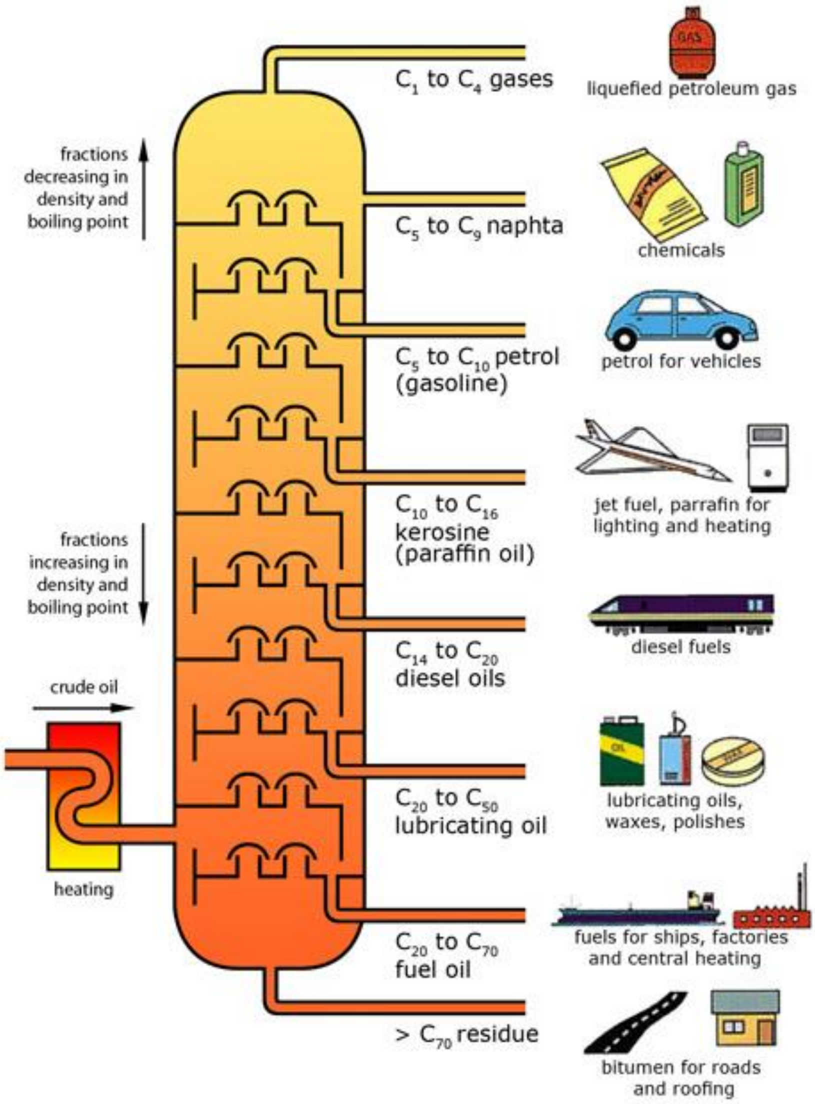
# FRACTIONAL DISTILLATION AND CRACKING

The term **fractional distillation** refers to a physical method used to separate various components of crude oil. Fractional distillation uses the different boiling temperatures of each component, or fraction, in the crude oil to enable the separation to occur.

Two types of cracking exist, they are known as thermal and catalytic. Cracking is the term used to describe how larger fractions are modified into more useful fractions.

## FRACTIONAL DISTILLATION

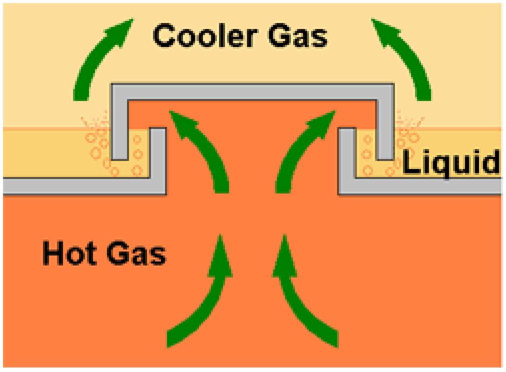
Fractional distillation is one of the main processes carried out in oil refineries and is performed in the **fractionating tower**, a diagram of which is shown below:

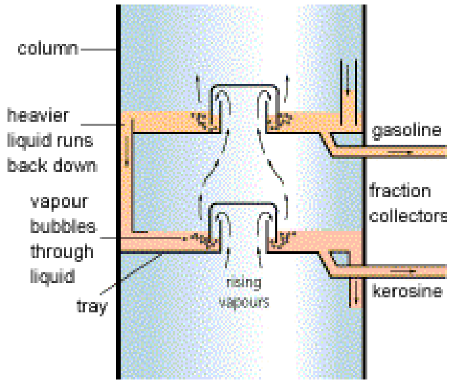


# THE PROCESS OF FRACTIONAL DISTILLATION EXPLAINED

The process begins by heating the crude oil to about 350$^0$C and pumping it into the bottom of the fractionating tower. The tower consists of a series of horizontal trays containing a large number of ***bubble caps***, which prevent the upward movement of gases by forcing the hydrocarbon vapours to bubble through condensed liquid hydrocarbon already in the tray. Very volatile fractions (ie: light fractions which evaporate at low temperatures) are already in the vapour state, these separate from the heavier liquid fractions by rising up the trays within the tower. As you move higher up the tower, each tray contains condensed hydrocarbon liquid of a progressively decreasing temperature. This allows gases to condense at the appropriate temperature along the tower and at the same time, allows lighter fraction to rise higher in the column.

A diagram of how a bubble cap works is shown below:




When vapour reaches the bubble cap two things may happen:

(a) If the boiling temperature of the gas is similar to that of the liquid in the trays, condensation will occur and the products can be collected from the tray at that particular level in the tower.

(b) If the boiling temperature of the gas is less than that of the liquid in the tray, the vapour will bubble through the liquid and continue to rise to higher levels in the column until it finds a liquid with a similar boiling temperature.

It is important to realise that fractional distillation does not separate all the individual components of crude oil. It produces mixtures of substances with similar boiling temperatures called fractions, which consist of a mixture of similar hydrocarbons.

# MAIN FRACTIONS AND BOILING TEMPERATURES

Boiling temperature depends on the strength of intermolecular forces (i.e.: the strength of attraction between molecules in the liquid and the size of the molecules). Since the main components of crude oil are non-polar alkanes, weak dispersion forces are the only intermolecular forces worthy of consideration.
The strength of dispersion forces will increase with molecular size, which can be expressed in terms of number of carbon atoms in the chain.

The table below shows some of the main fractions and their boiling temperatures.

| Temperature | Fraction Name | Chain Length |
|---|---|---|
| Room Temperature ($25^0C$) | Refinery Gas | $C_1$-$C_4$ |
| $110^0C$ | Gasoline | $C_5$-$C_6$ |
| $150^0C$ | Naphtha | $C_6$-$C_{10}$ |
| $180^0C$ | Kerosene | $C_{10}$-$C_{14}$ |
| $260^0C$ | Gas Oil | $C_{14}$-$C_{20}$ |
| $340^0C$ | Heavy Residue/Bitumen | $>C_{20}$ |

The heavy residue is either distilled again or used in the process of ***Cracking***.

# CRACKING

Cracking refers to a process, which breaks the carbon-carbon bonds in an alkane chain to produce smaller molecules. These products of cracking include smaller alkanes, alkenes and hydrogen gas.

Cracking can be achieved in two different ways:

1. **Thermal Cracking:**

   By exposing the alkane molecule to high temperatures. Unsaturated hydrocarbons such as ethene and propene can be produced by this method.

2. **Catalytic Cracking:**

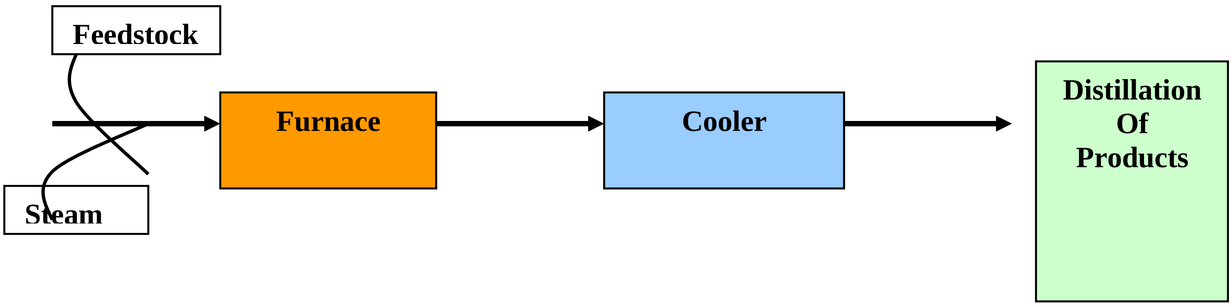
   By using a catalyst. Heavy fractions can be broken into the more useful lighter fractions such as octane, which are of greater use in the petrochemical industry. An advantage of catalytic cracking over thermal cracking is that the process can be performed at lower temperatures and provides greater control on the kind of products formed.

## THERMAL CRACKING

This method is used to produce important unsaturated hydrocarbons such as ethene from lower mass fractions of fractional distillation, which are sometimes referred to as ***feedstock***. Examples of feedstock are:

- Ethane ($C_2H_6$) and Propane ($C_3H_8$) from the refinery gas fraction
- Naphtha or gas oil fractions

Passing both steam and feedstock through a furnace at around 8000C and then cooling the products achieve the process. The products are then separated by distillation. Adjusting the conditions allows some control of the products of the process.
The diagram below summarises the process:



Typical reactions during thermal cracking may be:

$$C_2H_{6\,(g)} \rightleftharpoons C_2H_{4\,(g)} + H_{2\,(g)}$$

$$C_3H_{8\,(g)} \rightleftharpoons C_2H_{4\,(g)} + CH_{4\,(g)}$$

The heat of reaction ($\Delta H$) values for both the above reactions are positive. This indicates that both reactions are endothermic. They are also equilibrium reactions, so a high temperature will favour the production of the product ethene ($C_2H_4$). Also, since the forward reaction produces more particles, a low operating pressure would also favour the production of ethene.

If the gas mixture is left in the furnace for prolonged periods, the cracking process would continue and ethene and other products would decompose further into coke (carbon) and carbon dioxide among other substances. For this reason, the gas mixture is kept in the furnace for about one second and then cooled, thus minimising the further decomposition of ethene.

Ethyne (acetylene) is also produced but this can be converted into additional ethene by reacting it with hydrogen in the presence of a catalyst, according to the following reaction:

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$

Because of the presence of impurities such as sulphur, products such as hydrogen sulphide ($H_2S$) can be formed. Since this substance is acidic, it can be removed by treatment with sodium hydroxide according to the reaction:

$$2NaOH(aq) + H_2S(g) \rightarrow Na_2S(aq) + 2H_2O(l)$$

## CATALYTIC CRACKING

Some of the heavier fractions of distillation have little use for today's fuel needs, so these fractions are subjected to catalytic cracking so that more useful fractions may be obtained. Catalytic cracking is carried out at lower temperatures than thermal cracking using a catalyst to speed up the reaction so that equilibrium is achieved more rapidly. A ***zeolite*** catalyst is used as it allows more control over the range of products obtained in the process.

A typical reaction of catalytic cracking is as follows:

$$C_{29}H_{60}(g) \rightarrow C_8H_{18}(g) + C_8H_{16}(g) + C_{13}H_{26}(g)$$

From the above we notice that one alkane (octane) and two alkenes (octene and tredecene) are produced. Octane is used as the major component of petrol while any larger alkanes and alkenes are used as feedstock for thermal cracking and production of more ethene.

**QUESTION 1**
Write a balanced equation for the cracking of $C_{10}H_{22}$, where the products are ethene and a shorter alkane.

***Solution***

Since ethene is a two-carbon molecule, the alkane produced must be an eight-carbon molecule.

The reaction is as follows:

$$C_{10}H_{22}(g) \rightarrow C_8H_{18}(g) + C_2H_4(g)$$

**QUESTION 2**
Write a balanced equation for the thermal cracking of $C_{10}H_{22}$ where the only products are ethene and hydrogen gas.

***Solution***

From a ten-carbon alkane, five ethene molecules and a hydrogen molecule can be formed according to the reaction below:

$$C_{10}H_{22}(g) \rightarrow 5C_2H_4(g) + H_2(g)$$

**QUESTION 3**
Ethene can be obtained from the thermal cracking of propane according to the following reaction:

$$C_3H_{8\,(g)} \rightleftharpoons C_2H_{4\,(g)} + CH_{4\,(g)} \qquad \Delta H = +81 \text{ KJ mol}^{-1}$$

Different conditions can be used to maximise the yield of ethene. Choose two conditions and explain why the use of these conditions should produce more ethene.

***Solution***

Since the above is an endothermic reaction, an increase in temperature would cause the equilibrium to shift in favour of the forward reaction (endothermic). A high temperature is then a condition, which would increase the yield of ethene.

The product side of the above reaction produces two particles while the reactant side includes only one. A decrease in pressure would again shift the equilibrium in favour of the forward reaction. Low pressure is another condition, which will increase ethene yield.

**QUESTION 4**

Catalytic cracking of $C_{30}H_{62}$ yields octane, a fourteen-carbon alkene and another eight-carbon molecule. Deduce the equation for the catalytic cracking of $C_{30}H_{62}$.

***Solution***

Octane is an eight-carbon alkane containing eighteen hydrogen atoms. The fourteen-carbon alkene contains twenty-eight hydrogen atoms so the remaining eight-carbon molecule must contain sixteen hydrogen atoms, making it another alkene.

The reaction would be as follows:

$$C_{30}H_{62}(g) \rightarrow C_8H_{18}(g) + C_{14}H_{28}(g) + C_8H_{16}(g)$$