Topic 1.6

PETROLEUM AND ALKANES

Fractional Distillation
Cracking
Combustion

CRUDE OIL

1. Introduction

The vast majority of carbon-containing compounds in widespread use have been made from **crude oil**. Crude oil is also known as **petroleum**.

Crude oil is a **mixture of hydrocarbons**. **A hydrocarbon is a substance containing carbon and hydrogen only**. Most of the hydrocarbons in crude oil are **alkanes**. Alkanes are hydrocarbons containing only single bonds between the carbon atoms.

Each of the hydrocarbons present in crude oil has a slightly different use. Mixed together they are of no use at all. It is necessary, therefore, to separate them before they can be used productively. Crude oil is separated into its different components by a process called **fractional distillation**.

The products of fractional distillation are often converted into other, even more useful hydrocarbons by a process called **cracking**.

2. Fractional distillation

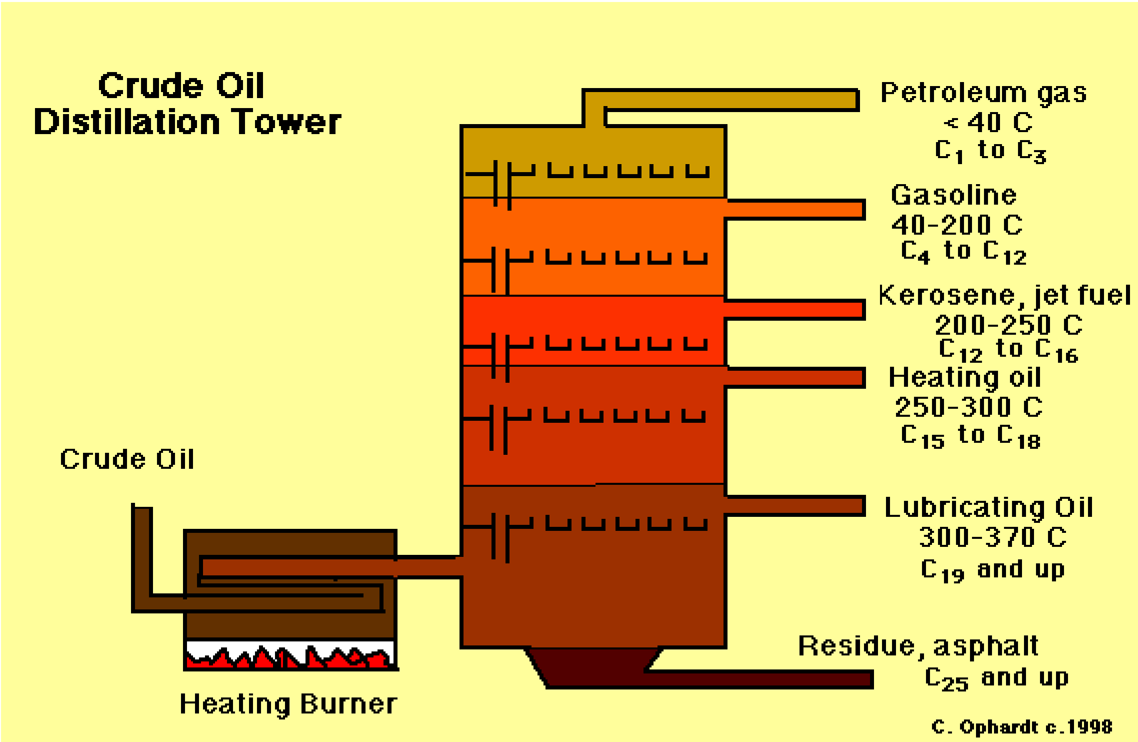
The different hydrocarbons in crude oil have different boiling points. This is because the chain length varies. The greater the number of carbon atoms in the chain, the longer the chain length. This results in more Van der Waal's forces acting between the molecules and a greater intermolecular attraction. Thus more energy is needed to separate the molecules and the boiling point is higher. It is the difference in boiling points of the different hydrocarbons in crude oil which is used to separate them from each other.

The crude oil is passed into a tall tower called a **fractionating column**. This is very hot near the base but much cooler near the top. When the crude oil is passed into the tower, near the bottom, most of the mixture boils and starts to rise up the tower. As they rise up the tower, they start to cool down and will gradually condense back into liquid form. They are then tapped off. The larger hydrocarbons, with higher boiling points, will condense first and be tapped off near the base of the column. The smaller hydrocarbons, with smaller boiling points, will condense later and be tapped off near the top of the column. Thus the separation is achieved. Not that the process involves breaking **intermolecular forces** only; the molecules themselves are unaffected by this process.

This process does not actually separate the crude oil mixture into pure hydrocarbon components, but into mixtures called **fractions**. **Fractions are mixtures of hydrocarbons with similar boiling points**. In many cases these fractions can be used directly, but sometimes further separation is required into purer components.

The following page shows a diagram of a typical fractionating column, and a table showing the most important fractions and their main uses:

<u>A fractionating column</u>



<u>Fractions from crude oil</u>

Name of fraction	Boiling range / °C	Number of hydrocarbons	Uses
Liquefied petroleum gas	Less than 25	1 – 4	Gas for camping/ cooking
Petrol or gasoline			Fuel for cars etc
Naphtha			Petrochemicals
Kerosine or paraffin			Plane fuel, petrochemicals
Diesel or gas oil			lorry, central heating fuel
Mineral/lubricating oil			Lubrication, petrochemicals
Fuel oil			Ship fuel, power stations
Wax and grease			Candles, grease, polish
Bitumen or tar	Above 450	More than 50	Road surfaces, roofing

The term **petrochemical** means that the compounds are converted into other chemicals for use as solvents, paints and various other things.

3. Cracking

Although all of the fractions produced from crude oil have their uses, some of the fractions are produced in greater quantities than needed, whilst others are not produced in sufficient quantities. The table below gives an example of the difference between the supply and demand of some important fractions:

Supply and demand for fractions

Fraction	Approximate supply/%	Approximate demand/%
Liquefied petroleum gases	2	4
Petrol and naphtha	16	27
Kerosine	13	8
Gas oil	19	23
Fuel oil and bitumen	50	38

This disparity can be corrected by breaking up some larger hydrocarbons in fuel oil into the smaller ones found in gas oil, or by breaking up some hydrocarbons in kerosene into the smaller ones found in petrol, naphtha or the liquefied petroleum gases. In other words the larger fractions (for which supply exceeds demand) can be broken up into smaller fractions (for which demand exceeds supply).

The process by which this is carried out is called **cracking**.

Cracking has the added advantage of producing other useful hydrocarbons not naturally present in crude oil, such as **alkenes** (widely used as petrochemicals), **cycloalkanes** and **branched alkanes** (widely used in motor fuels) and **aromatic hydrocarbons** (used as petrochemicals and as motor fuels).

Thus cracking is important for two reasons:

i) It converts low-demand fractions into higher demand fractions
ii) It makes useful hydrocarbons not naturally found in crude oil

There are two types of cracking: **thermal cracking** and **catalytic cracking**. Both involve the breaking of C-C bonds to form smaller molecules. C-C bonds are weaker than C-H bonds and so break more easily when heated.

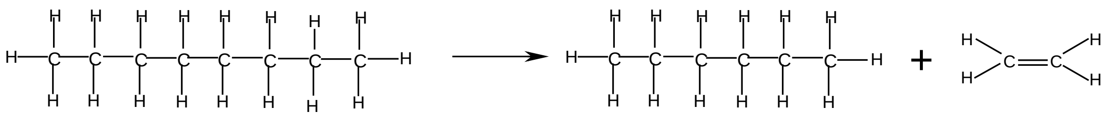
a) Thermal cracking

In thermal cracking, the bonds are broken using a **high temperature** (400 – 900°C) and a **high pressure** (70 atmospheres).

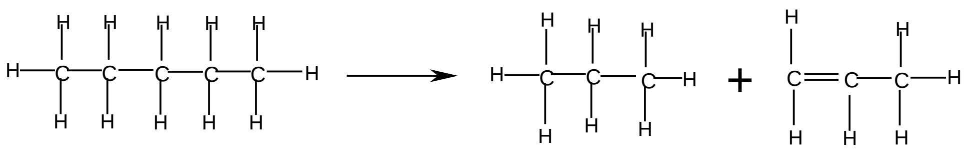
The high temperatures mean that the molecule breaks near the end of the chain, giving a **high percentage of small alkenes** such as ethene.

Most thermal cracking reactions involve the formation of one of more small alkane molecules and one alkene molecule. **Naphtha** (C_7 – C_{14}) is usually used as the starting material.

Eg $C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$



Eg $C_6H_{14} \rightarrow C_3H_8 + C_3H_6$



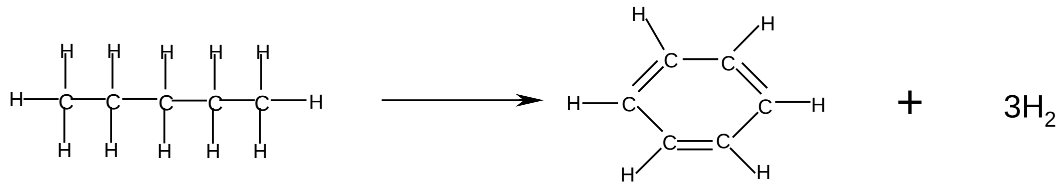
b) Catalytic cracking

In catalytic cracking, the bonds are broken using a **high temperature** (450 ^oC, which is generally lower than in thermal cracking), a **slight pressure** (slightly greater than 1 atmosphere), and a **zeolite catalyst**.

Catalytic cracking is cheaper and more efficient than thermal cracking as it uses a lower temperature and pressure.

The zeolite catalyst favours the formation of branched alkanes and cycloalkanes, which are widely used in **motor fuels**. The most important product of catalytic cracking is 2-methylheptane, which is the major component of petrol. It also produces **aromatic hydrocarbons** such as benzene, which have a variety of uses.

Eg



A table summarising the differences between thermal and catalytic cracking can is shown below:

Type of cracking	Thermal	Catalytic
Conditions	High temperature (400 – 900 ^oC) High pressure (70 atm)	High temperature (450 ^oC) Slight pressure (> 1 atm) Zeolite catalyst
Main products	High percentage of alkenes	Motor fuels (ie branched alkanes) Aromatic hydrocarbons

COMBUSTION OF ALKANES

1. **Alkanes as fuels**

Many of the fractions produced from crude oil are used as fuels. These fractions include:

fraction	uses
Liquefied petroleum gases	Camping gas, cooking gas
Petrol	Fuel for cars, motorbikes and machines
Kerosine	Fuel for aeroplanes, lamps, ovens
Diesel	Fuel for lorries, and central heating systems
Fuel oil	Fuel for ships, power stations
Wax	Fuel for candles

A fuel is a something that can be changed in a reacting vessel to produce useful energy.

Hydrocarbons, and especially alkanes, will react with oxygen in the air to give carbon dioxide and water. A reaction with oxygen is known as **combustion**. As alkanes are unreactive the reaction needs heat or a spark to get going.

These reactions are very **exothermic**, which means that heat energy is released. This heat energy can be used for direct heating (eg camping gas, central heating, candles). It can also be converted into mechanical energy (eg cars, lorries, ships), or even electrical energy (eg power stations).

Typical examples of combustion reactions include:

Reaction	Enthalpy change/ $kJmol^{-1}$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-890
$C_4H_{10} + 6\frac{1}{2}O_2 \rightarrow 4CO_2 + 5H_2O$	-2877
$C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$	-5470

The release of heat energy during these combustion reactions results in their widespread use as fuels.

2. Pollution problems associated with burning hydrocarbons

a) carbon dioxide

Although carbon dioxide is not poisonous and is naturally removed from the atmosphere by plants, the enormous quantities of hydrocarbons burned in recent years has caused carbon dioxide levels to rise significantly.

Carbon dioxide, along with various other compounds, prevents the earth's heat from escaping into space and is resulting in an increase in the earth's temperature. This is known as **global warming**. The result is the melting of the polar ice caps which is likely to cause severe flooding in the future, as well as serious damage to numerous ecosystems.

Gases which contribute towards global warming are known as **greenhouse gases**.

b) Water vapour

Water vapour is also produced in large quantities as a result of combustion of hydrocarbons and is also a **greenhouse gas**.

c) carbon monoxide and carbon

The combustion of hydrocarbons to produce carbon dioxide and water is called **complete combustion**, and it requires a lot of oxygen. If oxygen is not present in sufficiently large quantities, carbon monoxide or carbon is produced instead of carbon dioxide. This is called **incomplete combustion**.

Examples of incomplete combustion reactions are:

$C_4H_{10} + 4\frac{1}{2}O_2 \rightarrow 4CO + 5H_2O$	Incomplete combustion
$C_4H_{10} + 2\frac{1}{2}O_2 \rightarrow 4C + 5H_2O$	Incomplete combustion
$C_8H_{18} + 10\frac{1}{2}O_2 \rightarrow 8CO + 9H_2O$	Incomplete combustion
$C_8H_{18} + 8\frac{1}{2}O_2 \rightarrow 8C + 9H_2O$	Incomplete combustion

The less oxygen that is available, the more likely it is that incomplete combustion will occur. This is a particular problem in internal combustion engines where the air supply is limited. Incomplete combustion is a problem for three reasons:

i) Less energy is released by incomplete combustion than by complete combustion.
ii) Carbon monoxide is a pollutant – it is absorbed by the blood in place of oxygen, and hence reduces the ability of the blood to carry oxygen causing suffocation and eventually death.
iii) Carbon particles can cause breathing difficulties and cancer.

It is therefore desirable to ensure that the air supply is as good as possible when burning hydrocarbon fuels.

Occasionally incomplete combustion is desirable – such as with a Bunsen burner. Closing the air hole produces a yellow flame (the yellow colour results from hot carbon particles) and this makes the flame more visible and causes a more gentle heat. Usually, however, complete combustion is considered more desirable.

d) sulphur dioxide

Most crude oil deposits contain sulphur as an impurity. Oil refineries are increasingly treating the petrol fractions to lower the sulphur content, but some sulphur is still present in most hydrocarbon fuels. When the fuel is burned, the sulphur also burns, producing sulphur dioxide:

$S(s) + O_2(g) \rightarrow SO_2(g)$

This gas dissolves in rainwater forming a very acidic solution, known as **acid rain**. This causes various problems, including erosion of buildings and statues, killing of plants and trees, and killing of fish through contamination of lakes.

e) oxides of nitrogen

Most fuels are not burned in pure oxygen but in air, which contains 80% nitrogen. Although nitrogen is not a reactive gas, the high temperatures and the spark in combustion engines cause some of the nitrogen to react with the oxygen to produce nitric oxide and nitrogen dioxide:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Nitrogen dioxide (NO_2) also dissolves in rainwater to form an acidic solution and contributes to the problem of **acid rain**.

Nitrogen oxides can also combine with unburned hydrocarbons to produce a **photochemical smog**.

f) unburned hydrocarbons

Some of the hydrocarbon fuel is vaporised in the engine but escapes before it is burned. These unburned hydrocarbons cause various problems. They are toxic and can cause cancer if breathed in.

They also combine with oxides of nitrogen to produce a **photochemical smog**.

3. Ways of reducing pollution levels

A number of ways have been developed to reduce the polluting effects associated with the burning of fossil fuels. Two examples are given here:

a) Flue gas desulphurisation

Many factory chimneys contain alkaline materials such as lime (calcium oxide). These absorb the acidic gases such as SO_2 and thus prevent them from escaping:

$$SO_2 + CaO \rightarrow CaSO_3$$

Further reactions result in the formation of $CaSO_4$ (gypsum) which is used to make plaster.

b) Catalytic Converters

Most modern car exhausts are now fitted with **catalytic converters**. These are designed to convert some of the more harmful gases present in car exhausts into less harmful ones. Unburned hydrocarbons, carbon monoxide and the oxides of nitrogen can all be converted into less harmful gases inside these converters.

There are two main types of reaction taking place in a catalytic converter:

i) removal of carbon monoxide and nitrogen monoxide

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

Hence harmful NO and CO gases are converted into the less harmful nitrogen and carbon dioxide.

ii) removal of unburned hydrocarbons and nitrogen monoxide

eg $C_8H_{18} + 25NO \rightarrow 8CO_2 + 9H_2O + 12.5N_2$

Hence harmful unburned hydrocarbons and oxides of nitrogen are converted into the less harmful carbon dioxide, water and nitrogen.

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The reality is, however, that the burning of hydrocarbon fuels has caused and continues to worsen most of the planet's most serious environmental problems. Although technological innovations such as catalytic converters can limit some of the damage, the only action which will have any lasting effect is to reduce the reliance of rich Western countries, especially the USA, on fossil fuels. This will only happen if the potential of alternative sources of energy is more fully exploited, the political and economic power of oil barons is curbed and wealthy industrialised countries look at ways to reduce their energy consumption. Achieving these goals, however, has been socially and politically problematic.