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8.1.1 CRUDE OIL

Crude Oil

Mixture of Hydrocarbons

- **Crude oil** is a complex mixture of lots of different hydrocarbon compounds of different sizes
- It is a thick, sticky, black liquid that is found in porous rock (under the ground and under the sea)

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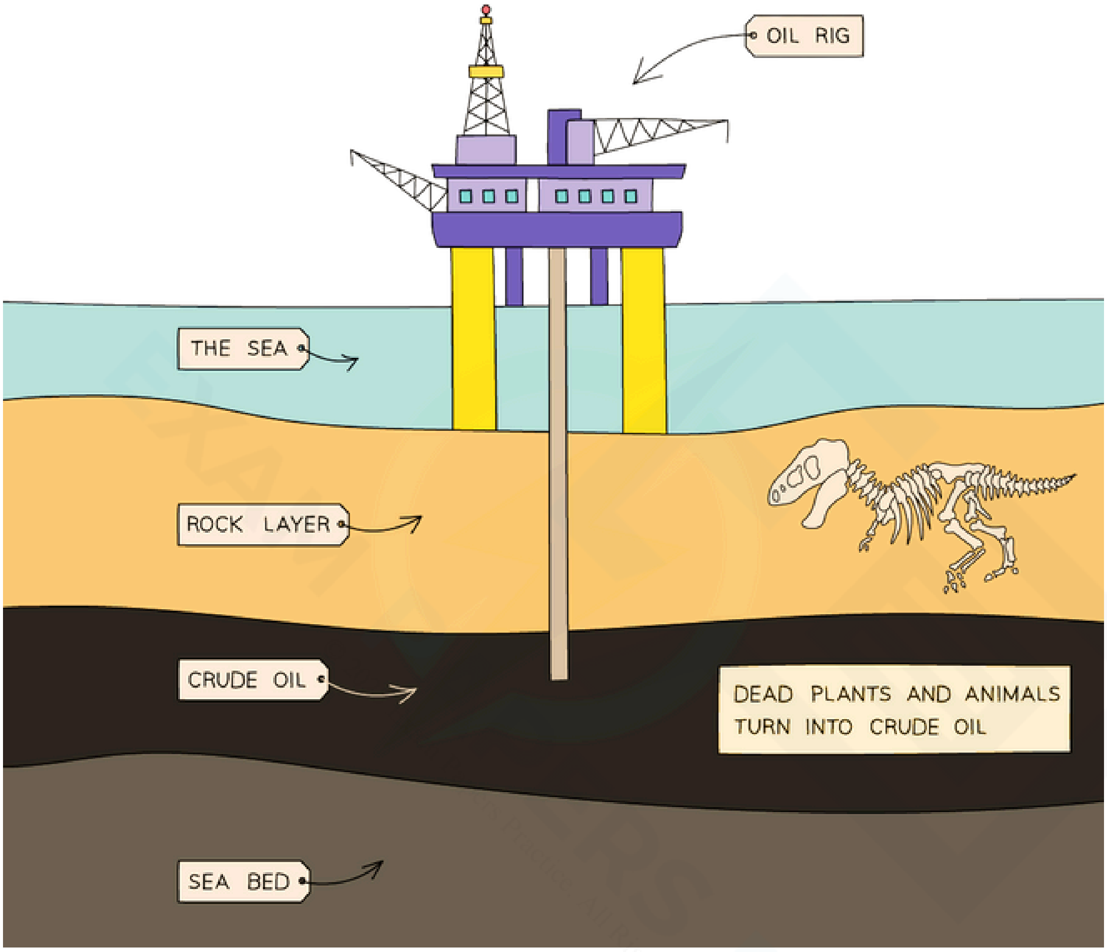

Diagram showing crude oil under the sea

Chains & Rings

- The hydrocarbon molecules in crude oil consist of a carbon **backbone** which can be in a **ring** or **chain**, with hydrogen atoms attached to the carbon atoms
- The mixture contains molecules with many **different** ring sizes and chain lengths

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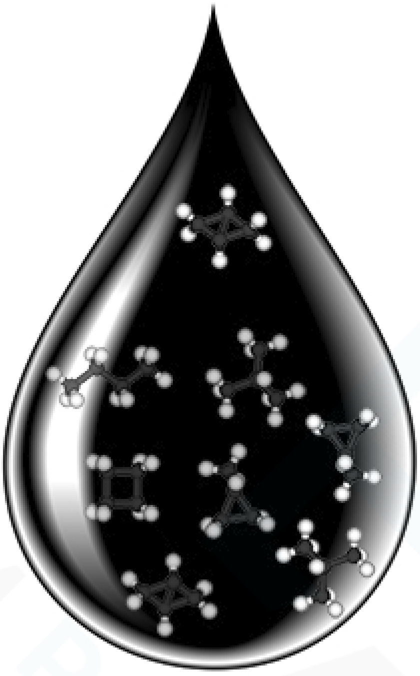

Crude oil is a mixture containing different sized hydrocarbon molecules

Useful Substances

- Crude oil is the main source of hydrocarbons which are used for producing **fuels** such as **petrol** and **diesel**.
- It is also a main source of **raw materials** (called **feedstock**) for the petrochemical industry

Finite Resource

- Crude oil formed over **millions** of years from the effects of high **pressures** and **temperatures** on the remains of plants and animals
- Since it is being used up much faster than it is being formed crude oil is a **finite** resource
- The petrochemical industry is hugely important for modern society and development
- The fuels that are used in most modern methods of transport (cars, trains, airplanes etc.) are all based on oil products
- Polymers, lubricants, solvents, detergents and adhesives are all products that are obtained from crude oil

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8.1.2 FRACTIONAL DISTILLATION OF CRUDE OIL

Fractional Distillation of Crude Oil

- Crude oil as a mixture is not a very useful substance but the different hydrocarbons that make up the mixture, called fractions, are enormously valuable, with each fraction having many different applications
- Each fraction consists of groups of hydrocarbons of **similar** chain lengths
- The fractions in petroleum are separated from each other in a process called **fractional distillation**
- The molecules in each fraction have similar **properties** and **boiling points**, which depend on the number of carbon atoms in the chain
- The size and length of each hydrocarbon molecule determines in which fraction it will be separated into
- The size of each molecule is directly related to how many carbon and hydrogen atoms the molecule contains
- Most fractions contain mainly **alkanes**, which are compounds of carbon and hydrogen with only **single** bonds between them

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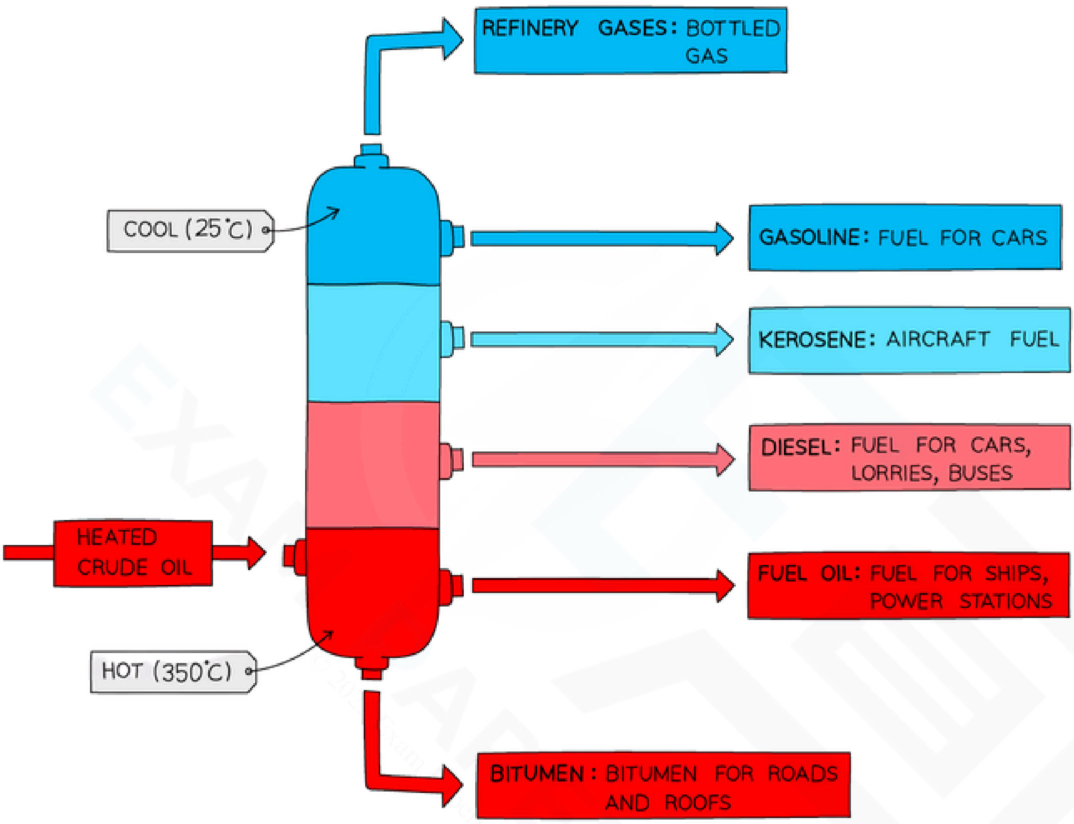

Diagram showing the process of fractional distillation to separate crude oil in a fractionating column

- Fractional distillation is carried out in a **fractionating column** which is very **hot** at the **bottom** and **cool** at the **top**
- Crude oil enters the fractionating column and is heated so **vapours rise**
- Vapours of hydrocarbons with very **high** boiling points will immediately condense into liquid at the higher temperatures lower down and are tapped off at the bottom of the column
- Vapours of hydrocarbons with **low** boiling points will rise up the column and condense at the top to be tapped off
- The different fractions condense at different heights according to their **boiling points** and are tapped off as liquids
- The fractions containing **smaller** hydrocarbons are collected at the top of the fractionating column as gases
- The fractions containing **bigger** hydrocarbons are collected at the lower sections of the fractionating column

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Exam Tip

As you move up a fractionating column the temperature decreases, so the compounds with higher boiling points come off lower down the column.

The Main Fractions

Uses of the different fractions obtained from petroleum (crude oil)

- The petrochemical industry is hugely important for modern society and development
- The fuels that are used in most modern methods of transport (cars, trains, airplanes etc.) are all based on oil products
- Polymers, lubricants, solvents, detergents and adhesives are all products that are obtained from crude oil
- The array of fractions in crude oil and the huge range of compounds we can produce from them all stem from carbon's ability to form multiple strong covalent bonds with itself leading a huge number of organic compounds
- The main fractions and their uses are described in the following table:

Uses of Crude Oil Fractions

Fraction	Use
Liquified petroleum gas	Domestic heating & cooking
Petrol	Fuel for cars (gasoline)
Kerosene	Jet fuel (paraffin)
Diesel	Diesel engines (gas oil)
Heavy fuel oil	Ships & power stations
Bitumen	Surfacing roads and roofs

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Exam Tip

You need to learn the names and uses of the main fractions obtained from crude oil: refinery gases(also known as liquid petroleum gases), gasoline, kerosene, diesel, fuel oil and bitumen. Gasoline and petrol are the same thing; gasoline is the term used in the USA.

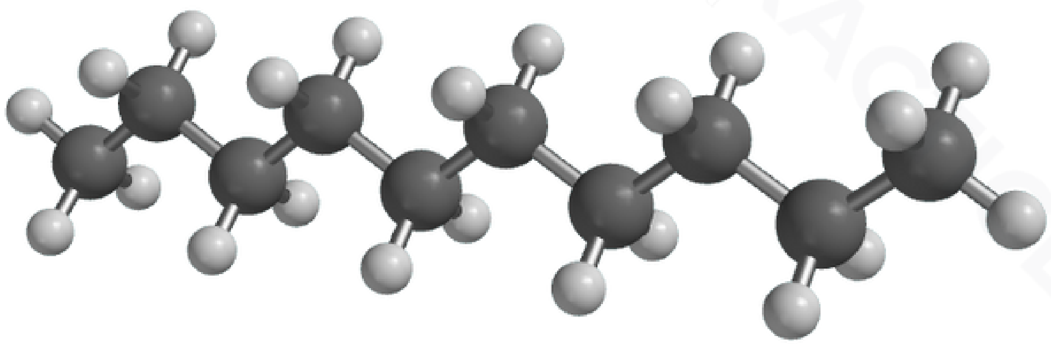
Trends in Properties

Properties of the main fractions of crude oil

- Some properties of hydrocarbons depend on the size of their molecules, including boiling point, viscosity and flammability
- These properties influence how hydrocarbons are used as fuels

Number of Carbon & Hydrogen Atoms

- The size and length of each hydrocarbon molecule determines in which fraction it will be separated into
- The size of each molecule is directly related to how many carbon and hydrogen atoms the molecule contains
- Most fractions contain mainly **alkanes**, which are compounds of carbon and hydrogen with only **single** bonds between them



Decane is an alkane, C10H22 and is a component in some fuels

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Boiling point

- As the molecules get larger, the **intermolecular forces** of **attraction** between the molecules becomes greater as there is more **surface area contact** between them
- This means that more heat is needed to separate the molecules, hence with increasing molecular size there is an **increase** in **boiling point**

Viscosity

- Viscosity refers to the ease of **flow** of a liquid
- **High** viscosity liquids are **thick** and flow less easily
- Viscosity also increases with increasing chain length
  - This is also due to the increased intermolecular forces of attraction as molecular size increases
  - Increased viscosity means that higher alkanes are useful as lubricants in machinery as they are less likely to burn and function to reduce friction between moving parts

Trends in the Main Fractions

FRACTION	NUMBER OF CARBON ATOMS	BOILING POINT RANGE /°C	BOILING POINT & VISCOSITY INCREASE GOING DOWN
REFINERY GAS	1 – 4	BELOW 25	↓
GASOLINE / PETROL	4 – 12	40 – 100	
NAPHTHA	7 – 14	90 – 150	
KEROSENE / PARAFFIN	12 – 16	150 – 240	
DIESEL / GAS OIL	14 – 18	220 – 300	
FUEL OIL	19 – 25	250 – 320	
LUBRICATING OIL	20 – 40	300 – 350	
BITUMEN	MORE THAN 70	MORE THAN 350	

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Ease of Ignition

- Molecular size again influences the ease of ignition or flammability of hydrocarbons
- Smaller hydrocarbon molecules are more **flammable** and are easier to ignite than larger molecules
- This makes them very useful as fuels, releasing large amounts of energy when they burn

Exam Tip

Makes sure you know the trends in the properties of crude oil fractions.

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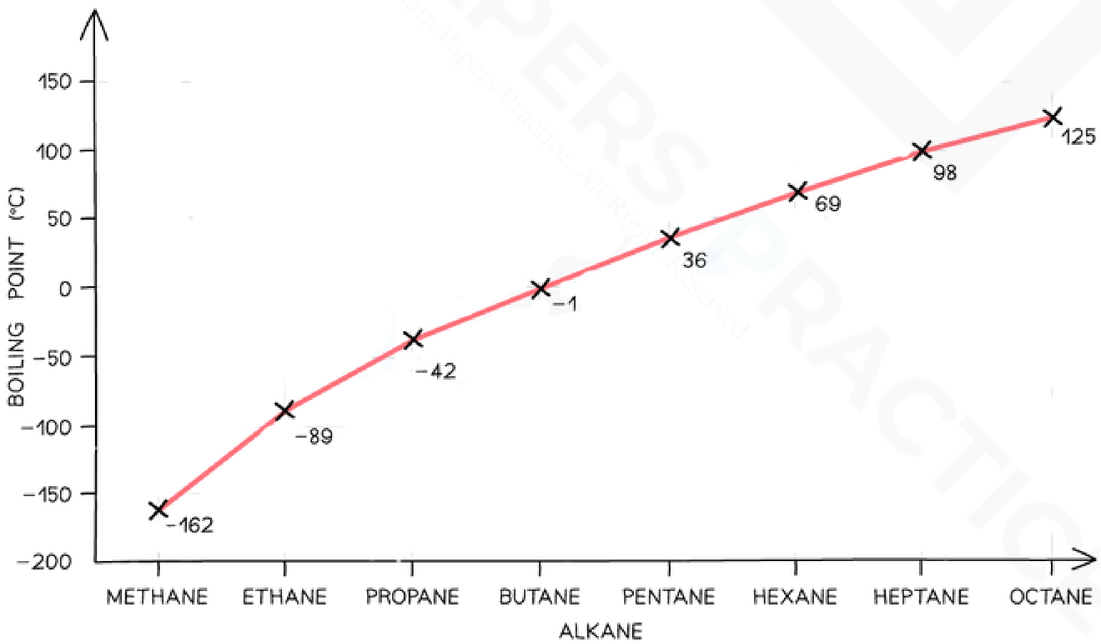
8.1.3 HOMOLOGOUS SERIES

Homologous Series

- Homologous series are **families** or **groups** of organic compounds that have similar **features** and chemical **properties** due to them having the same **functional group**
- All members of a homologous series have:
  - The same **general formula**
  - The difference in the molecular formula between one member and the next is **CH2**
  - Gradation in their **physical** properties
  - Same functional group
  - Similar **chemical properties**
- Gradation in the physical properties of a homologous series can be seen in the trend in **boiling points** of the alkanes

Boiling Point



A graph of the boiling points of the first eight alkanes showing a gradually increasing trend

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- Each alkane has a boiling point that is higher than the one before it
- As the molecules get larger, the **intermolecular forces** of **attraction** between the molecules becomes greater as there are more electrons in the molecules and greater **surface area contact** between them
- This means that more heat is needed to separate the molecules, hence with increasing molecular size there is an **increase** in **boiling point**

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8.1.4 COMBUSTION OF FUELS

Complete Combustion

- The combustion of fossil fuels is the major source of atmospheric pollution
- Fossil fuels include: **coal**, **oil**, **natural gas**, **oil shales** and tar sands
- Non-renewable fossil fuels are obtained from **crude oil** by fractional distillation
- Petrol is used as a fuel in **cars**, kerosene is used to fuel **aircraft** and diesel oil is used as a fuel in some cars, trucks and **heavy vehicles** such as tanks and trains
- Coal is used in power stations and also steel production
- Natural gas consists mainly of **methane**, CH_4
- There are finite amounts of fossil fuels and they all contribute to **pollution** and **global** warming
- All these fuels contain carbon, hydrogen and small quantities of sulfur

Combustion Products

- The burning of fossil fuels releases the gases **carbon dioxide**, **carbon monoxide**, **oxides of nitrogen** and **oxides of sulfur**
- In addition incomplete combustion of the fuels gives rise to **unburned hydrocarbons** and **carbon particulates**

Complete versus Incomplete Combustion

- A **fuel** is a substance which releases energy in an exothermic reaction
- When the fuel is a **hydrocarbon** then **water** and **carbon dioxide** are the products formed
- Hydrocarbon compounds undergo **complete** and **incomplete** combustion
- Complete combustion occurs when there is **excess oxygen**
- For example, the combustion equation for propane is:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Exam Tip

You don't need to learn these equations, but you do need to be able to predict the products of combustion given the composition of the fuel and the conditions.

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Incomplete Combustion

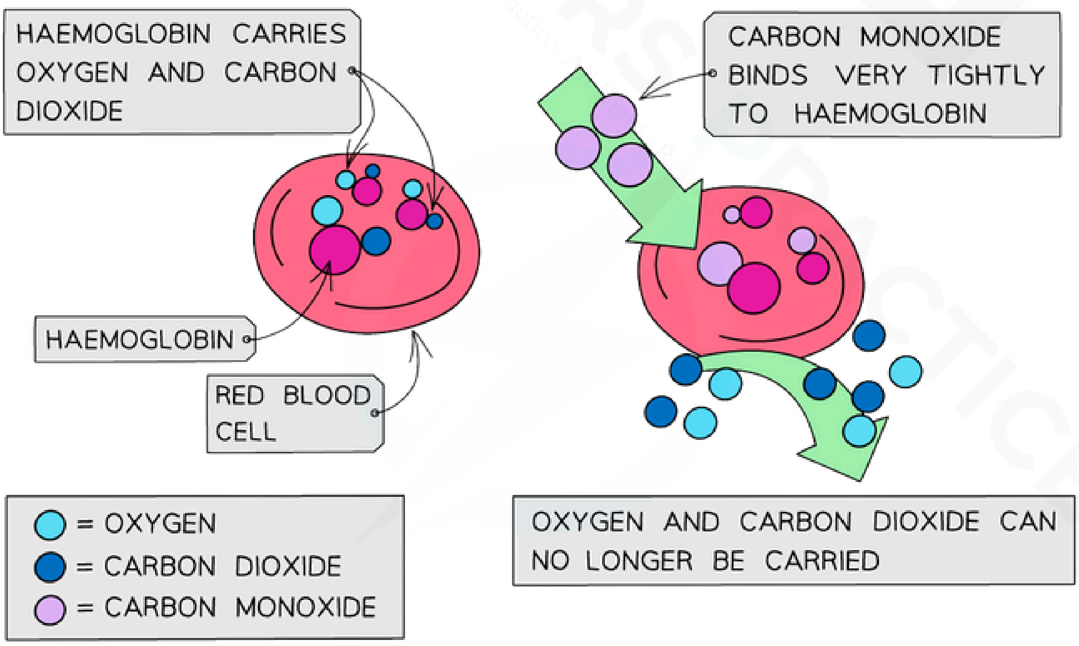
Incomplete Combustion

- Incomplete combustion occurs when there is **insufficient oxygen** to burn
- It occurs in some appliances such as **boilers** and **stoves** as well as in **internal combustion** engines
- The products of these reactions are unburnt fuel (soot), carbon monoxide and water
- Methane for example undergoes incomplete combustion in an oxygen-poor environment:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \rightarrow C + 2H_2O$$

- Carbon monoxide is a toxic and odourless gas which can cause dizziness, loss of consciousness and eventually death
    - The CO binds well to haemoglobin which therefore cannot bind oxygen and carbon dioxide
    - Oxygen is transported to organs
    - Carbon dioxide is removed as waste material from organs



The high affinity of CO to haemoglobin prevents it from binding to O2 and CO2

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Exam Tip

Though CO2 is not a **toxic** gas, it is still a **pollutant** causing **global warming** and **climate change.**

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8.1.5 ACID RAIN: NITROGEN OXIDES & SULFUR DIOXIDE

Formation of Sulfur Dioxide

Sulfur dioxide

- Sulfur dioxide is a **colourless**, **pungent** smelling gas that is a major air pollutant responsible for **acid rain**
- The sulfur dioxide released mixes with clouds and readily dissolves in **rainwater**
- SO2 is a non-metal oxide so it forms an **acidic** solution in water, hence forming **acid rain**
- **Sources**: combustion of fossil fuels – especially coal
- **Fossil fuels** are often contaminated with small amounts of **sulfur impurities**
- When these contaminated fossil fuels are **combusted**, the sulfur in the fuels get **oxidised** to **sulfur dioxide**

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

- **Adverse effects**: acid rain which causes corrosion to metal structures, buildings and statues made of carbonate rocks, damage to aquatic organisms. Pollutes crops and water supplies, irritates lungs, throats and eyes

Acid Rain

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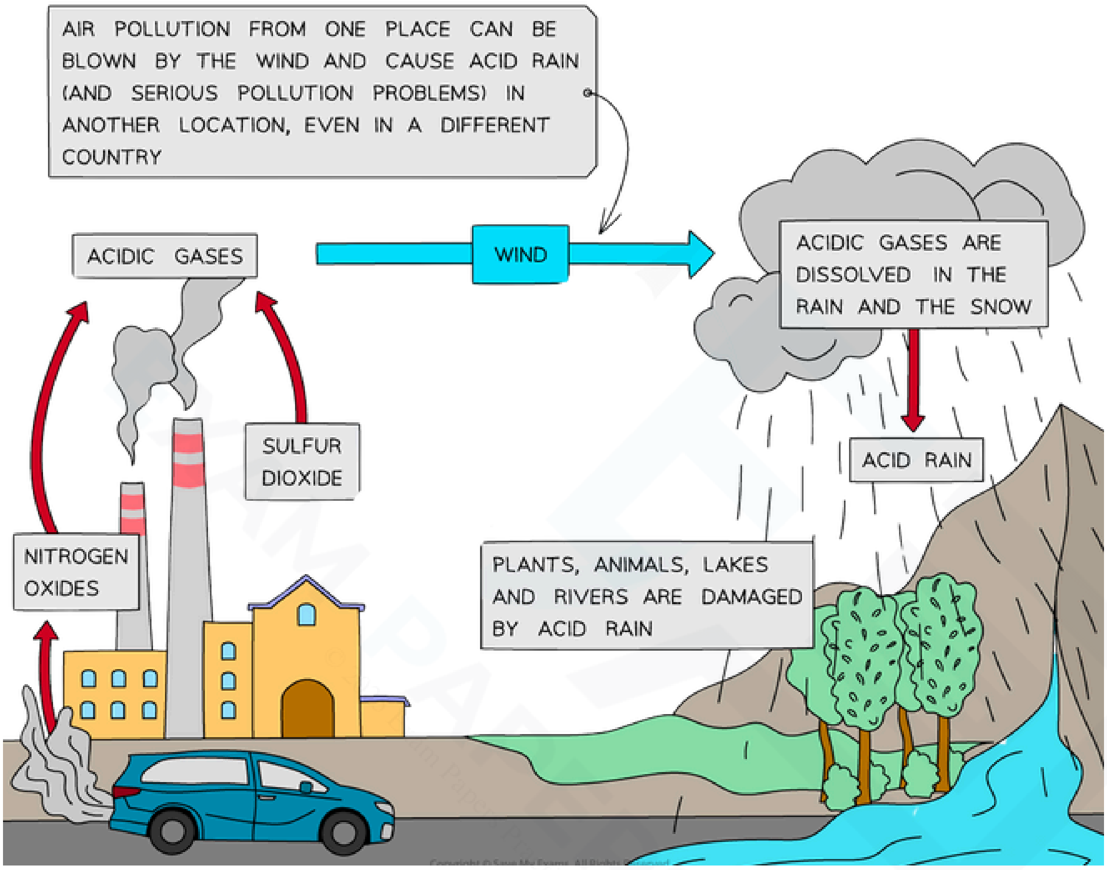

Formation of acid rain from nitrogen and sulfur oxides

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- The sulfur dioxide produced from the combustion of fossil fuels dissolves in rainwater droplets to form **sulfuric acid**

$$2SO_2 (g) + O_2 (g) + 2H_2O (l) \rightarrow 2H_2SO_4 (aq)$$

- Sulfuric acid is one of the components of acid rain which has several damaging impacts on the environment
- **Nitrogen dioxide** produced from car engines reacts with rain water to form a mixture of **nitrous** and **nitric acids**, which contribute to **acid rain**:

$$2NO_2 (g) + H_2O (l) \rightarrow HNO_2 (aq) + HNO_3 (aq)$$

- Lightning strikes can also trigger the formation of nitrogen monoxide and nitrogen dioxides in air
- Nitrogen dioxide gas reacts with rain water and more oxygen to form **nitric acid**

$$4NO_2 (g) + 2H_2O (l) + O_2 (g) \rightarrow 4HNO_3 (aq)$$

- When the clouds rise, the temperature decreases, and the droplets get larger
- When the droplets containing these acids are heavy enough, they will fall down as **acid rain**

Formation of Nitrogen Oxides

Nitrogen Oxides

- These compounds (NO and NO_2) are formed when nitrogen and oxygen react in the **high pressure** and **temperature** conditions of internal combustion engines and blast furnaces
- The temperature in an internal combustion engine can reach over 2000 °C
- Here, nitrogen and oxygen, which at normal temperatures don't react, combine to form **nitrogen monoxide**:

$$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$$

- **Nitrogen monoxide** reacts further forming **nitrogen dioxide**:

$$2NO (g) + O_2 (g) \rightleftharpoons 2NO_2 (g)$$

- **Nitrogen dioxide** gas reacts with rain water to form a mixture of **nitrous** and **nitric acids**, which contribute to **acid rain**:

$$2NO_2 (g) + H_2O (l) \rightarrow HNO_2 (aq) + HNO_3 (aq)$$

- Lightning strikes can also trigger the formation of nitrogen monoxide and nitrogen dioxides in air
- When the clouds rise, the temperature decreases, and the droplets get larger
- When the droplets containing these acids are heavy enough, they will fall down as **acid rain**

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Adverse Effects

- Acid rain with similar effects as SO2 as well as producing photochemical smog and breathing difficulties, in particular for people suffering from asthma

Catalytic Converters

- They contain a series of **transition metal catalysts** including platinum and rhodium
- The metal catalysts are in a **honeycomb** within the converter to increase the surface area available for reaction
- A series of redox reactions occurs which neutralises the pollutant gases
- Carbon monoxide is oxidised to carbon dioxide:

2CO + O2 → 2CO2

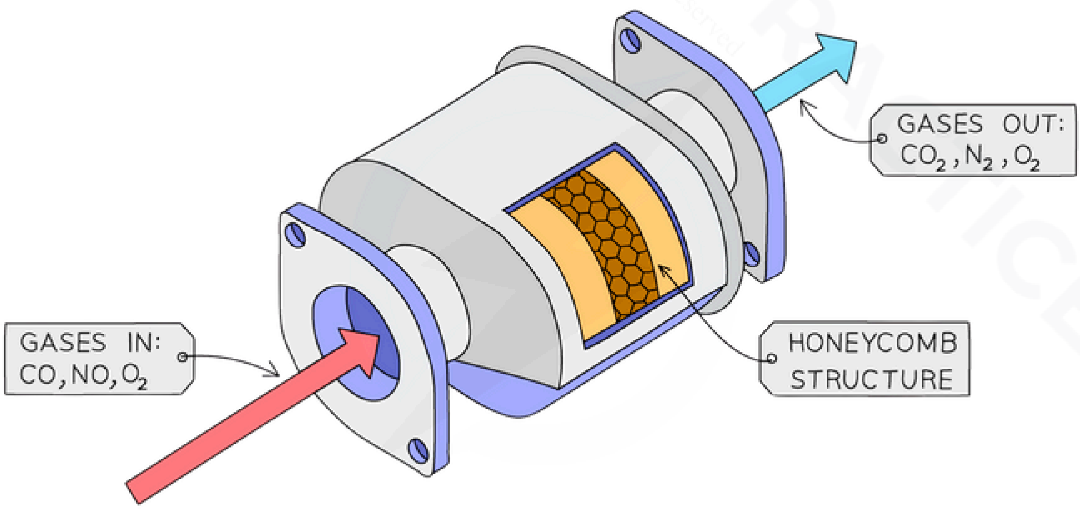
- Nitrogen oxides are reduced to N2 gas:

2NO → N2 + O2

2NO2 → N2 + 2O2

- Unburned hydrocarbons are oxidised to carbon dioxide and water:

C8H18 + 12½O2 → 8CO2 + 9H2O



Catalytic converters are designed to reduce the polluting gases produced in car exhausts

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Exam Tip

You don't need to learn all the equations given here. They are shown to illustrate some of the complex processes and variety of products from polluting sources.

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8.1.6 HYDROGEN VS FOSSIL FUELS

Hydrogen as a Fuel

Hydrogen as a fuel

- Hydrogen is used in rocket engines and in fuel cells to power some cars and buses
- It reacts with oxygen in an exothermic reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Hydrogen has a series of advantages and disadvantages regarding its use as a fuel
- **Advantages**:
  - It releases **more energy** per kilogram than any other fuel (except for nuclear fuels)
  - It does **not pollute** as it only produces water on combustion, no other product is formed
- **Disadvantages**:
  - **Expensive** to produce and requires energy for the production process
  - **Difficult** and **dangerous** to store and move around (usually stored as liquid hydrogen in highly pressurised containers)

Exam Tip

The economics of hydrogen production still make it an expensive fuel compared to fossil fuels.

Fossil Fuels

- A fuel is a substance which when burned, releases heat energy
- This heat can be transferred into electricity, which we use in our daily lives
- Most common fossil fuels include coal, natural gas and hydrocarbons such as methane and propane which are obtained from crude oil
- The main constituent of natural gas is **methane**, CH_4
- Most of the world's energy supply still comes from fossil fuels:

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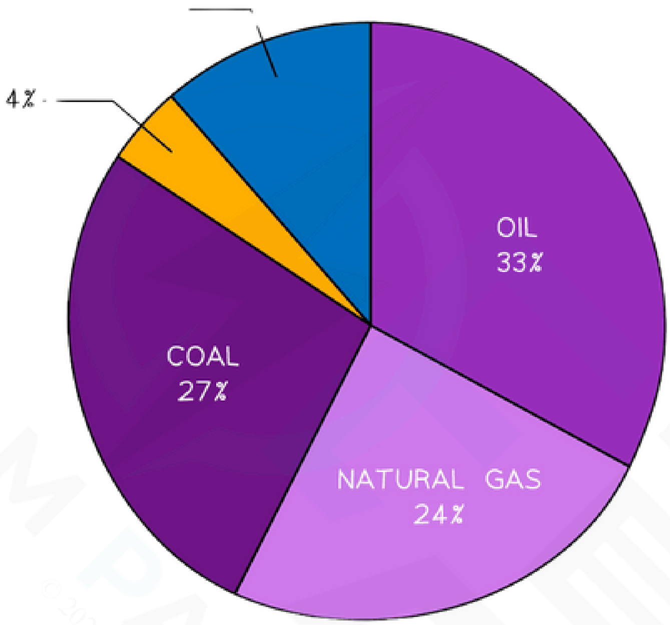

Over 80% of the world's energy supply still comes from fossil fuels

Exam Tip

The rate of extraction of fossil fuels outstrips their formation, so fossil fuels are a finite and non-replenishable resource within a human time scale.

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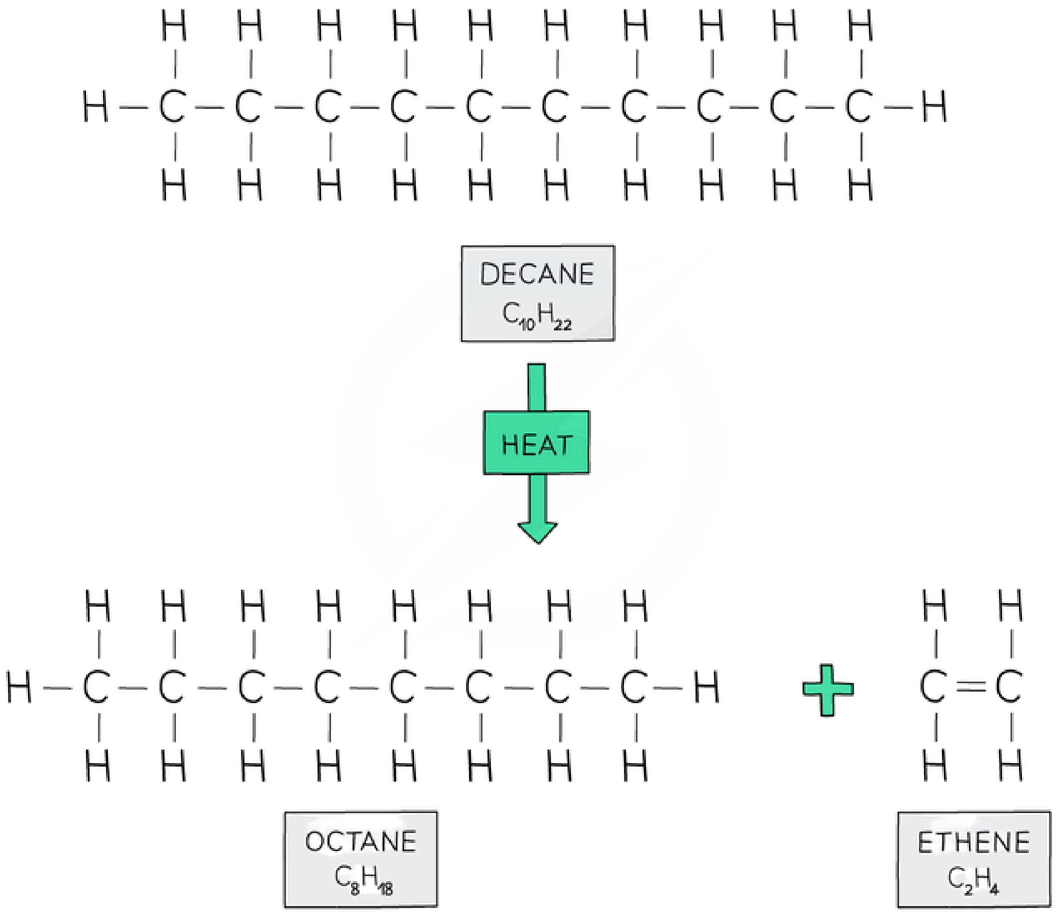
8.1.7 CRACKING

Cracking

- Saturated molecules contain **single** bonds only whereas unsaturated molecules contain **double** bonds between their carbon atoms
- **Alkanes** are saturated compounds and **alkenes** are unsaturated compounds
- Long chain alkane molecules are further processed to produce other products consisting of smaller chain molecules
- A process called **cracking** is used to convert them into short chain molecules which are more useful
- **Small alkenes** and **hydrogen** are produced using this process
- Kerosene and diesel oil are often cracked to produce petrol, other alkenes and hydrogen
- There are two methods used to crack alkanes: **catalytic** cracking and **steam** cracking
- As the names suggest, one method uses a catalyst and the other uses steam



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Decane is cracked to produce octane for petrol and ethene for ethanol synthesis

- **Catalytic cracking** involves heating the hydrocarbon molecules to around 470 – 550°C to **vaporise** them
- The vapours then pass over a hot powdered **catalyst** of aluminium oxide
- This process breaks covalent bonds in the molecules as they come into contact with the surface of the catalyst, causing **thermal decomposition** reactions
- The molecules are broken up in a random way which produces a mixture of smaller alkanes and alkenes
- Hydrogen and a higher proportion of alkenes are formed at higher temperatures and higher pressure
- In **steam or thermal cracking** the process is carried out at slightly higher temperatures and produces more ring structures and unsaturated compounds
- The vaporised hydrocarbons are mixed with steam and heated to a high temperature which induces cracking

Why Cracking is Necessary

- Crude oils vary considerably in their composition and some need more refining than others
- **Supply** is how much of a particular fraction can be produced from refining the crude oil
- **Demand** is how much customers want to buy
- General the demand for certain fractions outstrips the supply so this is why **cracking** is necessary to convert surplus unwanted fractions into more useful ones
- This is mostly larger, heavier fractions that are cracked into smaller lighter fractions

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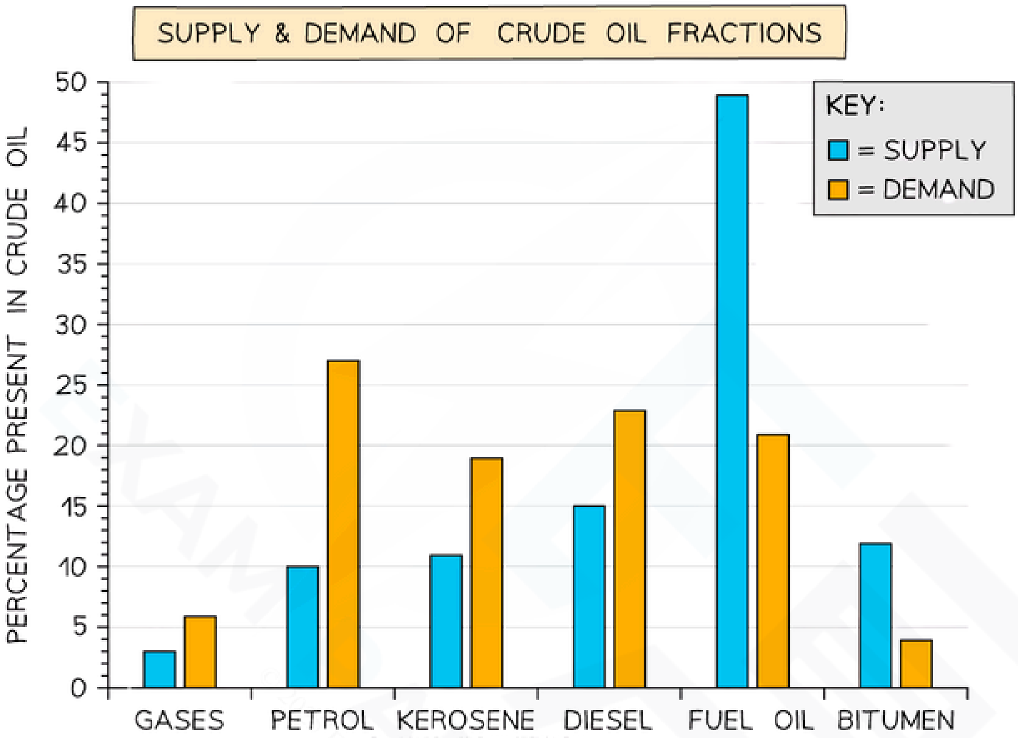

Supply & demand graph for crude oil fractions

- You can see from the chart that fuel oil and bitumen are surplus fractions so they are cracked and modified to produce petrol, kerosene and diesel

Exam Tip

Remember that cracking is an **endothermic** reaction.