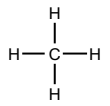
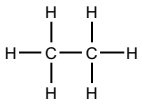
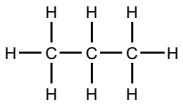
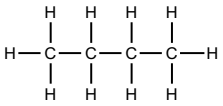
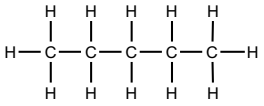
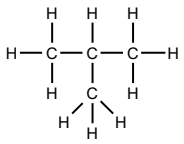
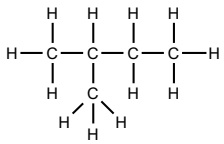
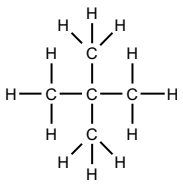
PETROLEUM & ALKANES

1) ALKANES

- Alkanes are a homologous series of saturated hydrocarbons with the general formula C_nH_{2n+2}.
- Alkanes are very unreactive, although they do burn and react with halogens (e.g. chlorine).

Boiling points of alkanes

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
 methane -162°C	 ethane -89°C	 propane -42°C	 butane -0.5°C	 pentane 36°C
			 methylpropane -12°C	 methylbutane 28°C
				 dimethylpropane 10°C

- The longer the carbon chain, the higher the boiling point due to stronger van der Waals' forces between molecules (because there are more electrons in the molecules).
- For alkanes that are isomers, the more branched the carbon chain, the lower the boiling point due to weaker van der Waals' forces between molecules (due to molecules not being able to pack as close together).

2) FRACTIONAL DISTILLATION OF PETROLEUM

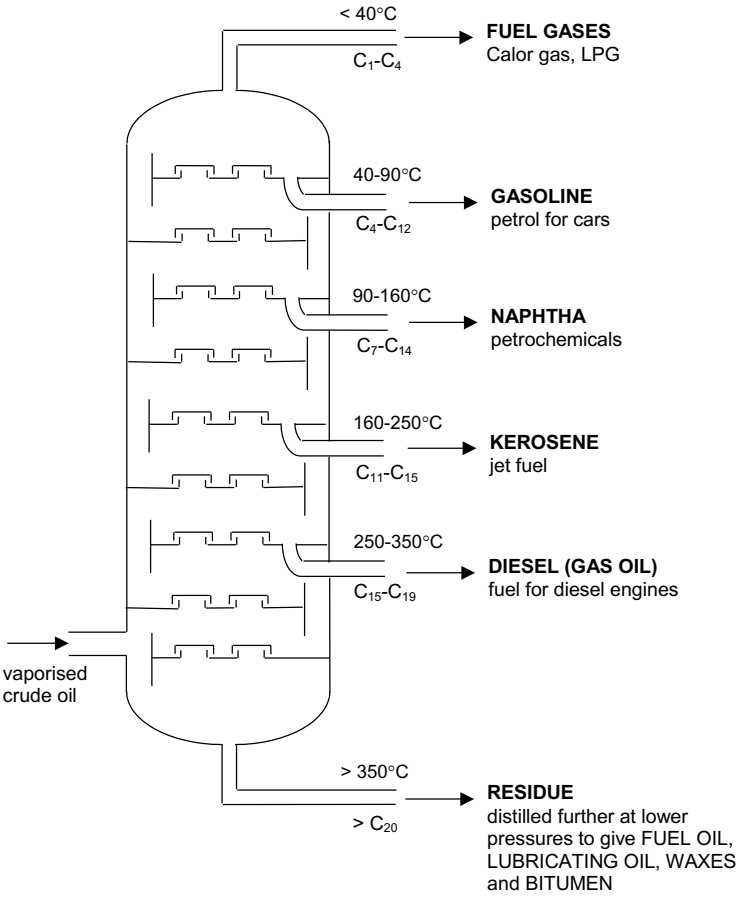
Petroleum

- Deposits of crude oil and natural gas usually occur together and they are formed by the slow decay of marine animals and plants, over millions of years, under heat and pressure in the absence of air.
- Although the exact composition of crude oils vary around the world, all are a complex mixture consisting mainly of alkanes (including cycloalkanes, some aromatics and other compounds containing some S and O).
- Crude oil has no use in its raw form, so to provide useful products its components must be partly separated (and if necessary modified) - the separation uses the differences in the physical properties of alkanes.

Fractional distillation

- The compounds in crude oil have different boiling points and this is used to separate them by fractional distillation at an oil refinery.
- C-H bonds are virtually non-polar, so there are only van der Waals' forces between molecules. As the alkane chain gets longer the melting and boiling points increase due to greater van der Waals' forces.

- The basic idea of the separation process is:
  - that crude oil is vaporised
  - the vapour is passed into a tower which is hot at the bottom and cold at the top
  - as the vapour rises it cools
  - molecules will condense at different heights as they have different boiling points
  - the larger the molecule (with higher boiling points), the lower down the column it condenses



- This produces fractions – a fraction is a mixture of hydrocarbons with similar boiling points.
- As the C chain gets longer, the hydrocarbons:
  - become more viscous
  - harder to ignite
  - less volatile
  - have higher boiling points

- The residue from the primary distillation (first distillation) contains useful substances, such as fuel oil, lubricating oil, waxes and bitumen, that boil above 350°C at atmospheric pressure. However, they would decompose at such high temperatures, so they separated further by distillation at lower pressure (vacuum distillation).

3) CRACKING

- The petroleum fractions with shorter C chains (e.g. petrol and naphtha) are in more demand than larger fractions.
- To make use of excess larger hydrocarbons and supply demand for shorter ones, longer hydrocarbons are cracked.
- Cracking is the thermal decomposition of alkanes.
- C-C bonds are broken in cracking.
- The products of cracking are more valuable than the starting materials (e.g. ethene used to make poly(ethene), branched alkanes for motor fuels, etc.)

Thermal cracking		**Catalytic cracking**
900°C	Temperature	450°C
70 atm	Pressure	1-2 atm
none	Catalyst	zeolites
alkenes	Products	motor fuels (aromatics, cyclic alkanes, branched alkanes)

4) REFORMING

- Reforming is a process where straight chain hydrocarbons are converted into branched chain alkanes and cyclic alkanes. Both these products burn more efficiently and are used in petrol for cars,

5) COMBUSTION

- Alkanes readily burn in the presence of oxygen, this combustion of alkanes being highly exothermic, explaining their use as fuels.
- The products of *complete* combustion are CO_2 and H_2O.

  e.g. $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ ΔH = -890 kJ/mol (i.e. very exothermic)
- If there is not enough oxygen then *incomplete* combustion occurs, producing CO (which is very toxic) and/or C:

  e.g. $CH_4(g) + {}^3/_2\ O_2(g) \rightarrow CO(g) + 2\ H_2O(l)$

  $CH_4(g) + O_2(g) \rightarrow C(s) + 2\ H_2O(l)$

Examples Write an equation for the complete combustion and two equations for the incomplete combustion of these alkanes:

propane (C_3H_8) .....

.....

.....

octane (C_8H_{18}) .....

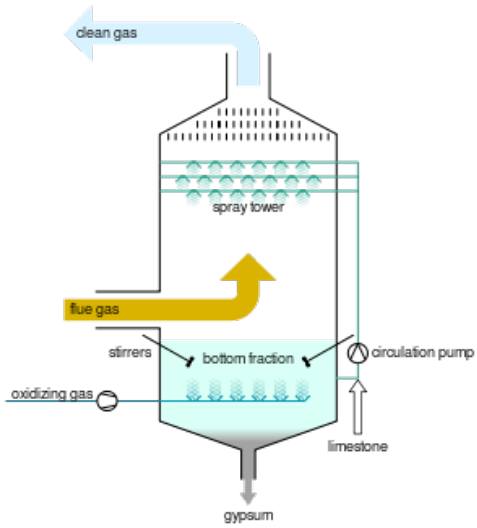
.....

.....

Pollutants from burning fossil fuels (e.g. fractions from oil)

Pollutant	How formed	Problem caused	Ways to reduce the problem
CO_2	complete combustion of fuels containing C	greenhouse gas	burn less fossil fuels
CO	incomplete combustion of fuels containing C	toxic	ensure a good supply of oxygen when burning fuels
C (soot)	incomplete combustion of fuels containing C	blackens buildings, can cause respiratory problems, global dimming	ensure a good supply of oxygen when burning fuels
H_2O	combustion of fuels containing H	not a problem	
SO_2	combustion of S containing compounds in fuel	acid rain	remove S from fuel before burning, flue gas desulfurisation
NO_x (NO, NO_2)	reaction of N_2 in the air with O_2 in the air at very high temperatures (in engines & furnaces)	acid rain	use catalytic converters in cars
unburned hydrocarbons	some of the fuel may not actually burn	wastes fuel	ensure engines are well-tuned and there is a good supply of oxygen

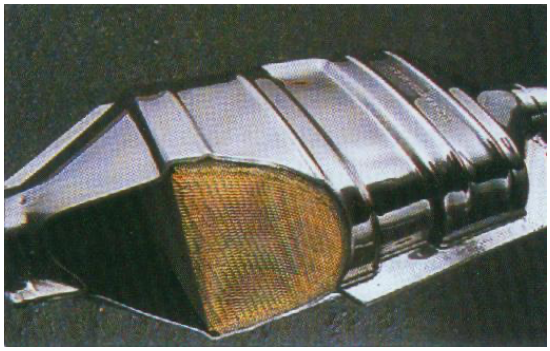
Formation of SO_2



- Sulfur containing impurities are found in petroleum fractions which produce SO_2 when they are burned, which lead to acid rain.
- SO_2 can be removed from the waste gases from furnaces (e.g. coal fired power stations) by flue gas desulfurisation.
- The gases pass through a scrubber containing calcium oxide or calcium carbonate which reacts with the sulfur dioxide,

  $CaO + SO_2 \rightarrow CaSO_3$ or $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$
- This is an acid-base reaction as $CaCO_3$ and CaO are bases and SO_2 is an acidic oxide (non-metal oxide).
- The reaction forms gypsum [calcium sulfate(IV)] which is used to make plasterboard

The internal combustion engine (e.g. cars)



- Petrol (gasoline fraction, which consists of liquid alkanes) is used in the internal combustion engine where the alkanes are vaporised and combusted with air.
- **Catalytic converters** remove CO, NO_x and unburned hydrocarbons (e.g. octane, C_8H_{18}) from the exhaust gases, turning them into CO_2, N_2 and H_2O.

  $2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2$

  $C_8H_{18} + 25\ NO \rightarrow 8\ CO_2 + 12½\ N_2 + 9\ H_2O$
- Converters have a ceramic honeycomb coated with a thin layer of catalyst metals (Pt, Pd, Rh) – to give a large surface area.

Global warming

- Greenhouse gases are gases that absorbs the IR radiation given off by the Earth, but do not absorb the higher frequency UV/visible radiation given off by the sun.
- Molecules that contain polar bonds absorb IR radiation to make bonds vibrate.
  - therefore, molecules such as CO_2 (the C=O bonds are polar), H_2O (the O-H bonds are polar) and CH_4 (the C-H bonds are slightly polar).
  - molecules such as O_2 and N_2 do not absorb IR radiation and are not greenhouse gases as they do not have polar bonds.
- The Earth is getting warmer and many scientists believe it is due to increasing amounts of greenhouse gases in the atmosphere.
- The burning of fossil fuels (including alkanes) releases carbon dioxide into the atmosphere. Carbon dioxide levels have risen significantly in recent years due to increasing burning of fossil fuels.
- Carbon dioxide is a particularly effective greenhouse gas and its increase is thought to be largely responsible for global warming.
- Methane levels have also increased significantly largely due to agriculture (e.g. rice production) and farming (e.g. cows).