9. Green Chemistry

Sustainability

The five principles of chemical sustainability:

(i) using industrial processes that reduce or eliminate hazardous chemicals and which involve the use of fewer chemicals

e.g. reduce the need to use finite raw materials such as crude oil

less harmful or corrosive reactants

Using more readily available starting materials

(ii) designing processes with a high atom economy that minimise the production of waste materials, often through discovering catalysts for reactions with higher atom economies

e.g. Designing processes with high atom economy that minimise production of waste products.

(iii) using renewable resources such as plant-based substances,

e.g. Develop ways of making polymers/ fuels from plant-based substances

(iv) making more efficient use of energy and seeking alternative energy sources such as solar energy, rather than consuming finite resources such as fossil fuels that will eventually be exhausted,

e.g. less toxic, corrosive waste products

Recycle heat in a process to heat the incoming reactants

(v) reducing waste and preventing pollution of the environment.

Ensuring that any waste products produced are non-toxic, and can be recycled or biodegraded by being broken down into harmless substances in the environment;

Develop biodegradable polymers

The 'Greenhouse Effect' and Global warming

A greenhouse gas absorbs Infra Red radiation re-radiating from the earth

- Carbon dioxide (CO_2), methane (CH_4) and water vapour (H_2O) are all greenhouse gases. (They trap the Earth's radiated infra red energy in the atmosphere).
- Water is the main greenhouse gas (but is natural), followed by carbon dioxide and methane.

Infrared radiation is absorbed by C=O, O–H and C–H bonds in H_2O, CO_2 and CH_4. The polarity of the molecules changes when their bonds vibrate.

The 'Greenhouse Effect' of a given gas is dependent both on its **atmospheric concentration** and its **ability to absorb infrared radiation** and also its **residence time.** (Time it stays in atmosphere)

Concentrations of Carbon dioxide in the atmosphere 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.

The Earth is thought to be getting warmer, and many scientists believe it is due to increasing amounts of greenhouse gases in the atmosphere.

Global warming could see rising sea levels, flooding, polar ice **melting,**
changing air currents, changing weather patterns, more extreme weather.

Human contributions to climate change are called **anthropogenic**

There has always been natural causes for climate change over hundreds of thousands of years, caused by changes in the sun's activity and volcanic activity.

Role of chemists in minimising climate change resulting from global warming

Chemists provide scientific evidence to governments to verify that global warming is taking place such as monitoring atmospheric changes

Chemists are investigating solutions to environmental problems, such as developing **carbon capture and storage, CCS.**

Chemists can monitor progress against initiatives such as the Kyoto protocol

Carbon Capture and Storage, CCS
Carbon dioxide could potentially be stored in a number of different ways
- removal of waste carbon dioxide as a liquid injected deep in the oceans or on the sea-bed.
- storage in geological formations or under the sea-bed by the reaction of carbon dioxide with metal oxides to form stable solid carbonates, which can be stored

Chemists can also develop
- alternative energy sources such as developing fuel cells or developing solar power or fuels that do not produce CO_2
- Develop more efficient engines for transport or lean burn engines
- Develop uses for carbon dioxide e.g. dry cleaning or making decaffeinated coffee OR blowing agent in polymer or making fizzy drinks.

Carbon Neutrality

The term carbon neutral refers to "an activity that has **no net annual carbon** (greenhouse gas) emissions **to the atmosphere**"

Ethanol as biofuel

A biofuel is a fuel produced from plants

Ethanol produced from fermentation is a biofuel.

It can be argued that ethanol produced from this method is classed as carbon–neutral as any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew.

Removal of CO_2 by photosynthesis

$\mathbf{6CO_2} + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

Production of CO_2 by fermentation and combustion

$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + \mathbf{2\ CO_2}$

$2\ CH_3CH_2OH + 6O_2 \rightarrow \mathbf{4CO_2} + 6H_2O$

Equations to show no net contribution to CO_2

This does not take into account any energy needed to irrigate plants, fractionally distil the ethanol from the reaction mixture or process the fuel. If the energy for this process comes from fossil fuels then the ethanol produced is not carbon neutral

Energy would be used to distil the ethanol water mixture after fermentation. Energy required to manufacture Fertilisers and insecticides to grow plants for biofuels in good yield. Energy is required to transport fuel to the power plant

Apparent benefits may be offset by unexpected and detrimental side effects. Note the advantages and disadvantages of using biofuels.

Advantages of using Biofuels

Reduction of use of fossil fuels which are finite resources
biofuels are renewable
Use of biodiesel is more carbon-neutral
Allows fossil fuels to be used as a feedstock for organic compounds
No risk of large scale pollution from exploitation of fossil fuels
new jobs created to grow crops on new farmland

Disadvantages of Biofuels

Less food crops may be grown
Land not used to grow food crops
Rain forests have to be cut down to provide land
May reduce biodiversity
Shortage of fertile soils

Hydrogen

A 'hydrogen economy' may contribute largely to future energy needs but limitations include:
(i) public and political acceptance of hydrogen as a fuel, with its risk of explosion.
(ii) handling and maintenance of hydrogen systems,
(iii) initial manufacture of hydrogen, requiring energy.

Hydrogen is readily available by the electrolysis of water, but this is expensive. To be a green fuel the electricity needed would need to be produced from renewable resources

The Ozone Layer

The naturally occurring ozone (O_3) layer in the upper atmosphere is beneficial as it filters out much of the sun's harmful UV radiation

Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog

Ozone is continuously being formed and broken down in the stratosphere by the action of ultraviolet radiation

$$O + O_2 \rightleftharpoons O_3$$

Ozone formation
UV light causes an O_2 molecule to split into free radicals

$$O_2 + \text{UV-light} \rightarrow O + O$$

When the free radical hits another O_2 molecule ozone forms

$$O + O_2 \rightarrow \mathbf{O_3}$$

Ozone depletion
This is the reverse of the formation reaction.. The energy is supplied by ultraviolet light

$$O_3 + \text{ultraviolet light} \rightarrow O_2 + O$$

There is a continuous cycle of formation and depletion of ozone

rate of ozone formation = rate of ozone removal

So there is a constant amount of ozone in the atmosphere

The frequency of ultra-violet light absorbed equals the frequency of biologically damaging ultra-violet radiation. These reactions therefore filter out harmful UV from reaching the Earth's surface and allow life to survive on earth.
UV light can increase risk of skin cancer and increase crop mutation.

Destruction of Ozone Layer

Radicals from CFCs, and NO*x* from thunderstorms or aircraft, may catalyse the breakdown of ozone

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break. The C-F bond is much harder to break than the C-Cl bond.

$$CF_2Cl_2 \rightarrow CF_2Cl^{\bullet} + Cl^{\bullet}$$

The chlorine free radical atoms **catalyse** the decomposition of ozone due to these reactions because they are regenerated. (They provide an alternative route with a lower activation energy)

They contributed to the formation of a hole in the ozone layer.

$$\mathbf{Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2}$$

$$\mathbf{ClO^{\bullet} + O^{\bullet} \rightarrow O_2 + Cl^{\bullet}}$$

Overall equation

$$\mathbf{O_3 + O^{\bullet} \rightarrow 2\,O_2}$$

The regenerated Cl radical means that one Cl radical could destroy many thousands of ozone molecules

Aircraft releasing NO is a problem because they release it closer to the ozone layer

$$\mathbf{NO + O_3 \rightarrow NO_2 + O_2}$$

$$\mathbf{NO_2 + O^{\bullet} \rightarrow O_2 + NO}$$

Overall equation

$$\mathbf{O_3 + O^{\bullet} \rightarrow 2\,O_2}$$

Legislation to ban the use of CFCs was supported by chemists and that they have now developed alternative chlorine-free compounds

HFCs (Hydro fluoro carbons) e.g.. CH_2FCF_3 are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond

CFC's still concern us because CFCs are still entering the atmosphere from disused items and are still used for some purposes and by some countries.
CFCs have a long lifetime in the atmosphere and it takes a long time for CFCs to reach upper atmosphere.