Polymers

PET- di-carboxylic acid + di-alcohol

Nylon- di-amine + di-carboxylic acid

Condensation polymerisation- produces 2 water (or something else)

Proteins

A proteins primary structure will determine how its chains fold and curl on itself.

- Primary structure- how amino acids are arranged in the protein

- Secondary structure- the regular arrangement of various sections of the protein chain (alpha helix, beta-pleated sheets), held together by ONLY hydrogen bonding.

- Alpha-helix occurs between a lone pair of electrons from oxygen atom of a carbonyl group (-C=O) and the polar hydrogen atom of an amide group (-N-H).

- Beta-pleaded sheets occur with sections of the polypeptide chain where the alpha amino acid have small side chains.

- Tertiary structure- the over 3D shape that forms as a result of the main chain folding and bonding back on itself. It is due to various bonds that form between some of the residue side chains. These bonds include disulphide bridges, hydrogen bonds, dipole-dipole forces, dispersion forces and ionic bonds. When sufficient heat is applied, the bonds than maintain its shape will be more likely to break. When a protein loses its shape in this way its said to be Denatured.

Disulfide bridge- consists of a covalent bond between two sulfur atoms from two **cysteine** residue side chains, when the cysteine residues align their –SH groups each lose a hydrogen atom (oxidation) leaving the two sulfur atoms free to join by a covalent bond. The disulphide bridge then strongly holds together the two parts of a polypeptide chain thus contributing to the protein’s tertiary structure. This also happens between side chains that contain groups like -OH, -COOH or –NH2. While these interactions are weaker than the disulphide bridges, they still contribute to a protein’s tertiary structure. Similarly, dipole-dipole and even ionic bonds can occur between residue side chains.

Quaternary structure- how its subunits are oriented and arranged with respect to one another. Only applies to multi-subunit proteins, that is, proteins made from more than one polypeptide chain. Protein made from a single polypeptide will not have a quaternary structure.

Structure and function of a protein are both related to the specific sequence of amino acid in its primary structure.

Enzymes-

Many proteins found in living systems act as catalysts and are known as enzymes. Most enzymes tend to be very specific in the reactions they catalyse and much faster acting. Often it is their complex structure and particularly their specific shape that allows a given reagent molecule called the substrate, to fit onto a specific active site on the enzyme surface. It is for this reason that a particular enzyme will often only catalyse a specific reaction (enzyme specificity).

Enzymes are sensitive to both temperature and pH. These conditions affect an enzymes shape and hence affect its catalytic properties. For this reason, enzymes have a preferred operating range for both temperature and pH.

In an uncatalysed reaction, the rate always increases with increasing reactant concentration. In an enzyme catalysed reaction however, the rate does initially increase with increasing substrate concentration until at some point there is no further increase in rate. At this point all of the active sites on the available enzyme molecules are occupied by substrate molecules undergoing their catalysed reaction.

Biofuels (bioethanol and biodiesel)

-Produced from biomass and are considered as fossil fuel alternatives.

- renewable resource

- CO2 emissions from biofuels can be balanced with the Earth’s carbon cycle as the carbon in these fuels simply replaces atmospheric CO2 absorbed by plants.

- Petroleum based fuels frequently contains sulfur, and combustion releases sulfur dioxide, which has negative effect on human health and also leads to acid rain.

- Petroleum require extra treatment to remove or reduce their sulfur content. Biofuels do not require extra treatment as their sulfur content is negligible.

-Biofuels burn cleaner, produce less particulate emissions (soot) than do petroleum based fuels.

- Biodiesel combustion however is prone to producing slightly higher emissions of toxic nitrogen oxides.

Ethanol production-

1 volume Ethene (alkene) + 0.6 volume H2O vapour (steam) = Ethanol (alcohol)

-Two commonly used methods- acid catalysed addition of water to ethene and the enzyme catalysed fermentation of sugars.

- Ethanol produced from fermentation is a biofuel as it is manufactured using biomass whereas ethanol from the acid catalysed addition of water to ethene is not a biofuel as ethene originates from fossil fuel sources.

- Fermentation uses renewable resources whereas manufacturing ethanol from ethene uses non-renewable resources.

- Using enzymes in the fermentation process results in less energy use as well as reaction conditions and chemicals that are inherently safer.

- Fermentation is conducted at atmospheric pressure, ambient temperature and a moderate pH

- Manufacture of ethanol from ethene uses a high pressure (60-70 atp), ~300C, and a corrosive acid catalyst (H3PO4)

- Fermentation to produce ethanol

1. Hydrolysis of sucrose to glucose and fructose (isomers of C6H12O6). Catalysed by yeast enzyme invertase or sucrase.

2. Fermentation of glucose/fructose mixture to ethanol and carbon dioxide. Catalysed by yeast enzyme zymase.

-As fermentation is an exothermic reaction, cooling is required, as enzymes are sensitive to temperature.

Ethanol synthesis (from ethene)-

-Quicker methods for producing ethanol.

- Uses the acid catalysed addition of water to ethene, and is easily adapted as a continuous processs.

- Involves passing mixture of steam and ethene through a catalyst bed made of silica particles coated with pure phosphoric acid as catalyst.

- Ethene to water molar ratio of 1:0.6 is used, as higher concentrations of steam result in the undesirable dilution and washing away of the phosphoric acid catalyst coating on the silica particles.

- Used as feedstock for the manufacture of other industrial chemicals rather than as a fuel or beverage additive.

- Does not have the advantages of bioethanol as it is produced from non-renewable petroleum based resources (ethene) and its combustion does contribute to increasing atmospheric CO2 concentration.

Biodiesel

-Liquid consisting typically of the methyl or ethyl esters of naturally occurring fatty acids.

- Production is almost entirely by the base catalysed trans-esterification of triglycerides present in natural fats and oils.

Biodiesel: Base catalysed trans-esterification of triglycerides

-Water must be removed from the reaction mixture as its presence results in a side reaction involving the conversion of esters, free fatty acids, and triglycerides into soap.

- Soap formation is undesirable as its production wastes valuable reagent and its presence in the final reaction mixture causes biodiesel and its co-product glycerol to form an emulsion making them much harder to separate.

- Fatty acid + methanol <--> methyl ester (biodiesel) + water

-Catalyst is used to speed up reaction. Most biodiesel production uses a strong base such as sodium hydroxide to catalyse the reaction.

- Triglyceride + 3 methanol < --- > 3 methyl ester (biodiesel) + glycerol

-Stoichiometric ratio of alcohol to TG is 3:1, however alcohol is added to large excess, up to 6:1, as its higher concentration in the reaction mixture favours a high equilibrium yield of biodiesel.

-Biodiesel and glycerol are essentially insoluble in one another hence once the reaction is complete they form two separate layers. Biodiesel is separated from the top later while the denser glycerol forms a bottom layer. Most of the excess methanol, the base catalyst or any soap that may have formed remain in the glycerol layer with only small amounts in the biodiesel.

Based-catalysed transesterification-

-Transesterification is the process in which an ester reacts with an alcohol so that the alkyl section of the alcohol replaces the alkyl section on the ester that is attached to the O.

- Similar to the saponification reaction for soap making. If this base catalysed reaction is performed in the presence of methanol it transforms the triglycerides into biodiesel rather than soap.

- To favour the production of the biodiesel, the concentration of methanol is kept high.

- Water is removed from the system as its presence can lead to the triglyceride reaction with NaOH catalyst to form soap.

Lipase catalysed transesterification (enzymes)

-Lipase is an enzyme that catalyses the hydrolysis of fats.

- Enzymatic transesterification has advantages over the chemical catalysis of transesterification as it is less energy intensive and allows easy recovery of glycerol.

- Limitations of enzyme catalysed reactions include high cost of enzymes, low yield and long reaction time.

- Advantage over traditional base catalyst due to:

* Ability to operate at milder temperatures and milder pH
* Lipase can simultaneously catalyse the transesterification of TGs and the esterification of free fatty acids into biodiesel.
* Use significantly less energy as lower temperatures are involved and the products needs less or no refining.

-Lipase catalysts are slower acting so higher catalyst concentration is needed in order to achieve the faster reaction rates offered by traditional catalysts.

- Lipase catalysts are currently quite expensive

- Lipase recovery from within the final reaction mixture is difficult to achieve, fresh lipase must be used for each batch of biodiesel, which increases cost of production.

- If lipase is used in presence of high concentrations of alcohol, especially methanol, or glycerol, both of these reagents inhibit lipase and prevent its catalytic effect, this is problematic as glycerol is a product of transesterification and high methanol concentrations are typically used for maximising the equilibrium yield of biodiesel.

Haber process: Ammonia synthesis (from nitrogen and oxygen)

Contact process: Sulfuric acid synthesis (from sulfur, water and oxygen)

1. Molten sulfur is burnt in dry air at around 1000C. At this stage only SO2 is produced.
2. Sulfur dioxide is converted to sulfur trioxide according to the following equilibrium reaction.

2SO2 + O2 < -- > 2SO3 (exothermic)

Formation of SO3 is problematic as the forward reaction is exothermic. A high yield is favoured by low temperature and high pressure. However, a low temperature slows the reaction rate and using high pressures introduces excessive cost into the manufacturing process. Typically ratio of 1:1 is used to increase equilibrium yield of SO3 from SO2. The formation of SO3 is exothermic so it is necessary to use heat exchangers to extract heat from the gas mixture thus preventing its temperature from rising excessively.

1. The conversion of sulfur trioxide and water to sulfuric acid is achieved indirectly by initially absorbing SO3 into H2SO4 to produce an oily compound called oleum. Addition of water to oleum then produces 98% H2SO4.
2. Direct addition of SO3 into water only results in a low yielf and a difficult to manage mist of H2SO4.

Manufacture of ethyl ethanoate-

* From ethanoic acid + ethanol (high concentrated acid catalyst)

Factors that can lead to a reduced yield:

* Loss of reagent due to unwanted side reactions that unnecessarily consume reagents
* Physical loss of product. Due to the inability to completely separate or purify the product from the final reaction mixture.
* Equilibrium reactions that do not go to completion.
* Presence of impurities in the reagents meaning the amount of reagent added is less than the amount measured.

Biodiesel production- why 2 different types of catalyst