A2 Chemistry Notes – OCR Unit 4: Rings, Polymers and Analysis

Aromatic Chemistry:

- An arene is a hydrocarbon containing at least one benzene ring. Benzene is formed of a ring of six carbon atoms, each of which is bonded to a hydrogen atom. It has the molecular formula C_6H_6 and skeletal formula \bigcirc .
- The standard state of benzene is a colourless liquid with a sweet odour (chemistry involving benzene and its derivatives is known as aromatic chemistry). It is a carcinogen, causing anaemia and leukaemia, but can be used to make a wide range of chemicals with uses in industry, pharmaceuticals and as explosives.
- If one of the hydrogen atoms on a benzene ring is replaced by a functional group or alkyl chain, a benzene derivative is formed. Common groups attached to benzene rings include halogens, NO₂ and alkyl groups. Appropriate prefixes are added to the suffix -benzene to name the compounds; carbon atoms are numbered to avoid ambiguity and given the smallest possible numerical values.
- Benzene is produced naturally from volcanoes and forest fires, and is also present in crude oil and cigarette smoke.

Structure of Benzene:

- An original proposed structure of benzene by Friedrich August Kekulé von Stradonitz was that of cyclohexa-1,3,5-triene (⁽⁾). This model was inadequate because it disagreed with several observations:
 - Low reactivity: the Kekulé structure, containing double bonds, would be highly unstable and react easily with halogens or hydrogen halides; benzene does not readily react with halogens.
 - Bond length: the bonds between carbon atoms can be shown to be of uniform length at around 0.139nm (between the lengths of C–C and C=C bonds. The Kekulé model predicts uneven bond lengths as it has alternating double and single bonds.
 - Enthalpy changes: under the Kekulé structure, the enthalpy change of reaction for the hydrogenation of benzene to cyclohexane should be -360kJ mol⁻¹. Experimental data give an enthalpy change value of -208kJ mol⁻¹.
- The main conclusion that can be drawn from the above evidence is that benzene is more stable (i.e. lower in energy) than cyclohexa-1,3,5-triene. The modern, widely accepted structure for benzene is the delocalised model. In this model, the carbon atoms in the ring each form three σ -bonds (two with carbon atoms, one with hydrogen) using three of its four outer-shell electrons. This leaves one electron from each carbon atom in a 2p orbital. These orbitals overlap, giving a delocalised ring of electron density above and below the carbon atoms this is known as a π -system. The molecule has a trigonal planar structure around each carbon atom and is hexagonally planar overall.
- The overlap of the p orbitals results in a net lowering of the π electrons' energy. This explains the high stability of the benzene ring, as well as its tendency not to participate in addition reactions: an addition reaction would disrupt the π -system and be unlikely to result in a favourable lowering of energy.

Reactions of Benzene:

- The delocalised electrons in benzene attract electrophiles; to preserve the stability of the π -system benzene normally takes part in substitution reactions. In these, an electrophile replaces one or more of the hydrogen atoms bonded to the ring.

When an electrophile approaches the π -system, a pair of the delocalised π electrons is accepted by it, forming a covalent bond. This disrupts the π -system; the intermediate formed is highly unstable and immediately releases the hydrogen atom as a H⁺ ion. The general reaction mechanism for electrophilic addition to benzene is outlined in fig. 1.

- One specific example of an electrophilic substitution reaction is the formation of nitrobenzene ($C_6H_5NO_2$). The reagents required are benzene and concentrated nitric acid, as well as concentrated sulphuric acid (a catalyst). The temperature for the reaction is 50°C (any higher and more than one nitro group may substitute the benzene ring). The reaction takes place as follows:
- ene is outlined in n reaction is the the the required are entrated sulphuric 50°C (any higher enzene ring). The Iphuric and nitric
 - $\circ~$ The nitronium ion (NO2⁺) is formed from sulphuric and nitric acid in solution:

 $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O_2^-$

- $\circ\;$ The nitronium ion acts as a nucleophile and substitutes the by the above mechanism.
- \circ $\;$ The sulphuric acid catalyst is regenerated:

Н

$$^{+}$$
 + HSO₄ \rightarrow H₂SO₄

- When a halogen molecule such as Br₂ approaches a localised π -bond such as that in cyclohexene, the high electron density induces a dipole across the molecule; the δ^+ end of this is sufficiently charged to act as an electrophile. However, this does not occur with benzene. This is because the π -electrons are delocalised: the electron density is not as high as in cyclohexene, and the dipole induced is not strong enough for the δ^+ end to act as an electrophile. Thus, benzene is resistant to reaction with non-polar molecules. It will, however, react with stronger electrophiles such as positively charged species.
- In order to halogenate a benzene ring, a halogen carrier such as AIX₃ or FeX₃ (where X is a halogen) may be used as a catalyst:
 - The halogen carrier reacts with the molecular halogen to form, for example, a positively charged bromonium ion:

$$\text{FeBr}_3 + \text{Br}_2 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$$

- The bromonium ion then reacts with benzene via the above electrophilic substitution mechanism.
- \circ The H⁺ ion reacts with the FeBr₄⁻ ion, reforming FeBr₃ and HBr.
- $\circ~$ Iron (Fe) can also be used in this reaction as it will form an iron(III) halide which can act as a halogen carrier.

Phenols:

- A phenol is an organic compound containing a benzene ring with a hydroxyl (–OH) group attached to it. The oxygen in the –OH group must be directly bonded to a carbon in the ring, or the compound is known as an aromatic alcohol.



> A⁺

н

1.

2. A

- The simplest phenol is C₆H₅OH, known (unsurprisingly) as phenol. It is solid under standard conditions and is slightly water soluble due to hydrogen bonding between –OH groups. However, the large, non-polar benzene ring decreases its solubility.
- Phenol is weakly acidic when aqueous, dissociating to form H^+ ions: $C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$. It reacts as other weak acids do:
 - $\circ~$ With metals such as sodium to produce a salt (e.g. sodium phenoxide $C_6 H_5 O^{-} Na^{+})$ and hydrogen gas.
 - $\circ~$ With alkalis such as potassium hydroxide to produce an aqueous salt (e.g. potassium phenoxide).

Reactions of Phenol:

- Phenol reacts with halogens in a similar way to benzene: by electrophilic substitution. Unlike benzene, phenol will react with molecular halogens at room temperature forming, for example, 2,4,6-tribromophenol. The tribromophenol will form a white precipitate:



- The reason for phenol's high reactivity (thus why it forms tribromophenol instead of bromophenol) is due to the lone pair on the oxygen atom of the –OH group. This is in a 2p orbital, and is drawn in to the delocalised π -system of the benzene ring. This increases the electron density of the benzene ring, and allows it to induce a dipole across halogen molecules which is strong enough for the positive end to act as an electrophile.
- Phenol and its derivatives have a variety of uses: alkyl phenols are used in detergents; chlorophenols are used as antiseptics; salicylic acid (phenol with a methanoate group on the second carbon) is important in the synthesis of analgesics.

Carbonyl Compounds:

- Aldehydes and ketones both contain a carbonyl (C=O) group; in aldehydes this is on the end carbon, whilst in ketones it is located on one of the central carbon atoms.
- The C=O bond, like a C=C bond, is formed of a σ -bond from the overlap of sp orbitals, and a π -bond from p orbital overlap. However, unlike a C=C bond, a C=O bond is polar: the carbon atom is δ^+ whilst the oxygen atom is δ^- . This means that the electron density of the π -bond is higher around the oxygen atom.
- In aldehydes, the carbon atom of the carbonyl group is numbered 1; the molecule is named thus (with the suffix –al). In ketones, the molecule is named so as to give the carbonyl carbon the lowest possible number (the suffix –one is used).
- Aldehydes and ketones can also be aromatic. The simplest examples are benzaldehyde (C₆H₅CHO) and phenylethanone (C₆H₅C(O)CH₃). Note that an oxygen atom cannot be directly double-bonded to a benzene ring; this would disrupt the π -system.

Oxidation and Reduction of Alcohols, Aldehydes and Ketones:

- Primary and secondary alcohols can be oxidised using an oxidising agent such as acidified potassium dichromate (H^+/Cr_2O_7) . During the reaction, the potassium dichromate (i.e. $K_2Cr_2O_7$) changes colour from orange to green – this can be used to identify if oxidation has occurred. The H^+ ions (from H_2SO_4) catalyse the reaction.

- Primary alcohols, when heated gently with acidified potassium dichromate form aldehydes (e.g. $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$). If the aldehyde is the desired product, it must be removed by distillation to prevent further oxidation occurring.
- Carboxylic acids are formed when an aldehyde or primary alcohol is heated under reflux with acidified potassium dichromate (e.g. $CH_3CHO + [O] \rightarrow CH_3COOH + H_2O$).
- When a secondary aldehyde is oxidised by acidified potassium dichromate, a ketone is formed (e.g. CH₃CH(OH)CH₃ + [O] → CH₃C(O)CH₃ + H₂O). The reaction does not continue; ketones are resistant to oxidation, as are tertiary alcohols.
- A reducing agent such as aqueous sodium tetrahydroborate (NaBH₄ also known as sodium borohydride.) can be used to reduce aldehydes and ketones, reversing the avidation process on clockel is formed. The symbol for

oxidation process: an alcohol is formed. The symbol for a reducing agent is [H] (e.g. $CH_3CHO + 2[H] \rightarrow$ CH_3CH_2OH , or $CH_3C(O)CH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$). In these reactions, water is used as a solvent and a secondary reactant.

- The mechanism for the reduction of carbonyl compounds in nucleophiles addition. A curly arrow description of the mechanism is outlined in fig. 2:
 - The BH₄⁻ ion (from sodium borohydride) acts as a source of hydride (:H⁻) ions.
 - \circ A hydride ion acts as a nucleophile and attacks the δ⁺ end of the C=O dipole, where there is a lower electron density. It donates an electron pair; the π-bond breaks and forms an unstable intermediate with a negative charge.
 - The intermediate donates an electron pair to a water molecule, forming a dative covalent bond; the –OH bond in water breaks by heterolytic fission. This forms an alcohol and an OH⁻ ion.



Fig. 2

Chemical Tests on Carbonyl Compounds:

- 2,4-dinitrophenylhydrazine, or 2,4-DNP can be mixed with methanol and sulphuric acid to make a mixture known as Brady's reagent. When added to an aldehyde or ketone, the 2,4-DNP reacts with the carbonyl group to form an orange or yellow precipitate. Thus, Brady's reagent can be used to identify carbonyl compounds (it will not react with the C=O bond of an ester or carboxylic acid).
- The melting point of a carbonyl compound's 2,4-DNP derivative can be used to identify the compound more precisely. Firstly, the precipitate is filtered and recrystallized to remove any impurities. It is then heated and the melting point is recorded – this can be compared to a database to identify the compound. This method is effective because 2,4-DNP derivatives usually have very distinct melting points.
- The distinction between an aldehyde and a ketone can be achieved using Tollen's reagent. This is a solution prepared from sodium hydroxide and silver nitrate this forms a silver oxide precipitate which is in turn dissolved in ammonia. It easily oxidises aldehydes to carboxylic acids at room temperature. This causes a silver-grey precipitate to form the test is also known as the 'silver mirror test.' No reaction will occur with ketones, as these are resistant to oxidation.

Carboxylic Acids:

- Carboxylic acids contain the carboxyl group; –COOH. They are commonly found in nature: examples include citric or lactic acid. They are named with the suffix –oic acid; as with aldehydes and ketones, the carbon of the carboxyl group is numbered 1.
- Carboxylic acids are water-soluble due to the polar C=O and O–H bonds, which form hydrogen bonds with water molecules. Solubility decreases as the acids increase in size due to the larger non-polar hydrogen chains.
- Carboxylic acids dissolve in water to form H⁺ ions and carboxylate (R–COO⁻) ions.
 Compared to nitric acid or sulphuric acid they are very weak.
- Carboxylic acids, like other acids will react with reactive metals to produce hydrogen gas, and a salt known as a carboxylate. They will also react with bases (e.g. NaOH, forming a carboxylate and water) or metal carbonates (forming a carboxylate, water and carbon dioxide).

Esters:

- An ester is formed when an alcohol is heated under reflux with a carboxylic acid in the presence of an acid catalyst (typically sulphuric acid). During esterification a water molecule is removed to form an ester bond. Esters are named by combining the name of the alcohol (for the alkyl part) with that of the carboxylic acid (for the alkanoate part). For example, propanol and ethanoic acid form propyl ethanoate.
- Esters can also be prepared using acid anhydrides. These consist of two carboxylic acids bonded together by removal of a water molecule. They react with alcohols to form an ester and a carboxylic acid; this gives a better yield of ester than a standard carboxylic acid.
- An ester bond can be broken by hydrolysis the addition of a water molecule across the bond:
 - Acid hydrolysis: the ester is heated under reflux with dilute aqueous sulphuric or hydrochloric acid. This forms a carboxylic acid and an alkali, and is a reversible reaction (e.g. $CH_3COOCH_2CH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3CH_2OH$).
 - Alkaline hydrolysis: the ester is heated under reflux with aqueous sodium or potassium hydroxide. The ester reacts with the alkali and forms an alcohol, and the sodium (or potassium) salt of the carboxylic acid. (e.g. $CH_3COOCH_2CH_3 + NaOH \rightarrow CH3COO^{-}Na^{+} + CH_3CH_2OH$). The reaction with
 - sodium hydroxide is known as saponification it is a key part of soap-making.
- Esters typically have pleasant smells; they are often used in perfumes and as food flavourings. Many esters are produced naturally by plants, in leaves and flowers.

Fats and oils:

- Fats and oils are used in both plants and animals for insulation, lubrication and as an energy store. They are chemically similar; fats have melting points above room temperature whilst oils are liquids at room temperature.
- Triglycerides are contained in fats. They are formed from glycerol (propan-1,2,3-triol) and three fatty acids.
- Fatty acids are long-chain aliphatic carboxylic acids. They can be saturated (no double bonds), monounsaturated (one double bond) or polyunsaturated (multiple double bonds). Due to the nature of their synthesis, they normally have an even number of carbon atoms. The structure of fatty acids can be denoted in shorthand as *n:x* (*a*,*b*,...) where *n* is the number of carbon atoms, *x* is the number of double bonds

and the numbers in the brackets denote the position of the double bonds. For example, hexadeca-9,11-dienoic acid is denoted 16:2 (9,11).

- A triglyceride forms when a fatty acid joins to each alcohol group on a glycerol molecule by ester linkage. Normally in nature there are two or three different fatty acids, producing a wide variety of triglycerides.

Triglycerides, Diet and Health:

- Cis-trans isomerism is a special case of E/Z isomerism in which each carbon atom around a double bond carries a group which is the same (in the case of fatty acids, there is a hydrogen atom bonded to each carbon). If they are on the same side of the double bond the molecule is a cis isomer; if they are on opposite sides it is a trans isomer.
- Trans fatty acids are linear, so pack closely together and have higher melting points. Conversely, Cis fatty acids cannot pack as closely together, so have lower melting points.
- In industry, monounsaturated fats are often hydrogenated (and thus saturated) to raise their melting points, such as when vegetable oils are hydrogenated to form margarine. This can also change cis fats into their trans counterparts.
- Trans fats and saturated fats are thought to raise the concentration of LDLs (lowdensity lipoproteins) in the blood. These deposit cholesterol in the arterial walls and restrict blood flow. The proportion of HDLs (high-density lipoproteins) is also reduced; these are responsible for removing cholesterol from the blood. Thus, a diet high in trans and saturated fats can result in raised cholesterol and should be avoided.
- Triglycerides are used to form biodiesel. This is a methyl or ethyl ester of a fatty acid and is formed by transesterification: a triglyceride is reacted with methanol in the presence of an alkaline catalyst such as NaOH. This forms biodiesel as the methanol replaces the glycerol; the glycerol molecule is removed and can be used in the pharmaceutical or cosmetic industries.

Amines:

- Amines are derivatives of ammonia in which one or more of the hydrogen atoms are replaced by a hydrocarbon chain. They are common in nature due to their physiological effects: examples include adrenaline and nicotine.
- Amines can be primary, meaning that only one hydrogen atom is replaced, or secondary or tertiary, meaning that two and three Fig. 3
 hydrogen atoms respectively are replaced.
- The longest hydrocarbon chain is used to name the amine, with the suffix-amine. Other chains in secondary or tertiary amines are added before the name: the



secondary or tertiary amines are added before the name; their positions are denoted by *N*. For example the molecule illustrated in fig. 3 would be named N-ethyl-Nmethylpropylamine.

- Like ammonia, amines have a lone pair of electrons on the nitrogen atom. This can form a dative covalent bond with a H^+ ion; amines are weakly basic, accepting protons to form alkylammonium ions.
- Amines react with acids to form an alkylammonium salt. For example, ethylamine reacts with hydrochloric acid to form ethylammonium chloride ($CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$).

Reactions of Amines:

- Aliphatic primary amines can be prepared by gently warming halogenoalkanes with an excess of ammonia, using ethanol as a common solvent. The lone pair on the nitrogen atom in the ammonia acts as a nucleophile; the halogen atom is substituted for an NH₂ group, forming an amine and a halogen halide (e.g. $CH_3CI + NH_3 \rightarrow HCI +$ CH_3NH_2). The acid formed is neutralised by the ammonia to form an ammonium salt.
- Amines also have lone pairs of electrons, so can act as nucleophiles themselves; this means that when primary amines are formed, further reactions can form secondary and tertiary amines. If a primary amine is desired, the excess of ammonia minimises secondary and tertiary substitution.
- Aromatic amines are prepared by the reduction of nitroarenes such as nitrobenzene. A mixture of tin and hydrochloric acid is used as a reducing agent. For example, nitrobenzene is reduced to form phenylamine and water ($C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$). Fig. 4
- Phenylamine can be used in the synthesis of azo dyes. This is achieved in two steps:
 - Diazotisation: sodium nitrite and hydrochloric acid react to form nitrous acid (NaNO₂ + HCl → HNO₂ + NaCl). The nitrous acid reacts with more hydrochloric and phenylamine at temperatures below 10° C to form a diazonium salt, benzenediazonium chloride, and water (C₆H₅NH₂ + HNO₂ + 2HCl → C₆H₅N₂⁺Cl⁻ + 2H₂O).



 Coupling: the diazonium salt (illustrated in fig. 4) is reacted with a phenol under alkaline conditions. This produces a dye in which two benzene rings are linked by an azo group (–N=N–).

Amino Acids:

- Amino acids are molecules which comprise the monomer units in peptides and proteins. These are used extensively in living organisms for growth, repair and structural support, as well as carrying out metabolic functions.
 Fig. 5
- Amino acids have the general formula RCH(NH₂)COOH (fig. 5); they contain both an amine group and a carboxylic acid group. The variable R group has 20 different naturally occurring versions, with differing complexity.



- At a certain pH, the carboxyl and amine groups on the same



amino acid can interact, forming a zwitterion (fig. 6): the carboxyl group donates a proton to the amine group. This pH is known as the isoelectric point; there is no electric charge across the molecule (note that this means that only one amine and one carboxyl group will ionise). The isoelectric point is specific to each amino acid; changing the R group will change the isoelectric point.

 Amino acids are amphoteric – they can act as both acids and bases. This enables them to act as buffers: at pH values above the isoelectric point, the carboxyl group donates protons to the solution, lowering the pH. Conversely, at pH values below the isoelectric point the amine group accepts protons, raising the pH. This causes the molecule to become charged accordingly.

Polypeptides and Proteins:

- The carboxyl group of one amino acid can form a peptide bond with the amine group of another. In this reaction, a water molecule is removed (condensation) and a dipeptide is formed.
- A long chain of amino acids joined by peptide bonds is known as a polypeptide or protein. The variety of amino acids and the length of protein chains results in billions of possible permutations.
- Polypeptides can be broken down by hydrolysis. As with ester hydrolysis, there are two methods:
 - Acid hydrolysis: the polypeptide is heated under reflux with a concentrated aqueous acid (traditionally 6 mol dm⁻³ HCl for 24 hours). The amino acids formed are positively charged due to the H^+ ions present (i.e. RCH(NH₃⁺)COOH).
 - Alkaline hydrolysis: the polypeptide is heated is heated at just over 100°C with aqueous sodium hydroxide. A sodium hydroxide molecule is added across the peptide bonds, forming sodium salts of the constituent amino acids (i.e. RCH(NH₂)COO[¬]Na⁺).

Optical Isomerism:

- Optical isomerism is a special case of stereoisomerism which occurs around chiral centres. A chiral centre is a carbon atom which is bonded to four different groups;

molecules with a chiral centre have two nonsuperimposable isomers which are mirror images of one another, known as optical isomers (fig. 7).



- Optical isomers are chemically identical, but rotate plane-polarised light in different directions. Many organic molecules are optically active, such as amino acids (excluding glycine – HCH(NH₂)COOH).
- A mixture containing equal proportions of optical isomers is known as a racemic mixture. Racemic mixtures have no effect on plane-polarised light; the two rotational directions cancel each other out. A mixture containing only one optical isomer is known as enantiopure.
- A molecule with *n* chiral centres will have 2ⁿ optical isomers; two chiral centres give four optical isomers, three will give eight, etc.
- Optical isomerism is vitally important in the production of pharmaceutical compounds. In cases such as Thalidomide, one isomer can have a beneficial effect whilst the other can cause fatal problems.
- Drugs are normally produced containing only one optical isomer of a chiral compound; only one is pharmacologically active (i.e. has a beneficial effect on the body's function). This reduces the risk of undesirable side effects, and means that the required dose of the drug is halved.
- Several methods are used to synthesise a single isomer of a molecule:
 - The use of enzymes: these have a specific three-dimensional shape and will only synthesise one optical isomer.
 - Chiral pool synthesis: this uses naturally occurring chiral molecules such as amino acids to create an enantiopure mixture.
 - The use of transition element complexes to form chiral catalysts.

Condensation Polymerisation:

- Condensation polymers are formed when a small molecule (usually water) is eliminated to form a bond between monomer units. Condensation requires the formation of a bond between differing functional groups on differing molecules.
- Polyesters are a type of condensation polymer. These are formed when the interacting functional groups are a hydroxyl group (–OH) and a carboxylic acid group (–COOH). They can be formed in two different ways:

o From a diol and a dicarboxylic acid, a bond forms between the hydroxyl group

and the carboxyl group, giving a polyester with the repeat unit as shown in fig. 8. Examples include Terylene, formed from ethane-1,2-diol and benzene-1,4-dicarboxylic acid.





 From a single type of monomer: a hydroxycarboxylic acid. Again, the hydroxyl and carboxyl groups interact, removing a water molecule: the repeat unit is as shown in fig. 9. Examples include poly(lactic acid), PLA.



- Polyamides are condensation polymers formed from the interaction between carboxyl and amine groups. As with polyesters a water molecule is removed, and there are two possible structures:
 - $\circ~$ Combination of a diamine and a dicarboxylic acid. Examples include Kevlar and nylon.
 - Polymerisation of amino acids; this forms polypeptides.

Addition vs. Condensation Polymerisation:

- An addition polymer can be identified by the following features:
 - There will be a single type of monomer, containing a C=C double bond.
 - \circ The backbone of the polymer will be an unbroken line of carbon atoms.
 - There is no secondary product formed from the polymerisation reaction.
 - A condensation polymer can be identified by the following features:
 - There will either be one monomer type with two different functional groups or two monomer types with two functional groups each.
 - \circ The polymer will contain ester (–O–) or amide (–N–) linkages.
 - \circ A small molecule such as H₂O or HCl will be formed during the polymerisation.

Breaking down condensation polymers:

- Condensation polymers can be hydrolysed by hot aqueous solutions of acids or alkalis:
 - In acidic conditions, polyesters form the monomer units of the polymer. Polyamides form a dicarboxylic acid and an ammonium salt of the diamine.
 - Under alkaline conditions, ester linkages are hydrolysed to form a metal salt of the carboxylic acid, and a hydroxyl group (this is much faster than acid hydrolysis of polyesters). Polyamides form diamines, and salts of the carboxylic acids that make them up.
- Due to waste disposal issues (as many polymers do not naturally break down), biodegradable polymers which break down completely into carbon dioxide and water are being developed and produced. They are often polyesters of biological

molecules, such as poly(lactic acid) and poly(glycolic acid). This has the added benefit of the fact that they do not deplete crude oil reserves.

 Photodegradable polymers which break down when exposed to sunlight are also in production. They can be formed by blending light-sensitive additives into the polymer, or by incorporating carbonyl (C=O) bonds into the backbone of the polymer – these absorb light energy and break.

Separation by Chromatography:

- Chromatography is a technique used to separate out a mixture into its components. It is used extensively in analysis because only a small sample size is required, and pure components can be analysed further after separation.
- During chromatography, a mobile phase is used to pass the mixture over a stationary phase. Different components of the mixture have different affinities for the stationary phase; this separates out the mixture.
- There are two commonly used types of chromatography:
 - Thin-layer chromatography (TLC), in which a liquid mobile phase moves over a solid stationary phase.
 - Gas chromatography (GC), in which a gaseous mobile phase moves over a liquid stationary phase.
- Solid stationary phases separate components by adsorption different components bind to the surface of the solid at different points. Liquid stationary phases use the difference in solubility of the components to separate the mixture.

Thin-Layer Chromatography:

- The stationary phase during TLC is an adsorbent such as SiO_2 or Al_2O_3 coated onto an inert support such as glass or plastic. The mobile phase is a liquid solvent which moves up the plate.
- A TLC chromatogram is produced as follows:
 - The sample is dissolved and a small spot is placed at one end of the TLC plate.
 It is allowed to dry and the plate is placed in a jar containing a shallow layer of liquid. The jar is sealed to minimise evaporation.
 - The solvent moves up the plate, carrying the components in the sample. These adsorb to the plate's surface with different affinities, separating the mixture.
 - Each component appears as a spot on the TLC plate. If the components are colourless, a locating agent or UV fluorescence may be used to identify the fronts.
- A TLC chromatogram is interpreted using R_f values. These are calculated by dividing the distance moved by a component by that moved by the solvent front. R_f values can be compared to a database of know substances to identify the sample's components. Note that R_f values are different for different solvents.
- To compare if two mixtures are the same, two chromatograms can be run simultaneously: if the final chromatograms are identical, the mixtures likely to be also.
- Limitations of TLC include the fact that similar compounds may have similar R_f values, and that unknown compounds have no R_f values for comparison. Also, in order for a chromatogram to work, the solvent must dissolve all components of the mixture; choosing a suitable solvent may be difficult.

Gas Chromatography:

- In GC, the stationary phase is a solid or liquid coated onto the inside of a capillary tube, which is coiled to fit into an oven. The mobile phase is an inert carrier gas such as helium or nitrogen.
- The chromatogram is produced as follows:
 - The sample is injected into the chromatograph and vaporised. The carrier gas flushes the sample through the column.
 - Different components are slowed down different amounts by the stationary phase, either by adsorption or by dissolving. This causes them to separate whilst inside the column.
 - Each component leaves the column at a different time; this is detected and logged by a computer as the components leave the chromatogram.
- The retention time for a component of a sample is the time taken for the component to pass through the capillary column. This is displayed on a chromatogram as a peak, the area of which corresponds to the concentration of the component.
- Whilst GC is effective at separating compounds, it is difficult to conclusively identify them for several reasons. Like TLC, similar compounds have similar retention times, and unknown compounds are unidentifiable. Also, compounds present in smaller concentrations may be masked by others.
- Coupling a gas chromatograph and a mass spectrometer gives a much more powerful analytical tool: the mixture is separated with a GC and components are identified by their unique mass spectra.
- GC-MS can be used in forensic science, environmental analysis, airport security or space probes.

Introduction to NMR:

- Nuclear magnetic resonance is a spectroscopy technique which gives details about the environments of different atoms in a molecule. The two commonly used types of NMR are ¹H and ¹³C.
- NMR utilises a property of nucleons known as spin; a nucleon can have one of two spin states (up or down). In nuclei with odd numbers of nucleons the spin states are unbalanced (they do not all cancel each other out) and so the nucleus has an overall spin, which generates a magnetic field.
- In NMR, a sample is placed into a strong magnetic field. The nuclei can occupy a high-energy state where the spin opposes the magnetic field, or a low-energy one where the spin is aligned. A radio wave is used to provide the nuclei with energy; this, when at a precise quantity matching the energy difference (known as ΔE), excites the nuclei to the spin-opposed state. The nuclei relax back to their original state, emitting radio waves at the same frequency, which are detected by the spectrometer.
- The electrons surrounding a nucleus also have a small magnetic field, which shields the nucleus from the large magnetic field and alters the nucleus's ΔE value. This means that nuclei in different environments can be identified by their chemical shift (δ); the place in an NMR spectrum at which the nucleus absorbs energy.
- Chemical shift is measured in ppm (parts per million) and is relative to that of tetramethylsilane (TMS). This calibration standard is used because TMS contains four identical methyl groups which produce a distinct peak, and because TMS is volatile (so can be easily removed) and unreactive.

Solvents for NMR analysis normally carbon and hydrogen, which would interfere with the spectrum. Thus, deuterated solvents such as CDCl₃ are used to remove the interference from hydrogen nuclei; deuterium (an isotope of hydrogen, ²H) has an even number of nucleons so no spin.

Carbon-13 NMR:

- About 1.1% of naturally occurring carbon is the isotope carbon-13. This has an odd number of nucleons, so may be used in NMR to determine the structure of organic molecules.
- Carbon-13 is highly sensitive to nuclear shielding, so there are a large range of different chemical shifts depending on the groups attached to the carbon atoms. Carbon atoms in identical environments will produce the same peak. Electronegative groups give an especially large chemical shift.
- The number of peaks in a carbon-13 NMR spectrum corresponds to the number of different carbon environments in the molecule being analysed. The chemical shifts of these peaks can be compared with data to indicate the nature of the carbon environments and assist in identification of the molecule. The size of the peak does not give any useful information in ¹³C NMR.

Proton NMR:

- ¹H is by far the most abundant isotope of hydrogen, so sample sizes for proton NMR are much smaller than those for carbon-13 NMR.
- As in carbon-13 NMR, the number of peaks and their chemical shifts corresponds to the number and type of hydrogen environments. Proton NMR, however can give more information about the molecule:
 - The area under each peak is directly proportional to the relative number of protons in the peak's environment: the ratio of peak areas is the same as the ratio of hydrogen atoms.
 - As adjacent protons can align their spins in different ways (giving slightly different magnetic fields) the number of protons immediately adjacent to a hydrogen environment causes the environment's peak to split, in accordance with Pascal's triangle. For example, three hydrogen nuclei can align their spins in four different ways, so a peak for a hydrogen environment adjacent to three protons will be a quartet, split in the ratio 1:3:3:1. This is known as spin-spin coupling, and only occurs between non-equivalent protons.
- Protons in –OH or –NH groups give a very broad range of chemical shift values depending on solvent and sample concentration. This makes them difficult to analyse from a spectrum. These peaks can be removed by running a second spectrum with D_2O added: the deuterium replaces the hydrogen in the –OH and –NH groups and thus removes their peaks. Furthermore, –OH and –NH peaks do not split adjacent proton signals, and are not split themselves.

NMR in Medicine:

- NMR is used as a powerful medical diagnostic tool in the form of an MRI (magnetic resonance imaging) scanner. Instead of a sample, a patient is placed inside a large, cylindrical electromagnet and radio waves are passed through the. The protons in the body resonate and give a signal which can be used to build an image of the body.
- There are minimal hazards in MRI scanning, especially compared to harmful or invasive techniques such as X-rays or surgery. However, the strong magnets make MRI unsuitable for patients with ferromagnetic implants or items on their person.

- A three-dimensional image of a body or organ is built up by taking MRI scans of cross-sections and layering them on top of one another.