Topic 6: Organic Chemistry

Oil Refinery and Petrochemical Industry

- Fossil fuels are petroleum (crude oil), natural gas, and coal – these are burnt to obtain energy
- Petroleum and natural gas made up of hydrocarbons (substances made of only carbon and hydrogen) and are found together in between layers of rock
  - Hydrocarbons can be alkanes (C_nH_{2n+2}) or alkenes (C_nH_{2n})
  - Natural gas is methane, CH_4

Separation of petroleum using fractional distillation:

- Substances come out at different heights of the fractionating column based on molecule size and boiling point:
  - Small molecules → Lower boiling point → Top of column
  - Large molecules → Higher boiling point → Bottom of column
- As boiling points of fractions increase:
  - Molecules get bigger
  - Liquids flow less easily
  - Liquids burn less easily, and with more smoky flames

Properties of fractions:

Fraction	No. of Carbon Atoms	Boiling Point / ^oC	Uses
Petroleum Gases	1-4	< Room temperature	Bottled gas
Petrol/Gasoline	5-10	35-75	Fuel for vehicles
Naphtha	8-12	70-170	Production of alcohol, plastics, drugs
Kerosene/Paraffin	10-14	170-250	Jet fuel, oil stoves
Diesel Oil	15-25	250-340	Diesel fuel
Lubricating Oil	19-35	540-500	Engine lubricants
Bitumen (Asphalt)	>70	>500	Surface of roads

Cracking:

- The process of breaking large alkane molecules into smaller ones
- Products of cracking (of alkanes): alkene (always) + hydrogen/carbon/alkanes (sometimes)
- Types of cracking:
  - Thermal cracking
    - Alkanes are heated to 800-850^oC under high pressure
  - Catalytic cracking
    - Alkanes are passed over a catalyst at 300^oC
    - Catalysts are alumina (Al_2O_3) or silica (SiO_2)
- After cracking is complete, the mixture of products is separated by fractional distillation
- State symbols for products of cracking:
  - If C in hydrocarbon <= 4: Gas
  - If C in hydrocarbon > 4: Liquid
  - C (s)
  - H_2 (g)
- Important applications of cracking:

- Changing heavy unnecessary fractions → Lighter fractions in demand
- Changing naphtha into alkenes (especially ethene)
- Production of hydrogen gas

Chemical conversion: Process of changing hydrocarbons to other useful chemicals

- Changing hydrocarbons in petroleum (or those obtained during cracking) into other useful chemicals like alcohols, plastics, detergents, drugs

General Notes:

- Each portion of separated crude oil boils over a range of temperatures because each portion consists of a mixture of several hydrocarbons that each have their own boiling point
- Natural gas is odorless → distinctive smell is added to help detect gas leaks

<u>Organic Chemistry</u>

Note that 1 carbon atom can form 4 covalent bonds in a tetrahedral arrangement.

Characteristics of organic compounds:

- Organic compounds are covalent in nature → being non-polar, they do not dissolve in solution (insoluble in water)
    - However, organic molecules that contain hydroxyl groups can dissolve in water (like glucone and ethanol)
- Most organic compounds mix well with non-polar solvents like hexane
- Generally have lower melting and boiling points than inorganic compounds
- Generally thermally unstable → decompose into smaller molecules when heated
- Burn exothermically (give off heat) in excess air (oxygen) to produce carbon dioxide and water
- Reactions involving organic compounds take place at a slower rate than reactions of inorganic chemistry
    - Require heat and catalysts to speed up reactions

Homologous series:

- A series of organic compounds which follow a structural pattern (example: alkanes, a series of hydrocarbons
- Members of a homologous series exhibit similar physical and structural properties, but with gradual changes as the molecular size increases
- All members have the same general molecular formula (example: C_nH_{n+2} for alkanes)

Functional group:

- An atom/group of atoms/bond that is common to a homologous series
- Determines the main chemical properties of the entire series
- Example: All members of the alcohol homologous series contain the group (OH)

Saturation:

- A saturated organic compound contains carbon atoms joined only by single bonds
- Unsaturated organic compounds have double/triple bonds between carbon atoms

Formulae:

- Empirical: Shows ratio of atoms
- Molecular: Shows actual numbers of atoms (note that each atom is only represented once)

- $C2H_5OH$ (wrong)
- $C2H_6O$
- Note that molecular formula can be deduced using relative molecular mass and empirical formula

- Structural: Drawn out
  - "—" indicates one covalent bond
  - Even if the structural formula shows the molecule flat, doesn't mean it must be 2D

<u>Alkanes and Alkenes</u>

Alkanes:

- Saturated hydrocarbons with general formula C_nH_{2n+2}
- Examples (first 4 members of homologous series):
  - Methane CH4
  - Ethane C2H6
  - Propane C3H8
  - Butane C4H10
- Alkanes are chemically inert, but go through two types of reactions: combustion and substitution reactions
- Combustion reaction:
  - In a good supply of oxygen, alkanes burn to produce carbon dioxide and water
- Substitution reaction with chlorine:
  - Methane reacts with chlorine, in which each hydrogen atom can be replaced by a chlorine atom
  - UV light is the catalyst (sunlight, for example)
  - Example: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
    - 1 hydrogen atom replaced: chloromethane
    - 2 replaced: dichloromethane
    - 3 replaced: tricholoromethane
    - 4 replaced: tetrachloromethane

Alkenes:

- Unsaturated hydrocarbons with a carbon-carbon double bond (C=C) with general formula C_nH_{2n}
- Examples (first 3 members of homologous series):
  - Ethene C_2H_4
  - Propene C_3H_6
  - Butene C_4H_8
- Alkenes are chemically much more reactive (due to the presence of double bonds)
- Combustion reaction:
  - In excess oxygen, alkenes burn to produce carbon dioxide and water
  - Example: $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
- Addition reaction of hydrogen (aka hydrogenation):
  - Nickel is used as catalyst
  - Example: Addition of hydrogen to ethene produces ethane (C_2H_4 + H2 $\rightarrow$ $C2H_6$)
  - Essentially, double bonds are replaced with single bonds on carbon atoms
  - Application: Making margarine (vegetable oil is polyunsaturated and thus is liquid $\rightarrow$ addition of hydrogen creates a more solid substance)
- Addition reaction of water (aka hydration):

- In high temperatures and pressure, addition reaction of water (as steam) can occur, with phosphoric acid as the catalyst
  - Example: Addition of water to ethene to produce ethanol ($C_2H_4 + H_2O \rightarrow C_2H_5OH$)
- Addition reaction of bromine (bromine test):
  - Example: Ethene + Bromine → Dibromoethane ($C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$)
  - When liquid/aqueous bromine is shaken with an alkene, the brown color of the bromine disappears (turns colorless) due to the addition reaction (test for alkene)
- Polymerization:
  - Many alkene molecules can link up together (polymerize) to form a long chain – this is done by getting rid of the carbon double bonds
  - Example: Ethene → Polyethene

Combustion of hydrocarbons:
- Product of complete combustion is always: carbon dioxide + water
  - If burnt in limited supply of oxygen (air), you may get carbon monoxide and/or carbon (soot)
  - Smoke is produced in incomplete combustion because carbon is produced which results in smoke
- The greater the %mass of carbon in a compound, the sootier and less cleanly it combusts

Alcohols

Alcohols: Organic compounds that contain the hydroxyl group (OH)
- Names of all alcohols end in "–ol"
  - Alcohols with 2 OH groups are called *diols*
  - Alcohols with 3 OH groups are called *triols*
- General formula: $C_nH_{2n+1}OH$
- Examples of first 4 members (note that this is not molecular formula):
  - Methanol (CH_3OH)
  - Ethanol (C_2H_5OH)
  - Propanol (C_3H_7OH)
  - Butanol (C_4H_9OH)
  - All the above are liquid at room temperature, and are soluble in water

Preparation of ethanol:
- From ethene:
  - A mixture of ethene and steam (water) is passed over phosphoric acid (catalyst) at a high temperature (300^oC) and pressure (60atm)
  - $C_2H_4 + H_2 \rightarrow C_2H_5OH$
- By fermentation:
  - Fermentation: The slow process of decomposition of organic compounds induced by microorganisms (like yeast) through enzymatic reactions
  - In anaerobic respiration of yeast, glucose ($C_6H_{12}O_6$) is converted into ethanol ($2\ C_2H_5OH$) by the enzyme zymase

Chemical properties and reactions of alcohols:
- Combustion: C2H5OH + 3O2 → 3H2O + 2CO2
- Dehydration:

    - Alcohols can be dehydrated by heating with a dehydrating agent (ex: concentrated sulfuric acid)
    - (Reverse process of hydration, addition reaction of water)
    - Example: C2H5OH → C2H4 + H2O
- Oxidation:
    - Alcohols can be oxidized to form a carboxylic acid (example: ethanol → ethanoic acid)
    - Good oxidizing agent: Acidified potassium dichromate (VI)
    - Application: Oxygen from the air can oxidize alcohols, which is why wine left exposed to air becomes sour (forms ethanoic acid)
- Esterification:
    - Alcohol + Carboxylic Acid → Ester + Water

Carboxylic Acids

Carboxylic acids: Contain carboxyl group (COOH) as functional group, and all names end with "-oic acid" (2 carboxyl groups → "-doic acid", etc.)

- General formula: $C_nH_{2n+1}COOH$
- Examples (first 4 members):
    - Methanoic acid (HCOOH)
    - Ethanoic acid (CH_3COOH), aka acetic acid (vinegar is acetic acid in water)
    - Propanoic acid (C_2H_5COOH)
    - Butanoic acid (C_3H_7COOH)
    - The above are all liquids at room temperature, and do jot dissociate completely in water, and are thus weak acids

Preparation (of ethanoic acid):

- By oxidation (of alcohols):
    - Example: Ethanol is oxidized to form ethanoic acid ($C_2H_5OH + 2[O] \rightarrow CH_3COOH + H_2O$) where '[O]' is the oxygen atom from an oxidizing agent
- From methane:
    - Methanol and carbon monoxide can be reacted together to form ethanoic acid in the presence of a catalyst

Chemical properties and reactions:

- All acid reactions are relevant to carboxylic acids (ex: acid+base, acid+metal, acid+carbonate, etc.)
    - $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
    - $CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$
    - $CH_3COOH + CaCO_3 \rightarrow (CH_3COO)_2Ca + H_2O + CO_2$
- The name of the salt is derived from the name of the acid:
    - Ethanoic acid + Sodium Hydroxide → Sodium Ethanoate
    - Ethanoic acid + Magnesium → Magnesium Ethanoate

Ester formation:

- Carboxylic acids react with alcohols to form esters (colorless, sweet smelling liquids) and water
- This is a reversible reaction (forward reaction: esterification, backward reaction: hydrolysis)
- Examples:
    - Ethanoic acid + ethanol → Ethyl ethanoate + water
    - (CH3COOH + C2H5OH → CH3COOC2H5 + H2O)

    - Ethanoic acid + propanol → Propyl ethanoate + water
    - ($CH_3COOH + C_3H_7OH \rightarrow CH_3COOC_3H_7 + H_2O$)
    - Methanoic acid + butanol → Butyl methanoate + water
    - ($HCOOH + C_4H_9OH \rightarrow HCOOC_4H_9 + H_2O$)
- Catalyst: concentrated sulfuric acid, in high temperatures
- Naming esters:
    - Alcohol(-yl) Acid(-oate)

Redox in Organic Chemistry

Oxidation: gain of oxygen, loss of hydrogen

Reduction: gain of hydrogen, loss of oxygen

- When an alcohol is oxidized, it gains oxygen atom and loses hydrogen atoms (+water)
- When a carboxylic acid (+water) is reduced, it loses oxygen atom and gains hydrogen atoms

Isomerism

Isomers: Molecules that have the same molecular formula, but a different arrangement of atoms

Chain isomerism: Isomers that arise because of branching in carbon chains

Position isomerism: Isomers that arise because of varying positions of important groups on the carbon skeleton

Functional group isomerism: Molecules re-arrange to form two different functional groups

(Refer to notes)

Nomenclature

Straight-chained alkanes:

- Suffix: "-ane"
- Prefix (note: carbon atoms refers to total, as per molecular formula):
    - C_1 → meth
    - C_2 → eth
    - C_3 → prop
    - C_4 → but
    - C_5 → pent
    - C_6 → hex
    - C_7 → hept
    - C_8 → oct
    - C_9 → non
    - C_{10} → dec

Branched-chain alkanes:

- An alkane that has lost a hydrogen atom forms an alkyl group (suffix: "-yl")
- Prefix follows number of carbon atoms
- Examples:
    - Methyl CH_3

Alkane naming procedure (if molecular formula is C_nH_{2n+2}):

1. Name the longest unbranched carbon chain
2. Name the branched groups (with positions)

3. When more than 1 branched group is present, use prefixes “di-“, “tri-“, or “tetra-“ with commas between positions
    a. Example: 2,3-dimethylpentane
4. If the chain has 2 or more branched groups, write in alphabetical order
    a. Example: 3-ethyl-2-methylhexane

Alkene naming procedure (if molecular formula is C_nH_{2n}):

- Straight-chained alkene:
    - C atoms prefix + “-ene”
    - Position of the double bond must be stated (example: but-1-ene)
- Branch-chained alkene:
    - Identify longest carbon chain with double bond → Name the alkene with double bond position
    - Identify branched group → Name branched group with position)

Prefixes:

- Alkene (detected by functional group C=C): -ene
- Alcohol (detected by functional group OH): -ol
- Carboxylic acid (detected by functional group COOH): -oic