Chapter 22

Hydrocarbons

Student Learning Outcomes

After studying this chapter, students will be able to:

- State that the bonding in alkenes includes a double carbon-carbon covalent bond and that alkenes are unsaturated hydrocarbons.
- Describe the manufacture of alkenes by the cracking of large alkane molecules using a high temperature and a catalyst.
- Describe the reasons for the cracking of large alkane molecules.
- Describe the test to distinguish between saturated and unsaturated hydrocarbons by their reaction with aqueous bromine and $KMnO_4$.
- Describe the properties of alkenes in terms of addition reactions with:
  - o bromine or aqueous bromine
  - o hydrogen in the presence of a nickel catalyst
  - o steam in the presence of an acid catalyst and draw the structural or displayed formulae of the products
- Describe, using symbol equations, preparation of alkenes by elimination reaction in halogenoalkanes and alcohols.
- Identify alkynes as hydrocarbons containing triple carbon-carbon covalent bond and that alkynes are unsaturated hydrocarbons.
- Describe the use of ethyne as fuel for welding and in artificially ripening fruits.
- Describe separation of petroleum into useful fraction by fractional distillation.
- Describe how the properties of fractions obtained from petroleum change from the bottom to the top of the fractionating column, limited to:
  - o decreasing chain length
  - o higher volatility
  - o lower boiling points
  - o lower viscosity
- Name the uses of the fractions as:
  - o refinery gas fraction for gas used in heating and cooking
  - o gasoline/petrol fraction for fuel used in cars
  - o naphtha fraction as a chemical feedstock
  - o kerosene /paraffin fraction for jet fuel
  - o diesel oil/ gas oil fraction for fuel used in diesel engines.
  - o fuel oil fraction for fuel used in ships and home heating systems
  - o lubricating oil fraction for lubricants, waxes and polishes
  - o bitumen fraction for making roads
- Name fossil fuels; coal, natural gas and petroleum
- Name methane as main constituent of natural gas
- State that petroleum is a mixture of hydrocarbons, compounds containing hydrogen and carbon only

22.1 Alkenes

Alkenes are unsaturated hydrocarbons containing one or more carbon-carbon double bond. They are also called olefins. General formula for alkenes is C_nH_{2n}.They are known for their unique physical and chemical properties. They are widely used in the synthesis of various products, like plastics and fuels.

Preparation

Alkenes may be prepared either by dehydration of alcohols or dehydrohalogenation of alkyl halides. Dehydration means removal of water molecule while in dehydrohalogenation a molecule of hydrogen halide (HX) is removed from a molecule of alkyl halide. Alkenes can also be prepared by cracking of Alkanes.

1. By Dehydration of Alcohols

Dehydration of alcohols is carried out with a dehydrating agent like concentrated sulphuric acid.

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[H_2SO_4]{180^\circ C} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

2. By Dehydrohalogenation of Alkyl Halides

Dehydrohalogenation of alkyl halides is done with potassium hydroxide dissolved in ethanol.

$$\underset{\text{Chloroethane}}{CH_3-CH_2Cl} + KOH \xrightarrow[\text{Alcohol}]{180^\circ C} \underset{\text{Ethene}}{CH_2=CH_2} + KCl + H_2O$$

This is an example of Elimination reactions. These reactions occur when a molecule is removed from a saturated compound to produce an unsaturated compound.

Interesting Information

Alkenes occur abundantly in nature. Ethylene, for example, is a plant harmone that induces ripening in fruit. An alkene β-carotene is an orange pigment responsible for the colour of carrots.

3. By Cracking of Alkanes to Alkenes

Cracking is a process which is carried out to convert high molecular mass alkanes to lower alkanes and alkenes. The process is carried out by heating

alkanes at high temperature in the absence of oxygen and in the presence of zeolites as catalysts.

Cracking is important commercially because it produces smaller alkanes which are useful as fuel as well as alkenes (ethene and propene) which are useful starting materials to produce many commercially important chemicals.

For example, kerosene oil and diesel oil which contain higher molecular mass alkanes are often cracked to give petrol, alkenes and hydrogen gas.

$$\text{Kerosene oil} \xrightarrow[500^\circ C]{\text{Catalyst}} \text{Petrol} + \text{Alkenes} + \text{Hydrogen gas}$$

$$C_{15}H_{32} \xrightarrow[500^\circ C]{\text{Zeolite}} \underset{\text{Ethene}}{2C_2H_4} + \underset{\text{Propene}}{C_3H_6} + \underset{\text{Octane}}{C_8H_{18}}$$

22.2 Important Reactions of Alkenes

Alkenes are very reactive compounds. Their chemical reactivity is due to the presence of a carbon-carbon double bond. They undergo addition reactions. Addition reactions are those reactions in which reactants combine to form a single new product.

1. Addition of Hydrogen

Hydrogen is added to alkenes in the presence of nickel metal as a catalyst to give alkanes as the products. This reaction is called catalytic hydrogenation or catalytic reduction.

$$CH_2 = CH_2 + H_2 \xrightarrow[150\ ^\circ C,\ 2\ atm.\ pressure]{Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

2. Addition of Halogens

Halogens are readily added to alkenes in the presence of a non-polar solvent to give alkyl dihalides.

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\text{1.2 - Dibromoethane}}{\overset{Br}{\overset{|}{CH_2}} - \overset{Br}{\overset{|}{CH_2}}}$$

3. Oxidation with $KMnO_4$

Alkenes can also react with cold and dilute alkaline potassium permanganate to give an important compound called ethylene glycol or ethane-1,2-diol.

$$CH_2 = CH_2 + H_2O + [O] \xrightarrow{KMnO_4} \underset{\text{Ethan-1, 2-diol (Glycol)}}{CH_2(OH) - CH_2(OH)}$$

Both halogenation and oxidation reactions may be used to detect the presence of an alkene. The reddish brown colour of bromine or purple colour of potassium permanganate is rapidly discharged when either of two reacts with an alkene. Similarly alkenes also discharge the violet colour of iodine.

These reactions are not given by saturated compounds or alkanes. Thus they are used to distinguish between saturated and unsaturated compounds (alkenes).

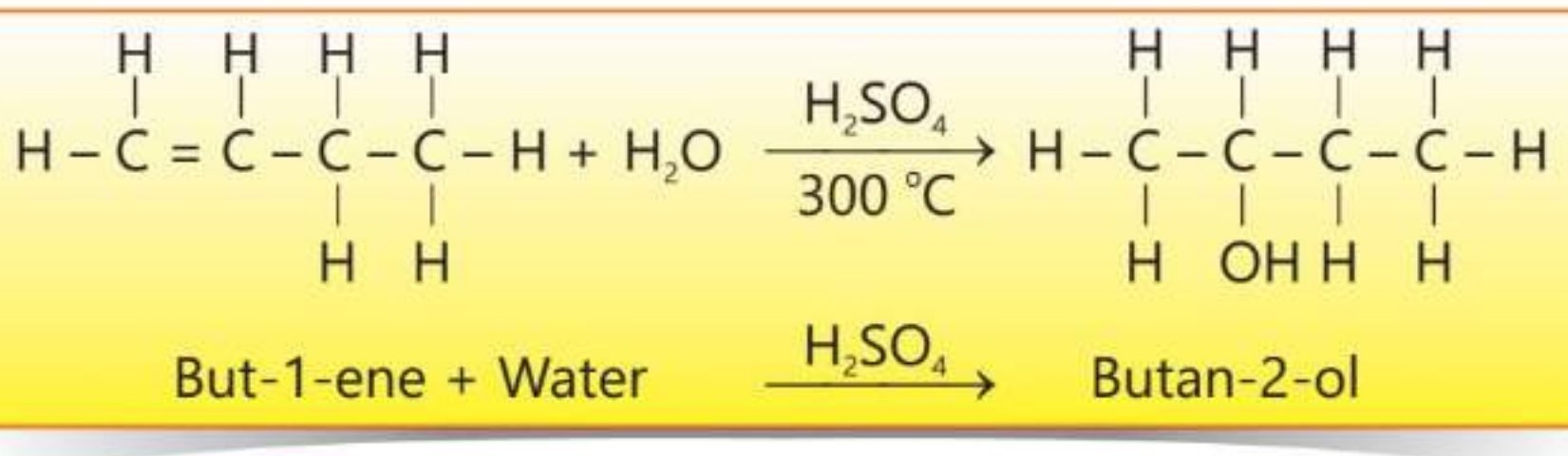
4. Addition of Hydrogen Halides

Like halogens, hydrogen halides can also be added to a double bond of an alkene. These reactions are known as hydrohalogenation of alkenes.

$$\underset{\text{Ethene}}{CH_2 = CH_2} + \underset{\substack{\text{Hydrogen}\\\text{Bromide}}}{HBr} \longrightarrow \underset{\text{Bromoethane}}{CH_3 - CH_2Br}$$

5. Addition of Water (Steam)

Alkenes react with water in the presence of sulphuric acid. The reaction takes place at around 300 °C. This is also called hydration reaction.



22.3 Alkynes

Alkynes are unsaturated hydrocarbons which contain at least one -C ≡ C- bond. They are represented by the general formula C_nH_{2n-2}. Just like alkenes,

alkynes are also named by counting the number of carbon atoms present in the longest continuous chain that contains the triple bond.

$CH \equiv CH$ Ethyne	$CH_3 - C \equiv CH$ Propyne
$CH \equiv C - CH_2 - CH_3$ But-1-yne	$CH_3 - C \equiv C - CH_3$ But-2-yne

The simplest unsaturated hydrocarbon containing a triple bond is called ethyne or acetylene gas. It is commonly used for welding and cutting purposes because it produces a large amount of heat when it is ignited in the presence of oxygen or air.

Figure 22.1: Acetylene torch

$$2CH \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + Heat$$

In the acetylene torch, acetylene gas burns in oxygen to produce CO_2 and H_2O. The high temperature of the oxy-acetylene flame speeds up the cutting and welding processes.

Acetylene gas is also used for ripening of green fruits. When solid calcium carbide reacts with moisture present in the air it produces acetylene gas which accelerates the ripening of the green fruits and induces a colour change.

Do You Know?

The use of calcium carbide in our country is prohibited because it is known to cause serious health problems like dizziness, vomiting and skin ulcer.

22.4 Sources of organic compounds

Organic compounds can be obtained from many sources. Coal, petroleum and natural gas are, however, three major sources of organic compounds. Natural gas and petroleum are chief sources of aliphatic hydrocarbons while coal is a major source of aromatic hydrocarbons. Natural gas is a mixture of many hydrocarbon gases, with methane (CH_4) being the largest component.

Petroleum: Petroleum and natural gas are mostly found together, held between the layers of non-porous rocks underground. When a well is drilled through the rock, the gas is released carrying with it some of more volatile liquids. After the flow of gases ceases, the liquid petroleum is then taken out with the help of pumps.

Liquid petroleum is a complex mixture of mainly aliphatic hydrocarbons. It has been estimated that when petroleum is boiled upto 400°C, at least 500 compounds can be obtained.

Although the principal products of petroleum refining are various types of fuels, yet a large number of other important chemicals can also be produced from these fuels. For example, petroleum products produce alkenes which are starting material to prepare plastics. Similarly, benzene, an aromatic hydrocarbon, may be produced from n-hexane. Benzene may be used to produce thousands of useful aromatic compounds like perfumes, drugs, dyes and photographic developers etc.

22.5 Refining of Petroleum

Petroleum in a crude state is a mixture of many hydrocarbons which do not burn easily. To make it useful, petroleum must be separated into different fractions by a process called refining of petroleum.

Refining process involves the fractional distillation of petroleum at about 400°C whereby it is separated into many useful fractions.

The first step in the refining process is neutralization of the crude oil by washing with acidic or basic solution as required. The neutralized oil is then heated in an electric furnance above 400°C and the resulting gases and vapours are allowed to pass into a tall fractionating column as shown in the Figure, 22.2. The column has a number of compartments divided into shelves having holes in them. These holes are covered with bubble caps.

When the oil is heated, the dissolved gases known as the refinery gases first go at the top of the fractionating column and escape there from the outlet shown in the Figure, 22.2. As the temperature rises, the vapour start going up in the column where the hydrocarbon fractions which have high boiling points are

easily condensed to liquids in the lower part of the column. The fraction which have lower boiling point ranges rise up near the top of the column as vapours, which are then condensed into liquid state. These condensed liquid fractions are collected on the various shelves from where they can be drained off into separate storage tanks. The fractions thus separated are not without impurities from the other fractions. They are then redistilled to have a better separation of hydrocarbons. Various fractions obtained in this process along with their boiling ranges are shown in the Table (22.1). The table gives the detailed information about the petroleum fractions and their uses for a variety of purposes.

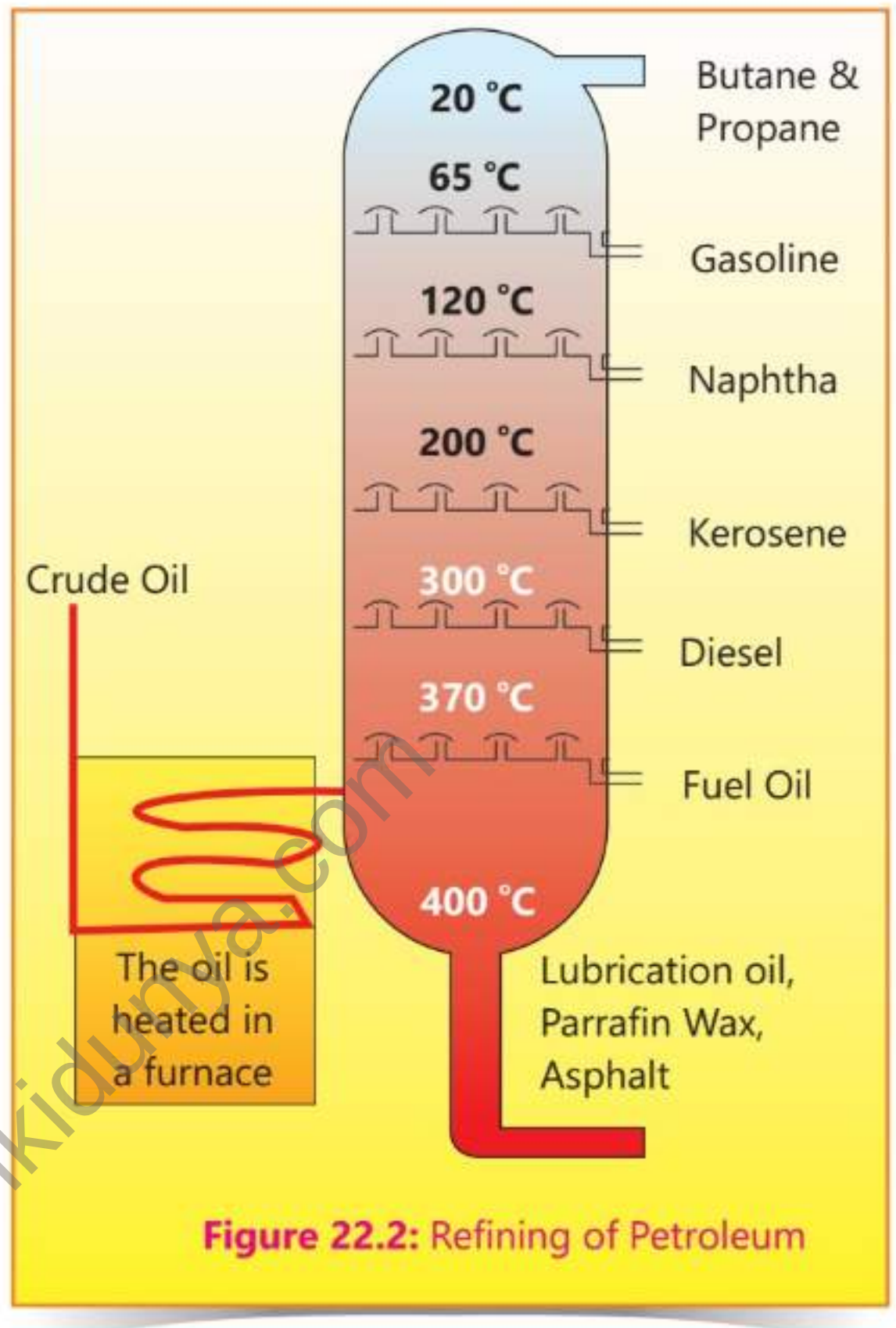


Figure 22.2: Refining of Petroleum

Table 22.1: Fractions of petroleum and their uses.

Name of the Fraction	Appropriate boiling range (°C)	Range of carbon atoms in each Fraction	Uses
Refinery gases	Below 0	1-4	Refinery gases are liquified and sold as fuels for stoves
Gasoline (petrol)	0-65	5-6	Used to drive automobiles
Naphtha	65-170	6-10	It is used as source of many useful hydrocarbons
Kerosene oil	170-250	10-14	It is a fuel used in jet engines.
Diesel oil	250-340	14-19	Used to run cars, buses and trucks

Name of the Fraction	Appropriate boiling range (°C)	Range of carbon atoms in each Fraction	Uses
Lubricating oil	340-500	19-35	Used in cars, buses and truck as lubricant, waxes and polishes
Fuel oil	340-500	Above 20	Used in ships and to run power plants
Bitumen	Above 500	Above 35	Used to construct roads and to water proof roofs and pipes.

1. Physical Properties of different Petroleum Fractions

Each petroleum fraction contains a mixture of hydrocarbons. They have similar physical properties which depend upon the following factors:

1. Number of carbon and hydrogen atoms present in the molecule of a fraction.
2. Volatility
3. Boiling point range
4. Viscosity

As the number of carbon and hydrogen atoms in the molecule of a hydrocarbon increases so does their molecular masses. This changes the strength of intermolecular forces between the molecules. Higher the molecular mass of a hydrocarbon stronger the intermolecular forces between its molecules. This fact affects the physical properties of hydrocarbons as well. Lower hydrocarbons have high volatility, low boiling points and lower viscosities. As the chain length increases their properties also show upward trends. So the fractions of the peroleum obtained at the top of the column have high volatilities, lower boiling ranges, lower viscosities and they are highly inflammable.

EXERCISE

A Multiple Choice Questions

Choose and tick the correct answer from the given choices.

1. Which of the following compounds is expected to give addition reaction?

   (a) $CH_3 - CH_3$ (b) $CH_2 = CH_2$

   (c) CH_4 (d) $CH_3 - CH_2 - CH_3$

2. Which of the followings is not used as a fuel?

   (a) LPG (b) CNG

   (c) Diesel (d) Asphalt

3. Indicate the type of the following reaction.

   $$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

   (a) Substitution (b) Oxidation

   (c) Reduction (d) Addition

4. Which species acts as a reducing agent in the reaction between ethene and $KMnO_4$?

   (a) H_2O (b) $CH_2 = CH_2$

   (c) $KMnO_4$ (d) NaOH

5. The product which will be formed when propene reacts with bromine molecule.

   (a) 1,2-Dibromopropane (b) 1,1-Dibromopropane

   (c) 2,3-Dibromopropane (d) 1,3-Dibromopropane

6. Select the name of the petroleum fraction which generates electricity in power plants.

   (a) Bitumen (b) Lubricating oil

   (c) Kerosene oil (d) Fuel oil

7. The molecule eliminated in the following reaction is:

   $$CH_3 - CH_2 - Br + KOH \xrightarrow[\text{Ethanol}]{} CH_2 = CH_2 + KBr + H_2O$$

   (a) Br_2 (b) H_2

   (c) HBr (d) H_2O

8. Fractional distillation of petroleum is based on:

(a) Viscosity (b) Boiling point range

(c) Flammability (d) Melting point range

B Short Answer Questions

22.1 Give two examples of addition reactions.

22.2 Give the names of the compounds obtained from coal tar and petroleum.

22.3 How ethene is oxidized by cold aqueous solution of potassium permanganate.

22.4 Differentiate between elimination and addition reactions.

22.5 Name the starting materials used to generate oxyacetylene flame:

22.6 How can an alkene be identified?

C Constructed Response Questions

22.1 What is the difference between the terms dehydration and dehydrohalogenation?

22.2 You have got two test tubes A and B containing a saturated and unsaturated compound (Alkene). How will you identify the two?

22.3 Why is oxyacetylene flame so hot?

22.4 Do you expect ethyne to decolourize a cold solution of $KMnO_4$?

22.5 How do chlorine and hydrogen chloride add to ethene?

D Descriptive Questions

22.1 Describe two methods of preparation for ethene.

22.2 Describe the fractional distillation of petroleum.

22.3 Which properties of petroleum fractions change with their boiling points?

22.4 Explain with examples the cracking of alkanes.

22.5 Give uses of acetylene.