9. Petroleum

9.1 Introduction to hydrocarbon chemistry

Compounds which consist of the elements carbon and hydrogen only are called hydrocarbons. They include common hydrocarbons like butane, C_4H_{10}, used as cooking gas; octane, C_8H_{18}, which is the main constituent of petrol and dodecane, $C_{12}H_{20}$, which is the main constituent of kerosene. The chemistries of coal, natural gas, petroleum and its direct products are essentially a study of hydrocarbon chemistry. We are aware of the importance of petroleum to the economy of many nations. This is particularly so for Nigeria, a member of the Organization of Petroleum Exporting Countries (OPEC). Moreover, petroleum, natural gas and coal are very important sources of energy and raw materials for the chemical industry. A close look at a service station will show you the importance of hydrocarbons to man.

9.2 Classification of hydrocarbons

Carbon is a tetravalent element. One carbon atom may combine with four atoms of a monovalent element or two atoms of a divalent element. Thus in the simplest hydrocarbon (methane) there are four C-H bonds which are arranged to form a tetrahedron. (Figure 9.1).

Plate 9.1 A service station displaying various petroleum products

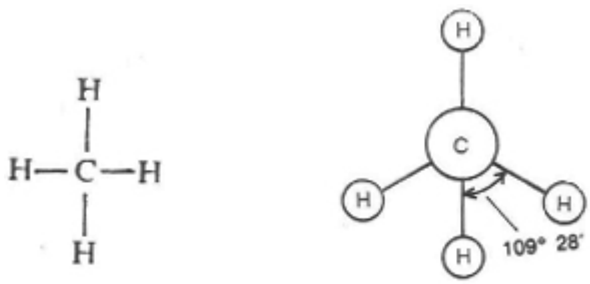
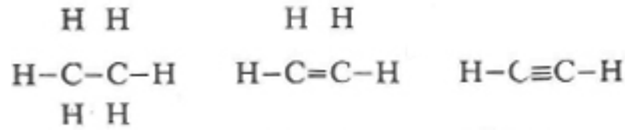


Figure 9.1 The structural formula and tetrahedral structure of carbon in methane

Carbon is a unique element. It has the ability to form chains by linking together several of its atoms. These chains may vary in length from as short as two carbon atoms as in ethane, C_2H_6, to hundreds of thousands of carbon atoms as in some giant (high molar mass) polymer molecules such as plastics.

Carbon also has the ability to form not only simple bonds, but also double and triple bonds between adjacent (neighbouring) carbon atoms. Thus in the hydrocarbons, the tetracovalency of carbon may be achieved through the formation of:

(1) four single bonds, in which all the C-H find C-C bonds are tetrahedrally arranged, or



alkane (ethane) alkene (ethene) alkyne (ethyne)

(Tetracovalency of carbon in alkanes, alkenes and alkynes.)
(2) two single bonds and one double bond, or
(3) one single bond and one triple bond, or
(4) cyclic arrangement of three or more carbon atoms.

The type of bonds which occur between the carbon atoms, and the arrangement of the carbon atoms in a given hydrocarbon compound provides chemists with a basis for classifying the hydrocarbons. Hydrocarbons are therefore classified as straight-chained (alkanes, alkenes and alkynes) and cyclic.

9.3 Alkanes

The hydrocarbons which contain single carbon-carbon bonds only are called alkanes. The simplest of these, methane, has already been mentioned. It has a tetrahedral structure with the hydrogen atom occupying the corners of a regular tetrahedron. Carbon occupies the centre of the tetrahedron. The bonds form an angle of 109Â° 28' with each other.

Alkanes have general formula $C_nH_{2n + 2}$. The molecular formula of all the members of the alkane group of hydrocarbons can be derived from this general formula. Any class of compounds which can be represented by a general formula is said to constitute a **homologous series.** The names and properties of some alkanes are listed in Table 9.1.

TABLE 9.1 Some properties of the alkanes

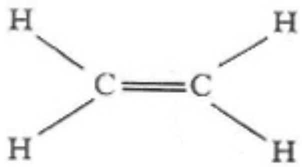
Alkane	Molecular Formula	Melting Point °C	Boiling Point °C	State at Room Temperature
Methane	CH_4	−183	−162	Gas
Ethane	C_2H_6	−183	−89	Gas
Propane	C_3H_8	−188	−42	Gas
Butane	C_4H_{10}	−138	−0.5	Gas
Pentane	C_5H_{12}	−130	36	Liquid
Hexane	C_6H_{14}	−95	69	Liquid
Heptane	C_7H_{16}	−91	98	Liquid
Octane	C_8H_{18}	−57	126	Liquid
Nonane	C_9H_{20}	−54	151	Liquid
Decane	$C_{10}H_{22}$	−30	174	Liquid

The physical properties of the alkanes listed in Table 9.1 illustrate a general feature among homologous series, i.e. that in a homologous series, there is a gradation of properties as we go from the lower to the higher molar mass members. In alkanes, the lower members: methane (C_1) â€“ butane (C_4) are gases; those immediately following butane (C_5-C_{17}) are liquids, while those containing carbon atoms equal to or higher than C_{18} are solid waxes. Other properties such as melting points and boiling points illustrate the gradation very clearly. This gradation of properties which is characteristic of the homologous series is found in all the classes of hydrocarbons.

The alkane molecules are relatively unreactive, due to their all-single-bond tetrahedral structure which is very stable. As a result of this, alkanes are described as **saturated hydrocarbons.**

9.4 Alkenes

Any hydrocarbon which contains one or more carbon to carbon double bond, C=C, in its molecule is classified as an alkene. The simplest alkene is ethene, C_2H_4.



All the carbon and hydrogen atoms forming the molecule lie on the same plane. The molecule is said to have a planar (flat) structure.

TABLE 9.2 Properties of the Alkenes

Alkene	Formula	Melting Point (°C)	Boiling Point (°C)	State at room temperature
Ethene (ethylene)	C_2H_4	−169	−104	Gas
Propene (propylene)	C_3H_6	−185	−48	Gas
1-butene (but-1-ene)	C_4H_8	−185	−6.3	Gas
1-pentene (pent-1-ene)	C_5H_{10}	−165	30	Liquid
1-hexene (hex-1-ene)	C_6H_{12}	−140	64	Liquid
1-heptene (hept-1-ene)	C_7H_{14}	−119	94	Liquid
1-octene (oct-1-ene)	C_8H_{16}	−107	121	Liquid

The alkenes have the general formula C_nH_{2n} . As tabulated in Table 9.2. the alkenes show a gradation in their physical properties. Ethene (C_2H_4)to butene (C_2H_8) are colourless, non-poisonous gases; the succeeding eleven members are liquids, while the rest are solids.

There is a general increase in melting and boiling points as we go from the lighter to the heavier members. The alkenes therefore form a homologous series.

The double bond in alkenes is not stable, and has the tendency to undergo reactions in order to attain the stable tetrahedral structure. Alkenes art therefore called **unsaturated hydrocarbons**.

9.5 Alkynes

A hydrocarbon which contains one or more carbon to carbon triple bond. C≡C, in its molecule is classified as an alkyne. The simplest alkyne is ethyne (acctylene), C_2H_2 which has the stucture:

$$H-C\equiv C-H$$

The molecule has a linear structure with all the C and H atoms arranged in a straight line. The properties of some alkynes are tabulated in Table 9.3.

The alkynes form a homologous series and have the general formula. C_nH_{2n-2}

TABLE 9.3 Properties of alkynes

Alkyne	Formula	melting Point (°C)	Boiling Point (°C)	Physical state at room temperature
ethyne	C_2H_2 or $HC\equiv CH$	−81	−84	Gas
propyne	$CH_3.C\equiv C-H$	−103	−23	Gas
1-butyne	$CH_3CH_2.C\equiv C-H$	−126	8.1	Gas
1-pentyne	$CH_3(CH_2)_2C\equiv C-H$	−106	40	Liquid
1-hexyne	$CH_3(CH_2)_3C\equiv C-H$	−132	71	Liquid

The triple bond of the alkynes is unstable and reacts with hydrogen to give the corresponding alkene first, and finally the alkane. It combines with other reagents in a similar manner. The alkyne, like the alkene, is therefore an unsaturated hydrocarbon. However, the triple bond is more unsaturated and hence more reactive than the alkene.

The chemistries of these hydrocarbons are discussed in greater details in a subsequent chapter.

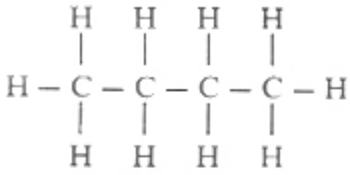
9.6 Straight and branched hydrocarbon chains

Consider the alkane butane, whose molecular formula is C_4H_{10}. To write its structural formula, we require to satisfy:

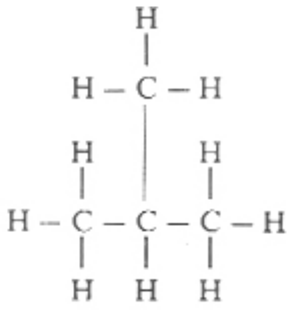
(1) the covalency of the four carbon atoms, and

(2) the covalency of each hydrogen atom.

These conditions are adequately met by two alternative structures as given below. The structure (a) butane, is a straight chain compound, while (b), 2methyl propane, is a branched chain compound.



(a) butane



(b) 2-methyl propane

These two structures though satisfying the same molecular formula, actually represent two different substances with distinct names and different properties.

Such compounds which have the same molecular formula but different structural formulae are called **isomers**.

The existence of two of more compounds with the same molecular formula but different structural formulae is called isomerism.

All hydrocarbons with four or more carbon atoms exhibit isomerism.

Exercise 9A

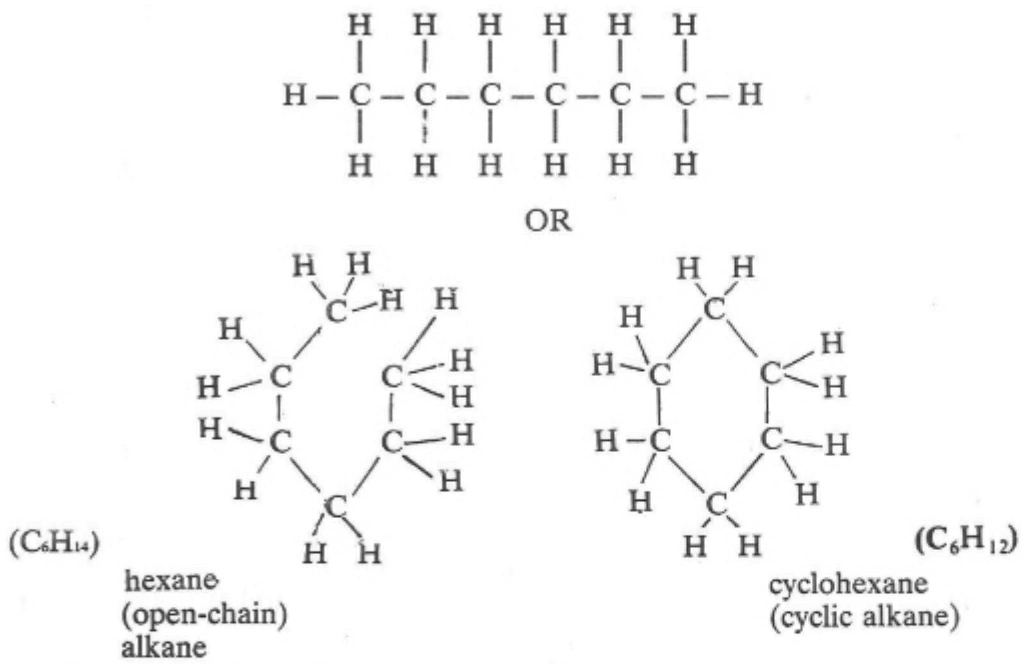
You are provided with a set of coloured balls. Let one colour represent carbon atoms while another set represent hydrogen atoms.

1. Prepare models to represent the following hydrocarbons: C_2H_6, C_2H_4 and C_2H_2. Ensure that the combining powers of C and H are satisfied. In each model prepared, hold one carbon atom in one hand. Attempt rotating the other carbon atom. Comment on the ease with which the second carbon atom rotates in each case.
2. Write down the molecular formula of pentane. Using the coloured balls provided, prepare models of all the possible structures of pentane. Show each new structure to your teacher to confirm that it is correct.
   (i) Write down each structure on paper.
   (ii) How many possible structures of pentane are in existence?

9.7 Open-chain (aliphatic) and cyclic

(ringed) hydrocarbons

The hydrocarbons studied above are all free at the two ends. They are referred to as open-chain or aliphatic hydrocarbons. In some classes of hydrocarbons, the two ends are linked up at the first and last carbon atoms so that a complete cyclic (ringed) structure is obtained. Such a compound is a cyclic hydrocarbon as illustrated below.



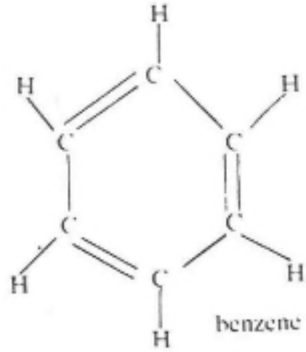
(a) Open-chain hydrocarbon. (b) Cyclic hydrocarbon.

The cyclic (ring) compounds are described by the suffix â€œcyclo-â€ before their names, as in cyclohexane, C_6H_{12}. The cycloalkanes form a homologous series of general formula C_nH_{2n}. The cycloalkenes have the general formula C_nH_{2n-2}

Note that cyclohexane, C_6H_{12}, is a saturated compound just like hexane, C_6H_{14}, but they are not isomers.

9.8 Aromatic hydrocarbons: benzene

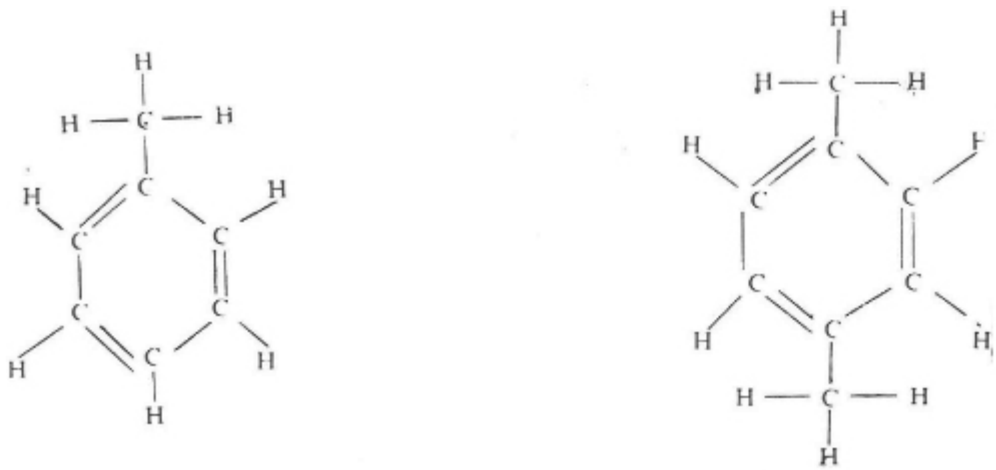
Benzene G_6H_6 is a ring compound with a difference. It contains three C=C double bonds arranged in a ring, which alternate with three single bonds. Thus, it has the structure:



benzene

The presence of the three alternate double and single bonds inside a six-carbon-membered ring gives benzene unique properties which distinguish it from the open-chain (aliphatic) and other cyclic hydrocarbons discussed earlier.

Other hydrocarbons derived from benzene are called benzene homologues. Examples of such compounds and their structures are:



methyl benzene 1,4-dimethylbenzene

Benzene homologues

The characteristics of the benzene homologues are greatly influenced by the presence of the benzene ring.

Benzene and its homologues are classified as *aromatic hydrocarbons.*

A summary scheme for the classification of the hydrocarbons is shown in Figure 9.2.

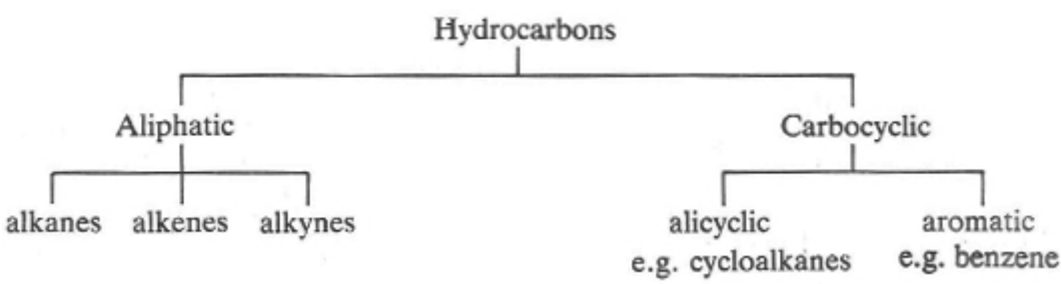


Figure 9.2 Classes of hydrocarbons

9.9 Origin of petroleum

Crude oil is sometimes called petroleum which means â€˜rock oilâ€™. It is obtained in rocks underneath the earth, where it was formed several millions of years ago. It is formed in conjunction with natural gas from dead marine organisms which are covered by sediments before being decomposed under conditions of high temperatures and pressures from thick layers of sediment. Figure 9.3.

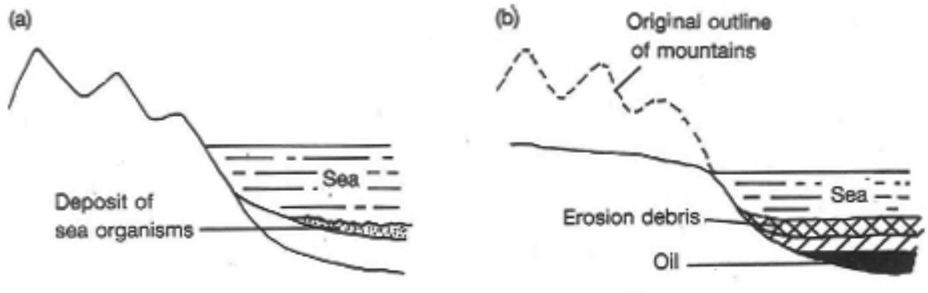


Figure 9.3. Origin of oil (a) bodies of marine organisms deposit and accumulate on the sea bed. (b) Over a period of millions of years, erosion of land causes movement and accumulation of sand and rocks over the marine organic matter.

The actual process of conversion is not well understood.

The oil and gas mixture migrate from porous sandstone and limestone till they are trapped by layers of impervious rock such as shale. In general petroleum is trapped in sedimentary rocks. A common shape of an oil trap is a dome-shaped layers of sedimentary rocks. The oil floats on salt water, while above the oil is the natural gas.

Crude oil is brought to the surface when a well is drilled into the earthâ€™s crust through the impervious cap, into the oil-bearing layer. Often, the gas and oil are forced to the surface by their own pressure. When this force is not large enough to bring the oil to the surface. mechanical pumps are used to bring up the oil to the surface.

9.10 Petroleum as a complex mixture of hydrocarbons

Crude oil is a dark brown, viscous liquid. It is not a single substance, but a mixture of different kinds of hydrocarbons. Depending on where it is obtained, it may also contain traces of nitrogen, oxygen, sulphur and chlorine as well as some metals. Sulphur-free petroleum such as the Nigerian crude is of high commercial value.

It is not easy to separate petroleum into its constituent hydrocarbons (which number at least seventy). However, crude oil may readily be separated into several distinct groups or fractions. Each fraction is in itself a mixture of hydrocarbons of close molecular masses and whose boiling points fall within a specific close range.

Experiment 9.1 Fractional distillation of Petroleum (Crude Oil)

Caution: The receiver must be kept far away from the bunsen burner as petrol is highly inflammable. If available, use a hot plate or heating mantle in place of bunsen burner.

Set up a fractional distillation apparatus as shown in Figure 9.4. Put about 50cm^3 of petroleum (or a mixture comprising 5 cm^3 petrol, 10 cm^3 kerosene, 10 cm^3 diesel oil. 10 cm^3 of engine oil and 15 cm^3 of grease into Flask A. Add some pieces of porous pot and stopper the distillation flask to be airtight. The thermometer should read up to 360Â°C. Connect up the entire apparatus. Heat the mixture slowly while watching the thermometer. Strike a match to ignite the gas escaping at the jet as shown in Figure 9.4.

Note the temperature when liquid first distills over into the receiver tube. Maintain the temperature at 100Â°C till no more distillate distills over. Remove the receiver tube and replace with another. Stopper the removed one and label the sample collected. Increase the temperature to 150Â° + 5Â°C and collect the distillate that distills over. Again remove and replace the receiver. Stopper the tube and label the sample you collected at 150Â°C. Increase the temperature to 200Â°C, 250Â°C and 300Â°C; collect the distillates as was done at 100Â°C and 150Â°C.

Finally, allow the residue in the flask to cool while you carry out the following investigations on the different fractions collected.

(i) Smell each fraction and record the smell.

(ii) Put 5 drops of each on a crucible lid and attempt igniting it by bringing a burning splint over it. How readily does it catch fire? What is the nature of the flame?

(iii) What is the order of viscosity of the fractions? (Assume viscocity to be indicated by the ease with which you can pour out each fraction).

(iv) When the residue has cooled sufficiently, scrape it out from the flask. Record its colour and smell. Test if it catches fire readily.

(v) Draw conclusions about the nature of crude oil.

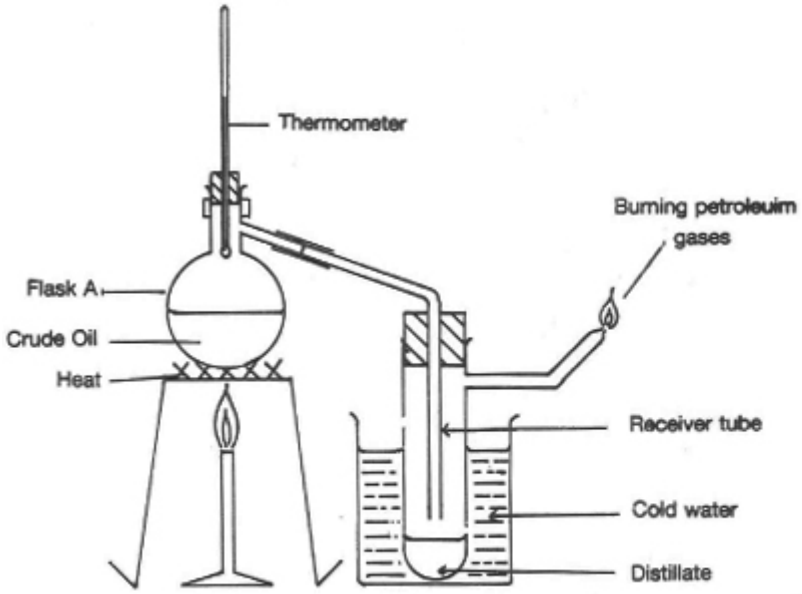


Figure 9.4 Fractional distillation of crude oil

9.11 Refining of petroleum

In the above experiment, crude oil (petroleum) has been separated into a number of component fractions, whose boiling points fall in the ranges:

70Â° â€“ 100Â°C
100Â° â€“ 150Â°C
150Â° â€“ 200Â°C
200Â° â€“ 250Â°C
250Â° â€“ 300Â°C

In the refinery the principle of fractional distillation is applied to separate crude oil into its various component fractions. The main fractions of petroleum are tabulated in Table 9.4.

TABLE 9.4 Main petroleum fractions

Fraction	Physical state at room temperature	Boiling range	Number of carbon atoms per molecule
Gases/Vapours	Gases	Below 40°C	$C_1 - C_4$
Low Boiling liquids	Liquid	100°C	$C_5 - C_6$
Gasoline-naphtha	Liquid	40° – 150°C	$C_5 - C_9$
Kerosene	Liquid	175 – 275°C	$C_{10} - C_{14}$
Diesel oil	Viscous liquid	230 – 305°C	$C_{14} - C_{18}$
Lubricating oils	Viscous liquid	>305°C	$C_{18} - C_{21}$
Heavy Waxes/ Asphalt	Solids	>400°C	C_{22} and above

In the refinery, the fractional distillation of crude oil is achieved with greater efficiency in an equipment called a fractionating column (Figure 9.5). The fractionating column is a long tower divided into various compartments. Each compartment carries a number of trays with holes in them, and each hole is covered by a cap. This hole-and-cap arrangement is called the **â€˜bubble capâ€™.** It ensures proper mixing of liquid and vapour The lower portion of the fractionating tower is maintained at a high temperature of about 340Â°C while, at the top of the tower the temperature is about 110Â°C.

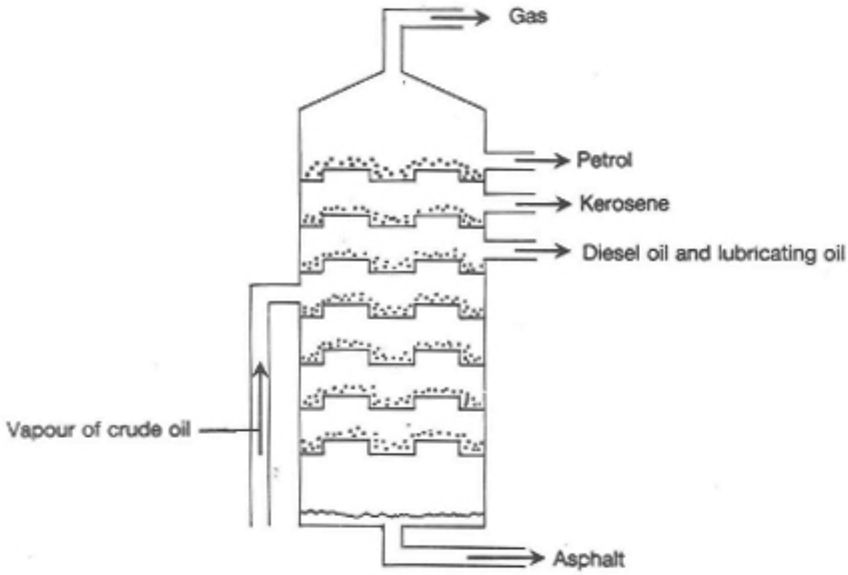


Figure 9.5 Fractionating column

The crude oil is first heated in a furnace and then passed into the lower part of the fractionating column. At the high temperature of the furnace most of the fractions in the oil boil. Thus they vapourize and rise up the column through the holes in the trays. As each fraction reaches the tray where the temperature is just below its own boiling point, it condenses and changes back into liquid on the bubble cap and in the trays. It is thus drawn off as a liquid fraction.

9.12 The nature and uses of petroleum fractions

The fractions of petroleum distillation may be classified into those that rise highest in the column (the light fractions) and those that condense on the lower trays (the heavy fractions). Going down the fractionating tower, the fractions obtained are as follows:

1. Refinery and petroleum gases

The very lightest fraction taken off at the top of the tower is refinery gas. It consists of hydrogen and the more volatile hydrocarbons: methane, ethane, propane, butane and ethene (C_1-C_4 hydrocarbons). These are all gases at ordinary temperatures.

The C_1 and C_2 hydrocarbons are used as fuel for heating in the refinery.

Propane and butane are bottled in cylinders under high pressure and sold in the liquefied form as cooking gas in homes. The â€˜Utilgasâ€™, â€˜Nidogasâ€™ and â€˜NNPCâ€™ gas which we buy in cylinders for cooking are liquefied mixtures of propane and butane.

2. Gasoline (Petrol)

Gasoline is currently one of the most important products from petroleum because of its use as fuel for motor cars. It is a mixture of C_6 to C_{10} hydrocarbons. However, its actual composition may vary widely. The boiling range is generally between 70-200Â°C. It is also useful as a solvent

3. Naphtha fraction

It may be further processed to produce petrol for motor vehicles; it is also a very important raw material for the manufacture of petrochemicals.

4. Kerosene

This is the fraction distilling at a temperature of 175Â°-275Â°C. It is a mixture of C_{10} - C_{14} hydrocarbons. It is used in lamps for lighting and also for heating.

It is also used as fuel for jet (aeroplane) engines and is a source of benzene and its homologues.

5. Diesel oil

The diesel oil fraction is used in diesel engines to drive trains, tractors and trailers. Diesel oil contains C_{14} to C_{18} hydrocarbons and its boiling range is 250-305Â°C.

6. Lubricating oil

This heavy fraction is made up of hydrocarbons exceeding C_{18}. It is usually further processed to obtain materials for waxes, candles, ointments, polishes and chemicals. This fraction is very important as the source of lubricating oil for engines. Its boiling range is over 305Â°C.

7. Residue

The residue left behind in the retort is drawn off the base of the fractionating column. It contains the heaviest fraction of all. This fraction includes fuel oil and bitumen and consists of high molar mass hydrocarbons with boiling points above 400Â°C.

The fuel oils are used for ships, factories and for central heating. Asphalt which is obtained from it is an important material for the construction of roads, roofing, water-proofing and other construction, works.

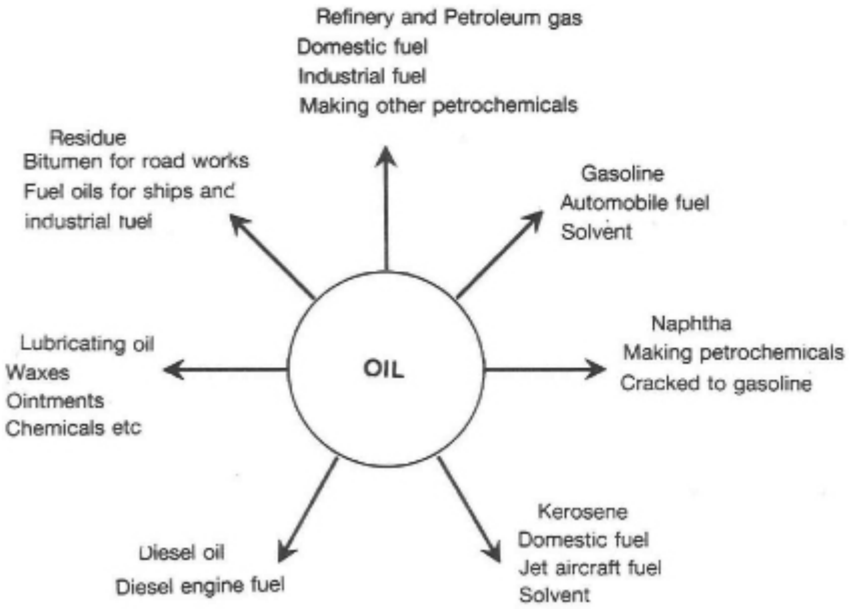


Figure 9.6 Oil fractions and their uses

9.13 Octane number (Octane rating) of gasoline

Petrol (gasoline) sold in Nigeria was until recently available in two grades, the â€˜superâ€™ (extra) grade and the â€˜regularâ€™ (ordinary) grade. Super petrol has an octane rating (or octane number) of 94-100, while the ordinary or regular gasoline has an octane number of 86-93. These figures suggest that the â€˜superâ€™ petrol is a higher grade of petrol than the â€˜ordinaryâ€™ or â€˜regularâ€™ petrol.

To understand the figures quoted above, let us first answer the question: What is â€˜octane number?â€™ The octane number of a given fuel is a quantitative expression of its performance in the high compression engine of a motor car.

Petrol (gasoline) is composed principally of C_7-C_9 hydrocarbons, i.e. heptanes, octanes and nonanes. C_5 and C_6 hydrocarbons as well as C_{10} hydrocarbons may be present in some cases. A particular hydrocarbon may be present as the straight-chain hydrocarbon and/or its branched chain isomer. Experiments show that the straight chain hydrocarbons (such as heptane) burn too rapidly in the engine, thus causing irregular (unsteady) motion of the pistons. This produces a rattling noise in the engine described as â€˜**engine knock**â€™ which may damage the engine of the car. Branched and cyclic hydrocarbons on the other hand, burn much more smoothly. For example 2,2,4-trimethyl pentane, C_8H_{18}, which was previously called iso-octane burns without causing engine knock.

Because it burns very smoothly in the high-compression engine, 2,2,4-trimethylpentane was selected as the standard on which the performances of other hydrocarbons and gasoline blends are rated, using the index called Octane numberâ€.

To establish the octane number index, heptane which causes severe knocking in engines is assigned a value of zero (0), while 2,2,4-trimethylpentane (iso-octane) which burns very smoothly in automobile engines is assigned a value of 100. A gasoline blend which has an octane number of 90, has exactly the same performance in an engine as a mixture of 90% 2,2,4-trimethylpentane (iso-octane) and 10% heptane.

Octane number is in fact a measure of the proportions of the branched and cyclic hydrocarbons relative to the straight-chain hydrocarbons in a given blend of gasoline.

9.14 Upgrading the quantity and quality of petroleum from crude oil

Until recently the principal product from crude oil refining was kerosene use for lighting and heating. The large increase in the use of automobiles in the past two decades has created a very high demand for petrol (gasoline).

Fractional distillation of crude oil yields only about 20% of gasoline and about 80% of other products. This quantity is insufficient to meet the current demand for the commodity. Moreover, petrol derived from the fractionating columns has a relatively low octane rating due to its low content of branched and cyclic hydrocarbons.

It is therefore often necessary to increase both the quantity and the quality of the gasoline yield from the refineries.

A number of methods are in practice for these purposes. One such method is to subject some of the other petroleum fractions to chemical reactions generally called conversion processes. The two most important conversion processes are cracking and, reforming.

Cracking of Oils

Cracking is the process by which a heavier hydrocarbon

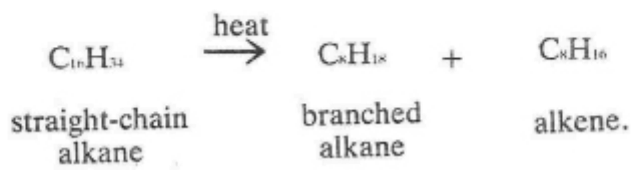
splits (or breaks up) into two or more lighter hydrocarbon molecules on heating.

In order to obtain gasoline from cracking of oils, the long-chain hydrocarbon molecule of the heavy fractions, such as diesel oil, are made to break on heating, yielding smaller molecules in the lower boiling (gasoline) range.

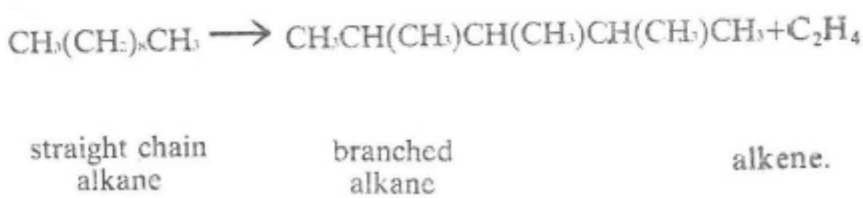
If the cracking process is carried out at high temperatures (500-700Â°C) and high pressures (300 atmospheres) the process is called **thermal cracking**. Cracking is now achieved much more efficiently even at lower temperatures and pressures, in the presence of catalysts. The catalyst is usually of silicaalumina but certain zeolite catalysts have also been recently introduced. Cracking in the presence of a catalyst is called **catalytic cracking** (cat-cracking).

Examples of cracking processes include:

(i) Cracking of a straight chain alkane molecule to give a branched alkane and alkene.



(ii) Conversion of straight chain alkane to branched chain alkane plus a gaseous alkene.



Catalytic cracking thus yields high quality petrol which is blended in calculated quantities to raise the performance of fuels in high compression car engines.

The cracking process is carried out in a special unit called the catalytic cracker (cat-cracker).

Reforming

In the reforming process, the gasoline fractions from the distillation column are heated under pressure. Unlike in cracking, the molecuics undergo internal rearrangement rather than splitting. This way, straight-chain hydrocarbon molecules are converted into ring structures (cyclization) or to branched chains (isomerization).

Examples of Reforming Reactions

(i) $C_6H_{14}(l) \longrightarrow C_6H_{12}(l) + H_2(g)$

hexane cyclohexane

(ii) $C_6H_{14}(l) \longrightarrow C_6H_6(l) + 3H_2(g)$

hexane benzene

(iii) $C_6H_{14}(l) \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2.CH_3\ (l)$

hexane 2.2-dimethylbutane

In the refinery plant, the reforming process is conducted in the presence of a catalyst, which is usually platinum. Hence the process is called catalytic reforming or platforming when platinum is specifically used. Recently some types of zeolite catalysts have been introduced. These zeolite catalysts promote both reforming and cracking and are therefore said to have a dual function.

In the catalytic reformer, gasoline and naphtha fractions from the distillation column are mixed with hydrogen and pumped under pressure, over a bed of catalyst at about 500Â°C.

The product from the reforming plant is called **reformate**. It is a very useful product in two main respects: (i) as a rich component in the blending of gasoline to raise octane number, and (ii) as a source of aromatic hydrocarbons such as benzene, toluene and xylenes which form raw materials for the manufacture of other chemicals.

As shown in the equations above this process yields a considerable quantity of hydrogen which is consumed in other processes within the refinery.

Other Conversion Processes

In addition to the cracking and reforming processes, there are other conversion processes which involve the linking together of small molecules to form larger molecules, e.g.; Petroleum gases $\longrightarrow$ gasoline.

9.15 Treatment processes

Apart from the distillation and conversion processes, there are other oil refining processes. Some of these are processes aimed at removing impurities from the oil and oil products. Two of the most important of these processes are known as

(i) desulphurization, and
(ii) dewaxing.

Desulphurization

Sulphur often occurs as an impurity in crude oil. The removal of this impurity from oil products is extremely important since if not removed it is converted to sulphur oxides (e.g. sulphur(IV) oxide) during combustion. This is an acidic gas which adversely affects breathing if inhaled in air, and also promotes the corrosion of metallic materials in engines and buildings.

To remove sulphur, the oil feedstock is treated with hydrogen in the presence of a catalyst. The sulphur is converted to H_2S gas.

$$C_5H_{11}SH(l) + 2H_2(g) \longrightarrow C_6H_{14}(l) + H_2S(g)$$

Sulphur-containing compound	desulphurized alkane	hydrogen sulphide

Nigerian crude oil contains little or no sulphur and thus requires no desulphurization. For this reason, Nigerian crude is considered to be of a highly desirable quality and consequently attracts a higher price per barrel than crude oil from some other countries with petroleum containing higher sulphur contents.

Dewaxing

This process involves the removal of paraffin wax from lubricating oils. The oil is dissolved in a suitable solvent, leaving behind the solid wax. The wax is used for the manufacture of petroleum jelly, candles and waxes.

Additives

The extra costs of production of high octane gasolines is responsible for the higher prices for good quality fuel. However the costs of obtaining good quality fuels are lowered substantially by adding to the gasolines, chemicals called additives which improve the quality of the poorer grade gasoline by eliminating engine knocking tendencies i.e. raise octane number. One such additive in regular use is tetraethyl lead(IV) $Pb(C_2H_5)_4$. When used in quantities of the order of 0.5 g lead per litre of petrol, it eliminates knocking in high compression engines.

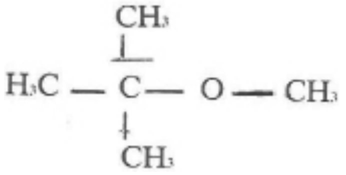
The use of lead in gasolines has in recent times come under severe attack by environmentalists because it has been found to cause serious environmental pollution problems. Lead poisoning leads to a loss of appetite, weakness, and damage to the circulatory and digestive systems and the brain. It may also affect proper brain functioning in children.

Car exhaust fumes are the principal sources of lead in the atmosphere. This arises because 75% of the lead used in petrol ends up in the exhaust gas. Most of it is released into the atmosphere.

Other additives such as 1,2-dichloroethane (CH_2C1CH_2Cl) and 1,2-dibromoethane (CH_2BrCH_2Br) are used in order to prevent the deposition of lead in car engines, but do not prevent the discharge of lead into the atmosphere.

In recent times there have been pressures on oil companies to stop the use of lead in gasoline, and use alternative safer additives. Some such alternative additives are already in use. Thus, for example, 2-methyl, 2-methoxypropane in some developed countries is being used to raise octane number. Improvements in cracking and reforming techniques have also yielded gasolines of octane numbers higher than 110, which perform better than isooctane.

It is expected that the use of lead compounds in petrol would be banned in many countries in the forseeable future.



Chapter Summary

1. Petroleum is a mixture of hydrocarbons, formed from dead marine organisms.
2. Hydrocarbons can be aliphatic or cyclic.
3. Aliphatic hydrocarbons can be alkanes (saturated), alkenes or alkynes (unsaturated).
4. Fractional distillation of petroleum yields:
   (i) refinery gases.
   (ii) petrol â€” used as fuel for internal combustion engines.
   (iii) naphtha â€” solvent, petrochemicals.
   (iv) kerosene â€” fuel for jet engines, domestic fuel.
   (v) lubricating oil â€” lubricants.
   (vi) diesel oil â€” fuel for diesel engines.
   (vii) wax â€” manufacture of candles, etc.
   (viii) asphalt â€” road surfacing.

   Cracking is the splitting of heavier petroleum fractions to yield more petrol.
5. Octane number is a rating for petrol performance in internal combustion engines. Heptane (octane number zero) and 2.2,4-trimethyl pentane. isooctane (octane number 100) are used as standards for assigning octane numbers to petrol samples.
6. Reforming of petrol involves internal rearrangement of molecules, cyclisation, isomerisation, to yield better quality petrol. Zeolite catalysts promote cracking and reforming.
7. Desulphurisation involves removal of sulphur impurity in petrol by heating with hydrogen. Sulphur escapes as hydrogen sulphide.

8. Dewaxing involves removal of waxy material from lubricating oils by dissolving out the waxy materials in suitable solvents.

Assessment

1. The Nigerian petroleum is in high demand because it is sulphur free. Why is sulphur free petroleum preferred to sulphur-containing petroleum? How is sulphur removed from petrol?
2. (a) List five fractions of petroleum refining and five corresponding uses of the fractions.
   (b) Explain the term octane number. Why is the addition of lead tetraethyl to petrol to increase its octane number no longer desirable?
3. (a) What is the source of petroleum?
   (b) What are the functions of (i) the bubble cap, (ii) trays in a petroleum fractionating column?
4. (i) Explain the term â€˜crackingâ€™.
   (ii) Under what conditions does cracking take place?
   (iii) Write an equation to illustrate cracking.
   (iv) What is the importance of cracking in the petroleum industry?

(WAEC)

A. Literature Project â€“ Petroleum Exploration in Nigeria

1. Organizing a school â€˜Science Clubâ€™

Your school probably has a Science Club. If you do, you will find membership of such a club to be greatly rewarding, particularly in carrying out your projects in applied chemistry. If such a club is not yet in existence in your school, it is necessary to start one as soon as you can. Industrial organizations are more likely to honour group requests for excursions or booklets than one coming from an individual. Moreover, chemistry is made more interesting when studied in the company of others.

Your club should have a president, a secretary, and a financial secretary to run the affairs of the club.

2. Industrial visits

Your club should as quickly as possible undertake a visit to:

(1) a refinery

(2) a petroleum pumping station

(3) any other nearby chemical industries such as a brewery, a distillery or a soap-making industry.

During your visit, take along a notebook. In the course of your tours, make a note of the following items:

(a) important sections visited;

(b) the functions of the section in relation to the entire operation:

(c) the key industrial chemical process in that section (including details not usually found in text books).

During your visit to the refinery or pumping station, collect samples of crude oil. Be sure to ask for and record its source. Request for any publications, photographs or samples that will serve as a souvenir of your visit.

After each visit, write a detailed report on the visit.

3 Collection of literature on oil operations in Nigeria

If your school has a library, it must have a good stock of written material or photographs on oil operations in Nigeria. However, your club should write to. the headquarters of the various oil companies (your school librarian may have all the current addresses), and request for pamphlets, brochures, bulletins and photographs on (i) oil exploration in Nigeria, and (ii) oil production in Nigeria.

The Shell company has a large volume of well-written and well illustrated publications which you will find very useful. These include: â€˜The Oil Ventureâ€™, â€˜Oil for Everybodyâ€™ etc. The Nigerian National Petroleum Corporation has a number of publications relating to the Nigerian oil industry which you can obtain on request. Read as many of these materials as you can. The Shell Company also has various films on different aspects of oil exploration and production. Some of these are listed in the pamphlets.

You can write an application to the Shell Company to borrow the films of your choice. You should state the date on which you will return the films and ensure that you do so if you do receive them. Your club can hire a projector to show these films during club meetings.

B. Experimental Project â€“ Crude Oil

4. Collection of samples of crude oil

During your visit to the refinery ensure that you collect some samples of crude oil.

Make a detailed report of the properties of this sample. This should include its colour, smell, flow properties, etc.

5. Distillation of samples of crude Oil

Place your sample of crude oil (about $50cm^3$) in a distilling flask. Connect it to the fractionating apparatus as shown in Figure 9.4 then distil the crude oil by heating the flask in an oil bath, or on a heating mantle, if available.

Collect distillates from temperature range of 100Â°C, 150Â°C, 200Â°C, 250Â°C and 300Â°C. The details of the distillation of crude oil is given in Experiment 9.1. Record the properties of each sample such as the smell, viscosity, inflammability, colour, etc.