Chapter 4

Chemical Fuels

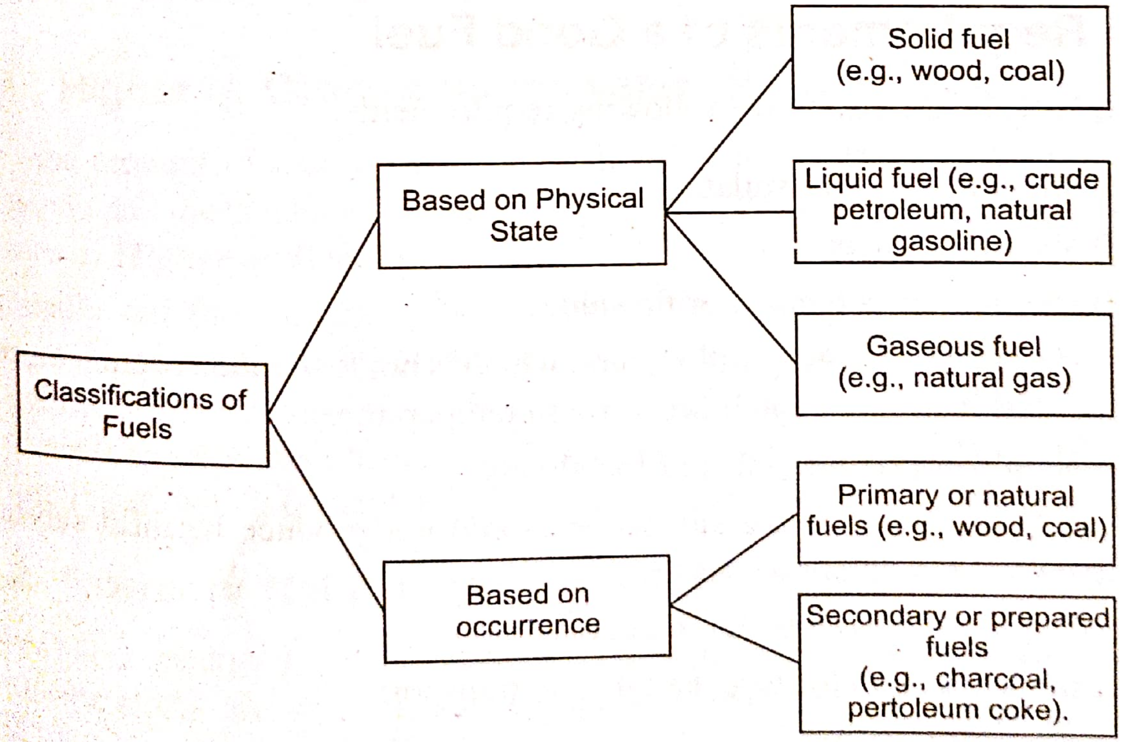
4.1 Introduction

Fuel

“A combustible substance containing carbon as the main constituent, which on proper burning liberates large amount of heat, which can be used economically for domestic as well as industrial purposes is called as ***Fuel***”.

4.2 Classification of Fuels

Fuels can be classified into two types based on physical state and based on occurrence.



4.3 Comparison Between Solid, Liquid and Gaseous Fuels

Solid fuels	Liquid fuels	Gaseous fuels
Slow combustion and not easy to control it.	Quick combustion and can be controlled.	Combustion is rapid and burning can be controlled.
Transportation is difficult.	Transportation is easy through pipe lines.	Transportation is easy through pipe lines and containers.
Storage is safe.	There is risk in storing.	There is greatest risk in storing.
Calorific value is comparatively low.	Calorific value is comparatively higher.	Calorific value is highest.
Cannot be used in internal combustion engines.	Can be used in internal combustion engines.	Can be used in internal combustion engines to a lesser extent.
On burning ash and more smoke are produced.	No ash is produced but some flue gases are produced.	No ash no smoke are produced.

4.4 Requirements of a Good Fuel

A good fuel should satisfy the following requirements:

- It should be easily available.
- It should be cheap.
- It should have a high calorific value.
- It should have a low ignition point, which is not lower than room temperature (so that it does not catch fire at room temperature).
- It should not burn too fast or too slowly.
- The combustion of the substance should not produce harmful substances like soot and poisonous gases.
- No residues should be left on combustion.
- It should be safe to store, handle and transport.

4.5 Calorific Value

"When a unit mass (or volume) of the fuel is burnt completely, the total quantity of heat liberated is known as ***calorific value***".

Units of heat

1. **Calorie:-** "Calorie" is the amount of heat required to raise the temperature of one gram of water through one degree centigrade (15 – 16°C).

2. **Kilocalorie:-** "Kilocalorie" is equal to 1000 calories. This is the unit of metric system and may be defined as "the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade" thus,1 k. cal = 1000 cal

3. **British Thermal unit:-** (B.Th.U) B.Th.U is defined as "The quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60 – 61°F). This is the English system unit.

$$1B.Th.U = 252cal$$

$$= 0.252k.cal$$

$$\therefore \quad 1k.cal = 3.968B.Th.U$$

4. **Centigrade heat unit (C.H.U):-** C.H.U is "the quantity of heat required to raise the temperature of 1 Pound of water through one degree centigrade." Thus 1000 cal=1 k.cal= 3.968 B.Th.U=2.2 C.H.U

4.5.1 Higher or Gross calorific value: (HCV or GCV)

"The total amount of heat produced; when unit mass of the fuel has been burnt completely and the products of combustion have been cooled to room temperature is known as ***Higher or Gross calorific value***".

Usually, all fuels contain some hydrogen and when the calorific value of hydrogen- containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature (15°C or 60°F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "***Higher or Gross calorific value***".

4.5.2 Lower or Net calorific value (LCV or NCV)

"The net heat produced, when unit mass (or volume) of the fuel is burnt completely and the products are permitted to escape is known as ***Lower or Net calorific value***".

In actual use of any fuel, the water vapour and moisture etc, are not condensed and escape as such along with hot combustion gases. Hence, a lesser amount of heat is available. Alternatively, Net or Lower calorific value (LCV)

LCV = HCV - Latent heat of water vapour formed

LCV = HCV - Mass of hydrogen × 9 × Latent heat of steam

Because 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of steam is 587 k.cal/kg or 1060 B.Th.U/lb of water vapour formed at room temperature (15°C or 60°F).

Units of calorific value:- The calorific value is generally expressed in calorie /gram (cal/gm) or kilocalorie/kg (kcal/kg) or British Thermal Unit/lb (B.Th.U/lb) in case of solid or liquid fuel.In case of gaseous fuels the units used are

Kilocalorie/ cubic meter (K.cal/m^3) or B.Th.U/ft^3)

$$1K.cal/Kg = 1.8 \times B.Th.U/lb$$
$$1K.cal/M^3 = 0.1077 \times B.Th.U/ft^3$$
$$1B.Th.U/ft^3 = 9.3K.cal/M^3$$

Dulong's formula

Dulong's formula is used for the calculation of calorific value

$$GCV = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240 \times S\right]$$

4.5.3 Problems on Calorific value

1. Calculate the gross and net calorific values of coal having the following composition: Carbon:87% Hydrogen:5% Sulphur:0.5%, Nitrogen:0.5% Oxygen:3% Ash:4%; latent heat of steam:587cal/gram.

Solution:

Given data:

Carbon:87% Hydrogen:5% Sulphur:0.5%, Nitrogen:0.5% Oxygen:3% Ash:4%; latent heat of steam:587 cal/gram.

Dulong's formula

$$GCV = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240 \times S\right]$$
$$GCV = \frac{1}{100}\left[8080 \times 87 + 34500\left(5 - \frac{3}{8}\right) + 2240 \times 0.5\right]$$

$$GCV = \frac{1}{100}\left[702960 + 34500\frac{37}{8} + 1120\right]$$

$$GCV = \frac{1}{100}[702960 + 159562.5 + 1120]$$

$$GCV = \frac{1}{100}[863642.5]$$

$$GCV = 8636.425 \text{ K.cal/kg}$$

$$LCV = [GCV - 0.09H \times 587] \text{ K.cal/kg}$$

2. Calculate the gross and net calorific values of coal having the following composition: Carbon: 85% Hydrogen: 8% Sulphur: 1%, Nitrogen: 2% Oxygen: 2% Ash: 2%; latent heat of steam: 587cal/gram.

4.6 Solid Fuels

4.6.1 Coal

A highly carbonaceous matter that has been formed as a result of alteration of vegetable matter [e.g plants] under certain favourable conditions. It is chiefly composed of C, H, N and O, besides non-combustible inorganic matter.

The combustion rate of solid fuels, like coal, is generally slow, because of the difficulty of thorough contact between the solid fuel and oxygen. The combustion rate can be increased by either of the following methods.

i) By increasing the rate of oxygen supply, but this method involves wastage of large proportion of heat carried by air itself. Hence in order to avoid the wastage of heat, it is necessary to use lower percentage of excess air for combustion.

ii) By finely powdering (or pulverizing) the coal, so that its free surface area is increased and the fuel comes in contact with air more easily. Generally, the pulverization method is more satisfactory for volatile coals. The volatile matter present in the coal is liberated quickly and burns, thereby helping the burning of fixed carbon.

4.6.2 Rank of Coal

- The amount of carbon content, volatile matter and impurities vary a great deal between different coal specimen.
- Primarily, on the basis on carbon content coal may be ranked into the following,

  Wood → Peat → Lignite → Bituminous Coal → Anthracite

(a) **Peat:-** It is a most inferior grade of coal, still remains in the first stage of coal formation. It is brownish in colour and contain un-decomposed woody matter. It is younger in age and carbon content varies between 30%-35%. The moisture con-tent is very high, more than 50%, and contains high amount of volatile matter.

(b) **Lignite or Brown Coal:-** This type is formed in the second stage of coal formation. It is brown in colour. Due to intense heat and pressure in the sub-surface region, peat is transformed into lignite after a very long period of separation from volatile matter and moisture. It contains low carbon content, varies between 35% to 45%.

The rest is high moisture content, volatile matter and impurities. It contains over 40% of moisture to its weight. It gives little heat but plenty of smoke and ash. It is older than peat but younger than anthracite and bituminous.

(c) **Bituminous:-** This is the penultimate stage of coal formation. Generally bituminous coal is black in colour. More compression and temperature transforms lignite into bituminous. The carbon content varies between 50% to 80%. It contain lower amount of moisture and volatile matter.

(d) **Anthracite:-** The best quality coal, formed in the last stage of coal formation It is lustrous black in colour, hard, compact and free from moisture and volatile matter. Carbon content of this coal may even exceed 95%. It is difficult to burn but, it burns with blue flame and, once ignited, gives ample heat but no smoke and little ash. Only 5% of world's coal deposit are of anthracite variety. It is mostly found in U.S.A., C.I.S. and U.K.

Fuel	**% of carbon**	**Calorific value (k.cal/kg)**	**Applications**
Wood	50	4000-4500	Domestic fuel
Peat	50-60	4125-5400	Used if deficiency of high rank coal is prevailing
Lignite	60-70	6500-7100	For steam generation in thermal power plants
Bituminous	80-90	8000-8500	In making coal gas and Metallurgical coke
Anthracite	90-98	8650-8700	In households and for steam raising

4.6.3 Analysis of coal

In order to assess the quality of coal, the following two types of analysis are made.

Proximate analysis

Proximate analysis involves in the following determinations.

1. **Moisture:-** About 1 gm of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105-110°C. The crucible is allowed to remain in oven for 1 hour and then taken out (with the help of a pair of tongs), cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).

   $$\text{Percentage of moisture} = \frac{\text{loss in weight}}{\text{Wt.of coal taken}} \times 100$$

2. **Volatile matter:-** The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at $925° \pm 20°C$. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside a desiccator and weighed a gain. Loss in weight is reported as volatile matter on percentage-basis.

   $$\text{Percentage of volatile matter} = \frac{\text{loss in weight}}{\text{Wt.of coal taken}} \times 100$$

3. **Ash:-** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at $700°C \pm 50°C$ for half-an-hour. The crucible is then taken out, cooled first in air, then in desiccator and weighed. Heating, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage basis. Thus,

   $$\text{Percentage of ash} = \frac{\text{Wt.of ash left}}{\text{Wt.of coal taken}} \times 100$$

4. **Fixed carbon:-**

   $$\text{Percentage of fixed carbon} = 100 - \%\text{ of (moisture + volatile matter + ash)}$$

Importance of proximate analysis:- Proximate analysis provides following valuable information's in assessing the quality of coal.

1. **Moisture:-** Moisture in coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel.
2. **Volatile matter:-** A high volatile matter content means that a high proportion of fuel will distill over as gas or vapour, a large proportion of which escapes

unburnt,so higher volatile content in coal is undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

3. **Ash:-** Ash is a useless, no combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air heat, thereby lowering the temperature. Hence lower the ash content, better the quality of coal.

4. **Fixed carbon:-** Higher the percentage of fixed carbon, greater is it's calorific and better the quality of coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter.

Ultimate analysis

Ultimate analysis involves in the following determinations.

1. **Carbon and Hydrogen:-** About 1-2 gm of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. 'C' and 'H' of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are adsorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increases in weights of these are then determined.

$$C + O \rightarrow CO_2 \; H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

$$12 \; 32 \quad 44 \quad 2 \quad 16 \quad 18$$

$$2KOH + CO_2 \rightarrow K_2CO + H_2O + O_2$$

$$CaCl_2 + 7H_2O \rightarrow CaCl_2.7H_2O$$

$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44}$$

$$\text{And percentage of H} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample taken} \times 18}$$

2. **Nitrogen:-** About 1 gm of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked flask called (Kjeldahl's flask). After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard $NaOH$ solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows.

$$\text{Percentage of N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 14}{\text{Weight of coal taken} \times 1000} \times 100$$

$$\text{Percentage of N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

3. **Sulphur:-** Sulphur is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, '*S*' is converted into sulphate. The washings are treated with Barium chloride solution when Barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of S} = \frac{\text{Weight of } BaSO_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

4. **Ash:-** Ash determination is carried out as in proximate analysis.
5. **Oxygen:-** It is obtained by difference

   Percentage of Oxygen $= 100-$ percentage of $(C+H+S+N+ash)$

Importance of ultimate analysis

1. **Carbon and Hydrogen:-** Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put.
2. **Nitrogen:-** Nitrogen has no calorific value, and hence its presence in coal undesirable. Thus, a good quality coal should have very little nitrogen content.
3. **Sulphur:-** Sulphur although contributes to the heating value of coal, yet on combustion products acids $(SO_2 \& SO_3)$ which have harmful effects of corroding the equipment's and also cause atmospheric pollution. Sulphur is usually, present to the extent of 0.5 to 3.0% and derived from ores like Iron pyrites, gypsum etc, and mines along with the coal.

   Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere and leads to corrosion.
4. **Oxygen:-** Oxygen content decreases the calorific value of coal. High oxygen content coal is characterized by high inherent moisture, low calorific value,

and low coking power. Moreover oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

4.6.4 Problems based on analysis

1. A sample of coal weighing 1.232 g was heated at 105°C for an hour and the residue weighed 1.186g. The residue was then heated in a muffle furnace at 940°C for seven minutes and the residue now weighed 1.126 g.

   Finally the residue was heated in presence of air at 750°C till a constant weight (0.080 g.) was attained. Calculate the results and explain what conclusions can you draw.

   Solution: Given data:

$$\begin{aligned}
\text{Sample weight} &= 1.232 \text{ gm}\\
\text{Residue weight} &= 1.186 \text{ gm}\\
\text{After heating residue weight} &= 1.126 \text{ gm}\\
\text{Mass of moisture in coal sample} &= 1.232 - 1.186 = 0.046 \text{ gm}\\
\text{Mass of volatile matter} &= 1.186 - 1.126 = 0.060 \text{ gm}\\
\text{Percentage of moisture} &= \frac{0.046 \times 100}{1.232} = 3.733\%\\
\text{Percentage of volatile matter} &= \frac{0.060 \times 100}{1.232} = 4.870\%\\
\text{Percentage of ash} &= \frac{0.080 \times 100}{1.232} = 6.494\%\\
\text{Percentage of fixed 'C'} &= 100 - (3.73 + 4.87 + 6.49)\\
&= 100 - 15.09\\
&= 84.91\%
\end{aligned}$$

4.6.5 Selection of coal

The following factors are considered for the selection of coal for different uses.

- The calorific value of a fuel should be high, so that large quantities of heat can be obtained from a small quantity of coal.
- It should have low moisture content.

- It should have low ash content since the presence of ash reduces the heating value of coal.
- Coal should have high calorific intensity.
- The size of coal should be uniform to facilitate handling and regulation of combustion.

4.7 Petroleum (or) Crude Oil

4.7.1 Introduction

Petroleum or crude oil (petra = rock;oleum = oil), is a dark greenish-brown, viscous oil found deep in earth's crust. It is composed mainly of various hydrocarbons (like straight-chain paraffins, cycloparaffins or napththalenes, olefins and aromatics), together with small amounts of organic compounds containing oxygen, nitrogen and sulphur. The oil is, usually, found floating upon a layer of brine and has a layer of gas on top of it. The average composition of crude petroleum is: $C = 79.5$ to 87.1%; $H = 11.5$ to 14.8%; $S = 0.1$ to 3.5%; $N + O =$ 0.1 to 0.5%.

4.7.2 Classification of petroleum

The chemical nature of the crude petroleum varies with the part of the world in which it is found. There appears, however, to be three principle varieties:

1. Paraffinic-base type crude is mainly composed of the saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ and a little of the naphthalenes and aromatics. The hydrocarbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are semi-solids, called 'waxes'.
2. Asphaltic-base type crude contains mainly cycloparaffins or naphthalenes with smaller amount of paraffin's and aromatic hydrocarbons.
3. Mixed-base type crude contains both paraffinic and asphaltic hydrocarbons and are, generally, rich in semi-solid waxes.

4.7.3 Origin of petroleum

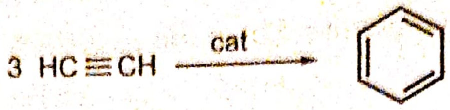
Carbidetheory (Inorganic theory)

Petroleum is originated from inorganic source. Molten metals react with coal deposits to form carbides which on further reactions such as hydrogenation, isomerization, and polymerization alkylation etc. form different hydrocarbons.

$$Ca + 2C \rightarrow CaC_2 \quad CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

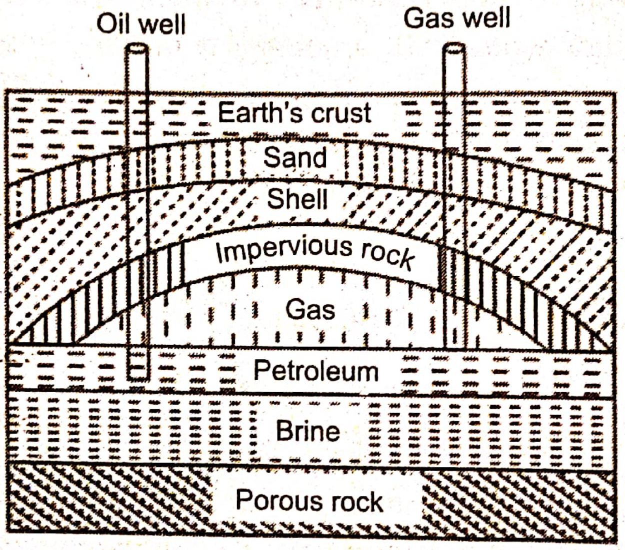
$$4Al + 3C \rightarrow Al_4C_3 \quad Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

$$Mg + 2C \rightarrow MgC_2 \quad MgC_2 + 2H_2O \rightarrow Mg(OH)_2 + C_2H_2$$



4.7.4 Mining of petroleum

It is done by drilling holes in the earth's crust and sinking pipes upto the oil-bearing porous rocks. Oil, usually, gushes out itself due to hydrostatic pressure of natural gas. Alternatively, it may be mechanically pumped up by using either lift pump or air-lift-pump. The latter consists of two co-axial pipes, lowered into the base of oil bed. Compressed air is forced through the outer pipe, whereby oil comes out through the inner pipe .The oil is conveyed to refinery by a system of pipelines.



Mining of petroleum

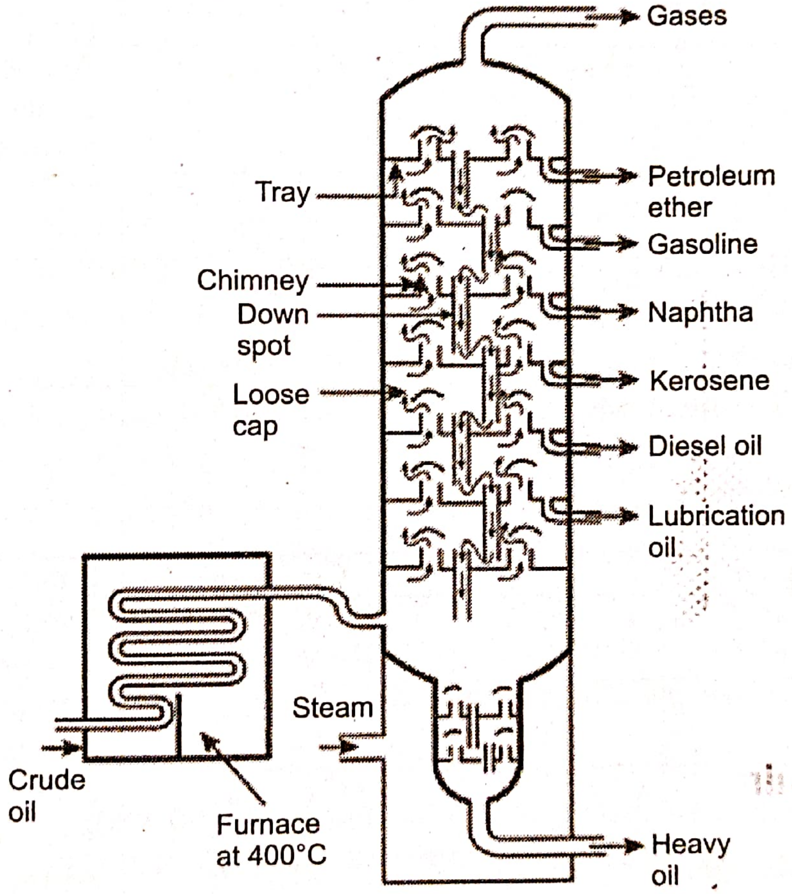
4.7.5 Refining of crude oil

The crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The process is called "refining of crude oil" and the plants set up for the purpose, are called the oil refineries. The process of refining involves the following steps:

Step 1. Separation of water (Cottrell's process):- The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

Step 2. Removal of harmful sulphur compounds;- It involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide(a solid), which is then removed by filtration.

Step 3. Fractional distillation:- The crude oil is then heated to about 400°C in an ion retort, whereby all volatile constituents, except the residue (alphalt or coke) are evaporated. The hot varpours are then passed up a "fractionating column", which a tall cylindrical tower is containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney, covered with a loose cap. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column. Higher boiling fractions condense first; while the lower boiling fractions turn-by-turn. Various principal fractionation products thus obtained are given in Table.



Fraction	Boiling range (°C)	Approximate composition	Uses
Uncondensed gases	Upto room temperature	$C_1 - C_4$	Fuel gases: refrigerants; production of carbon black, hydrogen; synthesis of organic chemicals.

Fraction	Boiling range (°C)	Approximate composition	Uses
Crude naphtha on refractionation yields,	30 - 150°	C_5-C_{10}	
(i) Petroleum ether	30 - 70°	C_5-C_6	Solvent
(ii) Petrol or gasoline	70 - 120°	C_6-C_8	Motor fuel; dry cleaning; petrol gas.
(iii) Benzene derivatives	120 - 150°	C_8-C_{10}	Solvent; dry cleaning
Kerosene oil	150 - 250°	$C_{11}-C_{16}$	Fuel; illuminant; oil gas
Heavy oil	250 - 400°	$C_{15}-C_{18}$	As fuel for diesel engines; converted to gasoline by cracking.
Refractionation gives,			
(i) Gas oil, (ii) Fuel oil, (iii) Diesel oil			
Residual oil on fractionation by vacuum distillation gives,	Above 400°	$C_{17}-C_{40}$	
(i) Lubricating oil		$C_{17}-C_{20}$	Lubrication
(ii) Paraffin wax		$C_{20}-C_{30}$	Candles; boot polish; wax paper; etc
(iii) Vaseline		$C_{20}-C_{30}$	Toilets; ointments; lubrication.
(iv) Pitch		$C_{30}-C_{40}$	Paints, road surfacing
Petroleum coke (on redistilling tar)			As fuel.

A brief description of three most important liquid fuels derived from petroleum is given on below:

(i) **Gasoline** or petrol is obtained between 40 – 120°C and is a mixture of hydrocarbons such as C_5H_{12} (pentane) to C_8H_{18} (octane). Its approximate composition is: $C = 84\%, H = 15\%, N+S+O = 1\%$. Its calorific value is about 11,250 kcal/kg. It is highly volatile, inflammable and used as fuel for internal combustion engines of automobiles and aeroplanes.

(ii) **Kerosene oil** is a fraction obtained between 180 – 250°C and is a mixture of hydrocarbons such as $C_{10}H_{22}$ (decane) to $C_{16}H_{34}$ (hexadecane). Its approximate composition is : $C = 84\%, H = 16\%$; with less than 0.1% S. Its specific gravity is 0.75-0.85. Its calorific value is 11,100 kcal/kg. Due to high boiling point range, kerosene does not vaporize easily. It is used as domestic fuel in stoves, as jet engine fuel and for making oil gas.

(iii) **Diesel oil** is a fraction obtained between 250 – 320°C and is a mixture $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbons. Its density is 0.86 to 0.95. Its calorific value is about 11,000 kcal/kg. It is used as a diesel engine fuel.

4.8 Knocking

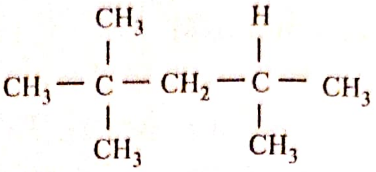
In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression-stroke to the volume at the end of compression-stroke of the piston is known the 'compression ratio'. The efficiency of an internal combustion engine increases with the increase in compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel-air mixture gets ignited instantaneously, producing on explosive violence, known as 'knocking'. The knocking results in loss of efficiency.

Chemical structure and knocking:- The tendency of fuel constituents to knock in the following paraffins (i.e. naphthalens) > aromatics.

Thus, olefins of the same carbon-chain length possess better anti-knock properties than the corresponding paraffins and so on.

Octane number (introduced by Edger in 1872) :- It has been found that n-heptane knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isooctane (2,2,4-trimethyl pentane),gives very little knocking, so its anti-knock value has been given as 100. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture isooctane and n-heptane, which matches the fuel under test in knocking characteristics. In this way, an '80-octane' fuel is one which has the same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

n-heptane
octane number = 0



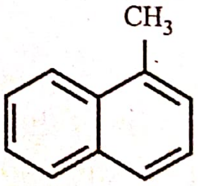
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

isooctane
octane number = 100

Cetane number:- Quality of diesel is expressed in terms of cetane number. Hexadecane ($C_{16}H_{34}$) (or) cetane which ignites rapidly and 1-methylnaphathalene which ignites slowly are taken as standard and the igniting property of the fuel under study is compared with that of the mixture of the two to find its cetane number.

$C_{16}H_{34}$

n-hexadecane
cetane number = 0

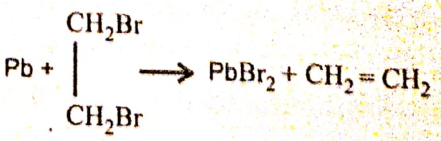


l-methyl naphthalene
cetane number = 0

4.9 Anti Knocking Agents

Improvement of anti-knock characteristics of a fuel: The octane number of I.C. fuels can be raised by the addition of such extremely poisonous materials as tetra ethyl lead, $(C_2H_5)_4Pb$ or TEL and diethyl telluride, $(C_2H_5)_2Te$. In motor spirit (or motor fuel), about 0.5 ml and in aviation fuels, about 1.0 to 1.ml of TEL is added per liter of petrol.

According to the most accepted theory, TEL is converted into a cloud of finely divided lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxide molecules formed, thereby slowing down the chain oxidation reaction and thus, decreasing the chances of any early detonation. However, deposit of lead oxide is harmful to the engine life. Consequently, in order to help the simultaneous elimination of lead oxide formed from the engine, a small amount of ethylene di bromide is also added to petrol. Ethylene di bromide removes lead oxide as volatile lead bromide along with the exhaust gases. The presence of sulphur compounds in petrol reduces the effectiveness of the TEL.



$$Pb + \begin{array}{c} CH_2Br \\ | \\ CH_2Br \end{array} \longrightarrow PbBr_2 + CH_2=CH_2$$

4.10 Gaseous Fuels

Gas fuels are the most convenient because they require the least amount of handling and are used in the simplest and most maintenance-free burner systems. Gas is delivered "on tap" via a distribution network and so is suited for areas with a high population or industrial density.

However, large individual consumers do have gasholders and some produce their own gas.

The following is a list of the types of gaseous fuel:

- Fuels naturally found in nature:
  - Natural gas
  - Methane from coal mines
- Fuel gases made from solid fuel:
  - Gases derived from coal
  - Gases derived from waste and biomass
  - From other industrial processes (blast furnace gas)
- Gases made from petroleum:
  - Liquefied Petroleum gas (LPG)
  - Refinery gases
  - Gases from oil gasification
- Gases from some fermentation process

Gaseous fuels in common use are liquefied petroleum gases (LPG), Natural gas, producer gas, blast furnace gas, coke oven gas etc. The calorific value of gaseous fuel is expressed in Kilocalories per normal cubic meter (Kcal/Nm^3) i.e. at normal temperature (20°C) and Pressure (760 mm Hg).

Properties of gaseous fuels

Since most gas combustion appliances cannot utilize the heat content of the water vapour, gross calorific value is of little interest. Fuel should be compared based on the net calorific value. This is especially true for natural gas, since increased hydrogen content results in high water formation during combustion.

Important gaseous fuels

The most important gaseous fuels are

1. Natural gas
2. Producer gas
3. Water gas
4. Coal gas
5. Bio gas

4.10.1 Natural gas

Natural gas is obtained from wells dug in the oil-bearing regions. When natural gas occurs along with petroleum in oil wells, it is called Wet gas. On the other hand, when the gas is associated with crude oil, it is called Dry gas. The wet gas is treated to remove propane, propene, butane and butane,which are used as LPG.

Before use the natural gas is purified to remove objectionable ingredients such as water, dust, grit, H_2S, CO_2, N_2 and heavier liquefiable hydrocarbons (propane, butane, etc.).

Composition

The average composition of natural gas is

$CH_4 = 70 - 90\%$

$C_2H_6 = 5 - 10\%$

$H_2 = 3\%$

$CO + CO_2 =$ rest.

The calorific value varies from 12,000 to 14,000 Kcal/m^3.

Uses

1. It is an excellent domestic fuel and can be conveyed over very large distances in pipelines.
2. It has recently been used in the manufacture of a number of chemicals by synthetic processes.
3. It is also used as raw material for the manufacture of carbon black (a filler for rubber) and hydrogen (used in ammonia synthesis).
4. Synthetic proteins are obtained by microbiological fermentation of methane.

Natural gas is mainly divided into two types

1. Liquefied Petroleum Gas (LPG)
2. Compressed Natural Gas(CNG)

Liquefied Petroleum Gas (LPG)

LPG is obtained as a byproduct during cracking of heavy oil or from natural gas. It contains hydrocarbons that are highly volatile but are easily liquefiable under high pressures.

The components that form LPG are n-Butane, Isobutane, Butylenes and Propane with traces of Propylene and Ethane. Its calorific value is about 27,800 kcal/m^3.

It is generally used as a domestic fuel for cooking and in industry. Though it is cheaper fuel and knock resistance.

Uses:- The largest use of LPG as domestic fuel and industrial fuel. However, there is an increasing trend to use LPG as motor fuel.

Advantages

- LPG is cheaper than petrol (up to 50%)
- It produces less exhaust emissions than petrol
- It is better for the engine and it can prolong engine life
- In some vehicles, it can provide better performance
- Has a higher octane rating than petrol (108 compared to 91)

Disadvantages

- It isn't highly available
- The initial cost for converting your vehicle to LPG can cost up to $3000. However the average car can repay the cost of the conversion in about 2 years
- It has a lower energy density than petrol
- No new passenger cars come readily fitted with LPG (they have to be converted)
- The gas tank takes up a considerable amount of space in the car boot

Compressed Natural Gas (CNG)

Natural gas is compressed to high pressure of about 1,000 atmospheres is known as CNG. A steel cylinder containing 15 kg of CNG contains about 2×10^4 L or 20 m^3 of natural gas at 1 atmospheric pressure.CNG is now being used as a substitute for petrol and diesel, since it is comparatively much less pollution causing fuel. During its combustion, no sulphur and nitrogen gases are evolved. Moreover, no carbon particles are ejected. Hence it is better fuel than petrol/diesel for automobiles. However, initial cost of engine designed to use CNG as a fuel is comparatively higher than that of engine designed to use petrol/diesel. In Delhi, it is mandatory for all buses, taxis and auto to use CNG as fuel.

Why is CNG preferred over LPG

1. CNG is a much safer fuel, since it ignites at higher temperature than petrol and diesel.
2. The conversion of gasoline operated automobiles into CNG operated vehicle is very easy.
3. The operating cost of CNG fuel is much lower compared to gasoline operation.
4. Combustion of CNG leads to lesser CO emissions than gasoline.
5. CNG mixes better with air than liquid fuels.
6. Emission from CNG operated vehicle contain no unregulated pollutants (e.g., smoke, $SO_2, SO_3, C_6H_6, HCHO$).

4.11 Biodiesel

Biodiesel is an alternative fuel which can be used in diesel engines with little or no modifications. It is a mixture of several alkyl esters produced from vegetable oils. The vegetable oil is heated with an alcohol (typically methanol or ethanol is used) and an aqueous solution of an alkali (potassium hydroxide or sodium hydroxide) added as a catalyst. The glycerol molecule from the vegetable oil is exchanged with methanol or ethanol to form another ester. This process is called transesterification.

4.11.1 Production of Bio-diesel

There are three basic technological routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil with alcohol.
- Direct acid catalyzed esterification of the oil with methanol.
- Conversion of the oil to fatty acids, and then to Alkyl esters with acid catalysis.

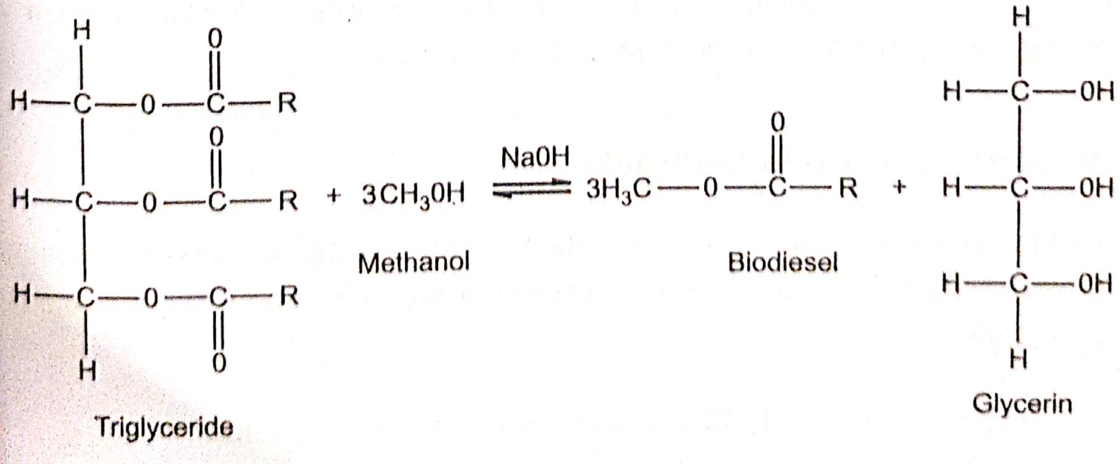
The process that is most widely used is the transesterification. In this process, vegetable oils and a short chain alcohol (methanol or ethanol mainly) in the presence of a catalyser (usually NaOH or KOH) are turned into alkyl esters and glycerine. This is not only the most economical route, but also:

- It has a high rate of reaction conversion (98%) with low reaction time and minimum side reactions.
- Presents direct conversion to alkyl ester without any intermediate steps.
- The reaction is carried out under low temperature (about 65°C) and low pressure (about 1.4 bar).
- There is no need to use advanced or special materials of construction.

Procedure

Moisture free oil or fat(with less than 5% free acid) and dry methanol or ethanol are taken in 1:3:5 molar ratio in a three-neck round bottom flask) with arrangement of magnetic stirrer and heating) and catalyst sodium methoxide maintained about 2% by weight. The mixture is heated at 60°C, and purified by using vacuum distillation.

The chemical reaction can be represented as following:



In general terms, 100 kg of vegetable oil reacting with 10 kg of alcohol yield 100 kg of biodiesel and 10 kg of Glycerine.

4.11.2 Advantages of Biodiesel

- Derivation from a renewable domestic resource, thus reducing dependence on and preserving petroleum
- Biodegradability
- Reduction of most exhaust emissions (Exception NOx)
- Higher flash point leading to safer handling and storage
- Excellent lubricity

4.11.3 Disadvantages of Biodiesel

- Inherent higher price
- High expensive Feedstock's
- Increased NOx exhaust emissions due to reduced excise taxes

4.12 Carbon Neutrality (or) Net zero carbon

Carbon neutrality is an effective way to deal with issues such as global warming and extreme climate disasters.

The amount of CO_2 released into the atmosphere is balanced by an equivalent amount being removed is called Carbon Neutrality.

(or)

Carbon neutrality is the achievement of net-zero cabon dioxide (CO_2) radiations by creating a balance between levels of emission and absorption of carbon from atmosphere.

(or)

Carbon neutrality means having a balance between emitting carbon and absorbing carbon from the atmosphere in carbon sinks.

Significance of Carbon neutrality

Achieving carbon neutrality is not only the key to avoiding the worst consequences of climate change - it also brings benefits to communities and society as a whole. They include:

1. Less environmental pollution and improvements to health.
2. A boost to sustainable economic growth and the creation of green jobs.
3. Enhanced food security by lessening the impact of climate change.

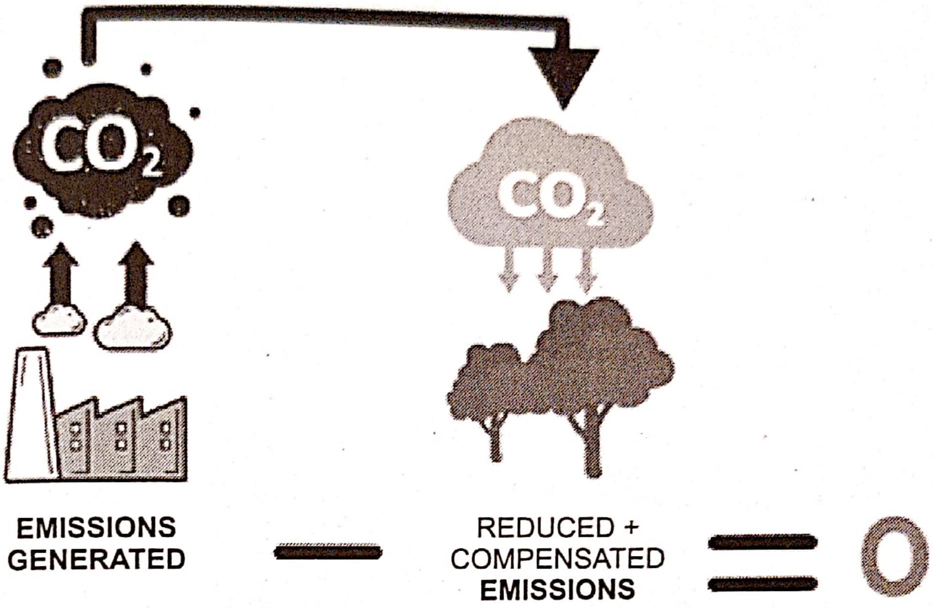


Figure. 4.1 **Carbon neutrality**

4. A halt to the loss of biodiversity and an improvement in the condition of the oceans.
5. It shows the company's commitment to decarbonisation and its desire to compensate for left-over impacts.
6. It improves the company's green credentials, differentiating it from the rest as an environmentally responsible brand.