Chapter 4: Fuels and Combustion

Fuel: A fuel is the substance which on combustion produces a large amount of heat.

$$\text{Fuel} + O_2 \quad \xrightarrow{\textit{high temp}} \quad \text{Combustion products} + \text{Heat}$$

As most of the fuels contain carbon or carbon and hydrogen, the combustion involves the oxidation of carbon to carbon dioxide and hydrogen to water. Sulphur, if present, is oxidised to sulphur dioxide while the mineral matter forms the ash.

Fuels like coal, crude oil, natural gas known as fossil fuels found under earth crust.

Chemical fuels: The fossil fuels, wood, vegetable oils etc. which produce heat on burning are known as chemical fuels.

Calorific Values
It is defined as the amount of heat obtained on complete combustion of unit mass of a solid or liquid fuel or unit volume of a gaseous fuel at STP.

Types of calorific values   (1)Gross calorific value (G.C.V.)
                                   (2)Net calorific value (N.C.V.)

Gross Calorific Value (G.C.V.)
Usually, fuel contains some hydrogen. The hydrogen atoms are bonded to carbon atoms in the fuel. When the fuel is burnt, hydrogen forms water vapours. The water vapours if cooled, we get certain amount of heat, as the water has high latent heat of 2450 joules/gm or 587 cal/gm.

Thus during the study of calorific value of a fuel, we get some heat directly by combustion of fuel and in addition we get certain amount of heat by cooling the products of combustion to 15°C.

Definition
Gross calorific value of a fuel can be defined as the total amount of heat obtained on complete combustion of unit mass of a solid or liquid fuel or unit volume of a gaseous fuel (STP) and on cooling the products of combustion to 15°C. The gross calorific value is also called as higher calorific value.

The G.C.V. is of only theoretical importance because in actual practice, we do not have any provision of cooling the products of combustion during combustion of a fuel in an engine, furnace or any other fuel burning device and the product gases leaves with some heat.

Net Calorific Value (N.C.V.)
A fuel containing hydrogen produces water, on combustion. Out of the total heat produced in combustion of the fuel, the water takes away a considerable portion of the heat for evaporation and actually less heat is available for heating.

There is no any furnace, engine or device designed to collect the heat being taken away by the water vapours. Therefore practically we get lower calorific value than the theoretically expected.

Definition

Net calorific value is defined as the amount of heat obtained practically on complete combustion of unit mass of solid or liquid fuel or unit volume of a gaseous fuel at STP and the products of combustion are allowed to escape with some heat. N.C.V. is also called as lower calorific value.

The N.C.V. and G.C.V. are related as under,

$$G.C.V. = N.C.V. + \left(\frac{9 \times h \times \text{latent heat of water}}{100} \right)$$

Where 'h' is the percentage of hydrogen in the fuel.
It should be noted that the unit of latent heat of water and unit of G.C.V., N.C.V. should be same.

Ex.1) The coal containing 5% hydrogen (dry / moisture free basis) and 10% moisture has gross calorific value of 33.5 MJ/kg. Calculate Net Calorific Value of Coal. Latent heat of water vapour is 2.45 MJ/kg.
Soln. :
GCV = 33.5 MJ/kg   Moisture = 10 %,   H % = 5,
As 18 gm moisture 2 gm H

$$\therefore \ 10 \text{ gm moisture} = \frac{100}{18} \times 2 = 1.11 \text{ gm or } 1.11\% \text{ hydrogen}$$

Total hydrogen % in coal = 5 + 1.11 = 6.11%

As, GCV = NCV + (0.09 H × 2.45)

33.5 = NCV + (0.09 × 6.11 × 2.45)

∴ NCV = 33.5 - 0.5499 × 2.45

= 32.15 MJ/kg   …Ans.

Characteristics of an Good/ideal fuel:

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

1. It should possess high calorific value.
2. It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.
3. It should not produce poisonous products during combustion. In other words, it should not cause pollution or combustion.

4. It should have moderate rate of combustion.
5. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
6. It should not leave behind much ash on combustion.
7. It should be easily available in plenty.
8. It should have low moisture content.
9. It should be cheap.
10. It should be easy to handle and transport.

Determination G.C.V. of Solid, Liquid Fuels by Bomb Calorimeter

Principle of Bomb Calorimeter :
A known weight of solid / liquid fuel is burnt in the presence of excess oxygen in the closed pot, and the products of combustion are cooled, to get GCV of the fuel.

Construction of Bomb Calorimeter
A Bomb calorimeter consists of,

a) Bomb Pot:
•It is a cylindrical, strong stainless steel pot having a lid. The lid can be fitted air tight to Bomb pot by screwing.
•There are two electrodes fitted through the lid and there is an oxygen inlet valve at its centre.
•One of the electrodes is provided with a ring to hold the crucible containing fuel. There is a thin resistance wire tied to the electrodes in loop form and the loop touches the fuel.
•The weighed fuel is burnt in the Bomb pot in the presence of high pressure oxygen.

b) Calorimeter
•There is a stainless steel or copper calorimeter in which the Bomb pot is kept. It contains a known volume of water and the water is kept circulating around the Bomb pot with the help of a stirrer.
•A Beckman thermometer or digital thermometer is kept in the water of calorimeter, which can record the rise in temperature of water due to absorbing heat generated in burning of fuel in Bomb pot.

c) Water and Air Jackets
•The calorimeter is surrounded by air jacket and water jacket to avoid heat losses due to radiation.
•There are insulator stands between calorimeter and water jacket.

d) Accessories
•There is a pellet press to convert the powder of solid fuel to pellet form. For a liquid fuel, a capsule of negligible weight can be used.
•There is a oxygen cylinder with pressure gauge to fill oxygen in the Bomb pot at the pressure of nearly 25 kg/cm^2.
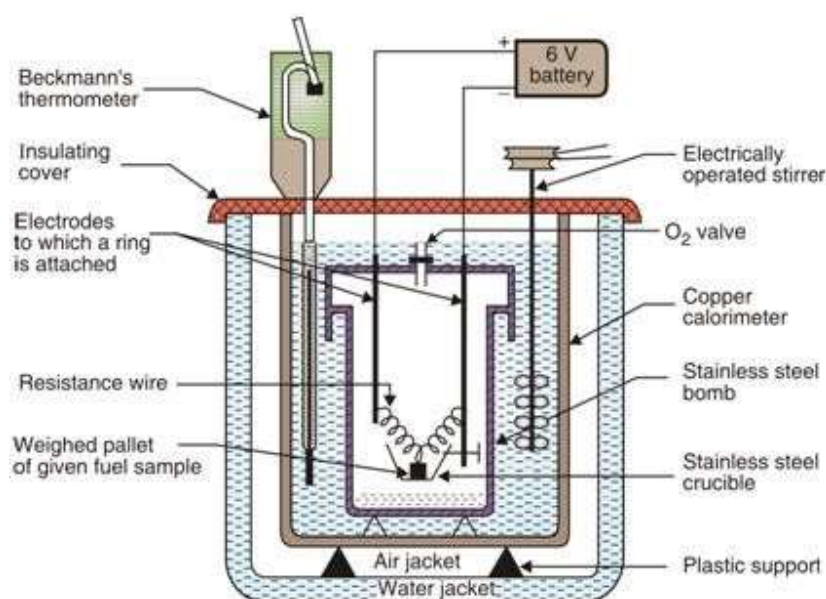•There is also a D.C. battery of about 6 volts, to start combustion of fuel.

Fig.1 : Bomb Calorimeter

Working of Bomb Calorimeter

(i) Weigh the pellet of solid fuel or liquid capsule and keep it in the crucible. Keep the crucible in the ring of the electrode. Tie the resistance wire between electrodes such that it touches to the fuel.

(ii) Add about 10 ml of distilled water at the bottom of Bomb pot and fix the lid tightly to Bomb by screwing.

(iii) Fill the Bomb with oxygen at the pressure about 25 kg/cm^2.

(iv) Place the Bomb in calorimeter. Add known volume of water in the calorimeter so that the Bomb gets immersed in the water.

(v) Place the calorimeter in the water jacket over the plastic studs. Keep the thermometer and stirrer in the water of calorimeter.

(vi) Put the plastic cover on the top and make electrical connections from battery to electrodes.

(vii) Operate the stirrer for 5 minutes and note the initial temperature of water.

(viii) Pass the current for about 5-10 seconds to heat the wire so that the fuel catches fire. If the fuel contains S and N elements, they get converted to SO_3 and N_2O_5. These gases get dissolved in the distilled water in Bomb to form H_2SO_4 and HNO_3 (along with liberation of little heat).

(ix) Note the maximum temperature reached. After that note the average rate of fall of temperature per minute and the time taken for reaching to initial temperature.

(x) Open the Bomb pot and wash the contents at its bottom into a beaker, to find out the amount of H_2SO_4 and HNO_3 formed.
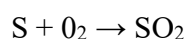
Calculations:

Ans. : Let,   mass of fuel in gm = x gm
    mass of water in calorimeter = W gms
    Water equivalent of calorimeter set = w gms.
    Gross Calorific value of fuel = L calories/gm
    Rise in temperature of water = $(t_2 - t_1)$
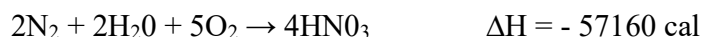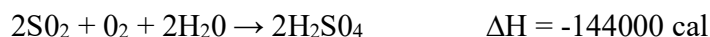   Heat liberated by burning fuel = Heat absorbed by water and calorimeter.

$$\therefore \quad xL = (W + w)(t_2 - t_1)$$
$$\therefore \quad G.C.V. = L = \frac{(W + w)(t_2 - t_1)}{x} \text{ cal/gm.}$$

Remember the units of W, w, x in grams.

Corrections

(i) Fuse wire correction: The heat liberated includes the heat given out by ignition of the fuse wire used.

(ii) Acid correction: Fuels containing sulphur and nitrogen are oxidized under high pressure and temperature of ignition to sulphuric acid and nitric acid.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta H = -144000 \text{ cal}$$

$$2N_2 + 2H_2O + 5O_2 \rightarrow 4HNO_3 \qquad \Delta H = -57160 \text{ cal}$$

Formation of these acids is an exothermic reaction, thus the measured heat also includes the heat given out during acid formation.

Amount of these acids can be analyzed from the washings. Sulphuric acid is precipitated as $BaSO_4$. Correction for 1 mg sulphur is 2.25 cal while for 1 ml N/10 HNO_3 is 1.43 cal.

(iii) Cooling correction: Time taken to cool the water from maximum temperature to room temperature is noted. From the rate of cooling (dt/min) and actual time for cooling (t min), the cooling correction dt x t is added to rise in temperature.

$$L(HCV) = \frac{(W + w)(t2 - t1 + t.\,dt) - (a + f)}{X} \; cal/g$$

Standard gross calorific values of some pure fuels are,
      Benzoic acid = 6325 cal/gm   Naphthalene = 9622 cal/gm,
      Salicylic acid = 5269 cal/gm   Camphor = 9292 cal/gm,

NCV for the fuel is calculated as below;

If 'h' is percentage of hydrogen in the fuel, then the heat taken by water formed during combustion to convert it into steam is = 0.09 h × 587 cal/gm

$$NCV = GCV - 0.09 \text{ h} \times 587 \text{ cal/gm or kcal/kg}$$

Ex.2) 0.072 gm of a fuel containing 80% Carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3°C to 29.1°C. If the calorimeter contains 250 gm of water and its water equivalent is 150 gm, calculate GCV of the fuel.
Soln. :
Rise in temperature $(t_2 - t_1)$ = 29.1 – 27.3 = 1.8°C
Mass of fuel = m = 0.072 gm
Water equivalent of calorimeter = 150 gm = w
Mass of water in calorimeter = 250 gm = W

$$GCV = \frac{(W + w)(t_2 - t_1)}{m} = \frac{(250 + 150) \times 1.8}{0.072} \text{ cal/gm}$$

      = 10,000 cal/gm.   …Ans.

Ex.3) A sample of coal containing 5% H2 when allowed to undergo combustion in Bomb Calorimeter, the following data were obtained.
weight of coal burnt = 0.95 gm
weight of water taken = 700 gm
water equivalent of bomb calorimeter = 2000 gm
rise in temperature = 2.48°C
cooling correction = 0.02°C
fuse wire correction = 10 cal
acid correction = 60 cal
Calculate Gross and Net Colorific Value of Coal.

Soln. :

$$w = 2000, \quad W = 700, \quad M = 0.95, \quad t_2 - t_1 \, C° = 2.48$$
$$h = 5\% \quad a = 60 \text{ cal}, \quad f = 10 \text{ cal}, \quad t.dc = 0.02,$$

$$\text{GCV of coal} = \frac{(W + w)(t_2 - t_1 + t_c) - (a + f)}{m}$$

$$= \frac{(700 + 2000)(2.45 + 0.02) - (60 + 10)}{0.95}$$

$$\therefore GCV = 7031.58 \text{ Cal/gm}$$
$$NCV = GCV - 0.09 \, h \times \text{Latent Heat}$$
$$= 7031.6 - 0.09 \times 5 \times 587$$
$$= 6767.45 \text{ cal/gm}$$
$$= 6767.45 \times 4.18 \times 1000$$
$$= 28288 \text{ Joules/gm} = 28288 \times 10^3 \text{ J/kg}$$
$$= 28.288 \text{ MJ/kg} \dots \text{Ans}$$

Calorific Value of Gaseous Fuels by Boy's Calorimeter

Principle of Boy's Calorimeter :
A gaseous fuel is burnt at a known constant rate in the calorimeter under such conditions that entire amount of heat produced is absorbed by circulating water.

Construction of Boy's Calorimeter :
It consists of following parts :
  (i)   Gas burner : There is a gas burner in which a known volume of gas is burnt at a known pressure. The gas is burnt at the rate of 3 to 4 litre per minute.
  (ii)   Combustion chamber (chimney) : Around the burner there is a combustion chamber which has a copper tubing coiled inside as well as outside of it. Water enters from top of the outer coil, moves to bottom of chimney and then goes up through the inner coil to the exit at top.
  (iii) Thermometers : There are two thermometers to measure temperatures of inlet water and outlet water.
       Insulating cover : The assembly is covered with an insulator to detach combustion chamber from atmosphere. There is a hole on top for exhaust gas, water inlet and condensed steam comes out from bottom outlet.
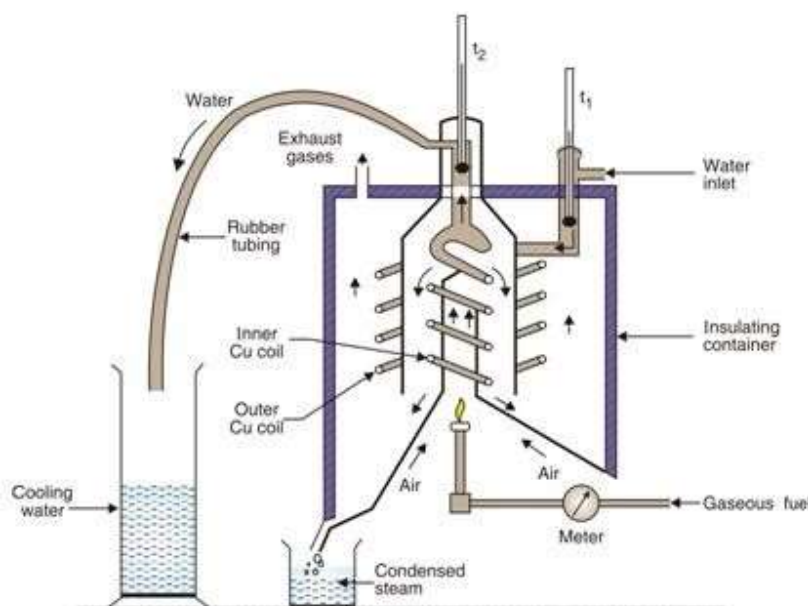
Fig.2 : Boy's gas calorimeter

Working of Boy's Calorimeter

(i) Start burning the gas at suitable pressure and adjust the rate of water flow such that the temperature of outgoing water remains constant.

(ii) Burn the gas for 5-10 minutes to have the steady temperatures of outgoing water.

(iii) After the steady conditions of outgoing water temperature, constant water circulation and gas flow rate reached, simultaneously note the following :

a) Volume of gas burnt at given temperature and pressure in certain time period.

b) Quantity of water passed through coil during this period.

c) Mass of water condensed from product gas during the period.

d) The steady rise in temperature of water $(t_2 - t_1)$.

Calculations :

First convert the volume of gas burnt to volume of gas at STP. Let this STP volume be V m³.

Let, W = mass of cooling water used in the period of observation, in kg.

Let m = mass of water condensate in kg. L = G.C.V. of the fuel.

Heat produced by combustion of fuel = heat absorbed by cooling water (assuming no heat loss, in the steady state conditions).

$$\therefore \quad VL = W(t_2 - t_1)$$

$$\therefore \quad L = \frac{W(t_2 - t_1)}{V} \text{ kcal/m}^3$$

The mass of condensate water per m³ of gas will be, $\frac{m}{V}$ kg/m³.

If this water had left as steam in product gases, it would have taken away

$$\text{Heat} = \frac{m}{V} \times 587 \text{ kcal/m}^3$$

$$\therefore \quad NCV = GCV - \frac{m}{V} \times 587$$

$$\boxed{NCV = \frac{W(t_2 - t_1)}{V} - \frac{m \times 587}{V} \text{ kcal/m}^3}$$

Ex.4) Observations in the Boy's gas calorimeter experiment on a gaseous fuel are given below; Find the G.C.V. and N.C.V. of the fuel, Volume of gas burnt (STP) = 0.08 m3

Mass of cooling water used = 29.5 kg

Rise in temperature of circulating water = 9.1°C

Mass of steam condensed = 0.04 kg

Soln. :

Given : V = 0.08 m   W = 29.5 kg, ³ $(t_2 - t_1$ m = 0.04 kg) = 9.1°C,

We have, $GCV = L = \dfrac{W(t_2 - t_1)}{V}$

$$\therefore \quad GCV = \frac{29.5 \times 9.1}{0.08} = 3355.6 \text{ kcal / m}^3$$

$$NCV = L - \frac{m}{V} 587 = 3355.6 - \frac{0.04}{0.08} \times 587 = 3062.1 \text{ kcal/m}^3$$

$$= 3062.1 \times 4.18 \times 1000 \text{ Joules/m}^3$$

$$= 12.8 \times 10^6 \text{ J/m}^3 = 12.8 \text{ MJ/m}^3 \qquad \text{...Ans.}$$

Ex. 5) In Boy's gas calorimeter's experiment when 0.1m3 of a fuel gas is burnt during which 25 kg of water is circulated. Temperature of incoming water and outgoing water is 20°C and 33°C respectively. Weight of steam condensed is 250 gm. Calculate gross calorific value and net calorific value, if heat liberated in condensing water vapour and cooling the condensate is 586 kcal/kg.

Soln. :

Given : Volume of gas burnet = 0.1 m³

Mass water circulated at NTP = W = 25 kg

Steady rise in temperature = $(t_2 - t_1)$ = 33 − 20 = 13°C

$$\text{Gross calorific value of gas} = \frac{W(t_2 - t_1)}{V}$$

$$= \frac{25 \times 13}{0.1} = 3250 \text{ kcal/ m}^3$$

$$\text{Net calorific value} = \text{G.C.V.} - \frac{m \times 586}{V}$$

$$= 3250 - \frac{0.25 \times 586}{0.1}$$

$$= 3250 - 1450 = 1785 \text{ kcal/m}^3 \qquad \text{...Ans.}$$

Coal

Coal is highly carboneous matter formed from vegetable matter buried in geomorphic changes, under pressure, by action of aerobic and anaerobic bacteria for a long time.

Analysis of Coal

Two types of analysis: Proximate and Ultimate

Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which:

(i) moisture %　　　　(ii) volatile matter %　　　(iii) ash %　　　　(iv) fixed carbon %, are found out.

Moisture %

(a) Principle : All moisture in coal escapes on heating coal at 110°C for 1 hour.

(b) Method : A known weight of powdered and air dried coal sample is taken in a crucible and it is placed in an oven for 1 hour at 110°C. Then the coal is cooled in a descicator and weighed out. If the initial weight of the coal is m gms and final weight is m1 gms. The loss in weight $(m - m_1)$ corresponds to moisture in coal.

(c) **Formula :** $\text{Moisture \%} = \dfrac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100 = \dfrac{m - m_1}{m} \times 100$

Silica Crucible

Descicator
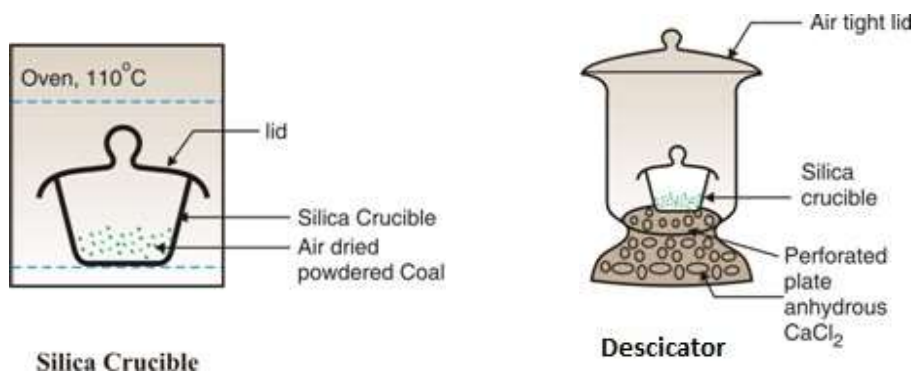
Volatile Matter (V.M.) %

(a) Principle : At 925°C, coal molecules under go thermal degradation to produce volatile matter.

(b) Method : Moisture free coal left in the crucible in first experiment (m_1) is covered with a lid loosely. Then it is heated at 925°C in a muffle furnace for 7 minutes. The crucible is taken out and cooled in a desicator. Then it is weighed (m_2 gms). The loss in weight ($m_1 – m_2$) is due to loss of volatile matter in the m gms of the coal sample. (Volatile matter is the thermally decomposed coal during burning of coal, that escapes without combustion, in the form of smoke).

(c) **Formula :** $\text{Volatile matter \%} = \dfrac{\text{Weight of volatile matter}}{\text{Weight of air dried coal}} \times 100 = \dfrac{m_1 - m_2}{m} \times 100$

The volatile matter % can also be determined by taking the fresh weight of the air dried coal but the loss in weight at 925°C, will be due to loss of moisture and volatile matter. If w is the weight of air dried coal and w_1 is the mass of coal left at 925°C heating, then

$$\text{Volatile matter \%} = \dfrac{\text{Loss in weight due to moisture and V.M.} \times 100}{\text{Weight of coal sample}} - \text{moisture \%}$$

$$= \dfrac{(w - w_1) \times 100}{w} - \text{moisture \%}$$

Ash %

(a) Principle : Inorganic matter in the coal gets oxidised to form metal oxides and silica, which is non-combustible and left as ash.

(b) Method : The residual coal in the above experiments is heated and burnt in a open crucible at above 750°C for half hour. The coal gets burnt. The ash left in crucible is cooled in a desicator and weighed (m_3 gm).

(c) **Formula :** $\text{Ash \%} = \dfrac{\text{weight of ash}}{\text{weight of coal}} \times 100 = \dfrac{m_3}{m} \times 100$

Fixed carbon %

Fixed carbon % = 100 – (% Moisture + % V. M. + % ash)

Significance (Importance of Proximate Analysis)

1. Moisture

      (i) Decreases calorific value of coal largely as it does not burn and takes away heat in the form of latent heat.

      (ii) It increases ignition point of coal.

Hence, a coal with lower moisture % is better quality.

2. Volatile Matter

      (iii) It decreases calorific value of coal.

      (ii) It elongates flame and decreases flame temperature.

      (iii) It forms smoke and pollutes air.

However, the coals containing 15-25% of V.M. on carbonisation give coke oven gas which is the source of various organic aromatic chemicals. Such coals have good caking property and coke can be obtained from the coals.

Overall, regarding burning of coal, the coal with lesser V.M. is better quality coal.

3.Ash
     (i)Ash reduces calorific value of coal as ash is non-burning part in coal.
     (ii)Ash disposal is a problem.
     (iii)Ash fuses to form clinker at high temperature, obstructing the air supply to coal burning in furnace.
Hence, lesser the ash %, better is the quality of coal.

4.Fixed Carbon
     Carbon is the burning part in coal and higher the FC%, higher is calorific value. Hence a good quality coal contains high FC%.
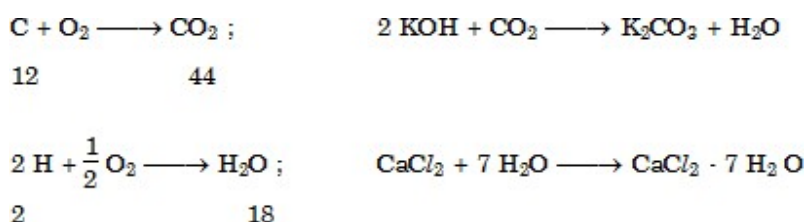

Ultimate Analysis of Coal
Definition : The analysis of coal in which percentages of C, H, N, S and O elements are found out, is known as ultimate analysis.

Carbon and Hydrogen.
(a) Method for determination :
• A known weight of powdered and air dried coal sample is burnt in the presence of pure oxygen, in a combustion apparatus. C and H are converted to CO_2 and H_2O vapours respectively.
• The gaseous products are allowed to pass through first the preweighed U-tube containing anhydrous $CaCl_2$ or magnesium per chlorate (absorbing H_2O vapours) and then through the KOH solution in a preweighed U-tube (absorption of CO_2).
• The increase in weight of U-tube containing anhydrous $CaCl_2$ corresponds to weight of water formed and increase in weight of U-tube containing KOH solution corresponds to CO_2 formed, by combusting the coal sample.

(b) Reactions :

$$C + O_2 \longrightarrow CO_2 ; \qquad\qquad 2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$
$$12 \qquad\qquad 44$$

$$2\,H + \frac{1}{2}O_2 \longrightarrow H_2O ; \qquad\qquad CaCl_2 + 7\,H_2O \longrightarrow CaCl_2 \cdot 7\,H_2O$$
$$2 \qquad\qquad 18$$

(c) Formulae for calculation :

$$C\,\% = \frac{\text{Weight of } CO_2 \text{ formed} \times 12 \times 100}{\text{Weight of coal sample} \times 44}$$

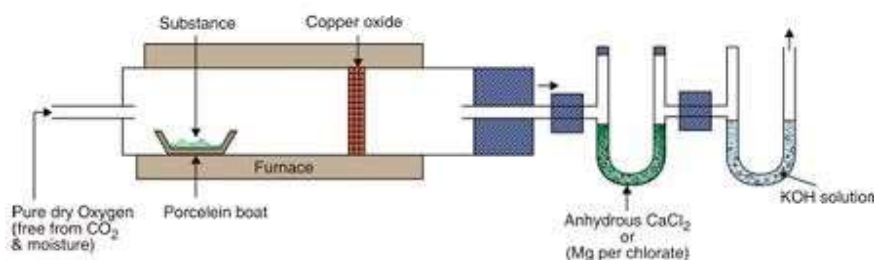$$H\,\% = \frac{\text{Weight of } H_2O \text{ formed} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

Fig. 4 : Combustion apparatus

Sulphur

Principle : Sulphur present in coal converts to first SO_3 which is soluble in water forming H_2SO_4. H_2SO_4 is then converted to $BaSO_4$ precipitate when treated with $BaCl_2$.

Sulphur is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of calorific value. The washings are treated with barium chloride solution, barium sulphate is precipitated. The precipitate is filtered, washed and dried.

$$\% \, S = \frac{wt. \, of \, BaSO4 \, formed \times 32 \times 100}{wt. \, of \, coal \, sample \, taken \times 233}$$

Nitrogen

Principle :

N in coal gets converted to ammonium sulphate, by action of hot concentrated H_2SO_4 and then on treatment with alkali solution, equivalent amount of NH_3 is liberated.

Method :

A known weight of powdered and air dried coal is heated with concentrated H_2SO_4 alongwith K_2SO_4 catalyst in a long necked Kjeldahl flask.

After the contents become clear, it is treated with alkali solution in a round bottom flask. The ammonia (basic gas) liberated is passed in known volume of standard acid solution.
The unused acid is determined by back titration with NaOH solution.

$$\underset{\text{(in coal)}}{N} \xrightarrow[K_2SO_4]{H_2SO_4, \, heat} (NH4)_2SO_4 \xrightarrow{alkali, \, heat} NH_3 \xrightarrow{Basic} \boxed{} \, acid \, solution$$

i) Mass of coal = m gm.
ii) V_2 ml = (Blank titration reading).
iii) V_1 ml = (Back titration reading, after passing NH_3)
iv) Volume of the acid consumed by NH_3 = ($V_2 - V_1$) ml.

Formula :

$$N \, \% \; = \; \frac{\text{Volume of acid consumed} \times \text{normality of NaOH} \times 1.4}{\text{Weigth of coal sample}}$$

OR

$$N \, \% \; = \; \frac{\text{Volume of acid} \times \text{change in normality of acid} \times 1.4}{\text{Weight of coal sample}}$$
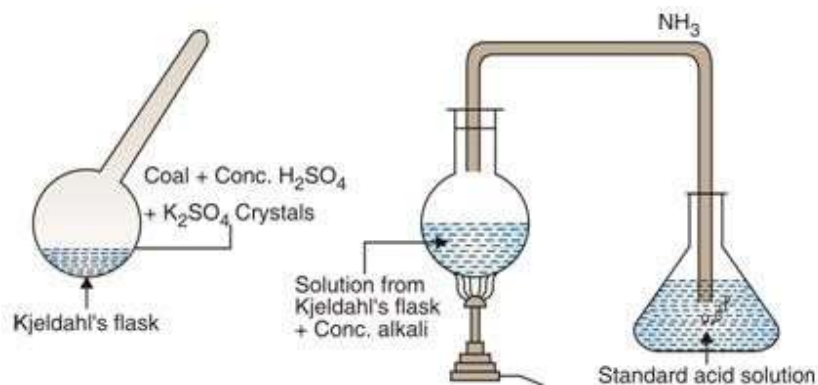
Fig. 5 : Estimation of nitrogen in coal

Ex. 6) 0.25 gm of a coal sample on burning in a combustion chamber in the current of pure oxygen was found to increase weight of U-tube with anhydrous CaCl2 by 0.075 gm and of KOH U-tube by 0.52gm. Find C and H percentages in coal.
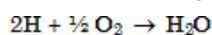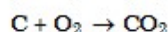
Soln. :

Given : Weight of coal = w = 0.25 gm

Increase in weight of U - tube containing

$CaCl_2$ = Weight of moisture formed = 0.075 gm

Increase in weight of KOH U-tube = Weight of CO_2 formed = 0.52 gm

$$2H + \tfrac{1}{2}O_2 \rightarrow H_2O$$
$$(2 \times 1) \quad (18)$$
$$C + O_2 \rightarrow CO_2$$
$$(12) \quad (44)$$

$$\% \text{ hydrogen} = \frac{\text{Weight of moisture formed}}{\text{Weight of coat}} \times \frac{2}{18} \times 100$$

$$= \frac{2}{18} \times \frac{0.075}{0.25} \times 100 = 0.33 \%$$

$$\% \text{ carbon} = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100$$

$$= \frac{12}{44} \times \frac{0.52}{0.25} \times 100 = 56.73 \% \qquad \text{...Ans.}$$

Ex. 7) One gram of coal sample was burnt in oxygen. Carbon Dioxide was absorbed in KOH and water vapour in CaCl2. The increase in weight of KOH and CaCl2 was 3.157 and 0.504 gm respectively. Determine % C and % H in the sample.

(C % = 86.1, H% = 5.6)

Soln. :

Given : Weight of CO_2 absorbed in KOH = 3.157 gm

Weight of H_2O absorbed in $CaCl_2$ = 0.504 gm

Weight of coal burnt = 1.0 gm

$$C \% = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100 = \frac{12}{44} \times \frac{3.157}{1} \times 100 = 86.1 \% \qquad \text{...Ans.}$$

$$H \% = \frac{2}{18} \times \frac{\text{Weight of } H_2O}{\text{Weight of coal}} \times 100 = \frac{2}{18} \times \frac{0.504}{1} \times 100 = 5.6 \% \qquad \text{...Ans.}$$

Ex. 8) Find the % of C and H in coal sample from the following data- 0.20 gm of coal on burning in a combustion tube in presence of pure oxygen was found to increase in the weight of CaCl2 tube by 0.08 gm and KOH tube by gm.

Soln. :

Given : W = Weight of coal = 0.2 gm

Weight of CO_2 = increase in weight of KOH = 0.12 gm

Weight of H_2O formed = increase in weight of $CaCl_2$ = 0.08 gm

$$C \% \text{ in coal} = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100 = \frac{12}{44} \times \frac{0.12}{0.2} \times 100 = 16.36 \% \quad \text{...Ans.}$$

$$H \% \text{ in coal} = \frac{2}{18} \times \frac{\text{Weight of } H_2O}{\text{Weight of coal}} \times 100 = \frac{2}{18} \times \frac{0.08}{0.2} \times 100 = 4.44 \% \quad \text{...Ans.}$$

Ex. 9) 2.4 gm of coal sample was weighed in silica crucible. After heating for one hour at 110°C, the residue weighed as 2.25 gm. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at 950°C. The residue weighed as 1.42 gm. The crucible was further heated without lid until a constant weight was obtained. The last residue was found to be 0.22 gm. Calculate the % results of the above analysis.

Soln. :

Given : W = weight of coal = 2.4 gm

$$\text{Weight of moisture} = W - \text{weight of residue at } 110°C = 2.4 - 2.25 = 0.15 \text{ gm.}$$

$$\text{Moisture} \% = \frac{\text{Weight of moisture}}{\text{Weight of coal}} \times 100 = \frac{0.15}{2.4} \times 100 = 6.25 \%$$

$$\text{Weight Volatile matter} = \text{Weight of coal after } 110°C - \text{Weight of residue at } 950°C$$

$$= 2.25 - 1.42 = 0.83 \text{ gm}$$

$$VM \% = \frac{\text{Weight of VM}}{\text{Weight of coal}} \times 100 = \frac{0.83}{2.4} \times 100 = 34.58 \%$$

$$\text{Weight of ash residue} = 0.22 \text{ gm}$$

$$Ash \% = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 = \frac{0.22}{2.4} \times 100 = 9.17 \%$$

$$\text{Fixed carbon} \% = 100 - (\text{Moisture} \% + VM \% + \text{ash} \%)$$

$$= 100 - (6.25 + 34.58 + 9.17) = 50 \%$$

The given coal contains,

Moisture % = 6.25   Ash % = 9.17

VM % = 34.58   Fixed carbon % = 50

Ex. 10) 0.5 gm of a coal sample on burning in a combustion chamber in the current of pure oxygen was found to increase weight of U tube with anhydrous CaCl2 by 0.145 gm and of KOH U tube by 0.90 gm. Find 'C' and 'H' percentage in coal.

Soln. : Weight of coal burnt = 0.5 gm

Weight of CO_2 formed = Increase in weight of U-tube containing KOH = 0.9 gm

Weight of H_2O formed = Increase in weight of U-tube containing anhydrous $CaCl_2$ = 0.145 gm

$$C \% \text{ in coal} = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100 = \frac{12}{44} \times \frac{0.9}{0.5} \times 100 = 49.99 \%$$

$$H \% \text{ in coal} = \frac{2}{18} \times \frac{\text{Weight of } H_2O}{\text{Weight of coal}} \times 100 = \frac{2}{18} \times \frac{0.145}{0.5} \times 100 = 3.22 \%$$

Petroleum or Crude Oil

An important primary liquid fuel.

•   It is a dark greenish-brown viscous oil found deep in the earth's crust.

- It is formed millions of years ago by anaerobic decay of of debris of plants and animals (which are buried due to volcanoes) under the influence of high temp. and pressure.
- Organic debris convert into alkanes, which on isomerisation, cycisation form crude oil.
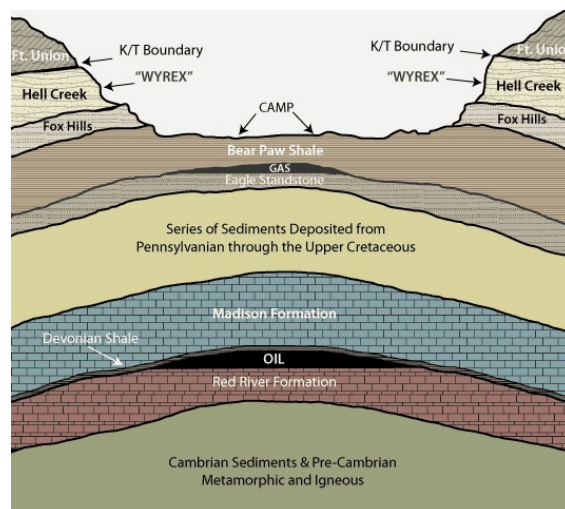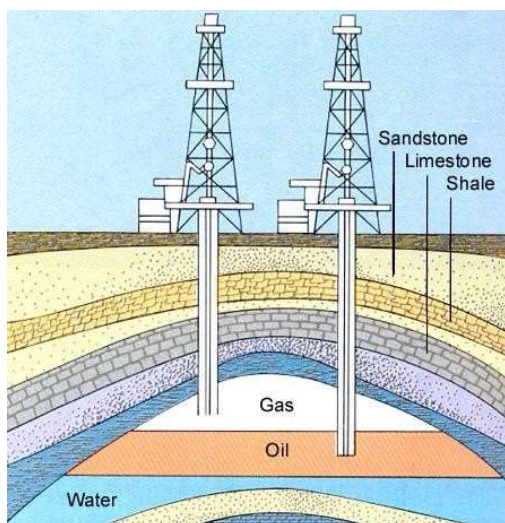
Composition of crude oil

Elemental composition

Element	Percent range
Carbon	80 to 87%
Hydrogen	11 to 15%
Nitrogen	0.4 to 0.9%
Oxygen	0.1 to 0.9%
Sulfur	0.1 to 3.0%
Metals	< 0.1%

Molecular composition

1. Open chain Alkanes
2. Cycloalkanes
3. Aromatics
4. Asphaltenes
5. Resins

Refining of petroleum

Ans. : Refining or fractionation is the process of separation of various fractions from crude oil, on the basis of fractional distillation. The crude oil contains a large number of hydrocarbons but by the process of refining, they are divided into few groups of molecular weights or boiling point ranges.

The refining consists of-

(i) Removal of water : First the emulsified water along with salts dissolved, is removed by passing the crude oil between highly charged electrodes. The colloidal water droplets unite on positive electrode to form large drops which separate from oil.

(ii) Removal of sulphur : Then the crude oil is treated with hot CuO to remove sulphur from the sulphur compounds in crude oil.

(ii) Fractionation : The principle of fractional distillation is that the vapours of higher boiling point compounds first get condensed into liquid, during the stepwise cooling. Various useful fractions like petrol, diesel, kerocene etc. are obtained by fractionation.
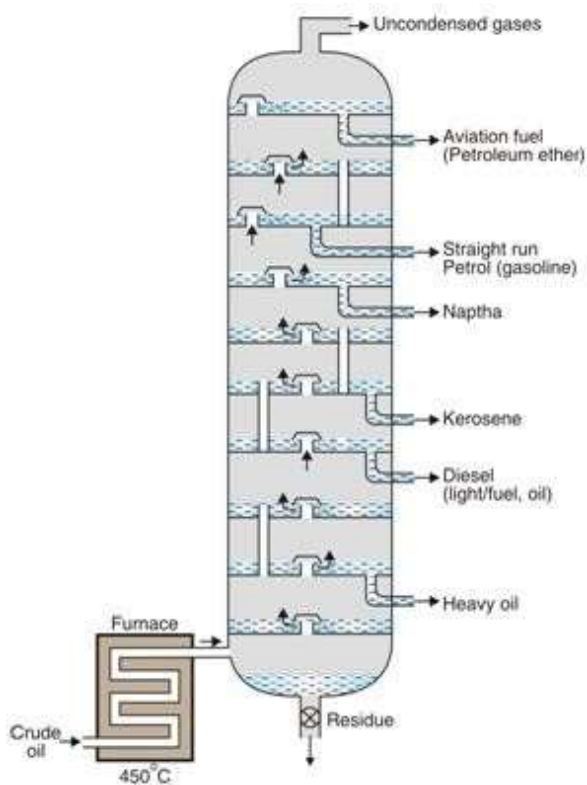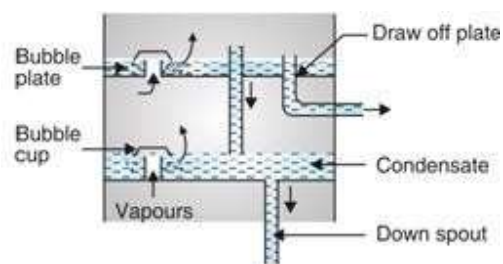
Fig. 6 (a) Fractionating tower

(b) Portion of fractionating tower

Working

(a) The crude oil is heated at about 400°C in a furnace or pipe still to convert it into vapours. The vapours enter into the fractionating column at the bottom.

(b) The vapours travel upwards through the bubble cups and gradually get cooled. The vapours of organic compounds with higher b.p. get condensed in bubble cups and the liquid deposits on the trays.

(c) The uncondensed vapours rise up and get condensed turn by turn on upper bubble trays. There is vigorous bubbling action on each tray. In case, large part of the vapours get condensed on a tray, then the extra liquid flows down to higher temperature lower trays and gets evaporated.

(d) From some bubble trays, the fractions like petrol, diesel, kerocene, naphtha, heavy oil etc. are taken out. Finally a small part of vapours comes out as uncondensed gases from the top where temperature is about 40°C.

(e) Heavy oil fraction can be further fractionated to get lubricating oils, vaseline, wax. The petrol obtained from refinery is called as straight run petrol but is not a good quality petrol.

(f) It is possible to convert any higher boiling fraction into petrol or LPG by the process known as cracking.

Fractions of Petroleum refining

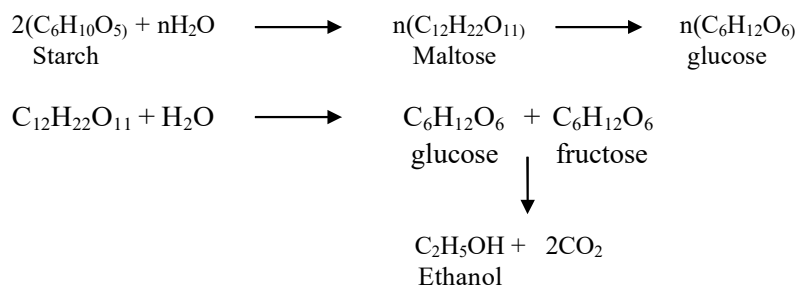| Sr. No	Name of fraction	Boiling range	Composition of hydrocarbon	Uses
1.	Uncondensed gases	Below 40°C	C_1 to C_4	Domestic and industrial fuel under 'LPG' name.
2.	Aviation fuel or petroleum ether	40° – 70°C	C_5 to C_7	Fuel for aeroplane, Helicopters, as solvent
3.	Petrol or gasoline	60° C – 120°C	C_5 to C_8	Fuel for petrol engines, dry cleaning, as solvent.
4.	Naphtha or solvent spirit	120° C – 180°C	C_7 to C_{10}	As solvent and for dry cleaning, for chemicals.
5.	Kerocene	180° C – 250°C	C_{10} to C_{16}	For illumination, domestic fuel, for oil gas and fuel of jet engines.
6.	Diesel	250° C – 320° C	C_{15} to C_{18}	Diesel engine fuel.
7.	Heavy oil	320° C – 400° C	C_{17} to C_{30}	For making petrol by cracking.

Cracking: It is the chemical process of breaking down higher hydrocarbon molecules to smaller molecules by either thermal process or by catalytic process.
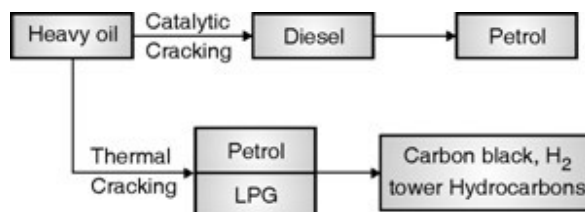
Power Alcohol
Definition : When ethyl alcohol is used as fuel in internal combustion engine, it is called as power alcohol.

Preparation:

$$2(C_6H_{10}O_5) + nH_2O \longrightarrow n(C_{12}H_{22}O_{11}) \longrightarrow n(C_6H_{12}O_6)$$
$$\text{Starch} \qquad\qquad \text{Maltose} \qquad\qquad \text{glucose}$$

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{glucose} \quad \text{fructose}$$
$$\downarrow$$
$$C_2H_5OH + 2CO_2$$
$$\text{Ethanol}$$

Advantages of Power Alcohol:

(i) Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about 65. Therefore addition of ethyl alcohol to petrol, increases its octane number.
(ii) Alcohol has property of absorbing any traces of water if present in petrol.
(iii) If a specially designed engine with higher compression ratio is used, then the disadvantage of lower C.V. of ethyl alcohol can be overcome.
(iv) Ethyl alcohol contains 'O' atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are reduced largely.
(v) Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign currency considerably.
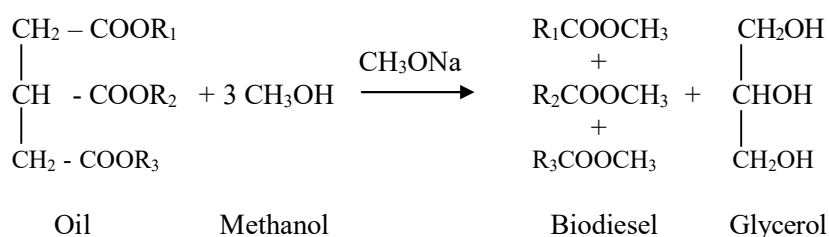(vi) Power alcohol is cheaper than petrol.

Disadvantages of Power Alcohol:

(i) Ethyl alcohol has C.V. 7000 cal/gm much lower than C.V. of petrol 11500 cal/gm. Use of power alcohol reduces power output upto 35%.
(ii) Ethyl alcohol has high surface tension and its atomisation, especially at lower temperatures, is difficult causing starting trouble.
(iii) Ethyl alcohol may undergo oxidation to form acetic acid, which corrodes engine parts.
(iv) Ethyl alcohol obtained by fermentation process directly cannot be mixed with petrol but it has to be dehydrated first.
(v) As ethyl alcohol contains 'O' atoms, the amount of air required for complete combustion of power alcohol is lesser and therefore carburettor and engine needs to be adjusted or modified, when only ethyl alcohol is used as fuel.

Biodiesel

Definition : Chemically biodiesel is the mixture of methyl esters of long chain carboxylic acids. Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using catalyst sodium metal or sodium methoxide. (Transesterification is the process of converting one ester to another ester).

Reaction for Biodiesel Formation :

During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps. The water soluble part can be easily separated from biodiesel by washing the mixture with water. The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.

$$
\begin{array}{l}
CH_2 - COOR_1 \\
| \\
CH \;\; - COOR_2 \;\; + 3\ CH_3OH \xrightarrow{\;CH_3ONa\;} \\
| \\
CH_2 - COOR_3
\end{array}
\quad
\begin{array}{l}
R_1COOCH_3 \quad\quad CH_2OH \\
\quad\quad + \quad\quad\quad\quad | \\
R_2COOCH_3 \;\; + \;\; CHOH \\
\quad\quad + \quad\quad\quad\quad | \\
R_3COOCH_3 \quad\quad CH_2OH
\end{array}
$$

Oil   Methanol   Biodiesel   Glycerol

Compounds present in biodiesel are like,

methyl palmitate	$H_3C - (CH_2)_{14} - COOCH_3$
methyl stearate	$H_3C - (CH_2)_{16} - COOCH_3$
methyl oleate	$H_3C - (CH_2)_7 - CH = CH - (CH_2)_7 - COOCH_3$
methyl linoleate	$H_3C - (CH_2)_5 - (CH = CH)_2 - (CH_2)_7 - COOCH_3$

Advantages of Biodiesel :
(i) Biodiesel is cheaper, as it is manufactured from cheap, nonedible or waste oil or animal fats.
(ii) It has high cetane numbers 46 to 54 and high C.V. of about 40 kJ/gm.
(iii) It is regenerative and environment friendly.
(iv) It does not give out particulate and CO pollutants, as 0 atoms in biodiesel help for complete combustion.
(v) It has certain extent of lubricity, due to higher oiliness of the esters.
(vi) Its use provides good market to vegetable oils and reduces our dependence on diesel on foreign countries, saving currency.
(vii) It is clean to use biodiesel in diesel engines.

Limitations of Biodiesel :
(i) Cloud and pour points of biodiesel are higher than diesel and can cause problem in fuel flow line. So it cannot be used in cold regions.
(ii) Biodiesel may have dissolving action rubber hoses, gaskets.
(iii) There is shortage of vegetable oils and the starting material if costly, the biodiesel will be costly.
(i) Biodiesel strongly adheres on metals and can become gummy.

Gaseous Fuels

Natural Gas

Composition : Average composition of a natural gas is; CH_4 C = 80 – 88 % $_2H_6$ = 4 – 6 %
  $C_3 H_8$ C = 3 – 4 % $_4 H_{10}$ = 1 – 4 %
  C_5 and C^+_5 hydrocarbons = 0.5 – 8 %
  Natural gas is also associated with 5 – 10 % of NH_3, CO_2, CO, H_2O, H_2, H_2S, N_2.

CNG:
Compressed natural gas is derived from 'dry' natural gas. The 'dry' natural gas is compressed and cooled to condense C^+_4 hydrocarbons and CO_2, NH_3, H_2O, etc. The remaining gas mainly contains CH_4 and small amounts of C_2 to C_4 hydrocarbons. This gaseous matter is scrubbed with monoethanolamine to separate H_2S from it.

2 HO – CH_2CH_2 – NH_2 + H_2S (HO – $CH_2 CH_2$ – NH_3)$_2$ S
Monoethanolamine (Monoethanolamine is recovered by heating the product). $\longrightarrow$

This H_2S free gas is compressed at high pressures like 1000 atm, in the cylinder. This gas in cylinder at high pressure, is called as compressed natural gas (CNG). A 15 kg CNG cylinder contains about 20 m^3 of gas at 1 atm.
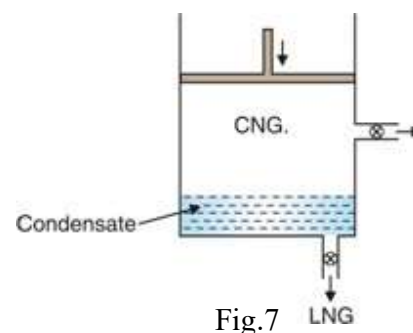

Fig.7

Composition : CH_4 = 88.5 %, C_2 to C_4 hydrocarbons and
    H_2 = 10 %, CO = 1%

Properties :
  (i) It has higher ignition point than petrol and it is safer to use.
  (ii) It mixes better with air than liquid fuels.
  (iii) Its calorific value is about 13000 kcal/m3.
  (iv) It can be used as fuel for petrol and diesel engines after modification in engines. i.e. gas kit fitting.
  (v) It burns completely to give no CO and SO_X emissions.
  (vi) CNG has higher ignition point than LPG, LNG, etc.

Uses :
(i) CNG is used as substitute fuel to petrol and diesel. City buses, rickshaws, cars run on CNG in metropolitan cities like Delhi, Mumbai, etc.
(ii) It can be used as industrial and domestic fuel.
(iii) It is the source of carbon black and hydrogen gas.
(iv) CNG use as fuel for engines, reduces CO, SO_X and particulate pollution.

LPG
Composition : LPG mainly contains propane and butanes along with little pentanes, hexanes.

Properties :

(i)LPG has C.V. about 25000 cal/lit.
(ii)To know the leakage of LPG from cylinder, a small amount of organic sulphur compound is mixed in LPG. The mercaptan or thioether has characteristic smell.
(iii)It burns with blue flame and it is clean to use.

Uses: LPG is used as domestic fuel, industrial fuel. LPG is useful as motor fuel.