

Fuels

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Introduction:

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

Defⁿ: Any source of heat energy, when heated in presence of Oxygen gives large amount of heat.

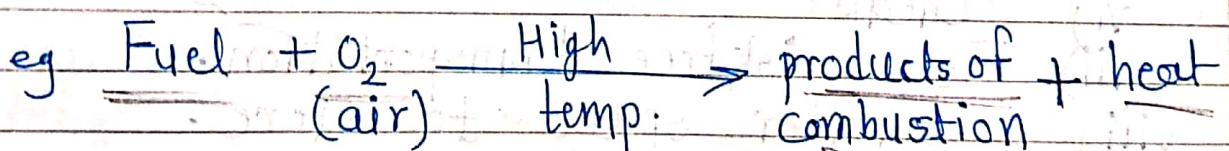
The heat obtained from or by burning of fuels is utilized for industrial & domestic purposes.

Most of the fuels contain mainly carbon element along with hydrogen, oxygen, nitrogen etc. The combustion of these produce ^{mainly} CO_2 & H_2O .

Chemical fuel:

e.g. coal, wood, charcoal, kerosene

The fossil fuels, wood, etc. which produces heat on burning are known as chemical fuels.



Nuclear fuels:

They/It produces energy by Nuclear fission reaction & not by combustion process.

The fuels like coal, crude oil, natural gas) are 'fossil fuels' which are found in earth crust as it is. So fuels are generally classified as,

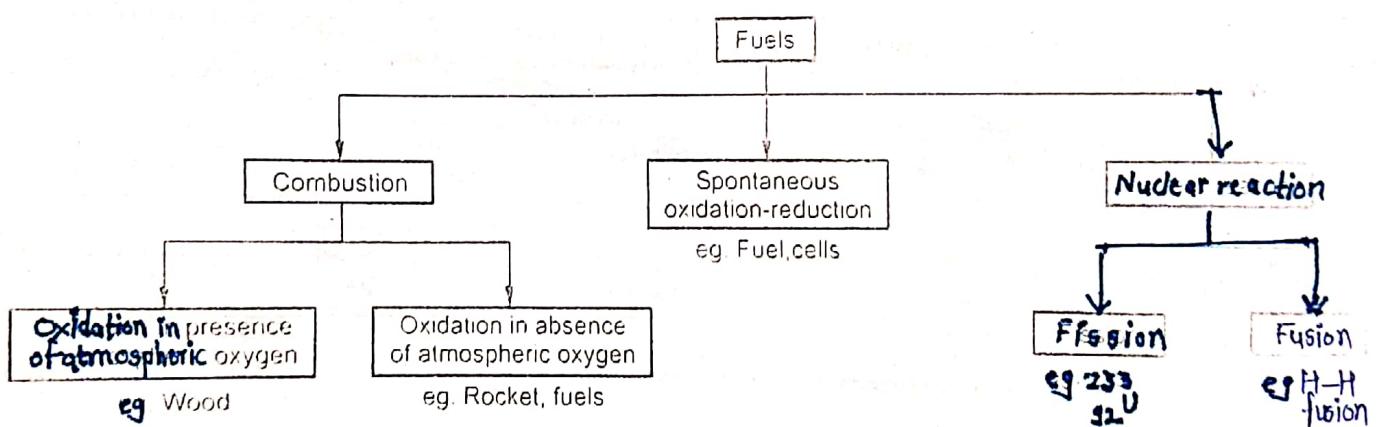
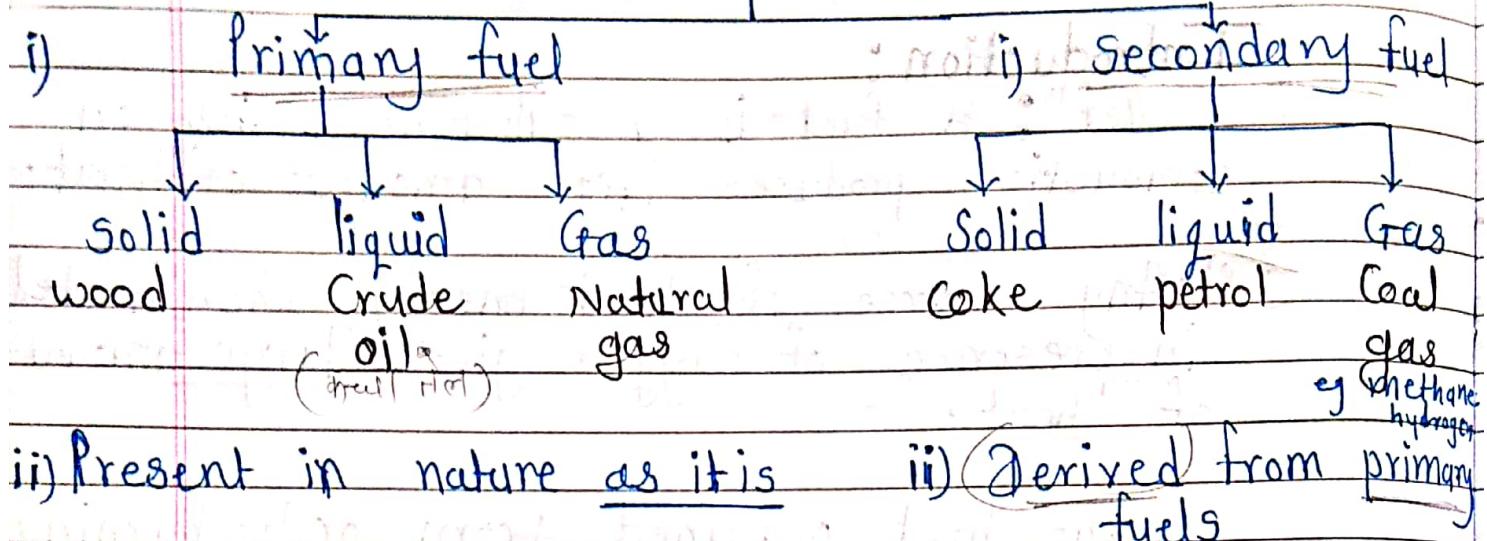


Fig. Classification of fuels based on chemical reaction

Classification of fuels



* Characteristics of an ideal fuel :

The properties of an ideal or good fuel are used in selection of a fuel for various purposes :

- i) High calorific value.
- ii) Moderate ignition point (temp.).
- iii) Velocity of combustion controllable.
- iv) Harmless products of combustion.
- v) No ash (non-combustible matter).
- vi) Cheap.
- vii) Easy, riskfree transportation.
- viii) Smaller space to store.
- ix) Air requirements.
- x) Use in internal combustion engine.
- xi) No moisture.
- xii) No volatile matter.

i) High calorific value:

- i) A good fuel has high calorific value, so that larger amount of heat will be obtained on burning smaller quantity of fuel.

ii) Solid fuels contain some quantity of non-combustible matter & it remains as ash, therefore solid fuels have lower calorific value than liquid & gaseous fuels.

II) Moderate ignition temp/ ignition point -

i) Ignition point is the minimum temp. at which continuous combustion of fuel starts.

ii) Gaseous fuels have very low I.P so it is risky to store & transport.

iii) Solid fuels have very high ignition point so it is difficult to start combustion. But liquid fuels have moderate I.P so. are preferable.

III) Velocity of combustion controllable:

A fuel is good if its combustion rate is controllable. By proper rate of combustion, the requirement of high temp. is attained easily such fuel can be used economically.

IV) Harmless products of combustion:

A good fuel does not liberate any polluting or poisonous gases.

Solid fuels may contain up to 2% sulphur which releases SO_x pollutant.

V) No ash (Non-combustible) matter:

A good fuel does not contain any non-combustible matter. If a fuel contains minerals, it leaves the matter like ash.

VI) Cheap:

A good fuel is cheap & easily available.

vii) Easy, risk free transportation:

A fuel/good fuel is easy to transport, risk free transportation.

Solid fuels are risk free in transportation.

Gaseous fuel can be easily piped but there is danger of explosion in transportation.

Liquid fuels are good in transport.

viii) Smaller space to store:

A good fuel requires smaller space to store.

Gaseous fuels occupy large volume in even small space at high pressure.

Liquid fuels occupy relatively lower volume.

ix) Air requirements:

A good fuel is one which burns completely with supply of sufficient air.

Solid fuels require large excess of air for complete combustion.

Liquid fuels require only a slight excess of air & gaseous fuels require only smallest amount of air for complete combustion.

x) Use in internal combustion engine:

The fuel which can be used in I.C. should be good.

Liquid & gaseous fuels are used in I.C. engine.

xi) No moisture:

If the fuel contains moisture, it decreases calorific value.

Liquid & gaseous fuel do not contain moisture so are good fuels.

xii) Volatile matter:

A good fuel does not contain any volatile matter which causes air pollution. Solid fuels usually contain V.M, if the combustion of a fuel is carried out in presence of insufficient air, then the smoke is rich with V.M.

Calorific value (cv):

Calorific value is the most important property of fuels it gives idea about efficiency of fuel to produce heat on combustion.

defⁿ:

It is defined as the amount of heat obtained on complete combustion of unit mass of solid or liquid or gaseous fuel at S.T.P

$$\text{S.T.P} \rightarrow T \rightarrow 273 \text{ K}$$

$$P \rightarrow 1 \text{ atm}$$

* Types of Calorific values of fuel:

- 1) Gross calorific value (G.C.V)
- 2) Net calorific value (N.C.V)

1) Gross calorific value (G.C.V) or Higher calorific value (H.C.V) →

Usually fuel contains some hydrogen. The hydrogen atoms are bonded to carbon atoms in the fuel. When the fuel burnt, hydrogen forms water vapours. The water vapours if cooled, we get certain amount of heat is known as latent heat of water & is 587 cal/gm of water or 587 kcal/kg of water.

— During the study of calorific value of fuel we get some heat directly by combustion of fuel & in addition to it we get certain amount of heat by cooling the products of combustion to 15°C .

Defⁿ:

The higher calorific value (H.C.V) or Gross calorific value (G.C.V) can be defined as the total amount of heat obtained on complete combustion of unit mass of solid or liquid or gaseous fuel at S.T.P & on cooling the products of combustion to 15°C .

2) Lower calorific value or Net calorific value (L.C.V) or (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 heat for evaporation & less amount of heat is available for heating.

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

Defⁿ:

The lower calorific value (L.C.V) or Net calorific value is defined as the amount of heat obtained practically on complete combustion of unit mass of solid or liquid or gaseous fuel at S.T.P & the products of combustion

are allowed to escape with some heat. The L.C.V & H.C.V are related as,

$$H.C.V = L.C.V - \frac{(g \times h \times \text{Latent heat of water})}{100}$$

where H is the percentage of hydrogen in the fuel.

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

$$1 \text{ cal/gm} = 1 \text{ kcal/kg} = 4.18 \text{ kJ/kg}$$

Latent heat of water is 587 cal/gm or 587 kcal/kg.

* Measurement of calorific value of solid/Liquid fuels (By Bomb calorimeter)

Calorific value of solid/liquid fuels can be determined by using Bomb calorimeter.

Principle of calorimeter —

Total heat liberated by complete combustion of known amount of fuel is absorbed by the known mass of water in calorimeter. From the rise in temp. of water the calorific value of the fuel can be determined.

Fig

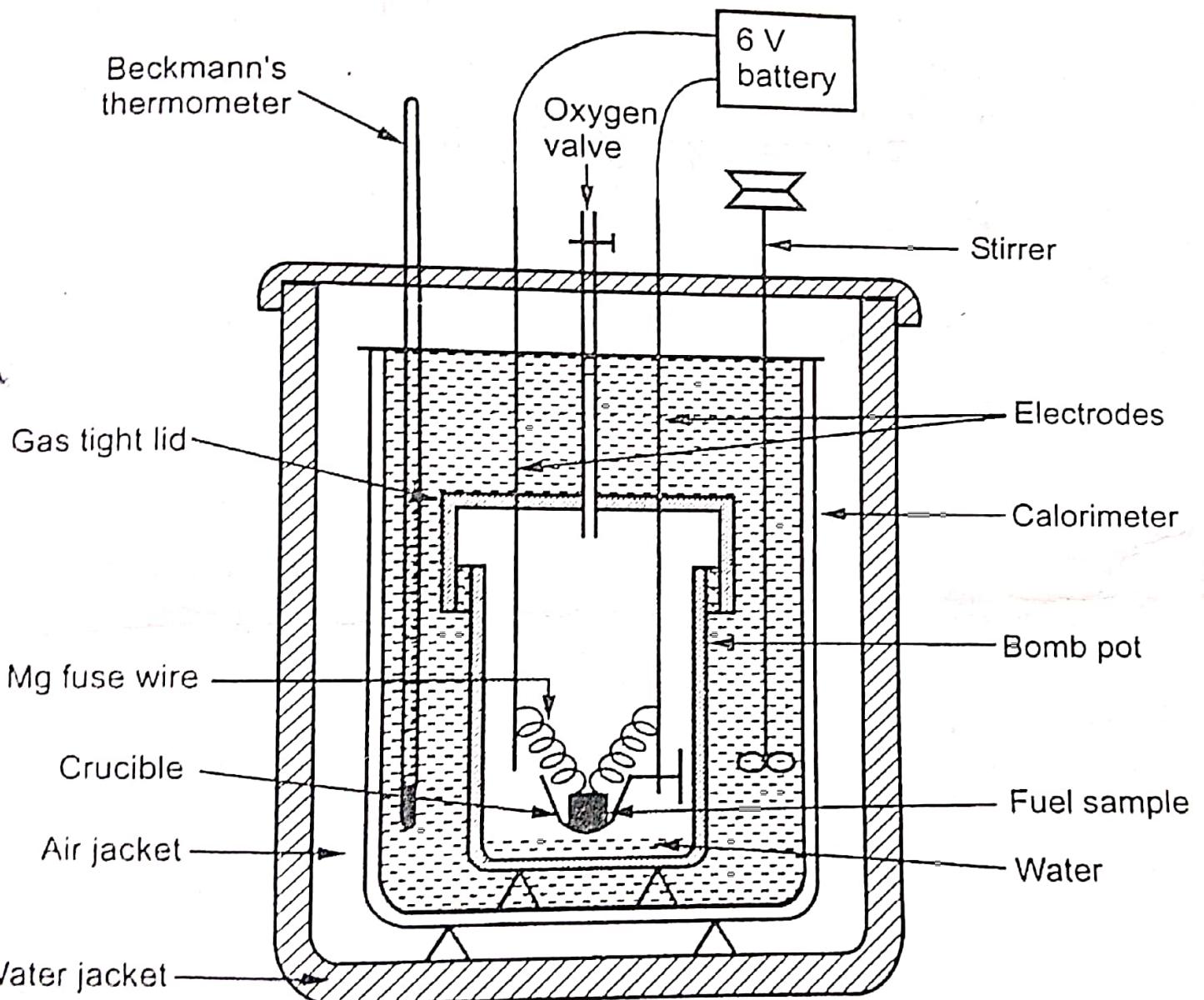


Fig. 1 : Bomb calorimeter

Construction —

- i) Bomb calorimeter consists of strong cylindrical stainless steel bomb in which combustion of the fuel is carried out.
- ii) Stainless steel bomb has gas tight lid.
- iii) The lid consists of two stainless steel electrodes & oxygen inlet valve.
- iv) A small ring is attached to one of the electrode. In this ring nickel or stainless steel crucible can be supported in which fuel of known volume/mass is taken.
- v) The entire bomb pot is placed in a copper calorimeter containing known mass of water.
- vi) Copper calorimeter is surrounded by air jacket & water jacket to prevent heat losses due to radiation.
- vii) The calorimeter also contains electric stirrer & Beekmann's thermometer.

Working —

- i) A known mass of fuel (about 0.5 to 1 gm) is taken in a crucible. This crucible is placed over the ring.
- ii) A fine magnesium wire is attached to the electrodes, touching the fuel sample.
- iii) About 10 ml of distilled water is added at the bottom of the bomb pot.
- iv) The lid of the bomb pot is tightly screwed & the bomb pot is filled with oxygen to 25 atmospheric pressure.
- v) The bomb pot is then placed in the copper calorimeter containing known mass of water.

- vi) The water in the calorimeter is stirred well & initial temp. of water is noted.
- vii) The electrodes are connected to 6 volts battery & current is passed for 5-10 sec. This ignites the magnesium fuse wire which provides ignition to the fuel.
- viii) The fuel sample burns completely & heat is liberated.
- ix) The heat liberated on combustion of the fuel is absorbed by the water in the calorimeter. Stirring of water in the calorimeter is continued for uniform distribution of heat & the maximum temperature attained is noted.

Calculation —

Let, mass of fuel in gm = X gm

Mass of water in calorimeter = W gms.

water equivalent of calorimeter set = w' gms

Higher/Gross calorific value of fuel = L calories/gm.

Rise in temp. of water = $(t_2 - t_1)$

Heat liberated by burning fuel = Heat absorbed by water & calorimeter.

$$\therefore XL = (W + w)(t_2 - t_1)$$

$$\therefore \text{H.C.V. / G.C.V. / L} = \frac{(W + w)(t_2 - t_1)}{X}$$

Express the units of W, w, X in grams.

If $\%H$ is the percentage of hydrogen in the fuel, then the heat taken by water formed during combustion to convert it in to steam is = $0.09 \times 587 \text{ cal/gm}$.

$$\& \text{NCV} = G \cdot C \cdot V - 0.09 \times 587 \text{ cal/gm or kcal/kg}$$

Water equivalent of calorimeter (w) —

Signi- The heat evolved during combustion is also transferred to the apparatus (calorimeter, stirrer, thermometer) which is in contact with water. Along with water, it is essential to know the heat utilized to raise the temp of instrument, measured in terms of water. This is known as Water equivalent of calorimeter. The water equivalent of calorimeter & other apparatus is determined experimentally, by burning a known weight of standard substance (whose calorific value is known) in the bomb calorimeter under identical conditions as used for sample fuel. The fuel used for this purpose are benzoic acid ($HCV = 6325 \text{ kcal/kg}$) & naphthalene ($HCV = 9688 \text{ kcal/kg}$).

The water equivalent is calculated by substituting the value in above $G \cdot C \cdot V$ eqn.

Corrections —

1) fuse wire correction — (t_f)

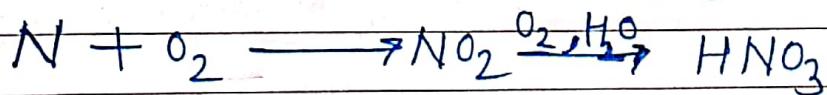
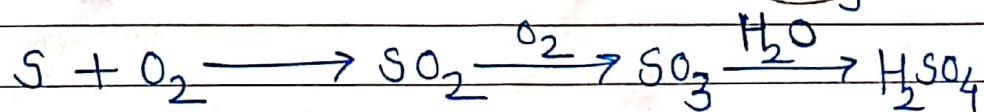
The heat liberated by burning of magnesium fuse wire is associated with

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fuse wire correction. This additional heat given out, other than the burning of fuel, hence need to be subtracted.

2) Acid correction (t_a)

Fuels containing S & N are oxidized, under high pressure & temperature in the bomb pot to form H_2SO_4 & HNO_3 resp. Formation of H_2SO_4 & HNO_3 is exothermic therefore, the measured heat also includes the heat given out during the acid formation. This additional heat has to be subtracted, in order to know the heat given out by the combustion of fuel only.



3) Cooling correction (t_c) —

The heat liberated by combustion of fuel should be transferred completely to water. The temp. reaches to the maximum in the bomb calorimeter & then cooling begins. Therefore cooling correction is added to the observed rise in temp. Cooling correction (t_c) is calculated by the product ($t \times dt$)

where, t = Time taken to cool the water in the calorimeter from \max^m temp. to room temp. in minutes

dt = rate of cooling ($\frac{^\circ C}{\text{min}}$ per min.)

Then, the corrected formula is given as,

$$\text{G.C.V.(L)} = (W + \omega) (t_2 - t_1 + t_c) - (t_q + t_f)$$

cal/gm
or kcal/kg

* Measurement of calorific value of volatile liquid/gaseous fuels (by Boy's gas calorimeter)

fig

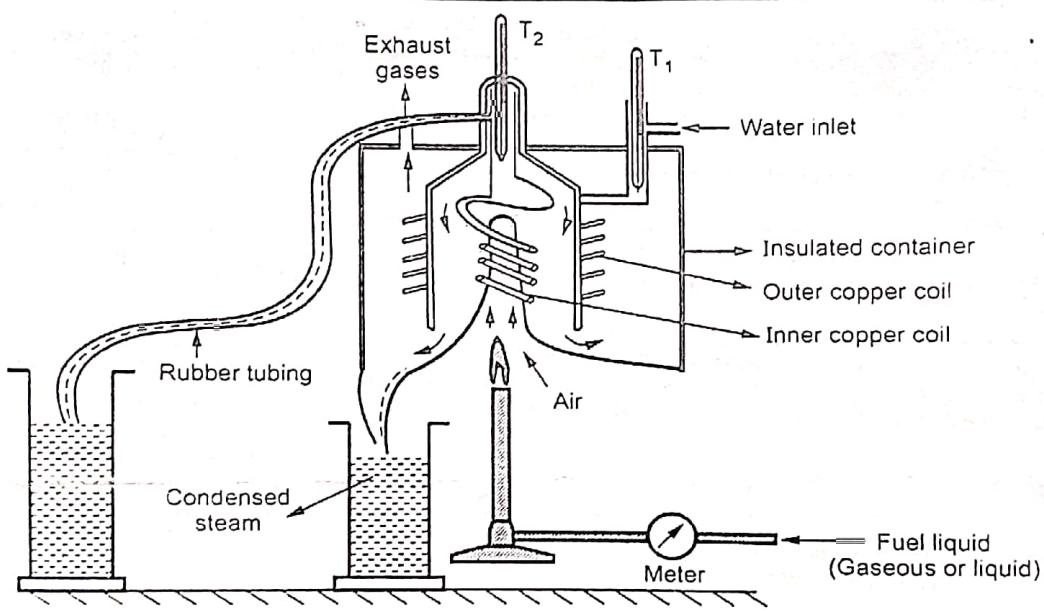


Fig: Boy's gas calorimeter

Construction —

- i) The apparatus consist of suitable gas burner as shown in fig. A known volume of gas at known pressure can be burnt in it.
- ii) Burner is surrounded by combustion chamber.
- iii) Combustion chamber has a copper tubing coiled inside as well as outside, water at constant rate is passed through the coil.
- iv) Water enters from the top of the outer coil. It moves to the bottom

of the combustion chamber & then goes up through the inner coil to the exit from ~~the~~ top.

- v) The thermometer T_1 & T_2 gives the temp. of the incoming & outgoing water resp.
- vi) During circulation of water through the cooling coil, the circulating water takes away ~~the~~ whole heat of the burner.
- vii) Any steam formed during combustion get condensed as water, which is collected.
- viii) The entire assembly is enclosed in an insulated container.

Working —

- i) Start burning the gas at suitable pressure & adjust the rate of water flow such that the temp. of outgoing water remains constant.
- ii) Burn the gas for 5-10 min to have the steady temp. of outgoing water.
- iii) After the steady conditions of outgoing water temp., constant water circulation & gas flow rate reached, simultaneously note the following readings
- a) volume of gas burnt at given temp. & pressure in certain time period.
- b) Quantity of water passed through coil during ~~the~~ this period.
- c) Mass of water condensed from product gas during the period.
- d) The steady rise in temp. of water ($t_2 - t_1$)

Calculations

Let,

- i) Volume of gas burnt at STP = $V \text{ m}^3$
- ii) The quantity of water passing through the coil, during the same time period = $w \text{ kg}$
- iii) The initial temp of incoming water = $t_1^\circ \text{ C}$
- iv) Final temp of outgoing water = $t_2^\circ \text{ C}$

Thus rise in temp = $(t_2 - t_1)^\circ \text{ C}$

- v) Mass of water condensed = $m \text{ kg}$
- vi) L = Higher or gross calorific value of fuel

Heat produced by combustion of fuel = Heat absorbed by circulating water

$$VL = w(t_2 - t_1)$$

$$\therefore GCV / HCV (l) = \frac{w(t_2 - t_1)}{V} \text{ kcal/m}^3$$

Mass of steam condensed per m^3 of gas = $\frac{m}{V} \text{ kg}$

Latent heat of steam per m^3 of gas = $\frac{mx587}{V} \text{ kcal}$

$$\therefore \left[NCV / LCV = GCV - \frac{mx587}{V} \right] \text{ kcal/m}^3$$

* Solid Fuel:-

Coal:-

Coal mainly contains C, H, O along with N, S & non combustible inorganic matter. Coal is highly carbaceous matter (Major constituent is carbon) that has resulted from alteration of vegetable matter (e.g. plants) under certain favourable conditions.

Formation & Classification of coal:-

The formation of coal is not a rapid process but it is very slow process requires millions of years. The plants were converted into coal under the combined effect of high pressure, temp. & bacteria.

The process is called coalification.

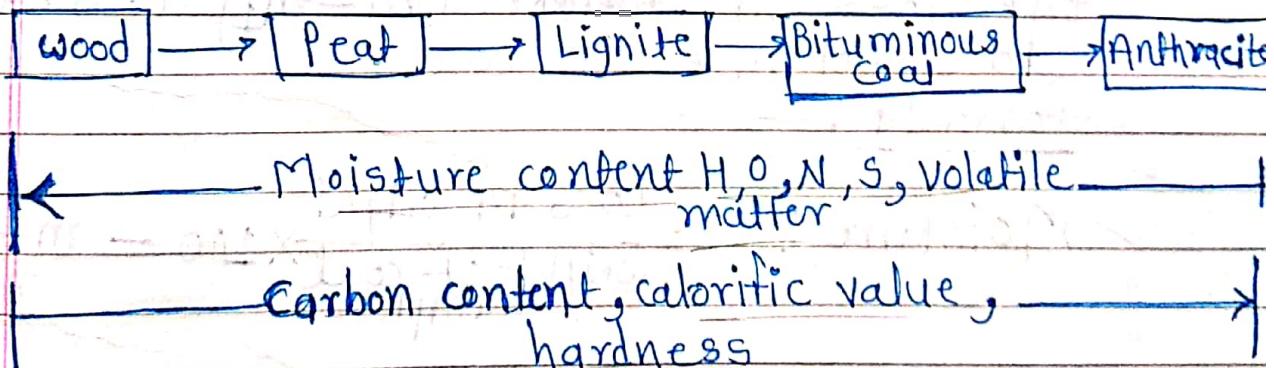


fig: Stages of coalification

Analysis of coal:-

The composition of coal varies with source & age of the coal. In order to decide the quality, rank & price two types of analysis are carried out -

- i) Proximate analysis :-
ii) Ultimate analysis :-

Proximate analysis —

defn Proximate analysis of coal deals with the determination of percentage moisture, volatile matter, ash & fixed carbon.

i) % Moisture :— or Moisture %

Principle :— All moisture in coal escapes on heating coal at 110°C for 1 hours.

Method :—

If know weight of powdered & air dried coal sample is taken in a crucible & it is placed in an oven for 1 hour at 110°C . Then the coal is cooled in a desiccator & weighted. If the initial weight of the coal is m gm & final weight m_1 gms. Then the loss in weight ($m - m_1$) corresponds to moisture in coal.

Formula :—

$$\text{Moisture \%} = \frac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100 = \frac{m - m_1}{m} \times 100$$

ii) Volatile matter (V.M) % —

Principle —

At 925°C , coal molecules undergo thermal degradation to produce volatile matter.

Method —

Moisture free coal left in crucible in first experiment (m_1) is covered with lid, then it is heated at 925°C in a

~~geographic form~~
~~smoke~~
muffle furnace for 7 min. The crucible is taken out & cooled in desiccator. Then it is weighted as (m_2 gm). The loss in weight ($m_1 - m_2$) is due to loss of volatile matter in the m gm of coal sample.

formula —

$$\text{Volatile matter \%} = \frac{\text{weight of volatile matter}}{\text{weight of air dried coal}} \times 100$$

$$V.M \% = \frac{m_1 - m_2}{m} \times 100$$

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

$$V.M \% = \frac{\text{Loss in weight due to moisture} \times 100}{\text{weight of coal sample}}$$

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

iii) Ash %
Principle — Inorganic matter in the coal get oxidised to form metal oxides & silica, which is non combustible & left as ash.

Method —

The residual coal in the above

experiments is heated & burnt in a open crucible crucible at above 750°C for half hour. The coal gets burnt. The ash left in crucible is cooled in desiccator & weighted as m_3 gm
formula —

$$\text{Ash \%} = \frac{\text{weight of ash}}{\text{weight of coal}} \times 100$$

$$= \frac{m_3}{m} \times 100$$

iv) Fixed carbon % —

This is the actual amount of carbon available for combustion, after loss of some carbon in the form of volatile matter. It is found as,

$$\text{FC \%} = 100 - (\text{moisture \%} + \text{V.M \%} + \text{ash \%})$$

~~A~~ Ultimate analysis of coal —

Defn — The analysis of coal in which percentages of C, H, N, S & O elements are found out is known as ultimate analysis.

1) C, H in coal —

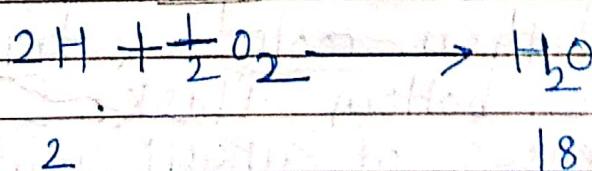
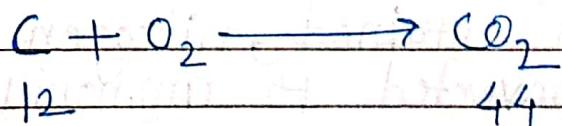
Principle — The carbon in the coal gets converted to CO_2 & hydrogen to H_2O vapours, on burning in the presence

of pure O_2 . (without coal sample)

Method for determination —

- i) A known weight of powdered & air dried coal sample is burnt in the presence of pure oxygen, in a combustion apparatus. C & H are converted to CO_2 & H_2O vapours resp.
- ii) The gaseous products are allowed to pass through first preweighted 'U' tube containing anhydrous $CaCl_2$ or magnesium perchlorate absorbing H_2O vapours & then through the KOH soln in a pre-weighted 'U' tube absorbing CO_2 .
- iii) The increase in weight of 'U' tube containing anhydrous $CaCl_2$ corresponds to weight of water formed & increase in weight of 'U' tube containing KOH soln corresponds to CO_2 formed by combusting the coal sample.

Reactions —



Coal $\xrightarrow[\text{pure } O_2]{\text{burnt in combustion}} \text{products}$
 $(CO_2, H_2O \text{ etc})$

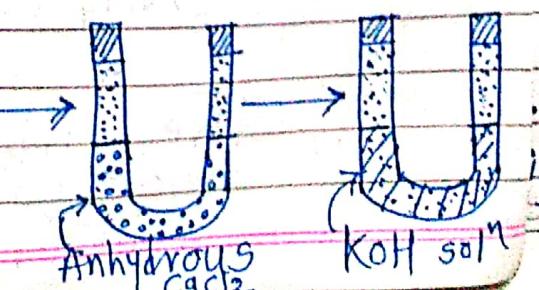


Fig Determination of C & H

formulae for calculation —

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

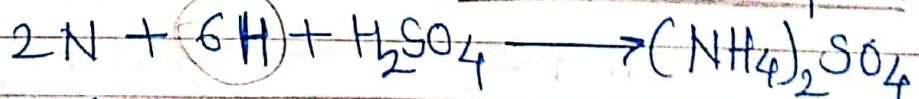
$$H\% = \frac{\text{weight of } H_2O \text{ formed} \times 2 \times 100}{\text{weight of coal sample} \times 18}$$

2) Nitrogen in Coal — (By kjeldahl method)

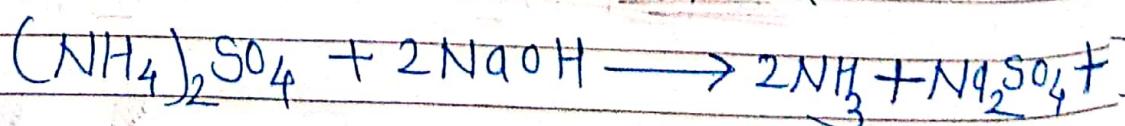
Principle — N in coal gets converted to ammonium sulphate, by action of hot concentrated H_2SO_4 & then treatment with alkali solⁿ, equivalent amount of NH_3 is liberated.

Method —

- Known quantity of coal (1 gm) is heated with concentrated H_2SO_4 in presence of catalyst like Se in a kjeldahl task till a clear solⁿ is obtained when a clear solⁿ is obtained, nitrogen in the coal get converted to ammonium sulphate.



- The solⁿ then cooled & transferred to a round bottom flask & then treated with excess of alkali which causes the liberation of ammonia.



- The liberated ammonia is absorbed in a known volume of acid (H_2SO_4) depending up on the

Back titration - Passing NH_3

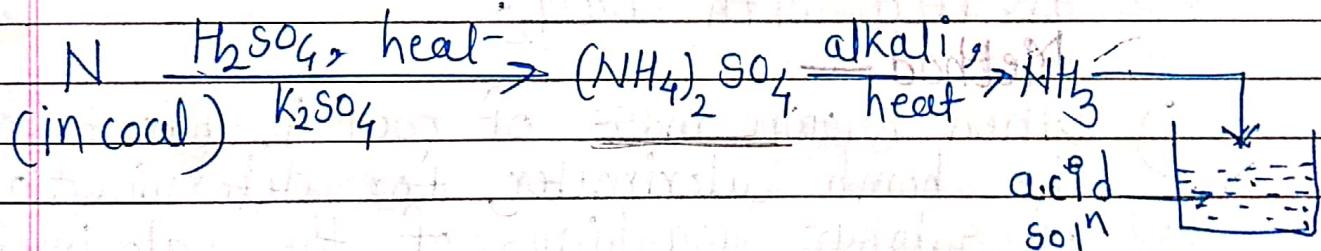
amount of ammonia liberated, equivalent amount of acid will be required to absorb it.



- iv) The unused acid is determined by titrating against standard NaOH is referred as back titration.

v) For determining the amount of acid neutralised by ammonia blank titration is carried out. In this the same quantity of acid (H_2SO_4)^{which} is used to absorb NH_3 (without passing ammonia) is titrated against the same NaOH.

vi) From the amount of the acid neutralised by NH_3 , the amount of NH_3 liberated, the amount of nitrogen present in coal can be calculated.



- 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 = $(V_2 - V_1)m$

formula —

$$N\% = \frac{\text{Volume of acid consumed} \times \text{normality of NaOH} \times 1.4}{\text{weight of coal sample}} \times \frac{\text{Atomic mass of C}}{12}$$

$$N = \frac{1.3 \times 10^6}{10^6} = 1.3$$

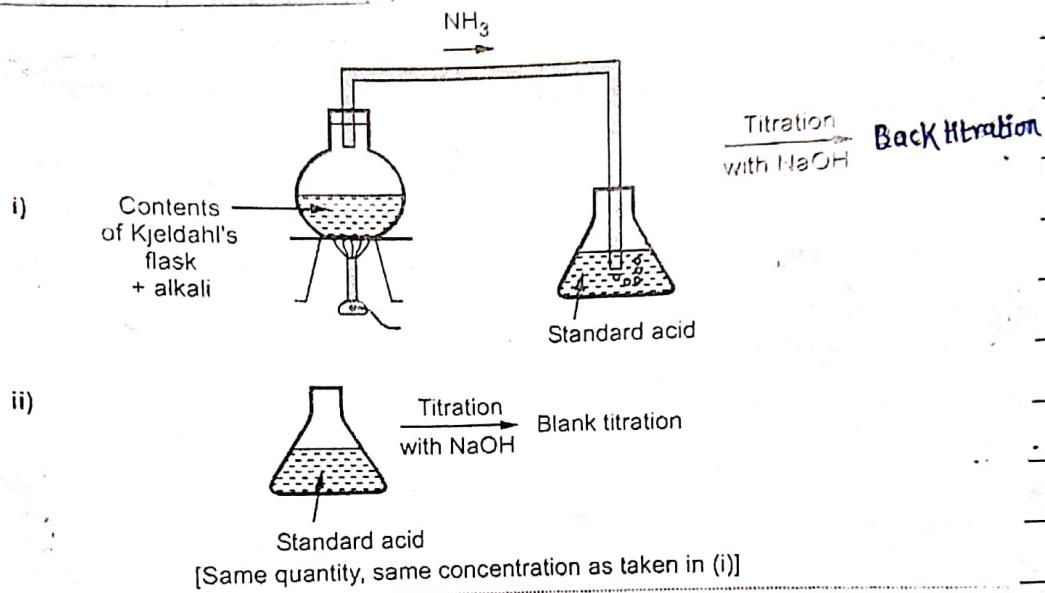


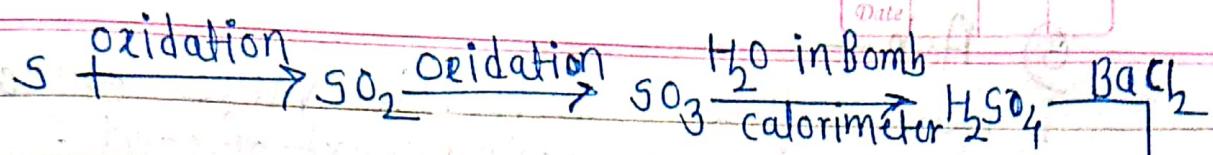
Fig. Estimation of Nitrogen

3) Sulphur in Coal:-

Principle— Sulphur present in coal converts to first SO₂ which is soluble in water forming H₂SO₃. H₂SO₃ is then converted to BaSO₄ precipitate when treated with BaCl₂.

Method—

- i) When known mass of coal is burnt in the bomb calorimeter, for determination of sulphur washings of the calorimeter are collected. During this determination, the sulphur is converted to sulphate.
- ii) The washing from bomb pot is treated with barium sulphate chloride soln, which form barium sulphate (BaSO₄) precipitate. The precipitate is filtered, washed with water, dried & its weight taken. From the weight of BaSO₄, amount of sulphur can be calculated.



formula —

$$S\% = \frac{\text{weight of BaSO}_4 \text{ ppt} \times 32 \times 100}{\text{weight of coal sample} \times 233}$$

atomic mass of S

PPT.

1) Ash % — As carried out under proximate analysis.

5) O % — It is obtained by the difference,

$$O\% = 100 - (C\% + H\% + N\% + \cancel{S\%} + S\%)$$

★ Significance of proximate analysis —

1) Moisture —

- i) It decreases the calorific value of coal largely as it does not burn & takes away heat in the form of latent heat.
- ii) It increases ignition point of coal. Hence coal with lower moisture % is of better quality.

2) Volatile matter —

- i) It decreases calorific value of coal & also decrease flame temp.
- ii) It forms smoke & polluted air. So, the coal with lesser V.M. is better quality of coal.

③ Ash —

- i) Ash reduces calorific value of coal as ash is non burning part of coal.
- ii) Ash disposal is problem.
Hence lesser the % ash better is the quality of coal.

④ Fixed carbon —

Carbon is burning part in coal & higher F.C. higher is calorific value. Hence good quality coal contains high F.C %.

Significance of ultimate analysis —

Carbon :— Greater the % of carbon in coal, better is the quality of coal & calorific val.

Hydrogen :—

Most of the hydrogen in coal is in the form of moisture & volatile matter. only a small percentages of hydrogen is combustible. Hence it decreases C.V of coal. Smaller the H% better is the coal quality.

Nitrogen :—

Nitrogen does not burn during coal combustion & therefore has no calorific value. Hence good quality of coal contains negligible N %.

Sulphur :—

Although sulphur can burn & increase calorific value of coal but it causes SO_2 pollution & causes acid rain, corrosion of metallic equipment. Hence lower the % of 'S' in coal, better is coal quality.

Oxygen -

Most of the oxygen in coal is in the form of moisture. It decreases calorific value of coal hence lower the O% better is coal quality.

Important formulae

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

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

$$\text{Moisture \%} = \frac{\text{weight of moisture}}{\text{weight of coal}} \times 100$$

$$\text{Ash \%} = \frac{\text{weight of ash}}{\text{weight of coal}} \times 100$$

$$\text{Fixed carbon (F.C)\%} = 100 - (\text{moisture\%} + \text{V.M\%} + \text{ash\%})$$

$$\text{Sulphur in coal S\%} = \frac{\text{weight of } BaSO_4 \times 32}{\text{weight of coal} \times 233} \times 100$$

$$\text{Volatile matter (V.M)} = \frac{\text{Weight of V.M}}{\text{weight of coal}} \times 100$$

$$N\% = \frac{\text{Volume of acid consumed} \times \text{normality of acid}}{\text{weight of coal}} \times 1.4$$

~~★~~ Liquid fuels:

Petroleum/ Crude oil :

Petroleum is a dark, greenish-brown viscous oil found deep in the earth's crust (Peta - rock, Oleum - oil). It is very important liquid fuel as it is a source of many domestic & industrial fuels.

It is mainly composed of various hydrocarbons like paraffins, cycloparaffins aromatic hydrocarbons with small amount of compound containing oxygen, nitrogen, & sulphur.

The composition of petroleum in terms of its constituent element is -

$$C = 80-87\%$$

$$H = 11-15\% \quad N, O = 0.1-3\%$$

$$S = 0.1-3\%$$

Mining of petroleum is done by drilling holes in the earth's crust.

~~Refining of petroleum~~

Crude oil is not directly used as a fuel or for manufacturing chemicals, as it is a complex mixture mixture of several hydrocarbons in solid, liquid & gaseous form. It also contain small amount of oxygen, nitrogen, sulphur, salt & water.

Therefore, the crude oil is first refined.

Defn: Refining is the process in which

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the petroleum is separated into its components by fractional distillation along with the separation of impurities. The process is carried out in an oil refinery in 3 steps.

Step I — Separation of water —

The crude oil obtained from well is in the form of stable emulsion of oil & salt water. De-emulsification is done to separate oil from water. It consists of passing the emulsion through highly charged electrodes, to separate out from the oil.

Step II — Removal of harmful sulphur comp.

Harmful sulphur comp. are removed by treating oil with copper oxide. It results in the formation of copper sulphide precipitate which is removed by filtration.

Step III — Fractional Distillation —

Principle :— The vapours of higher boiling point fractions condense first during the stepwise cooling.

process —

- i) The crude oil is heated to about ~~400°C~~ in a furnace then the volatile constituents are vaporized & leaving the asphalt or ~~rock~~ coke as residue.
- ii) The hot vapours are then passed through a fractionating column which is tall, cylindrical tower in which a

- number of horizontal stainless steel trays are fixed at short distance.
- iii) Each tray is provided with bubble cup which is covered with a loose cap.
 - ix) As vapours moves up through bubble cups, & gradually get cooled.
 - v) Higher boiling fractions will condense first while lower boiling fractions will condense later.
 - v) The heavier components with higher boiling points condense & the excess condense components flows down to the next lower tray through 'down spout' pipes & get evaporated.
 - vi) Various fractions like heavy oil, diesel, kerosene, naphtha, petrol etc are taken out from trays. Uncondensed gases are collected from top.
 - vii) Heavy oils are further subjected to fractional distillation to get useful fractions like vaseline, greases, paraffin wax etc.

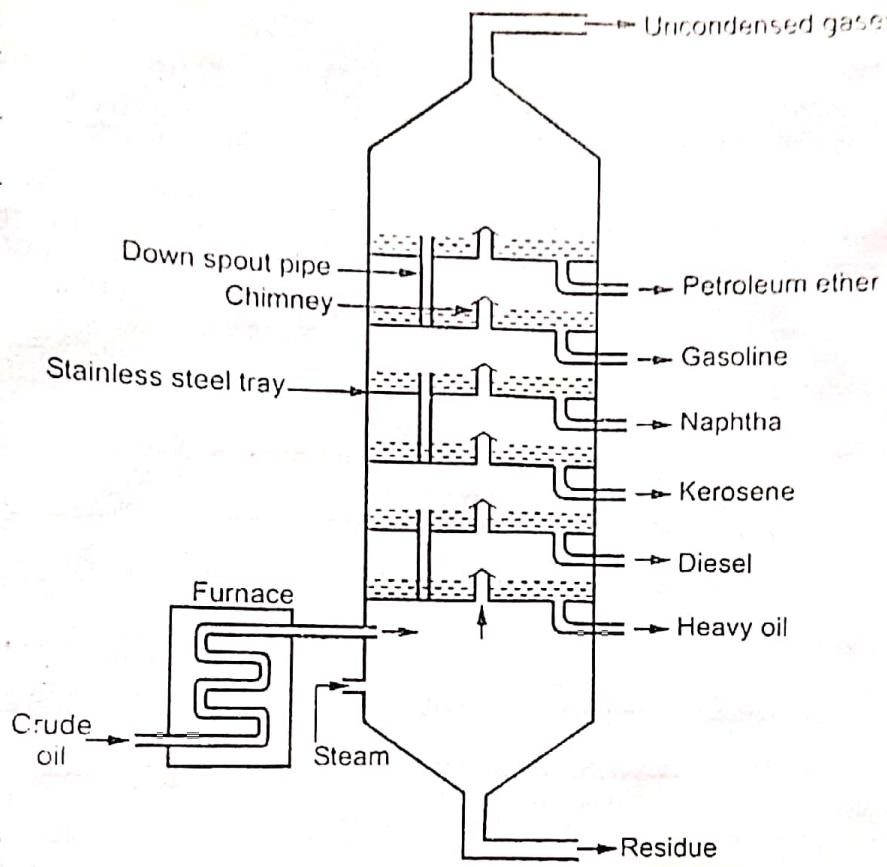


Various products obtained during fractional distillation are as:

sr no.	Name of fraction	Boiling range	Approximate composition in terms of hydrocarbon
1)	Uncondensed gases	Below 30°C	$\text{C}_1 \text{ to } \text{C}_4$
2)	Petroleum ether	$30\text{--}70^{\circ}\text{C}$	$\text{C}_5 \text{--} \text{C}_7$
3)	Gasoline / Petrol	$40\text{--}120^{\circ}\text{C}$	$\text{C}_5 \text{--} \text{C}_9$
4)	Naphtha / solvent spirit	$120\text{--}180^{\circ}\text{C}$	$\text{C}_9 \text{--} \text{C}_{10}$
5)	Kerosene oil	$180\text{--}250^{\circ}\text{C}$	$\text{C}_{10} \text{--} \text{C}_{16}$
6)	Diesel	$250\text{--}320^{\circ}\text{C}$	$\text{C}_{16} \text{--} \text{C}_{18}$
7)	Heavy oil on re-fractionation gives a) Lubricating oil b) Petroleum jelly (Vaseline) c) Grease d) Paraffin wax	$320\text{--}400^{\circ}\text{C}$	$\text{C}_{17} \text{--} \text{C}_{30}$
8)	Residue a) Asphalt b) Petroleum coke	Above 400°C	Above C_{30}

Various products obtained during fractional distillation are as follows

Uses
Domestic/Industrial fuel under the name LPG
As a solvent
As a motor fuel as solvent, dry cleaning agent.
As a solvent in dry cleaning
For illumination, domestic fuel, jet engine fuel.
Fuel for diesel engines
For making petrol by cracking
As lubricant in cosmetics, in medicine
As lubricant in candles, boot polishes wax paper etc.
Water proofing of roofs, road making, As a fuel in moulding arc light rods.



Fig—Fractional Distillation

* Various products obtained during fractional distillation are as :-

Name of fraction Boiling range

★ Gaseous fuels :-

Gaseous fuels have high calorific value. They burn clean without producing smoke or ash.

They are highly inflammable hence special care is required for their storage.

Compressed Natural Gas (CNG)

Compressed natural gas (CNG) is dry natural gas compressed to a high pressure of about 1000 atmosphere.

Compositions —

It contains 70-90% methane, 10-20% ethane, 2-8% propane & small quantity of other higher hydrocarbons up to C₅.

Properties —

- 1) CNG on combustion, evolves no pollutants like sulphur, nitrogen or carbon particles.
- 2) Ignition temp. of CNG is higher (about 550°C) & requires more air for ignition.
- 3) CNG mixes better with air than liquid fuels.
- 4) CNG requires heavier tanks for storage & hence not suitable for small vehicles.

Applications :-

- 1) CNG is used as automobile fuel.
- 2) It can be used for production of hydrogen & carbon black.
- 3) It can be used as industrial fuel.

* Hydrogen Gas as a future fuel :-

Hydrogen is considered as a future fuel because -

- i) It is non toxic & clean burning
- ii) It has high calorific value as compared to fossil fuels.
- iii) It is the most abundant element on earth

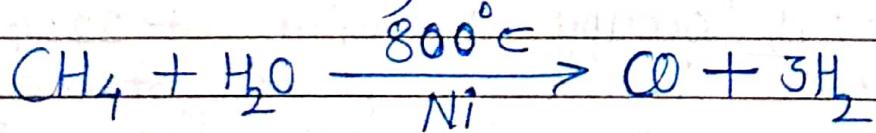
The major problem associated with hydrogen are :

- A) Its production
- B) Its storage & transport

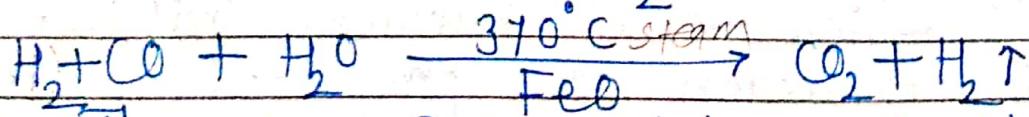
A) Production of Hydrogen —

i) Steam reforming of methane —

Methane from natural gas is mixed with steam & passed over Nickel catalyst at 800°C to produce water gas (mixture of $\text{CO} + \text{H}_2$)



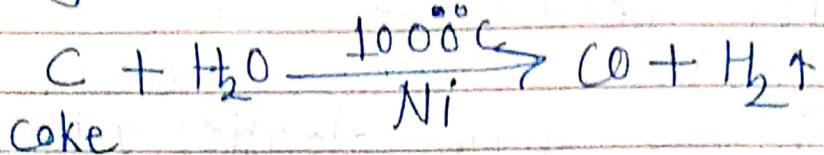
Water gas on further reacⁿ with steam at 370°C in presence of FeO catalyst produces additional H_2 .



The CO_2 & H_2 mixture is then compressed & cooled to get liquid CO_2 & H_2 gas. CO_2 can also be removed by dissolving in water under pressure

2) Steam reforming of coke -

Hydrogen can be prepared by passing steam over red hot coke.



B) Storage & transport of Hydrogen -

I) Physical storage -

- a) In the form of compressed H_2
- b) In the form of liquified H_2
- c) By adsorption on porous carbon materials.

II) Chemical storage -

- a) In the form of metal hydrides.
- b) In the form of sodium alanates.

The difficulties in storage & transport of hydrogen are -

- i) Hydrogen is the lightest gas i.e. 2 gms of H_2 occupy a volume of 22.4 lit at STP. Hence it has to be stored in cylinder in compressed form. The cost of compression is high.
- ii) High pressure H_2 gas in steel cylinder leads to decarburisation because of which steel becomes brittle.
- iii) Hydrogen gas on cooling to -252.6°C can be converted to its liquid form. Liquid H_2 is stored & transported in cryogenic tanks. Also cost of cooling is very high.
- iv) Hydrogen gas is highly inflammable.

Use of H₂ as a fuel :-

- 1) H₂ can be used as a rocket fuel.
- 2) It can be used as a fuel in internal combustion engine & in fuel cell.
- 3) H₂ if used as fuel in IC engine, it will produce no air pollution but not used commonly because of its cost & large H₂ cylinders to carry.
- 4) Because of lower molecular weight it is used as rocket fuel. But can be stored in liquid form in the rocket.
- 5) H₂ is required for manufacture of NH₃ on large scale which is used for making fertilizers & chemicals.
- 6) In industries used for:
 - i) for cutting of metals under water
 - ii) As reducing agent, it is required for reduction reactions, hydrogenation of C=C & other multiple bond.
 - iii) Annealing of metals
- 7) For production of CH₃OH, HCHO etc useful organic chemicals.

Alternative fuels:-

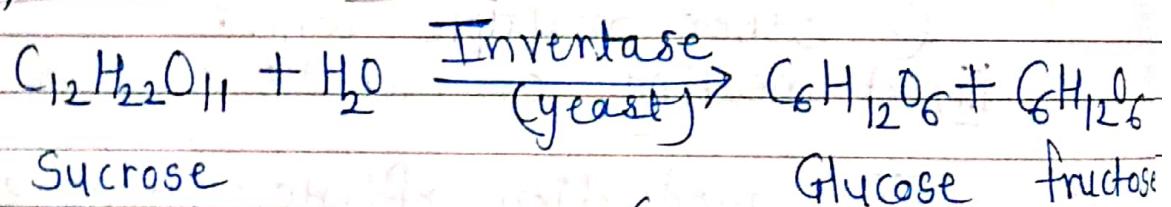
Power alcohol, biodiesel are the emerging alternative fuels.

1) Power alcohol —

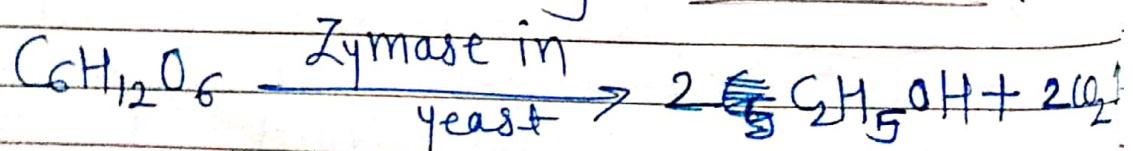
Lower alcohol — When (ethyl alcohol) is blended with petrol (about 20-25 %) & is used as a fuel for internal combustion engines, it is known as power alcohol.

Production of ethyl alcohol -

Introduction of ethyl alcohol—
Ethyl alcohol is obtained from molasses which contains sucrose. Sucrose is converted into glucose & fructose by means of enzyme invertase from yeast at 30°C .



The enzyme Zymase (from yeast) converts glucose & fructose into ethanol & carbon dioxide by fermentation.



Advantages of power alcohol -

- 1) Ethanol has higher octane no. about 90 as compared to petrol with octane no. 60-70. Hence addition of ethanol to petrol will improve octane no. giving better antiknocking properties.

- 2) Alcohol burns clean, hence when blended with petrol, it reduces the emission of harmful gases.
- 3) Alcohol is capable of absorbing moisture hence it removes all traces of moisture in the petrol.
- 4) Deposition of carbon & gummy products on internal parts of engine is reduced when alcohol is used as fuel.
- 5) Alcohol reduces chances of overheating of engine thus extending engine life.
- 6) Ethanol is a renewable source of energy It reduces dependency on foreign countries for petrol.

Disadvantages of power alcohol →

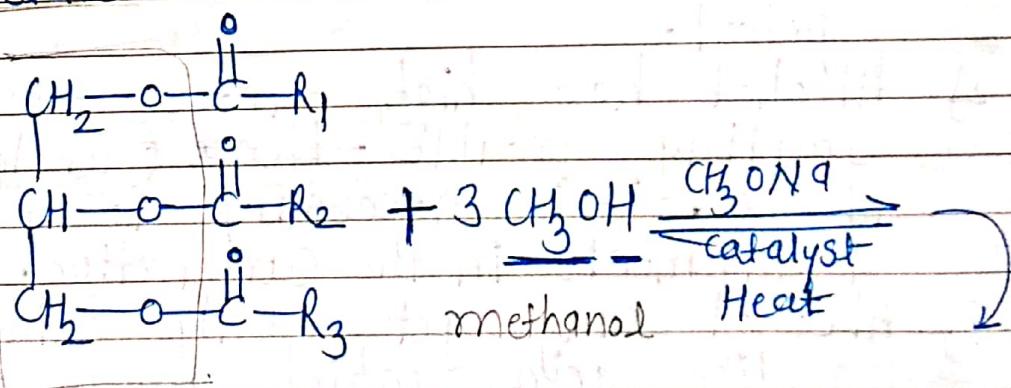
- 1) Ethanol lower the calorific value of petrol.
- 2) Alcohol has high surface tension causes starting trouble → Hence it at low temp. Hence, it is necessary to make special arrangements in the carburettor.
- 3) Alcohol may get easily oxidized to acetic acid which may causes corrosion of engine parts.
- 4) As ethyl alcohol contains 'o' atoms, air required for complete combustion of power alcohol is less than that required for petrol. Hence modification of air inlet is required.

2) Biodiesel :-

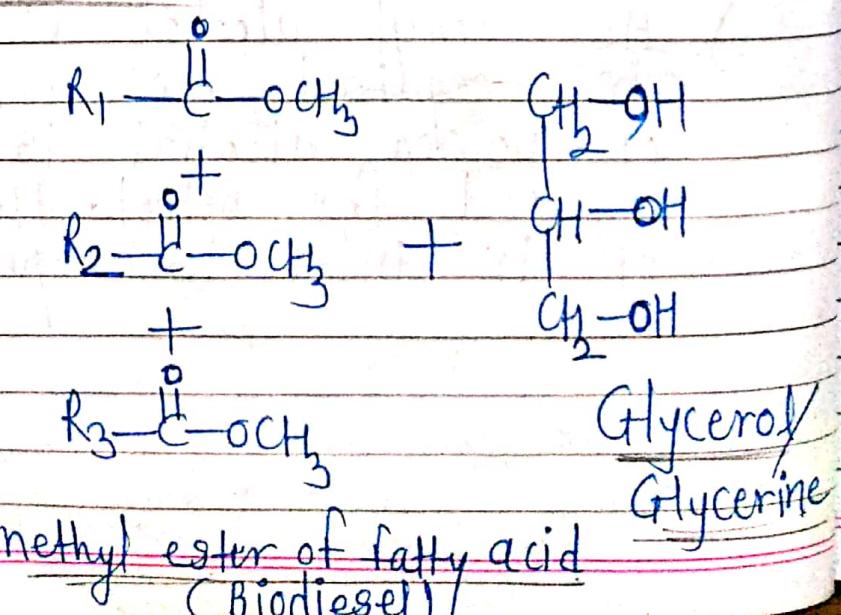
Biodiesel is a biofuel obtained from renewable sources of energy such as vegetable oils or animal oils (fats) by transesterification.

It is mainly used as fuel for diesel engine.

Vegetable/animal oil can be converted in to biodiesel by the process known as trans-esterification. In this process, animal/vegetable oils are heated with excess of methanol in presence of catalyst like sodium methoxide or potassium methoxide & it should be free from moisture.



Animal/vegetable oil



Where R_1 , R_2 & R_3 are the alkyl groups.
They may be same or different,
depending up on the type of oil.

Preparation of Biodiesel -

- 1) Filtered cheap, nonedible vegetable/animal oil is taken in reaction vessel & heated to about 110°C to remove moisture.
- 2) About 2% sodium methoxide & 20% methanol is added to the reaction vessel.
- 3) The mixture is refluxed at $60-70^\circ\text{C}$ for about 1 to 7 hours, depending up on the type of oil used.
- 4) Mixture is cooled & mixed with water to dissolve glycerine formed in the reaction.
- 5) Water insoluble biodiesel phase is then separated from water phase through a separating funnel.
- 6) Biodiesel obtained is further processed by adding suitable antioxidants to avoid oxidation & increase stability.

Advantages :-

- 1) It is non-conventional & renewable source of energy obtained from domestic sources. It reduces dependency on foreign countries for diesel.
- 2) It is non toxic, free from sulphur.
- 3) It burns clean. Oxygen present in fuel helps in burning.
- 4) It has better lubricity.
- 5) It has higher cetane no. than that of oils.

Limitations :

- 1) Biodiesel has higher cloud & pour point than conventional diesel can causes problem in fuel flow lines, so it can not be used in cold regions.
- 2) Biodiesel may have dissolving action with rubber articles.
- 3) Biodiesel strongly adheres on metals & can becomes gummy.

Numericals : Fuels

Bomb & Boy's calorimeter

1) Calculate the HCV (in kJ/kg) of 0.75 gm of fuel containing 80% carbon when burnt in a bomb calorimeter increased the temp. of water from 27.3 to 29.7 °C. The calorimeter contains 250 gms of water & its water equivalent is 150 grams.

$$\rightarrow \text{Sol}^n \quad \begin{aligned} \text{Weight of fuel} &= x = 0.75 \text{ gm} \\ \text{Weight of water} &= W = 250 \text{ gm} \\ \text{Water equivalent} &= \omega = 150 \text{ gm} \\ t_1 &= 27.3^\circ\text{C} \\ t_2 &= 29.7^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \text{HCV (L)} &= \frac{(W + \omega)(t_2 - t_1)}{x} \text{ cal/gm} \\ &= \frac{(250 + 150)(29.7 - 27.3)}{0.75} \\ &= 1280 \text{ cal/gm} = 1280 \text{ kcal/kg} \\ &= 1280 \times 4.187 \text{ kJ/kg} \\ &= 5359.36 \text{ kJ/kg} \end{aligned}$$

2) 10.60 gm of a fuel on complete combustion in a bomb calorimeter increased the temp of water in the calorimeter from 26.3 °C to 28.4 °C. The calorimeter contains 500 g of water & water equivalent of the calorimeter is 1500 g. The corrections are as follows.

$$\text{Cooling correction} = 0.02^\circ\text{C}$$

$$\text{Fuse wire correction} = 15 \text{ cal}$$

$$\text{Acid correction} = 65 \text{ cal}$$

If the fuel contains 5% H, calculate GCV & NCV of the fuel.

Sol' \rightarrow weight of fuel burnt = $x = 10.60 \text{ g}$
 weight of water in calorimeter = $W = 500 \text{ gm}$
 water equivalent of calorimeter = $\omega = 1500 \text{ g}$
 Initial temp. of water = $t_1^\circ\text{C} = 26.3^\circ\text{C}$
 Final temp. of water = $t_2^\circ\text{C} = 28.4^\circ\text{C}$
 Cooling correction = $t_c = 0.02^\circ\text{C}$
 Fuse wire correction = $t_f = 15 \text{ cal}$
 Acid correction = $t_a = 65 \text{ cal}$
 % H in fuel = 5

$$\text{GCV} = \frac{(W + \omega)(t_2 - t_1 + t_c) - (t_a + t_f)}{x}$$

$$= \frac{(500 + 1500)(28.4 - 26.3 + 0.02) - (65 + 15)}{0.60}$$

$$= \frac{2000 \cancel{\times} 2.12 - 80}{0.60}$$

$$= \frac{4240 - 80}{0.60} = 6933.33 \text{ cal/gm}$$

$$\text{NCV} = \text{GCV} - 0.09 \text{ H} \times \text{Latent heat}$$

$$= 6933.33 - 0.09 \times 5 \times 587$$

$$= 6933.33 - 264.15$$

$$= 6669.18 \text{ cal/g}$$

3) 0.85 g of coal sample containing 3.4% H on complete combustion in a bomb calorimeter increased the temp. of the surrounding water from 22.1°C to 25.1°C . The calorimeter contains 1700 gm of water & the water equivalent of the calorimeter is 600 g. The corrections are as follows -

cooling correction = 0.015°C

Fuse wire correction = 10 cal

Acid correction = 75 cal

Calculate GCV & NCV of coal

\Rightarrow weight of fuel burnt = $x = 0.85 \text{ g}$

Weight of water in calorimeter = $W = 1700 \text{ g}$

Water equivalent of calorimeter = $w = 600 \text{ g}$

Initial temp of water = $t_1 = 22.1^{\circ}\text{C}$

Final temp of water = $t_2 = 25.1^{\circ}\text{C}$

cooling correction = $t_c = 0.015^{\circ}\text{C}$

Fuse wire correction = $t_f = 10 \text{ cal}$

Acid correction = $t_a = 75 \text{ cal}$

$$GCV = \frac{(W+w)(t_2 - t_1 + t_c) - (t_a + t_f)}{x}$$

$$= \frac{(1700+600)(25.1 - 22.1 + 0.015) - (75+10)}{0.85}$$

$$GCV = 8058.23 \text{ cal/g}$$

$$NCV = GCV - 0.09H \times \text{Latent heat}$$

$$= 8058.23 - 0.09 \times 3.4 \times 587$$

$$= 7878.61 \text{ cal/g}$$

* Numericals on Boys gas calorimeter.

1) Boys gas calorimeter experiment:

Volume of gas burnt = 0.1 m^3 at STP

Mass of cooling water used = 28 kg

Temp. of inlet water = 24.2°C

Temp. of outlet water = 32.4°C

Mass of steam condensed = 0.05 kg

Calculate GCV & NCV of the gas

Given :

Volume of gas burnt (V) = 0.1 m^3

Mass of cooling water (W) = 28 kg

Temp. of inlet water (t_1) = 24.2°C

Temp. of outlet water (t_2) = 32.4°C

Mass of steam condensed (m) = 0.05 kg

$$\begin{aligned} \text{GCV} &= \frac{W(t_2 - t_1)}{V} \\ &= \frac{28(32.4 - 24.2)}{0.1} = \frac{28 \times 8.2}{0.1} \\ &= 2296 \text{ kcal/m}^3 \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - \frac{m \times 587}{V} \\ &= 2296 - \frac{0.05 \times 587}{0.1} \\ &= 2296 - 293.5 \\ &= 2002.5 \text{ kcal/m}^3 \end{aligned}$$

2) The following observations were noted in Boys gas calorimeter experiment on a gaseous fuel.

Volume of gas burnt at STP = 0.08 m^3

Mass of cooling water = 30 kg

Rise in temp. of water = 8.2°C

Mass of steam condensed = 0.04 kg

Calculate GCV & NCV of the fuel.

Soln

Given:

Volume of gas burnt at STP (V) = 0.08 m^3

Mass of cooling water = (w) = 30 kg

Rise in temp. of water = ($t_2 - t_1$) = 8.2°C

Mass of steam condensed (m) = 0.04 kg

$$GCV = \frac{w(t_2 - t_1)}{V} = \frac{30(8.2)}{0.08}$$

$$= 3075 \cancel{\text{kcal}}/\text{m}^3$$

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

$$= 3075 - \frac{0.04 \times 587}{0.08}$$

$$= 2781.5 \text{ kcal}/\text{m}^3$$

Numericals on proximate & Ultimate analysis

i) A sample of coal on analysis gave the following results: 1 gm of an air dried sample, on heating for an hour at 110°C in a silica crucible, left a dry residue of 0.98 gm. The crucible was covered with a vented lid & the heating was continued for another 7 min. at $950 \pm 20^{\circ}\text{C}$, when a residue of 0.85 gm was obtained. The crucible was then heated strongly in air until a constant weight was realized. The final residue weighed 0.15 gm. Calculate the proximate analysis result on i) air-dry basis

ii) oven-dry basis

Solⁿ

$$\text{Weight of coal} = 1.00 \text{ gm}$$

$$\text{Weight of moisture} = 1 - 0.98 = 0.02 \text{ gm}$$

$$\text{Weight of Volatile matter} = 0.98 - 0.85 = 0.13 \text{ gm}$$

$$\text{Weight of ash} = 0.15 \text{ gm}$$

a) Proximate analysis on air dry basis —

Here, weight of coal is taken on air dry basis = 1 gm

$$\therefore \% \text{ moisture} = \frac{\text{Weight of moisture}}{\text{Weight of coal}} \times 100 \\ = \frac{0.02}{1} \times 100 = 2 \%$$

$$\% \text{ VM} = \frac{\text{Weight of VM}}{\text{Weight of coal}} \times 100 \\ = \frac{0.13}{1} \times 100 = 13 \%$$

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

$$= \frac{0.15}{1} \times 100 = 15\%$$

$$\begin{aligned}\% \text{ Fixed Carbon} &= 100 - (\% \text{ moisture} + \% \text{ VM} + \% \text{ ash}) \\ &= 100 - (2 + 13 + 15) \\ &= 70\%\end{aligned}$$

b) Proximate analysis on oven dry basis -

Here, weight of coal is considered on oven dry basis (i.e moisture free basis) = 0.98 gm

$$\begin{aligned}\% \text{ VM} &= \frac{\text{weight of VM}}{\text{weight of coal}} \times 100 \\ &= \frac{0.13}{0.98} \times 100 = \underline{13.26}\% \end{aligned}$$

$$\begin{aligned}\% \text{ Ash} &= \frac{\text{weight of ash}}{\text{weight of coal}} \times 100 \\ &= \frac{0.15}{0.98} \times 100 = \underline{15.31}\% \end{aligned}$$

$$\begin{aligned}\% \text{ Fixed carbon} &= 100 - (\% \text{ VM} + \% \text{ ash}) \\ &= 100 - (13.26 + 15.31) \\ &= 71.43\%\end{aligned}$$

2) 1.20 g of coal sample was heated in a silica crucible in an electric oven at 110°C for 1 hour. The weight of the residue was 1.15 g. The residue was then ignited to a constant weight of 0.09 g. In an another experiment 1.20 g of the same coal sample was heated in a silica crucible covered with a vented lid at 950°C for exactly 7 min. The weight of the residue was 0.82 g. Calculate the % moisture, volatile

matter, ash & fixed carbon.

\rightarrow SOM % Moisture (%M) = $\frac{\text{Loss in weight of coal}}{\text{Initial weight of coal}} \times 100$

$$= \frac{1.20 - 1.15}{1.20} \times 100$$
$$= \frac{0.05}{1.20} \times 100 = 4.16 \%$$

% Ash (%A) = $\frac{\text{Weight of residue}}{\text{Initial wt of coal}} \times 100$

$$= \frac{0.09}{1.20} \times 100 = 7.50 \%$$

% Volatile matter (%VM) = $\frac{\text{Loss in wt of coal}}{\text{Initial wt of coal}} \times 100$ - % moisture

$$= \frac{1.20 - 0.82}{1.20} \times 100 - 4.16$$
$$= 31.66 - 4.16 = 27.50 \%$$

% Fixed carbon = $100 - \% [M + VM + A]$

$$= 100 - [4.16 + 27.50 + 7.50]$$
$$= 100 - 39.16$$
$$= 60.84 \%$$

3) A sample of coal was analysed as follows:
Exactly 1.5 gm was weighed in to a silica crucible. After heating for one hour at 118°C , the residue weighed ~~1.435~~ gm. The crucible next was covered with vented lid & strongly heated for exactly 7 min at $950 \pm 20^{\circ}\text{C}$. The residue weighed 1.027 gm. The crucible was then heated without cover, until a constant

Weight was obtained. The last residue was found to be 0.117 gm. Calculate the percentage results of above analysis.

→ Solⁿ: weight of the coal = $1.5 - 1.435$

= 0.065 gm

Weight of the volatile matter (VM) = $1.435 - 1.027$

Weight of ash = 0.117 gm
= 0.408 gm

% Moisture = $\frac{\text{weight of moisture}}{\text{weight of coal}} \times 100$

$$= \frac{0.065}{1.5} \times 100 = 4.33\%$$

% VM = $\frac{\text{weight of VM}}{\text{weight of coal}} \times 100$

$$= \frac{0.408}{1.5} \times 100 = 27.2\%$$

% ash = $\frac{\text{weight of ash}}{\text{weight of coal}} \times 100$

$$= \frac{0.117}{1.5} \times 100 = 7.8\%$$

% Fixed Carbon = $100 - (\% \text{ moisture} + \% \text{ VM} + \% \text{ ash})$

$$= 100 - (4.33 + 27.2 + 7.8)$$

$$= 100 - 39.33$$

$$= 60.667\%$$

Numericals on Ultimate Analysis :-

1) 0.20 g coal sample on complete combustion in presence of continuous oxygen supply increased the weight of V tube containing CaCl_2 by 0.10 g & V tube containing KOH by 0.52 g. Calculate % of C & H present in coal.

$$\text{Soln} \rightarrow \% \text{ C} = \frac{12 \times \text{Increase in wt. of tube containing KOH}}{44 \times \text{Initial weight of coal}} \times 100$$

$$= \frac{12}{44} \times \frac{0.52}{0.20} \times 100 = 70.90\%$$

$$\% \text{ H} = \frac{2 \times \text{Increase in wt of tube containing } \text{CaCl}_2}{18 \times \text{Initial wt of coal}} \times 100$$

$$= \frac{2}{18} \times \frac{0.10}{0.20} \times 100 = 5.55\%$$

2) 1.2 g of coal sample in Kjeldahl's experiment liberated ammonia which was observed in H_2SO_4 . The resultant soln required 10 ml 0.1 N NaOH for complete neutralisation. The blank titration reading was 50 ml. Calculate % N in coal.

$$\% \text{ N} = \left[\frac{\text{Blank titration reading} - \text{Back titration reading}}{\text{Initial weight of coal}} \right] \times \text{Normality} \times 1.4$$

$$= \frac{(50 - 10) \times 0.1 \times 1.4}{1.2} = 4.66\%$$

3) 1.0 g of coal sample was completely combusted in a bomb calorimeter. The solution from the bomb pot on treatment with BaCl_2 soln formed a precipitate of BaSO_4 . After washing & drying the weight of BaSO_4 precipitate was found to be

0.3 g. calculate % S in the given coal sample

→ Solⁿ

$$\% \text{ sulphur} = \frac{32}{233} \times \frac{\text{weight of } \text{BaSO}_4 \text{ formed}}{\text{Initial weight of coal}} \times 100$$
$$= \frac{32}{233} \times \frac{0.3}{0.1} \times 100$$
$$= 4.12\%$$
