UNIT- 4

Ques:- A sample - - - - - - - - - - - - - - - - - sample.

Ans:-

Impurity	Quantity (mg/L)	Eq. wt.	Hardness
$Ca(HCO_3)_2$	40.5	81	$40.5\times\frac{50}{81} = 25$
$Mg(HCO_3)_2$	46.5	73	$46.5\times\frac{50}{73} = 31.8$
$CaSO_4$	32.1	68	$32.1\times\frac{50}{68} = 23.6$
$CaCl_2$	22.5	55.5	$22.5\times\frac{50}{55.5} = 20.27$
$MgCl_2$	19.0	47.5	$19.\times\frac{50}{47.5} = 20$
$MgSO_4$	27.6	60	$27.6\times\frac{50}{60} = 23$

Temporary Hardness = due to $[Mg(HCO_3)_2 + Ca(HCO_3)_2]$

= 25 + 31.8

= 56.8 ppm

Permanent Hardness = due to $[CaSO_4 + MgSO_4 + CaCl_2 + MgCl_2$

= 23.60 + 23 + 20.27 + 20

= 86.87 ppm

Total Hardness = Temp. + Permanent

= 56.8 + 86.87

= 143.67 ppm Ans

Ques2:- What do you mean by term Permutit ? Explain zeolite process for water softening.
A zeolite softener was 90% exhausted by removing the hardness ~~of~~ completely when 10,000 litres of hard water was passed through it. The exhausted zeolite bed required 200 litres of 3% sodium chloride solution for its complete regeneration. Calculate the hardness of water sample.

Ans:- The word Permutit means boiling stone. Zeolites are hydrated Sodium Alumina Silicates. They have porous structure with molecular formula $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ ($x = 2$ to 10) & ($y = 2$ to 6).
Represented as Na_2Ze (Ze = the insoluble framework);
Na = loosely held sodium ions.

Zeolite process of water softening :-

Principle of Zeolite process :- They exchange their loosely held sodium ions reversibly with the hardness producing cations in water (Ca^{+2} & Mg^{+2})

Water Softening :-

$$\underset{\text{(Zeolite)}}{Na_2Ze} + \underset{\text{(Calcium salts)}}{Ca^{+2}} \longrightarrow \underset{\text{(Released in water)}}{2Na^+} + \underset{\text{(Calcium Zeolite)}}{CaZe}$$

$$\underset{\text{(Zeolite)}}{Na_2Ze} + \underset{\text{(magnesium salts)}}{Mg^{+2}} \longrightarrow \underset{\text{(Released in water)}}{2Na^+} + \underset{\text{(Magnesium zeolite)}}{MgZe}$$

NUMERICAL :-

3% NaCl solution = 30 gm/L NaCl
Amount of NaCl in 200 L = 200 × 30
= 6000 gm

$CaCO_3$ equivalents $= 6000 \times \frac{50}{58.5}$

$= 5128.20$ gm

Hardness of 10,000 L of water $= 5128.20 \times \frac{1000}{10000}$

$=$ ~~[illegible]~~ ppm

$= \boxed{512.82}$ ppm

Ques3:- What is the basic principle of Lime Soda process?. Give its working.
Calulate the quantities of lime (74%) and soda (94%) required for cold softening of 125,000 L of water with the following analysis using 10 ppm of $NaAlO_2$ as coagulant. Analysis of raw water: $Ca^{+2} = 160$ ppm, $Mg^{+2} = 48$ ppm, $CO_2 = 66$ ppm, $HCO^- = 264$ ppm, $H^+ = 20$ ppm, $NaCl = 4.7$ ppm. Analysis of treated water: $CO^{-2} = 45$ ppm, $OH^- = 68$ ppm.

Ans:- Principle:- By adding calulated amounts of lime $Ca(OH)_2$ + Soda Na_2CO_3.
all the calcium salts are precipitated out as calcium carbonate; all the magnesium salts are precipated as magnesium hydroxide $Mg(OH)_2$ which can be easily filtered out.

WORKING :-

Constituent	Reactions	Need
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$	L
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2 + 2H_2O$	2L

$CaCl_2$	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$	S
$CaSO_4$	$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$	S
$MgSO_4$	$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_3$	L+S
$MgCl_2$	$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$	L+S
CO_2	$CO_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + H_2O$	L
HCO_3^-	$2HCO_3^- + Ca(OH)_2 \rightarrow CaCO_3 + H_2O + CO_3^{-2}$	L-S
$FeSO_4$	$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$ $2Fe(OH)_2 + H_2O + O_2 \rightarrow 2Fe(OH)_3\downarrow$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$	L+S
$Al_2(SO_4)_3$	$2Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4$ $3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3\downarrow + 3Na_2SO_4$	L+S
$NaAlO_2$	$NaAlO_2 + H_2O \rightarrow Al(OH)_2 + NaOH$ $2NaOH$ = is equivalent to $Ca(OH)_2$	-L

NUMERICAL :-

Impurity	Quantity	Eq. wt.	$CaCO_3$ eq. (Mg/L)	L or S
Ca^{+2}	160	20	$160 \times \frac{50}{20} = 400$	S
Mg^{+2}	48	12	$48 \times \frac{50}{12} = 200$	L+S
CO_2	66	22	$66 \times \frac{50}{22} = 150$	L

HCO_3^-	264	61	$264 \times \frac{50}{61}$ = 216·39	L-S
H^+	20	1	$20 \times \frac{50}{1}$ = 100	L+S
CO_3^{2-}	45	30	$45 \times \frac{50}{30}$ = 75	S
OH^-	68	17	$68 \times \frac{50}{17}$ = 200	L+S
$NaAlO_2$	10	82	$10 \times \frac{50}{82}$ = 6·09	-L
NaCl	4.7	-(58·5)	No Hardness	-

$$\text{Lime} = \frac{74}{100}\left[Mg^{+2} + CO_2 + HCO_3^- + H^+ - \underset{+OH^-}{NaAlO_2}\right] \text{ all as. } CaCO_3 \text{ eq.} \times \frac{100}{\%\ \text{purity}} \times \frac{\text{Vol. water}}{10^6}$$

$$= \frac{74}{100}\left[200 + 150 + 216·39 + 100 + 200 - 6·09\right] \times \frac{100}{74} \times \frac{125000}{10^6}$$

$$= \boxed{107·53} \text{ kg.}$$

$$\text{Soda} = \frac{106}{100}\left[Ca^{+2} + Mg^{+2} - HCO_3^- + CO_3^{-2} + OH^-\right] \times \frac{100}{\%\ \text{purity}} \times \frac{\text{Vol. of water}}{10^6}$$

$$= \frac{166}{100}\left[400 + 200 - 216·39 + 200 + 75\right] \times \frac{100}{94} \times \frac{125000}{10^6}$$

$$= \boxed{97·39} \text{ kg}$$

Ques4:- What are ion exchange resins?. With the help of neat sketch, discuss ion exchange process for water softening, compare its merit over zeolites process.

Ans:- Ion Exchange Resin :- used for producing demineralised or deionised water. These are high molecular weight, insoluble, cross-linked, organic polymers having porous structures.

They are of two types :-

(i) Cation Exchange Resin (ii) Anion Exchange Resin.

classmate
Date
Page

(i) Cation Exchange Resin :- Have loosely held H^+ ions, which are reversibly exchanged by hardness producing cations (Ca^{+2} & Mg^{+2}) in water.

(ii) Anion Exchange Resin :- Have loosely held OH^- ions which are reversibly exchanged by hardness producing anions (Cl^-, SO_4^{-2} & HCO_3^-) in water.

Principle :- They are capable of exchanging hardness producing ions (cations & anions) in water with their H^+ & OH^- ions.

Working :- Ion exchange process consists of two columns -
(i) Cation exchanger column
(ii) Anion exchanger column

REACTIONS :- Step-I Water softening

Cation Exchanger :-

$$2R\text{-}H + Ca^{+2} \rightleftharpoons R_2\text{-}Ca + 2H^+$$
$$2R\text{-}H + Mg^{+2} \rightleftharpoons R_2\text{-}Mg + 2H^+$$

Anion Exchanger :-

$$R\text{-}OH + Cl \rightleftharpoons RCl + OH^-$$
$$2R\text{-}OH + SO_4^{-2} \rightleftharpoons R_2SO_4 + OH^-$$

(R = Insoluble Matrix)

Step II → Regeneration of ion - exchangers :-

Regeneration of cation exchanger by Acid :- $R_2\text{-}Ca + 2H^+ \rightleftharpoons 2R\text{-}H + Ca^{+2}$
" " anion " " Base :- $R\text{-}Cl + OH^- \rightleftharpoons R\text{-}OH + Cl^-$

Limitations :- ① Initial cost is high
② Used for small scale treatment of water.

* Ion- Exchange Process	Zeolite Process
1. Remove all positive & negative ions from water.	Removes only cations causing hardness in water.
2. No sodium salts in treated water.	Treated water contains high amount of sodium salts.
3. Initial cost is High	Lower.
4. Running cost is Higher.	Lower, as NaCl is very cheap.
5. Acidic water can be purified.	Can't be purified.

Ques5:- Write a short note on Reverse Osmosis.

Ans :- Osmosis :- Solvent from dil. solution passes to the conc. solution through a semi-permeable membrane to equalize the conc. of both.

Reverse Osmosis :- Pressure higher than osmotic pressure is applied on the conc. solution side, so that the flow of solvent is reversed, i.e from concentrated solution to the dilute solution. mainly used for distillation of sea water.

Ques6:- What is meant by calorific value of a fuel? What are its units? or define Gross Calorific value and Net Calorific value? Calculate GCV and LCV of the coal sample having C = 80%, H = 9%, O = 4%, N = 1.5%, S = 2.5% and Ash = 3%.

Ans :- Calorific value is defined as the amount of heat energy released during complete combustion of a unit mass of a fuel. It is expressed in KJ/Kg.

There are two ~~units~~ types — of fuel –

(i) Gross Calorific value (GCV)
(ii) Net Calorific value (NCV)

GCV :- It is the quantity of heat liberated by the combustion of unit volume of gas.

NCV :- It is the practical amount of energy which may be realised at atmospheric (constant) press.

Numerical :-

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

$$= \frac{1}{100}\left[8080 \times 80 + 34500\left(9 - \frac{4}{8}\right) + 2240 \times 2.5\right]$$

$$= 9452.5 \quad cal/g$$

LCV = G

Ques 7 :- How the calorific value of a solid fuel is determined using bomb calorimeter? Draw a neat diagram of bomb calorimeter.

Ans :- **Bomb's Calorimeter** :-

Construction -

It consists of :-

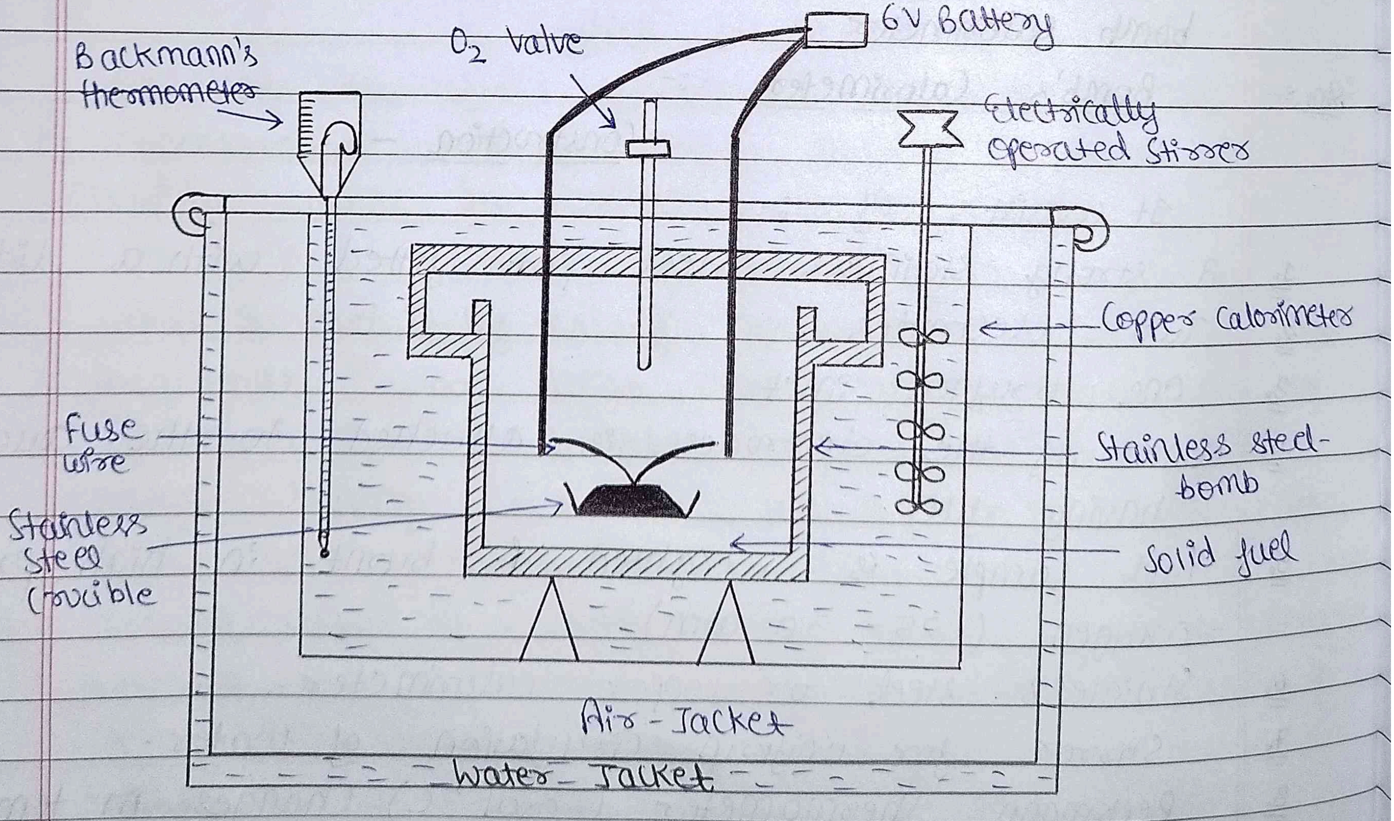
1. A strong stainless steel pot fitted with a lid.
2. Two electrodes.
3. One oxygen inlet.
4. One of the electrodes is attached to the crucible having fuel.
5. Fuel sample is weighted & burnt in high pressure oxygen (25 - 30 atm).
6. Stainless steel or copper calorimeter.
7. Stirrer for uniform circulation of water.
8. Beckmann thermometer (0.01 °C) changes in temperature can be easily

classmate
Date
Page

9. water & air Jackets to avoid heat losses.
10. 6V battery to start Combustion of fuel.

Working :-

1. weigh fuel sample & keep it in crucible.
2. fix the lid tightly of bomb pot.
3. fill the bomb with oxygen (25 - 30 atm pressure).
4. Place the bomb in calorimeter.
5. And known volume of water in the calorimeter.
6. Keep the thermometer & stirrer in the water
7. Place the calorimeter in the water jacket.
8. Put the plastic cover on the top & make electrical connections.
9. Stir for 5 minutes & note the initial temperature of water
10. Note the maximum temp. reached.



Bomb's Calorimeter

Calculations :-

Let the weight of the fuel sample taken = x g
weight of water in the calorimeter = W g
Water equivalent of the calorimeter = w g
Stirrer, bom, thermometer
Initial temp. of water = t_1°C
final temp. of water = t_2°C

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

$$NCV = GCV - 0.09 \times H\% \times 587 \quad \text{Cal/gm}$$

Ques8:- A sample of coal contains C = 93%, H = 6%, ash = 1%. The following - - - - - - - - - - - - Cal/gm.

Ans:-

$$GCV = \frac{(W+w)(t_2-t_1+C_c)-(C_A+C_F+C_T)}{x}$$

$$= \frac{(2200+570)(2.3+0.047)-(62.6+3.8+1.6)}{1.029}$$

$$= \frac{(2770)(2.347)-(68)}{1.029}$$

$$= \frac{6433.19}{1.029}$$

$$GCV = \boxed{6251.885} \text{ Cal/gm}$$

$$LCV = HCV - 0.09\,(H\%) \times \text{Latent heat of steam}$$

$$LCV = 6251.885 - 0.09 \times 580$$

$$= 6256.445 - 313.28$$

$$= \boxed{5938.685} \quad \text{Cal/gm}$$

Ques9:- A sample of coal contains C = 70%, O = 20%, H = 8%, S = 1%, N = 0.5%, ash = 0.5%, Calculate GCV and NCV of coal.

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

$= \frac{1}{100}\left[8080 \times 70 + 34500\left(8 - \frac{20}{8}\right) + 2240 \times 1\right]$

$= \frac{1}{100}\left[565600 + \frac{34500 \times 44}{8} + 2240\right]$

$\boxed{GCV = 7575.9}$ cal/g

$NCV = GCV - 0.09\,(H\%) \times 587$

$= 7575.9 - 0.09 \times 8 \times 587$

$= 7575.9 - 422.64$

$\boxed{NCV = 7153.26}$ cal/g

Ques10:- What is rank of coal? Describe proximate and ultimate analysis of coal and its usefulness.

Ans:- On the basis of % of C, coal can be classified into following categories —

* Wood, peat, Lignite, Bituminous, Anthracite

Proximate analysis of coal :- Proximate analysis is the study or analysis of coal sample in which following things are determined :-

(i) % Moisture (ii) % volatile matter
(iii) % Ash content (iv) % Fixed carbon are found.

\# (i) % Moisture :- All moisture in coal escapes on heating coal at 110°C for 1 hr.

Procedure :-

$$\text{Known coal sample (powdered and dried) (weighed sample)} \xrightarrow[\substack{110^\circ C \\ 1\text{ hour}}]{\text{Heat}} \text{Cool in desiccator} \rightarrow \text{weigh}$$

$$\% \text{ moisture} = \frac{\text{Loss in weight}}{\text{weight of coal sample}} \times 100$$

(ii) % Volatile matter :- At 925°C in muffle furnace, coal undergoes thermal degradation to form volatile matter.

$$\boxed{\begin{array}{l}\text{Moisture free coal} \\ \text{left in first exp.}\end{array} \xrightarrow[\substack{925^\circ C \\ 7\text{ minute}}]{\text{Heat}} \begin{array}{l}\text{Coal the crucible} \\ \text{in desiccator}\end{array} \longrightarrow \text{weigh}}$$

$$\% \text{ volatile matter} = \frac{\text{weight of volatile matter}}{\text{weight of coal sample}} \times 100$$

(iii) % Ash :- The residual coal in above exp. is heated and burned above 750°C for 30 minutes. The ash is left behind. Cool and weigh.

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

(iv) % fixed carbon :- 100 − (% moisture + % volatile matter + % Ash)

ULTIMATE ANALYSIS OF COAL

Analysis of coal in which % of C, H, O, N, S elements are found out is known as ultimate analysis.

(i) Determination of C and H :-

$$\begin{array}{l}\text{Known coal sample} \\ \text{(Powdered and dried)}\end{array} \xrightarrow[\text{oxygen}]{\text{Heat}} \begin{array}{l}\text{C is converted} \\ \text{to } CO_2 \text{ and H} \\ \text{into } H_2O\end{array} \longrightarrow \begin{array}{l}\text{Gaseous products are} \\ \text{absorbed by pre-weigh} \\ \text{U-tubes containing} \\ \text{anhydrous } CaCl_2 \text{ which} \\ \text{absorbs } H_2O \text{ and KOH} \\ \text{which absorb } CO_2\end{array}$$

Increase in weight is calculated

classmate
Date
Page

$$\% C = \frac{12}{144} \times \frac{\text{weight of } CO_2 \text{ formed}}{\text{weight of coal sample}} \times 100$$

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

(ii) Determination of N (Kjeldahl method) :-

Known coal sample (powdered and dried) in Kjeldahl flask $\xrightarrow[\text{conc. } H_2SO_4,\ K_2SO_4]{\text{Heat}}$ Clear solution $\longrightarrow$ Alkali $\longrightarrow$ NH_3 is liberated

$\downarrow$

Pass through ~~Known volume~~ of Standard acid.

$\longleftarrow$ Unused acid is determined by back titration with NaOH

$$\boxed{\% N = \frac{1.4 \times \text{Normality} \times \text{Vol. of acid}}{\text{weight of coal sample}}}$$

(iii) Determination of S :-

$$S \xrightarrow{O_2} SO_2 \xrightarrow{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 \downarrow + 2HCl$$

(white ppt.)

$BaSO_4$ is filtered, dried and weighted.

$$\boxed{\% S = \frac{32}{233} \times \frac{\text{Weight of } BaSO_4 \text{ precipitate}}{\text{Weight of coal sample}} \times 100}$$

(iv) % Ash :-

Known Coal Sample (powdered and dried) $\xrightarrow[\text{30 minute}]{750°C \text{ (Heat)}}$ Residue left $\longrightarrow$ weigh

$$\boxed{\%\ \text{Ash} = \frac{\text{weight of residue}}{\text{weight of coal sample}} \times 100}$$

(iv) **Determination of O :-**

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

Ques11:- Calculate the mass of air needed for complete combustion of 5.0 kg of coal containing 80% carbon 15% hydrogen and rest oxygen.

Ans :- % O (present in coal) = 100 - (80 + 15)

= 5%

weight of carbon (in coal) = $5000 \times \frac{80}{100}$

= 4000 gm

weight of hydrogen (in coal) = $5000 \times \frac{15}{100}$

= 750 gm.

weight of oxygen (present in coal) = $500 \times \frac{5}{100}$

= 250 gm

Net O_2 required = $\left[\frac{32}{12} \times C + 8 \times H - O\right]$ gm

$= \left[\frac{32}{12} \times 4000 + 8 \times (750) - 250\right]$

= 10666.67 + 6000 - 250

= $\boxed{16416.67}$ gm.

weight of air (needed) = Net O_2 required $\times \frac{100}{23}$

$= 16416.67 \times \frac{100}{23}$

$= \boxed{71376.82\ \text{gm}}$

Ques12:- A coal sample has following — — — — — — value.

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

$= \frac{1}{100}\left[8080 \times 90 + 34500 \times \left(H\% - \frac{3}{8} \right) + 2240 \times 0.5 \right]$

$= 7272 + 345\,H - 129.375 + 1120$ K cal/g

$= 8262.62 + 345\,H$ —(1)

Also, $GCV = LCV + 0.09\,H\% \times$ Latent heat of steam

$= 8490.5 + 0.09\,H \times 587$

$= 8490.5 + 52.83\,H$ —(2)

from Eq^n (1) & Eq^n (2)

$8262.62 + 345\,H = 8490.5 + 52.83\,H$

$292.17\,H = 227.88$

$\boxed{H = 0.77}$ %

So, $GCV = 8262.62 + 345 \times 0.77$

$= 8262.62 + 265.65$

$= \boxed{8528.27}$ K cal/g

Ques13:- What is biogas? How biogas is produced? with the help of diagram, explain Biogas plant.

Ans: It is a mixture of gas produced by the micro-organism during the anaerobic fermentation of biodegradable materials. Anaerobic fermentation is a biochemical process in which particular kinds of bacteria digest biomass is an oxygen-free environment resulting in production of CH_4, CO_2, H_2 and traces of other gases along with decomposed mass.

Composition of Biogas -

Name of gas	(%)
Methane (CH_4)	50-70
Carbondioxide (CO_2)	30-40
Hydrogen (H_2)	10-5
Nitrogen	2-1
Water vapour (H_2O)	0.3
Hydrogen sulphide (H_2S)	Traces

Raw material used :-

Cow dung, sewage, crop residues, vegetable wastes, water hyacinth, Polutry droppings.

The fixed Dome Type Biogas Plant :-

Consists of following parts -

1. Digester Tank
2. Slurry mixing Tank
3. Spent slurry Tank

In the digester, anaerobic fermentation starts with the release of biogas. It takes 30 to 60 days for the slurry to fill the digester, depending upon the temp. within the digester. During time the biogas formed is collected in the dome under pressure. When the pressure of biogas exceeds certain limit, the biogas forces the spent slurry into the overflow tank.
The biogas is withdrawn from the dome through an outlet pipe. Its flow is regulated by a gas valve.

$$\left\{\begin{matrix}\text{Animal Dung} + \\ \text{Plant waste} + \\ \text{water}\end{matrix}\right\} \xrightarrow[\text{35°C temp.}]{\text{Anaerobic fermentation}} \left\{\begin{matrix}\text{Biogas or Gobargas} \\ (CH_4 + CO_2 + H_2 + H_2S + N_2)\end{matrix}\right\}$$