FUELS

Introduction, Classification, Calorific value

Characteristic of a Good Fuel

Comparison between Solid, Liquid and Gaseous Fuels

Bomb Calorimeter

Coal: Classification, Selection Criteria, Proximate and Ultimate Analysis, Pulverized Coal.

Petroleum: Classification, Types of Cracking, Knocking, Octane and Cetane Number

LPG, Natural Gas, Producer Gas, Water Gas, Bio Gas.

Numerical Problems based on Calorific Value, Bomb Calorimeter, Proximate and Ultimate Analysis.

What is Fuel?

- Fuel is a combustible substance , containing carbon as the main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes.

- Examples: Wood, Charcoal, Coal, Kerosene, Petrol, Diesel, Producer Gas, Bio Gas etc.

Classification of Fuels

According to Occurrence

- **Natural / Primary fuels**
  - Solid
    - Wood
    - Peat
    - Lignite
    - Coal
  - Liquid
    - Crude Oil
  - Gas
    - Natural Gas
- **Artificial / secondary Fuels**
  - Solid
    - Coke
    - Charcoal
    - Petroleum
    - Coke
    - Coal
  - Liquid
    - Kerosene
    - Diesel
    - Petrol
    - Fuel Oil
    - L.P.G.
  - Gas
    - Coal Gas
    - Water Gas
    - Oil Gas
    - Bio Gas

Calorific Value

The total quantity of heat liberated, when a unit mass (volume) of the fuel is burnt completely.

Units

1) Calorie – The amount of heat required to raise the temperature of one gram of water through one degree centigrade (15 – 16 ^{0}C).
2) Kilocalorie – The amount of heat required to raise the temperature of one kilogram of water through one degree centigrade (15 – 16 ^{0}C).

3) British Thermal Unit (B.Th.U.) – The amount of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60 – 61 ^{0}F).

1B.Th.U. = 252 cal

4) Centigrade Heat Unit (C.H.U.) – The amount of heat required to raise the temperature of one pound of water through one degree centigrade (15 – 16 ^{0}C).

1 C.H.U. = 454.5 cal

HCV and LCV

- Usually All fuels contains hydrogen and when the calorific value of it is determined, H converts to steam.
- **Higher or Gross Calorific Value (HCV)** – The total amount of heat produced, when unit mass / volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature.
- **Lower or Net Calorific Value (LCV)** – The net heat produced, when unit mass / volume of the fuel has been burnt completely and the products of combustion have been permitted to escape.

LCV = HCV – Heat of vaporisation

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O$$

2gm 18 gm

1 gm 9 gm

Weight of water produced from 1 gm of hydrogen is 9 gm.

Let 'a' be the percent of hydrogen in the sample then weight of the water produced will be 9a/100.

Since amount of heat per Kg. of steam is the latent heat of vaporization of water corresponding to a standard temperature of 25^{o}C is 587 Kcal/Kg,

LCV = HCV – mass of hydrogen $\times$ 9 $\times$ latent heat of steam

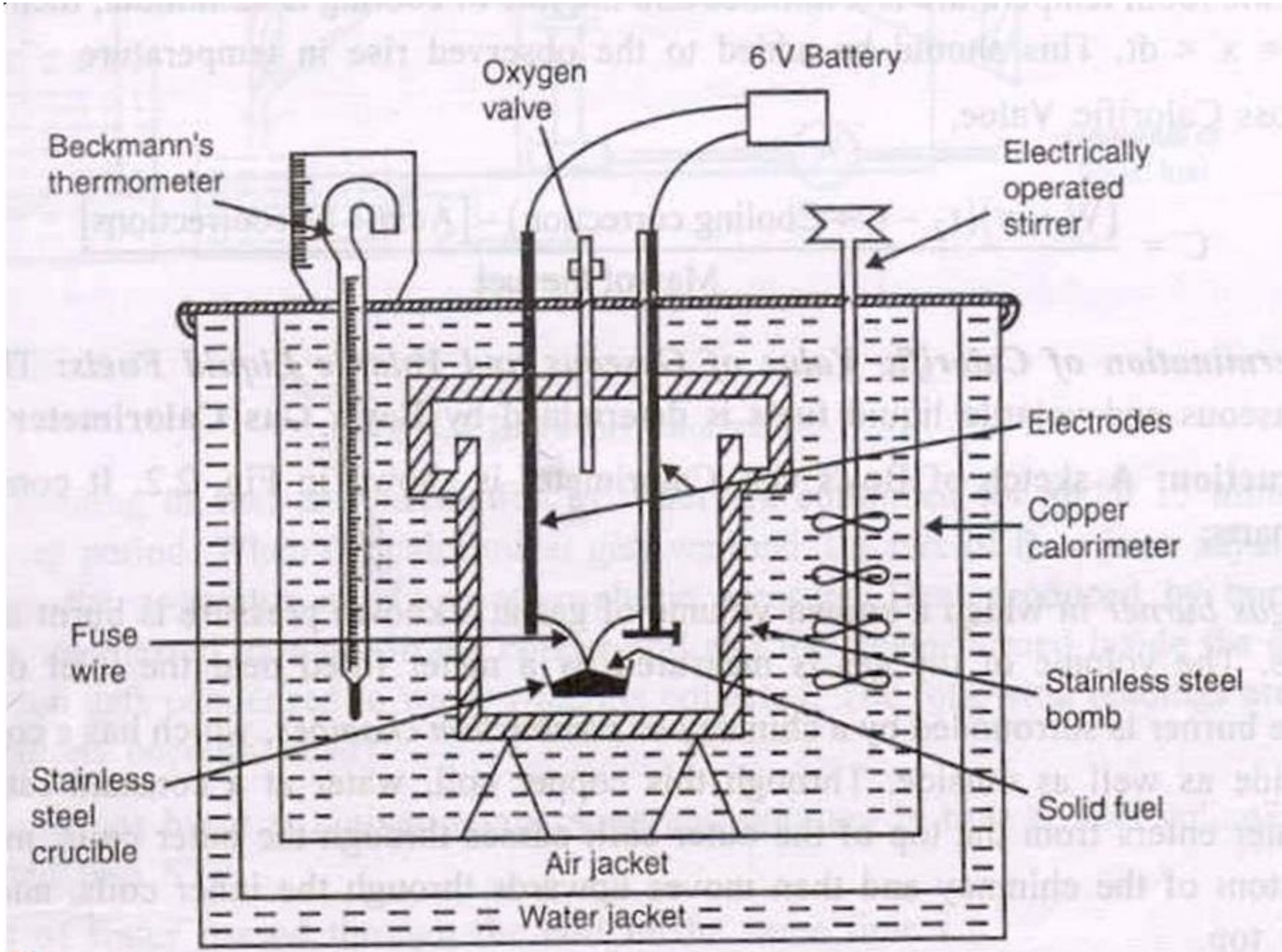
Characteristics of Good Fuel

- High Calorific Value
- Moderate ignition Temperature
- Low Moisture Content
- Low Non-Combustible Matter Content
- Moderate Velocity of Combustion
- Non Harmful Products of Combustion
- Low Cost
- Easy to Transport
- Controllable Combustion
- No Spontaneous Combustion
- Low Storage Cost
- Uniform Size (solid)

Comparison Between Solid, Liquid and Gaseous Fuels

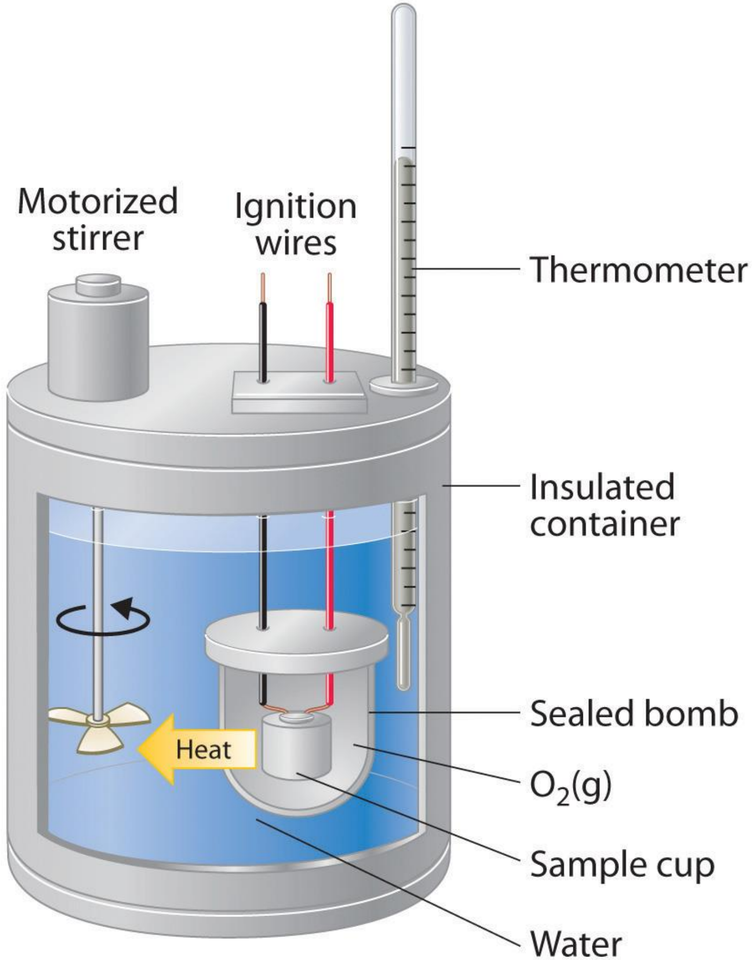
Solid Fuels	Liquid Fuels	Gaseous Fuels
Easily available and cheap	Costly than Solids	Costly
Convenient transport, storage and handling	Sophisticated storage and transport	Sophisticated storage and transport
Least risk of fire hazards	Large risk	Highest
Slow combustion	Quick	Quick
Combustion can not be stopped easily	Easily stopped	Easily stopped
Requirement of labor	Lesser handling cost	Lesser handling cost
Production of ash and smoke	No ash and smoke	No ash and smoke
Cannot be used in internal combustion engine	Can be used	Can be used
Large excess of air required for burning	Slight excess	Slight excess
Least thermal efficiency	Higher thermal efficiency	Highest thermal efficiency

Bomb Calorimeter



Working

1. Known mass (0.5–1.0 g) of fuel is taken
2. Magnesium wire is stretched
3. 10 ml distilled water is added in bomb
4. Bomb lid is screwed
5. Oxygen up to 25atm pressure is filled
6. Lower bomb in calorimeter having known mass of water ($\approx$ 2 L)
7. Stirrer started
8. Initial temperature of water noted
9. Connection completed
10. Sample burns and heat is liberated
11. Maximum temperature attained is recorded
12. Washings collected


Motorized stirrer
Ignition wires
Thermometer
Insulated container
Sealed bomb
Heat
O2(g)
Sample cup
Water

Calculations

m = Mass of fuel sample (in gms)

W = Mass of water in calorimeter

w = water equivalent of calorimeter, stirrer, thermometer, bomb etc. (in gms)

t_1 = Initial temperature of water

t_2 = Final temperature of water

H = Higher Calorific value

L = Lower calorific value

Heat liberated = m. H

Heat absorbed = $(W + w)(t_2 - t_1)$

$m.H = (W + w)(t_2 - t_1)$

$H = (W + w)(t_2 - t_1)/m$ cal/g

L = H – Heat of vaporisation

$= (W + w)(t_2 - t_1)/m - 0.09 \times a \times 587$

Corrections

1. Fuse Wire Correction – to be subtracted
2. Acid Correction – Oxidation of S and N present in fuels takes place as exothermic

$$S + 2H + 2O_2 \rightarrow H_2SO_4 + Heat$$
$$2N + 2H + 3O_2 \rightarrow 2HNO_3 + Heat$$

Washings are boiled, cooled, titrated with N/10 $Ba(OH)_2$ using phenolphthalein as indicator.

Add 20 ml N/10 Na_2CO_3 , boil, cool, filter, wash .

Titrate with N/10 HCl using methyl orange as indicator.

1 ml N/10 $Ba(OH)_2$ = 3.60 cal

1 ml N/10 Na_2CO_3 = 1.43 cal

1 mg of S from $BaSO_4$ ppt = 2.25 cal

3. Cooling Correction – Time taken to cool the water in calorimeter noted (t). Rate of cooling (dt per minute) multiplied by t gives cooling correction.

$$L = \frac{(W + w)(t_2 - t_1 + \text{cooling corr.}) - (\text{Acid corr.} + \text{Fuse wire corr.})}{m}$$

Numerical –

0.92 g coal sample was burnt in a bomb having 550 g water in calorimeter and water equivalent of 2200 g. Rise in temperature took place from 26.50 to 28.92 ^{0}C. Fuse wire correction and acid corrections were recorded as 10.0 cal and 50.0 cal respectively. Calculate gross and net calorific value of the coal, assuming latent heat of condensation of steam as 587 cal/g. Percentage of Hydrogen in the sample is 6 %.

Solution –

m = 0.92 g, W = 550 g, w = 2200 g,

$(t_2 - t_1) = 28.92 - 26.5 = 2.42\ ^0C$

Fuse wire correction = 10.0 cal

Acid corrections =50.0 cal

$H = (W + w)(t_2 - t_1) - (\text{Acid corr.} + \text{Fuse wire corr.}) / m \quad \text{cal/g}$

$= (500 + 2200)(2.42) - (10 + 50) / 0.92$

$= 7168.5$ cal/g

$L = H - 0.09 \times a \times 587$

$= 7168.5 - 0.09 \times 6 \times 587$

$= 6851.52$ cal/g

Numerical– On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water increased from 26.5 to 29.2 ^{0}C. water equivalent of calorimeter is 385 g. if the fuel contains 0.7% hydrogen, calculate its gross and net calorific value.

<u>Solution</u> – m = 0.83 g, W = 3500g, w = 385 g,

$(t_2 - t_1) = 29.2 - 26.5 = 2.7\ ^0C$

$H = (W + w)(t_2 - t_1) / m$ cal/g

$= (3500 + 385)(2.7) / 0.92$

$= 12638$ cal/g

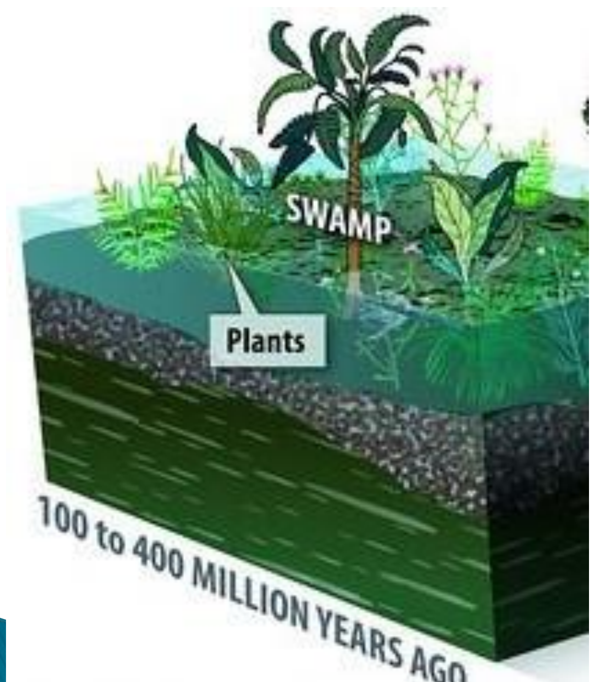
$L = H - 0.09 \times a \times 587$

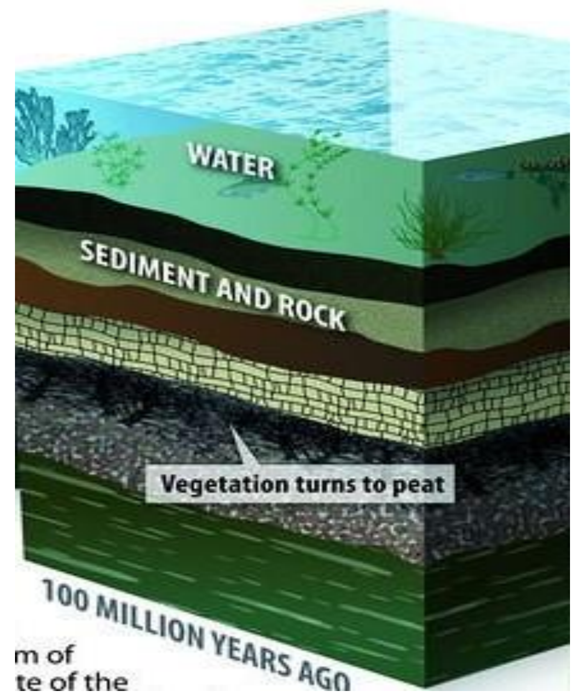
$= 12638 - 0.09 \times 0.7 \times 587$

$= 12601$ cal/g

Coal

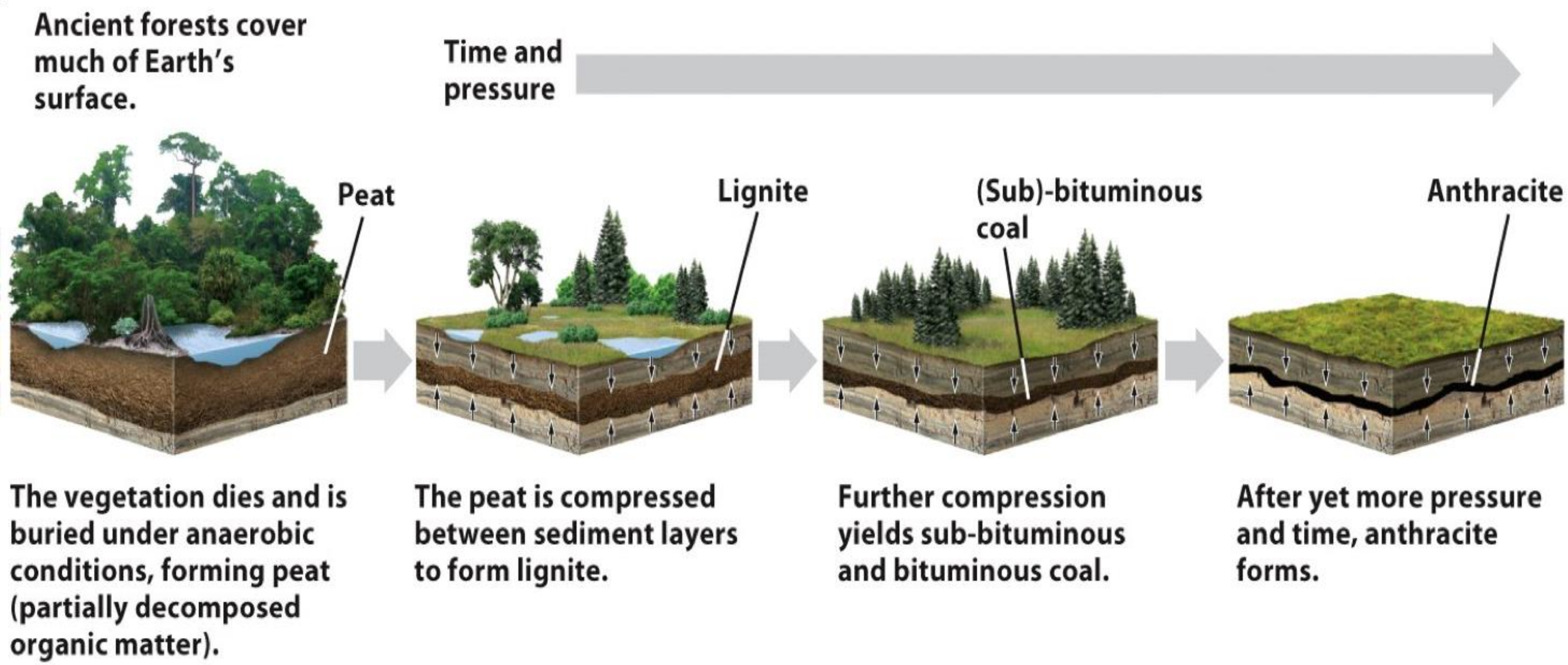
- Highly carbonaceous matter that has been formed as a result of alteration of vegetable matter under certain favorable conditions.
- Chiefly composed of C, H, N and O, besides some non-combustible matter.





Classification of Coal by Rank

Wood → Peat → Lignite → Bituminous → Anthracite



Compositions of varieties of Coal

Fuel	Moisture of air-dried sample at 40 ^{0}C	C (%)	H (%)	N (3%)	O (%)	Calorific value (kcal/kg)
Peat	25	57	5.7	2	35	4125-5400
Lignite	20	67	5	1.5	25	6500-7100
Sub-bituminous coal	11	77	5	1.8	15	7000-7500
Bituminous coal	4	83	5	2	10	8000-8500
Semi-bituminous coal	1	90	4.5	1.5	5	8350-8500
Anthracite	1.5	94	3	0.7	3	8650-8700

Criteria of Selection of Coal

1. Calorific Value: High

Large amount of heat from small quantity of coal

Reduces cost of handling and storage

2. Moisture content: Low

It reduces heating value

Loss of money (paying same rate as coal)

3. Ash content: Low

Non-combustible

Reduces heating value of coal

Increases storage, handling and disposal cost

1% ash causes 1.5% loss of heat

(i) Compositions of Ash:

Important in metallurgy as it affects metal and slag composition

(ii) Fusion temperature of ash: important in boilers

If fuse at working temp, clinker formation, which restricts air flow.

They also sticks to boiler causing problem in heat transfer.

4. Calorific intensity: The maximum temp reached when the coal is completely burnt in the theoretical amount of air.

Initial heat preheats the air causing increased intensity.

5. <u>Size of coal</u>: Uniform

Regulated combustion and handling

Smaller particle interfere in flow of air

6. <u>Sulphur and phosphorus content</u>: Low

Especially in metallurgy

It can get transferred to metal

Gases produced are corrosive and polluting

7. <u>Coking quality</u>-

a) The coals which on heating, in the absence of air, becomes soft, plastic and fuse together to large coherent masses, are called <u>caking coals</u>.

Difficult to be oxidised

b) The coals which on heating, in the absence of air, becomes porous, hard, strong and usable for metallurgical purposes, are called <u>coking coals</u>.

All coking coals are caking, but all caking coals are not coking coals.

Analysis of Coal – Proximate analysis

Moisture

1. Weigh ≈1 g finely powdered air-dried coal sample in a crucible.
2. Place in an electric oven at 105–110 ^{0}C for 1 hr, without lid.
3. Take out, cool in a dessicator, weigh.

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

Volatile matter

1. Dried sample covered with lid is placed in furnace at 925 ± 20 ^{0}C, for 7 min.
2. Take out crucible, cool in air, then in dessicator, weigh again.

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal sample}} \times 100$$

Ash

1. Residual coal heated without lid in a furnace at 700 ± 50 ^{0}C for 30 min.
2. Take out crucible, cool in air, then in dessicator, weigh.
3. Process is repeated till constant weight is obtained.

$$\% \text{ ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal sample}} \times 100$$

Fixed carbon

% of Fixed carbon = 100 – % of (moisture + volatile matter + ash)

Importance of Proximate analysis

Moisture – It evaporates during burning of coal and takes away a part of heat as latent heat of vaporization. Lowers effective calorific value. Lesser the better but 10% required to create uniform fuel-bed and less fly-ash.

Volatile matter – Same as above. Burns with long flame, high smoke, low calorific value.

Ash – A useless, non-combustible matter, which reduces calorific value. Also hinders flow of air and heat, thus lowering temp. Forms clinkers . Additional cost of transportation, storage, handling, disposal , wear of furnace walls.

Fixed Carbon – Higher % desired.

Analysis of Coal – Ultimate analysis

Carbon and Hydrogen

1–2 g accurately weighed coal sample burnt in current of oxygen in combustion apparatus.

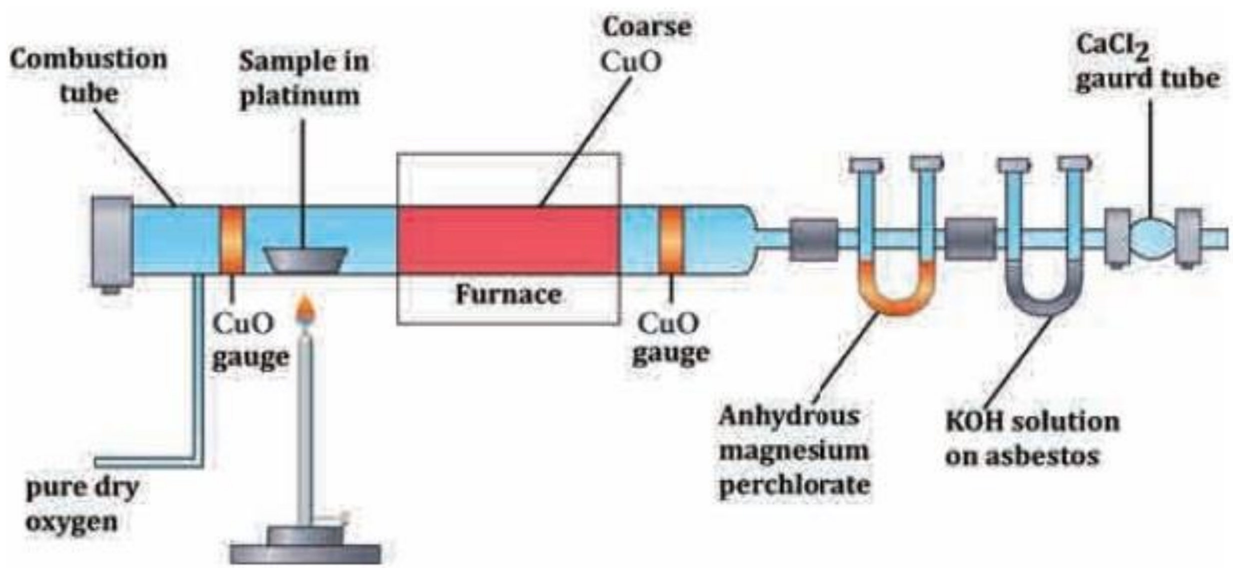


Fig 11.2 Estimation of Carbon and Hydrogen

C converts to CO_2 which gets absorbed in KOH tube and H converts to H_2O which gets absorbed in $CaCl_2$ tube.

$$C + O_2 \rightarrow CO_2 \qquad\qquad H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

12 44 2 18

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

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

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

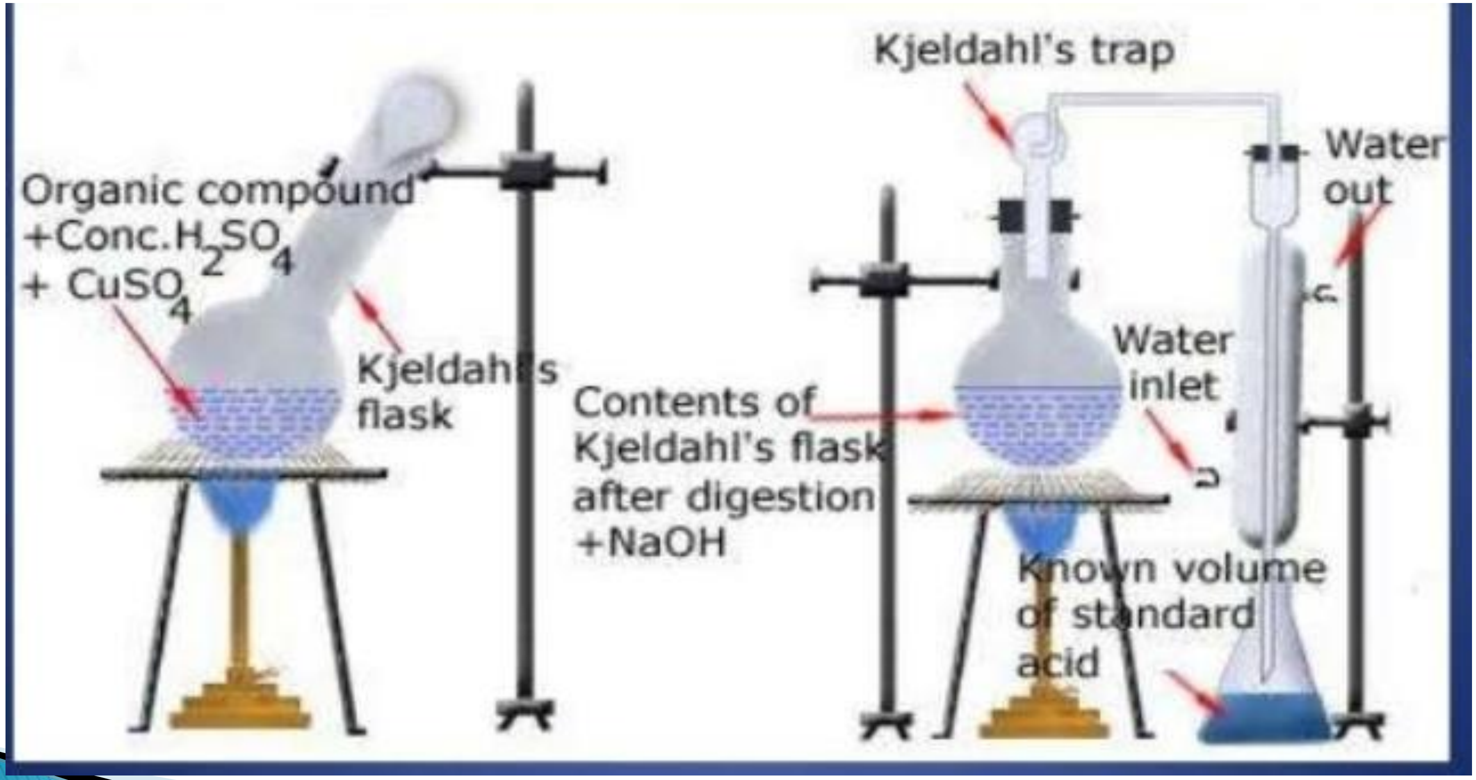
$$\%\, H = \frac{\text{Increase in weight of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

Nitrogen

Heat ≈1 g coal with conc. H_2SO_4 and $K_2SO_4/CuSO_4$ (catalyst) in Kjeldahl's flask.

$$\text{Nitrogen} + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

After it gets clear, transfer contents to another flask having excess of KOH/NaOH.



$$(NH_4)_2SO_4 + 2NaOH_4 \rightarrow \underset{\text{salt}}{Na_2SO_4} + 2NH_3 + 2H_2O$$

Distill liberated NH_3 and absorb in a known volume of standard acid .

Determine unused acid by back titration with standard NaOH.

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

Sulphur

1. Washings obtained from bomb calorimeter are treated with $BaCl_2$
2. Precipitates of obtained $BaSO_4$ are filtered, washed and heated till constant weight

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

Ash

Same as in proximate analysis

Oxygen

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

Importance of Ultimate analysis

1. Carbon and Hydrogen – Greater C and H %, better the coal. But as H is considered as volatile matter, it affects the area where coal is used.
2. Nitrogen – No calorific value, thus undesirable.
3. Sulphur – Contributes to the heating value but produces acids (corroding), enters in metals during metallurgy and also cause environmental pollution.
4. Oxygen – Decreases the calorific value. High oxygen means high moisture, low calorific value, low coking power.

1% increase in oxygen content decreases 1.7% calorific value.

2.5 g of coal was heated for 1 hr at 110 ^{0}C and the residue was found to be 2.415 g. The crucible was then covered and heated to 925 ± 20 ^{0}C and residue found to be 1.528 g. The crucible was again heated without lid until a constant weight is obtained. The last residue weighs 0.245 g. Calculate the percentage results of the above analysis.

Solution –

$$\% \text{ Moisture} = \frac{\text{loss in weight} \times 100}{\text{Wt. of coal taken}} = \frac{(2.5 - 2.415) \times 100}{2.5}$$

$$= 3.4\%$$

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight} \times 100}{\text{Wt. of coal taken}} = \frac{(2.415 - 1.528) \times 100}{2.5}$$

$$= 35.48\%$$

$$\% \text{ ash} = \frac{\text{weight of ash left}}{\text{Wt. of coal taken}} \times 100 = 0.245 \times 100 / 2.5 = 9.8\%$$

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

$$= 100 - (3.4 + 35.48 + 9.8) = 51.32\ \%$$

Nitrogen estimation of 1 g coal sample was done by Kjeldahl method. Evolved ammonia was collected in 25ml N/10 sulphuric acid. To neutralize excess acid, 15ml of 0.1N sodium hydroxide was required. Determine the % of nitrogen in the sample.

Solution –

$$N_1V_1 = N_2V_2$$

$$(NaOH) \qquad (H_2SO_4)$$

$$15 \times 0.1 = 0.1 \times V_2$$

$$V_2 = 15 \text{ ml}$$

Volume of H_2SO_4 used to neutralize ammonia = 25–15 = 10ml

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

$$= \frac{10 \times 0.1 \times 1.4}{1.0} = 1.4 \%$$

0.5 g of coal sample was used in bomb calorimeter for determination of calorific value. Washings were treated with barium chloride to get a precipitate of barium sulphate. It was filtered, dried and weighed and found to be 0.05 g. Calculate the percentage of sulphur in the coal sample.

<u>Solution</u> –

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

$$= \frac{0.05 \times 32 \times 100}{0.5 \times 233} = 1.3734\ \%$$