FUELS & Determination of Efficiency

Subject : Chemistry II
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Unit V: Fuels

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1. **Definition of Fuel**
2. **Classification of Fuels**
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4. **Calorific Value of Fuels**
5. **(Net Calorific & Gross Calorific Value)**
6. **Determination of Calorific Values(i.e. (Bomb Calorimeter)**

What is Fuels ?

Fuels are combustible substance, containing carbon as main constituent's which upon proper burning gives large amount of heat which can be used economically for domestic &Industrial process.

Alternatively, Material which posse's chemical energy is known as fuel.
For Example:
Wood, Charcoal, Coal, Kerosene
Petrol, Diesel, Oil and Gas etc.

How Fuels are Classified ?

Fuels can be classified based on their **Occurrence** & **Physical states.**
Based on **Occurrence** they are of **two** type:

Primary Fuels: Fuels which occur in nature as such are called primary Fuels. **i.e. Wood, Peat, Coal, Petroleum & Natural Gas.**

Secondary Fuels: The Fuels which are derived from the primary fuels after by further chemical process are called secondary fuels. **i.e. Coke, Charcoal, Kerosene, Coal Gas, Producer Gas etc.**

How Fuels are Classified ?

Based on their physical states Fuels can be classified in to three major categories.

Solid Fuels	Wood, Peat, Lignite etc.
Liquid Fuels	Crude Oil, Tar, Diesel, Petrol, Kerosene etc.
Gaseous Fuels	Natural Gas, Coal Gas, Biomass Gas etc.

What is Calorific value of Fuels ?

The calorific value of a fuel is the measure of the amount of heat released during complete combustion of a unit mass of Fuels expressed in kilojoules per kilograms (kj/kg.). Calorific value usually determined by a Calorimeter, but a theoretical value can be calculated from the following equation:

$$\text{Calorific Value (kcal/kg. of Fuels)} = \frac{8100C + 34000\left(H - \frac{O}{8}\right)}{100}$$

What is Calorific value of Fuels ?

Calorific Value (kcal/kg. of Fuels) =

$$\frac{8100C + 34000(H - \frac{O}{8})}{100}$$

Where **C**, **H** and **O** are percentage of these elements in **1 Kg** of Fuels. Carbon yields **8080 kcal/kg** when completely burned, hydrogen **34000 kcal/kg**; oxygen is assumed to be already attached to its proportion of hydrogen: that is, an amount of hydrogen equal to **one-eighth the weight of the oxygen is nullified**. The Sulphur compounds are assumed to have their combustion heat nullified by the oxy-nitrogen ones.

What is Calorific value of Fuels ?

Another variant of the formula is as follows:

> **Calorific Value (kcal/kg. of Fuels)**
> **=**
> **7500 C + 33800 (H-O/8)**

C, H, O being fractions of a kilogram per kilogram of fuel.
To convert the **kilocalories per kilogram** values to **SI units** as widely used:
1kcal/kg. = 4.187 kJ/kg.
For example, a fuel of 10500 kcal/kg in SI units:
10 500 kcal/kg=10 500 × 4.187 kJ/kg = 44 000 kJ/kg

Type of Calorific value of Fuels

There are two type of Calorific value of Fuels :

1. Gross Calorific Value (GCV/HCV)
2. Net Calorific Value (NCV/LCV)

1. Gross Calorific Value (GCV) :

When **1 kg** of fuel is burned, product of combustion is cooled down to room temperature. Heat obtained by this complete combustion is known as higher calorific value. *Gross calorific value (GCV) assumes all vapor produced during the combustion process is fully condensed.*

2. Net Calorific Value (NCV/LCV):

When 1 kg of fuel is burned, heat obtained by this combustion is known as lower calorific value or net calorific value. Here product of combustion is not cooled down to room temperature, steam generated during combustion is not condensed and heat carried away by combustion is not recovered.

Net calorific value (NCV) assumes the water leaves with the combustion products without fully being condensed.

Type of Calorific value of Fuels

[LCV] = [HCV]- [Latent Heat of Water Vapor]

Since one part by weight of Hydrogen gives nine parts by weight of water. i.e.

$$H_2 + 1/2 \, O_2 = H_2O$$

Therefore,
[LCV] =[HCV]- [Weight of Hydrogen] x 9x Latent Heat of steam
       =[HCV]- [Weight of Hydrogen] x 9x 587

Typical Gross Calorific Values

The typical Gross Calorific Values of some for different fuels are as follows:

Gross Calorific Values of some Typical Fuels	
Kerosene	10277 kcal/kg
Diesel Oil	10,800 kcal/kg
Gasoline	10,516 kcal/kg
Coal Gas	8126 kcal/kg
Wood	47800 kcal/kg
Methanol	4732 kcal/kg
Hydrogen	34178 kcal/kg
Methane	13289 kcal/kg

Determination of Calorific Value

The Calorific value of solid & nonvolatile Liquid Fuels are determined by Bomb Calorimeter.

Principle:

A known amount of the fuel brunt in presence of excesses of O_2 and heat liberated is transferred to to a known amount of water. The calorific values of fuels then determined by applying the principle Of calorimetry i.e. *Heat gained = Heat loss.*

Calculation:

Let weight of the fuel sample taken   = m gm.
Weight of water in Calorimeter   = W gm.
Water equivalent of the Calorimeter, stirrer, bomb, thermometer   = w gm.
Initial temperature of water = t_1 ^{0}C
Final temperature of Water = t_2 ^{0}C
Specific heat of Water   = S
Gross Calorific values   = C cal/gm.
Heat gained by Water   = $W.\Delta t.S = W.(t_2-t_1)S$
Heat gained by Calorimeter   = $w.(t_2-t_1)S$
Heat liberated by the Fuels   = $m.\theta$ *cal*

Ignition wires

Oxygen Supply

Water jacket

Beckman thermometer

Stirrer motor

Inner bucket

Beckman thermometer

Stirrers

Inner Bucket

Ignition coil

Steel bomb
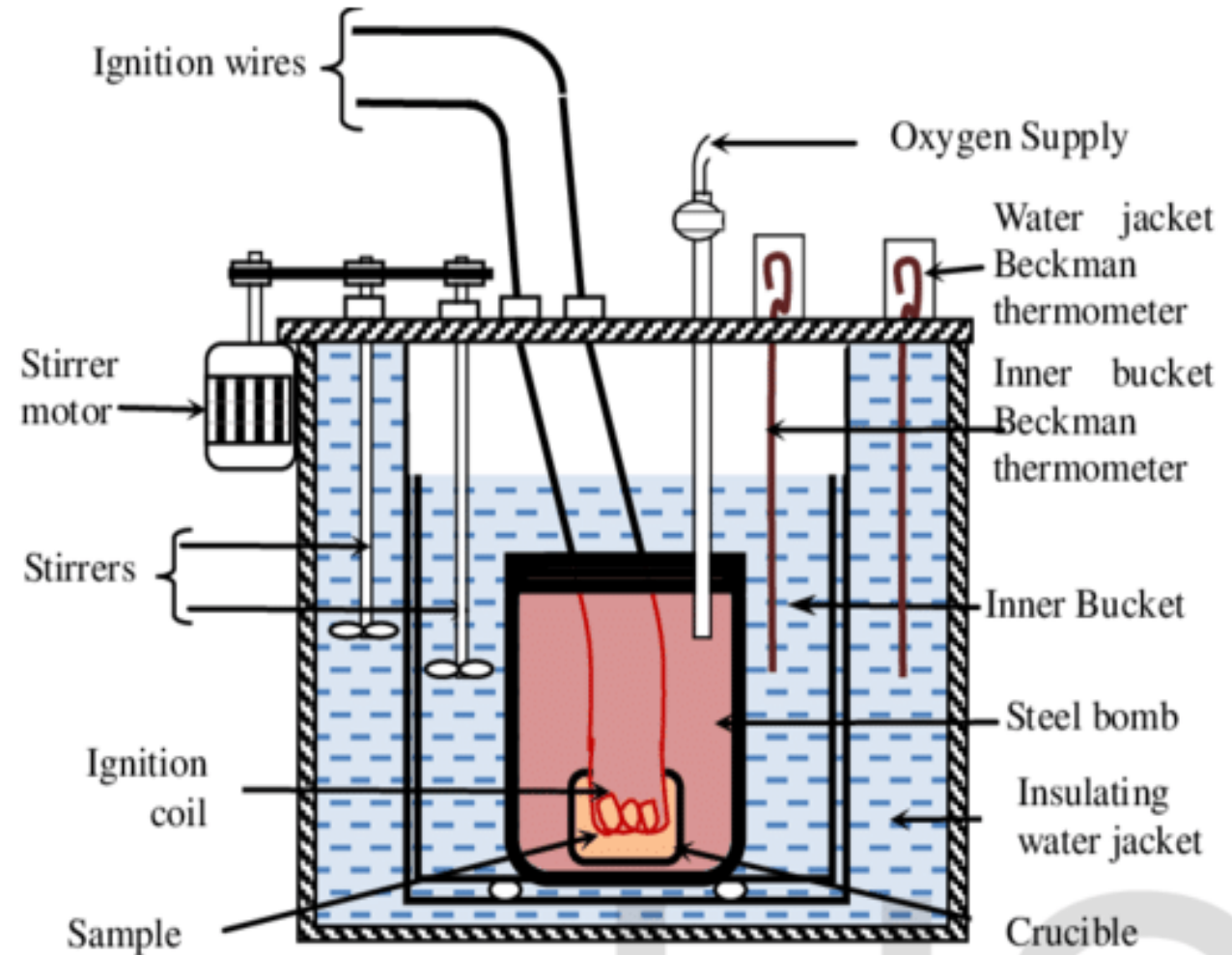
Insulating water jacket

Sample

Crucible

Fig. 1 Omega sieko Adiabatic Bomb Calorimeter

Determination of Calorific Value

Then according to the principle of Calorimetry we Can write the equation as thus:

[Heat Liberated by the Fuel]=[Heat gained by Water & Calorimeter]
Therefore,
mθ = (W+w)(t$_2$-t$_1$).S cal
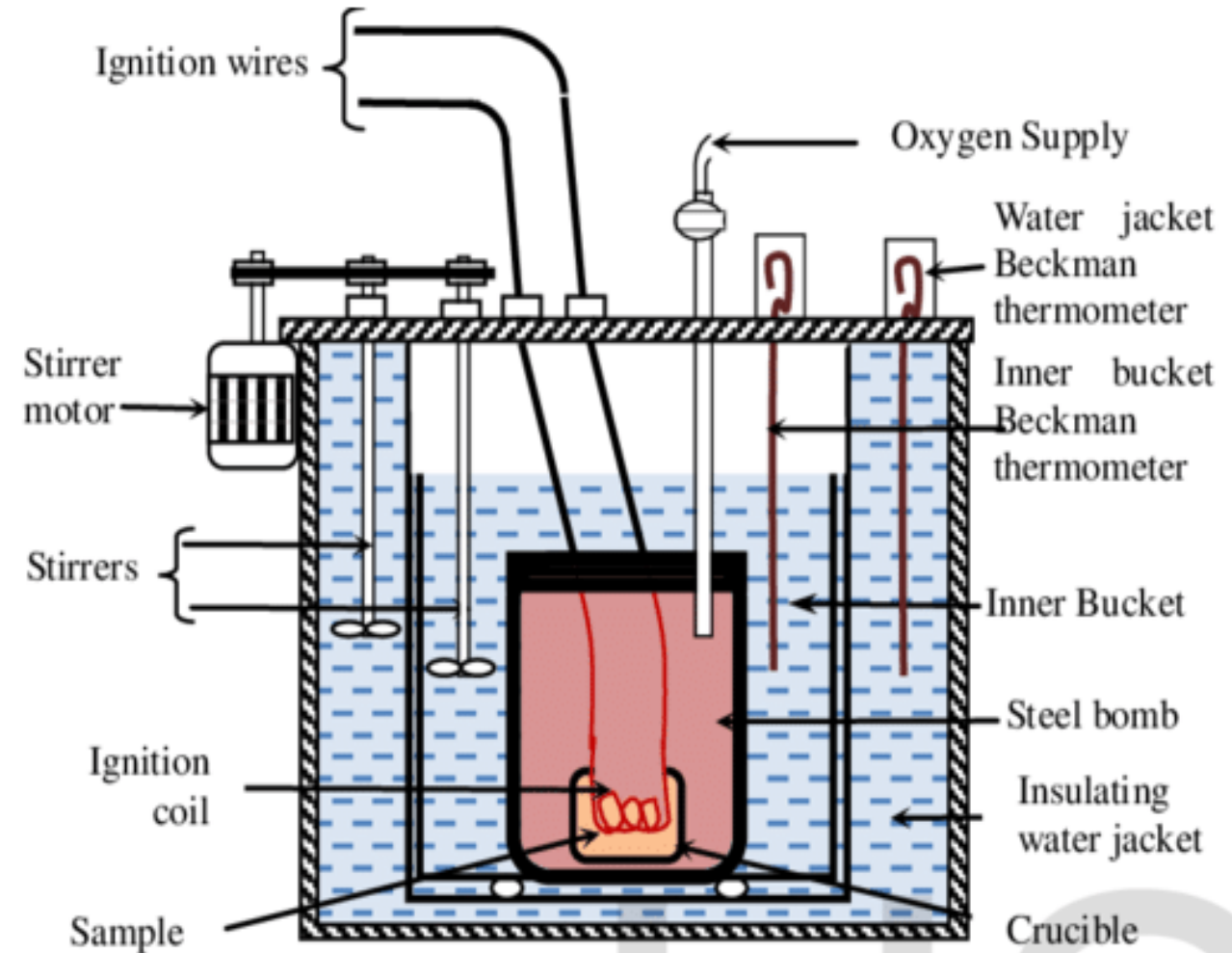
$\theta = \frac{(W+w)(t_2-t_1).S}{m}$ cal

N.B: The water equivalent of Calorimeter is determined by burning a fuel of known calorific value and use above equation.
Following may use for this purpose:
Benzoic Acid (HCV = 6,325 cal/gm.)
Naphthalene (HCV = 9,622 cal/gm)
Salicylic Acid (HCV = 5269 cal/gm.)

Fig. 1 Omega sieko Adiabatic Bomb Calorimeter

Determination of Calorific Value

Net Calorific Value (NCV):
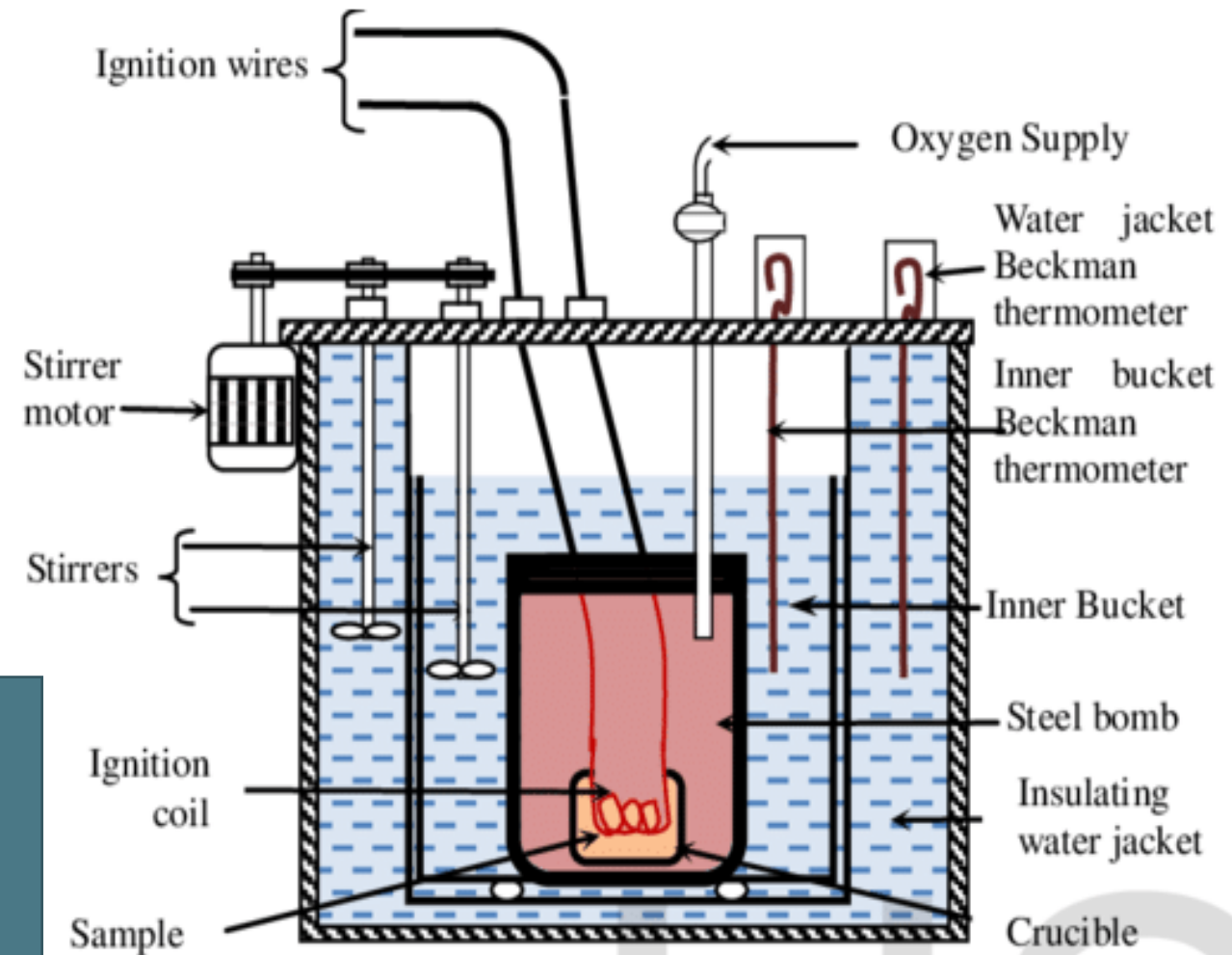
Let % of H in the Fuel   =   H
Weight of Water produced from the 1 gm. of the Fuel   =   9H/100 gm.
Heat liberated during condensation of steam
                 = 0.09.H x 587 cal.

Therefore,

NCV   =   GCV – Latent heat of water formed
      =   θ- 0.09.H x 587 cal/gm.

For the more accurate results the following correction has been recommended:
❖ Fuse Wire Correction
❖ Acid Correction &
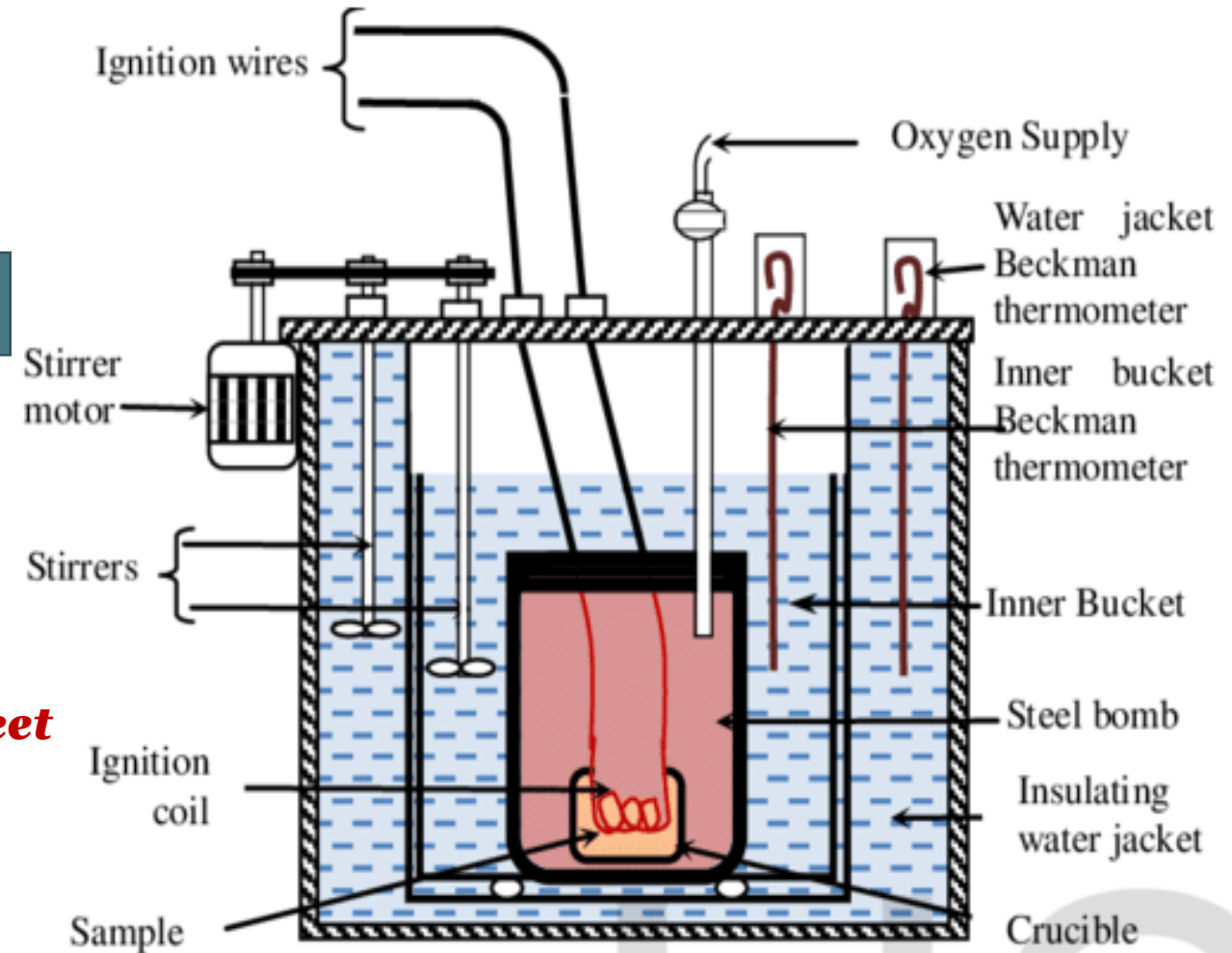❖ Cooling Correction

Fig. 1 Omega sieko Adiabatic Bomb Calorimeter

Determination of Calorific Value

This correction should add to the formula then Gross Calorific Value become:

$$GCV = \frac{(W+w)(t_2 - t1) + (\text{cooling Correction}) - (\text{Acid+Fuse Corrections})}{\text{Mass of the Fuels}}$$

N.B : Problem will be provided in the separate sheet

Ignition wires

Oxygen Supply

Water jacket

Beckman thermometer

Stirrer motor

Inner bucket

Beckman thermometer

Stirrers

Inner Bucket

Ignition coil

Steel bomb

Insulating water jacket

Sample

Crucible

Fig. 1 Omega sieko Adiabatic Bomb Calorimeter

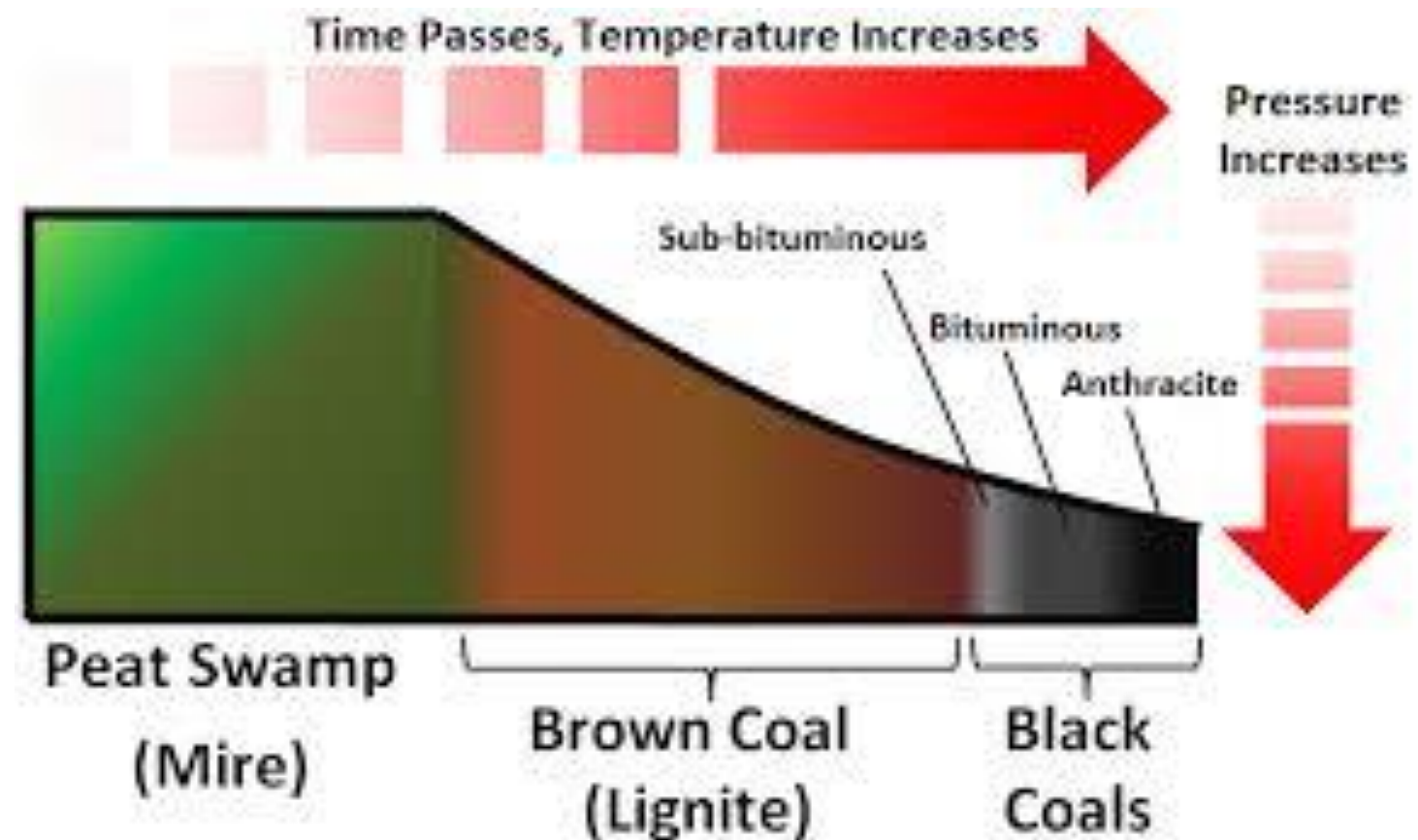# What is Coal

Coal is highly Carbonaceous Fossil Fuel that has been produced as a result of Vegetable debris Under favorable conditions of High temperature and pressure over million of years. It is chiefly composed of C, H, N and O besides noncombustible Inorganic matter.

How Coal is Formed ?

Coal is formed when dead plant matter decays into **peat** and is converted into **coal** by the **heat and pressure** of deep burial over **millions** of years.

Time Passes, Temperature Increases

Pressure Increases

Sub-bituminous

Bituminous

Anthracite

Peat Swamp (Mire)

Brown Coal (Lignite)

Black Coals

How Coal is Formed ?

The quality of each coal deposit is determined by:

- ❑ Types of vegetation from which the coal originated
- ❑ Depths of burial
- ❑ Temperatures and pressures at those depths
- ❑ Length of time the coal has been forming in the deposit

High temperatures and pressures caused physical and chemical changes in the vegetation, transforming it into coal.

Classification of Coal(s)

Coals are mainly classified based on their degree of coalification from the parent material, wood. When wood is converted into coal there is gradual increase in the concentration of CARBON (C) and decrease in % of oxygen & nitrogen. Coal is given a ranking depending upon the carbon content of the coal wood to anthracite.

Classification of Coal(s)

% of Carbon & Energy content of Coal(s)		
Type (s)	**%C**	**Energy Content(Btu/lbs)**
Lignite	30	5000-7000
Subbituminous	40	8000-10,000
Bituminous	50-70	11000-15000
Wood	90	14000

Selection of Coal

- ❑ **Calorific Value** should be high
- ❑ **Moisture** content should be low
- ❑ **Ash** content should be low
- ❑ **Sulphur & Phosphorous** Contents should be low
- ❑ **Size** of Coal should be Uniform

Analysis of Coal

In order to assess the quality of Coal, the following two types of analysis are made:

1. **Proximate Analysis**

2. **Ultimate Analysis**

1. **Proximate Analysis of Coal:**

❖ Determine only fixed Carbon, Volatile matter, Moisture & Ash
❖ Useful to find out heating value (GCV)
❖ Simple Analysis Equipment

Analysis of Coal

$$\% \text{ of moisture} = \frac{\text{Loss in Weight}}{\text{Wt. of Coal is taken}} \times 100$$

Excess moisture in Coal may cause the following:

❖ **Moisture is undesirable in Coal**

❖ **Lower the Calorific Value**

❖ **Cause difficulty in Handling**

❖ **Quench fire in the furnace**

Analysis of Coal

% of Volatile matter (VM) $= \dfrac{\text{Loss in Weight}}{\text{Wt. of Coal is taken}} \times 100$

Excess of VM in Coal cause the following:
- ❖ **Large proportion of Coal burnt like a gas**
- ❖ **Long Flame, High Smoke and Low heat Value**
- ❖ **High Volatile Matter (HVM) in coal is desirable in Coal Gas Manufacture.**

Analysis of Coal

$$\% \text{ of Ash} = \frac{\text{Weight of ash Left}}{\text{Wt. of Coal taken}} \times 100$$

High % of ash is undesirable and influence the following:

- ❖ Reduce the Calorific Value of Coal
- ❖ In Furnace, block the passes of air and reduce the combustion of Coal
- ❖ Major loss in heat value of Coal and form ash lump as well.

Analysis of Coal

% of Fixed Carbon = 100-[% of moisture +VM + Ash]

% of Fixed Carbon in Coals dealt the Followings:
- ❖ Fixed Carbon increase from Lignite to Anthracite
- ❖ Higher the % of Fixed C greater is its Calorific Value
- ❖ Fixed C % helps in the designing of the FURNACE and Fire-Box Chambers.

VM : Volatile Matter

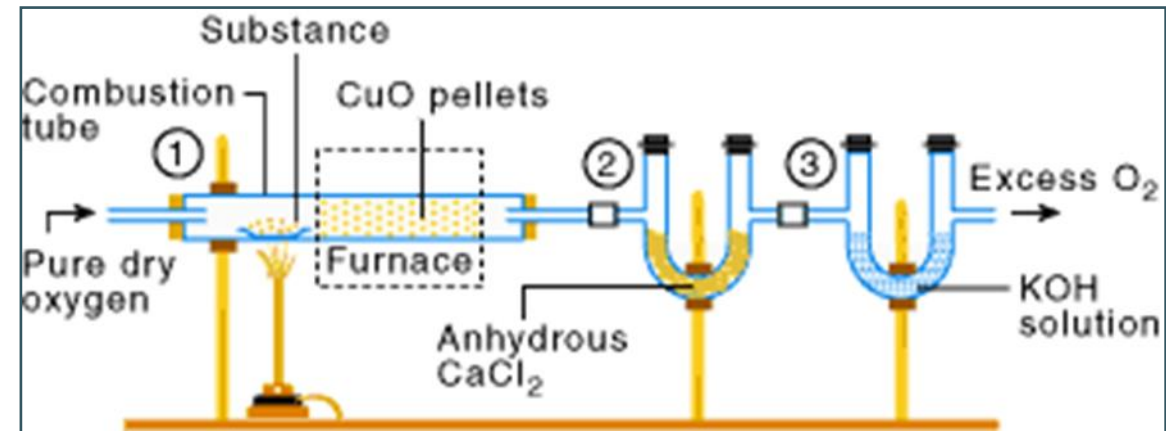## 2. Ultimate Analysis Of Coal :

The Ultimate Analysis determine all elemental composition of the Coal which include the estimation of C, H, S, N and O.
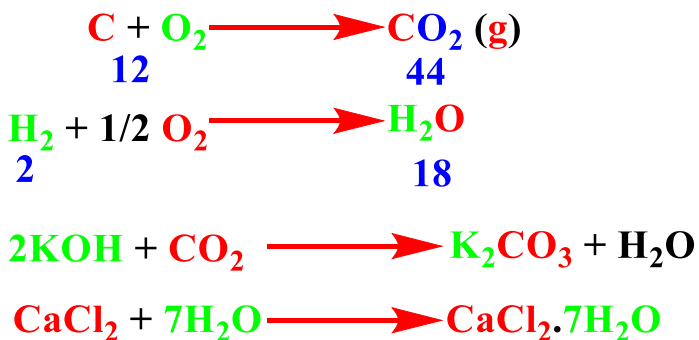
Estimation of Carbon(C) & Hydrogen(H):

- ❖ A Known amount of Coal is taken in a Combustion tube.
- ❖ C and H burnt in presence of excess Oxygen and Converted into CO_2 and H_2O.
- ❖ These gaseous products are absorbed in $CaCl_2$ and KOH tube of known weight.

2. Ultimate Analysis Of Coal :

Estimation of Carbon(C) & Hydrogen(H):

$$C + O_2 \longrightarrow CO_2 \text{ (g)}$$
$$12 \qquad\qquad 44$$

$$H_2 + 1/2\ O_2 \longrightarrow H_2O$$
$$2 \qquad\qquad\qquad 18$$

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

$$CaCl_2 + 7H_2O \longrightarrow CaCl_2.7H_2O$$

44 gm. Of CO2 contain = 12 gm of C

Y gm of CO2 contain $= \dfrac{12}{44} \times Y$

% of C $= \dfrac{12}{44} \times \dfrac{Y}{\text{Weight of Coal taken}} \times 100$
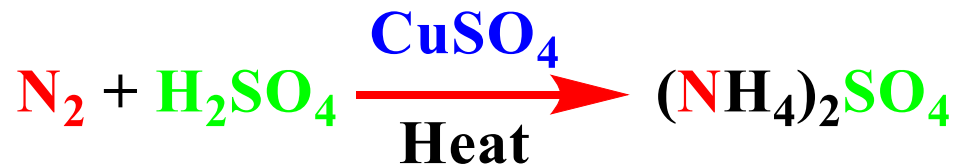
% of H $= \dfrac{2}{18} \times \dfrac{Z}{\text{Weight of Coal taken}} \times 100$
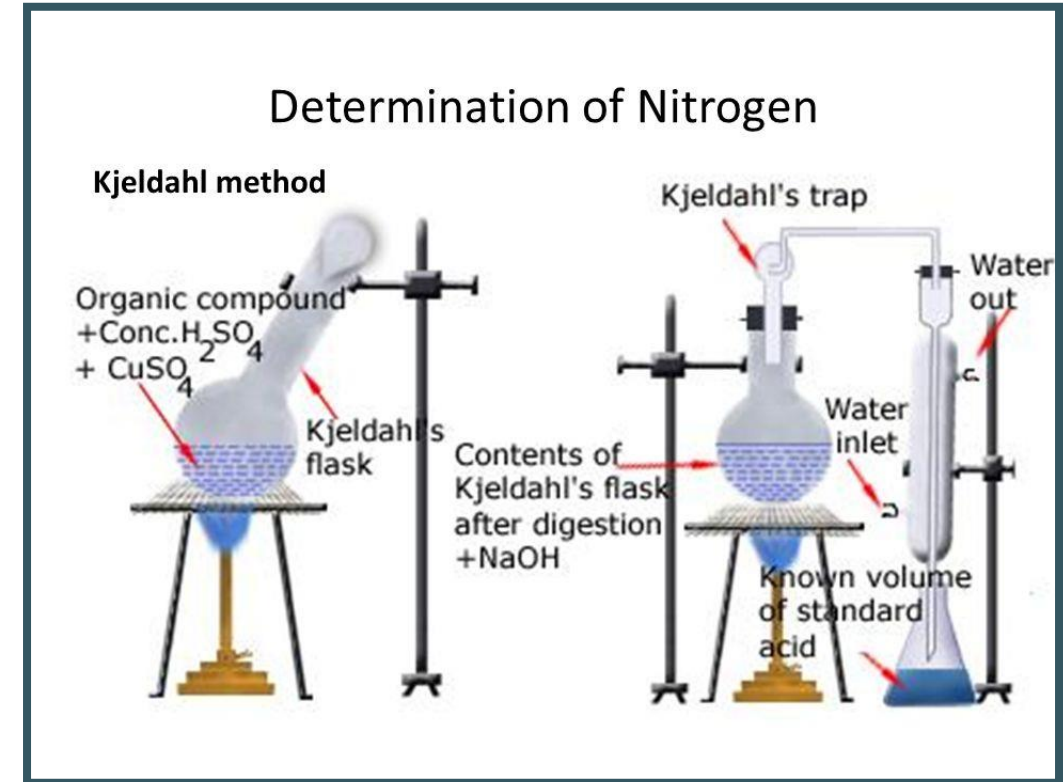
Analysis of Coal

2. Ultimate Analysis Of Coal :

Estimation of Nitrogen (N):

Nitrogen present in Coal is estimated by Kjeldhals methods. The known wt. of Coal has been taken digestion tube and treated with con. Sulphuric acid along with $CuSO_4$.(cat.) which turn the nitrogen content of coal in to $(NH_4)_2SO_4$ **(Fig. 1)**.

$$N_2 + H_2SO_4 \xrightarrow[\text{Heat}]{CuSO_4} (NH_4)_2SO_4$$

The content then then transferred into Kjeldhals flask and the solution is heated with excess of NaOH **(Fig. 1)**. The ammonia (NH_3(g) thus liberated and absorbed by known volume of a standard solution of an acid.

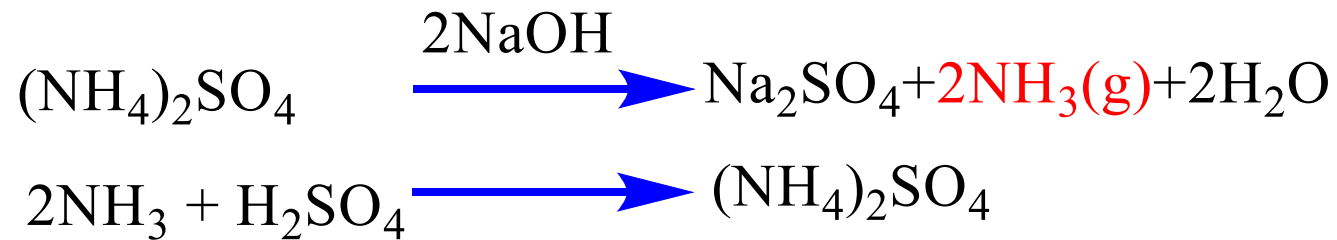**Fig.1 Kjeldhals method for estimation of N_2**

2. Ultimate Analysis Of Coal :

Estimation of Nitrogen (N):

$$(NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3(g) + 2H_2O$$
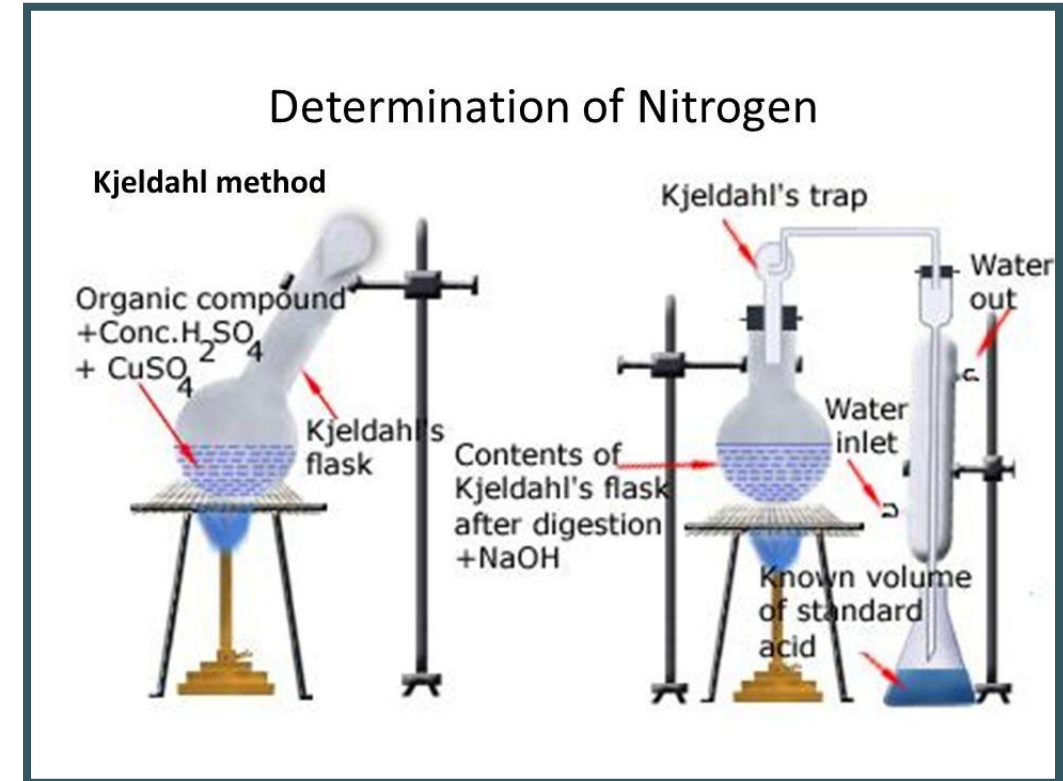
$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The unused acid is then determined by titrating with NaOH From the volume of acid used by ammonia liberated, the % of nitrogen can be calculated.

$$\% \text{ of } N = \frac{1.4V \times N}{W}$$

V = acid used in Titration(mL)

N = Normality of Std. Acid

W = Wt. of Sample (gm.)

Determination of Nitrogen

Kjeldahl method

Kjeldahl's trap

Organic compound +Conc.H_2SO_4 + $CuSO_4$

Kjeldahl's flask

Contents of Kjeldahl's flask after digestion +NaOH

Water out

Water inlet

Known volume of standard acid

Fig.1 Kjeldhals method for estimation of N₂

Analysis of Coal

2. Ultimate Analysis Of Coal :

Estimation of Sulphur:

$$\% \text{ of S} = \frac{\text{Wt.of BaSo4 obtaind x 32}}{\text{Wt.of whole Sample taken in Bomb}} \text{ x 100}$$

$$\% \text{ of O} = 100 - \% \text{ of [C+H+N+Ash]}$$

Ash is determined as prescribed in Proximate Analysis

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