LECTURE NOTES

ON

FUELS

ENGINEERING CHEMISTRY

B.Tech 1st year

By

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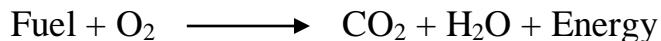## Assistant Professor

University of Lucknow | Centennial Celebrations
लखनऊ विश्वविद्यालय | शताब्दी उत्सव

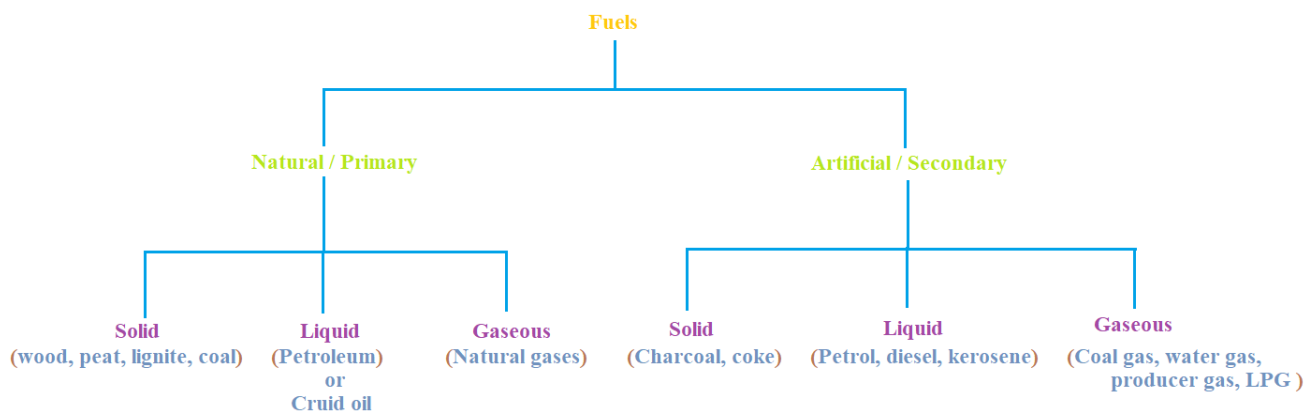# Faculty of Engineering & Technology

University of Lucknow

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Introduction

A fuel is a substance that contains carbon and hydrogen undergoes combustion in presence of oxygen to gives large amount of energy.

$$\text{Fuel} + O_2 \longrightarrow CO_2 + H_2O + \text{Energy}$$

Classification of Fuel

On the basis of occurrence fuel is classified into two categories; natural or primary fuels and artificial or secondary fuels.

i)   **Natural/primary fuels**: These fuels are naturally present.

ii)   **Artificial/ secondary fuels**: They are synthesized by primary fuels.

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                              Fuels
                                |
             _____|_____
            |                                       |
     Natural / Primary                       Artificial / Secondary
            |                                       |
    _____|_____                       _____|_____
   |        |        |                      |        |        |
 Solid    Liquid   Gaseous               Solid    Liquid   Gaseous
(wood,  (Petroleum) (Natural gases)    (Charcoal, (Petrol, diesel, (Coal gas, water gas,
peat,      or                           coke)     kerosene)     producer gas, LPG )
lignite, Cruid oil
coal)
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Characteristics of Good Fuel

i)   Fuel should have high calorific value.

ii)   Must have moderate ignition temperature.

iii)   Fuel should have low moisture content.

iv)   Available in bulk at low cost.

v)   Should not burn spontaneously.

vi)   Fuel should burn efficiently, without releasing hazardous pollutants.

vii)   Handling, storage and transportation should be easy.

Unit of heat

i)   **Calorie**: it is the amount of heat required to raise the temperature of 1 gram of water through one degree centigrade.

ii)   **British Thermal Unit (BTU):** it is the amount of heat required to raise the temperature of 1 pond of water to one degree Fahrenheit.

   1 B.T.U. = 252 cal = 0.252 kcal

   1 kcal = 3.968 B.T.U.

iii)   **Centigrade Heat Unit (CHU):** it is define as the amount of heat required to raise the temperature of 1 pond of water to one degree centigrade.

1 kcal = 3.968 B.T.U. = 2.2 C.H.U.

Calorific value

Calorific value of fuel can be define as the amount of heat evolved when one unit mass or volume of the fuel undergoes completely combustion in presence of oxygen.

i) **High or gross calorific value (HCV or GCV)**: it is defined as amount of heat evolve when one unit mass or volume of the fuel is completely burnt and combustible products are cooled to room temperature (25ºC or 77ºF).

ii) **Low or net calorific value (LCV or NCV)**: it is defined as amount of heat evolve when one unit mass or volume of the fuel is completely burnt and combustible products are permitted to escape. Therefore net calorific value is lower than gross calorific value.

LCV = HCV – latent heat of water vapour
LCV = HCV – mass of hydrogen × 9 × latent heat of steam (587 kcal/kg)

One part by mass of hydrogen produced nine parts by mass of water molecule. Therefore,

**LCV = HCV – H/100 × 9 × 587 kcal/kg**
H = percentage of hydrogen in fuel

Determination of calorific value

i) **Bomb calorimeter**

Bomb calorimeter is used to determine calorific value of solid and liquid fuels experimentally. A bomb calorimeter contains a cylindrical bomb made by stainless steel. Combustion takes place in this cylinder. The lid contains two stainless steel electrodes. Oxygen is supplied through oxygen valve for combustion. The electrode is attached with a small ring which supports nickel or stainless steel made crucible. The bomb is taken in a copper calorimeter which is surrounded by air and water jacket in order to prevent heat loss by radiation. The copper calorimeter also contains electrically operated stirrer and Beckmann's thermometer (take reading with temperature difference up to 0.01ºC.
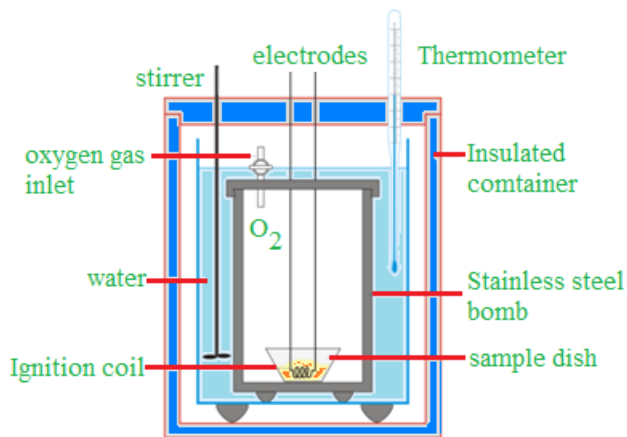
Working: In a crucible, a known amount of the fuel is placed in the nickel or stainless steel crucible which is supported by a ring. A fine magnesium wire touches the fuel sample, which is already connected to the electrodes. The bomb lid is lightly screwed and filled with oxygen at about 25 atm pressure, is placed in copper calorimeter containing a known amount of water. The electrically operated stirrer is driven and notes the initial temperature of water (T_1). After that both the electrodes are connected to a battery to complete the circuit. The fuel sample is burn and heat is liberated. To maintain the uniform temperature, water is continuously stirred and the final temperature (T_2) of water is noted.

Calculation:

Mass of fuel (solid or liquid)= x g

Mass of water taken = W g

Water equivalent of calorimeter = w g

Initial temperature of water in calorimeter = T_1 K

Final temperature of water in calorimeter = T_2 K

High or gross calorific value = $\dfrac{(W+w)(T2-T1)}{x}$ **cal/g**

LCV = HCV – H/100 × 9 × 587 kcal/kg

H = percentage of hydrogen in fuel

Corrections:

$$\text{HCV or GCV} = \frac{(W+w)(T2-T1-Tc) - (Cs+Cn+Cf+Cc)}{x}$$

Where

T_c = cooling corrections

Cs = Corrections for sulphuric acid (H_2SO_4)

Cn = Corrections for nitric acid (HNO_3)

Cf = Corrections for fuse wire

Cc = Corrections for cotton thread

ii) **Theoretical calculation by Dulong's formula**:

The theoretical calculation of calorific value of a fuel can be approximately calculated by Dulong's formula, based on the percentage of the constituents (C, H, O and S) present in the fuel.

As per Dulong's formula

$$\text{HCV} = \frac{1}{100} \left[8080\, C + 34500 \left(H - \frac{O}{8} \right) + 2240\, S \right] \text{kcal/kg}$$

Where, C, H, O and S are percentage of carbon, hydrogen, oxygen and sulphur present in fuel. In above formula the oxygen is assumed to be present in combined form with hydrogen or in form of water (H_2O).

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

2g   16g   18g

1g   8g   9g
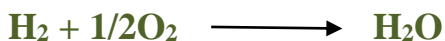
Total mass of hydrogen in fuel – fixed hydrogen

Total mass of hydrogen in fuel – (1/8) mass of oxygen in the fuel

∴ 8 part of oxygen combine with 1 part of hydrogen to form H_2O.

Fixed hydrogen $= \dfrac{Mass\ of\ oxygen\ in\ the\ fuel}{8}$

Then the amount of hydrogen available for combustion

= total mass of hydrogen in fuel – fixed hydrogen

= [H-O/8]

LCV = HCV – H/100 × 9 × 587 kcal/kg

Analysis of Coal

The quality of coal can be analyzed by two analysis; proximate and ultimate analysis.

Proximate analysis:

In this analysis moisture, volatile matter, ash and fixed carbon can be determined.

Moisture: A known amount of finely powdered air-dried coal sample is taken in crucible. The crucible is placed inside an electric hot air-oven, at 105° to 110°C for 1 hour. The crucible is then taken out, cooled in desiccators and weighed. Difference in the weight of sample gives the information about the weight loss due to removal of moisture.

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

Lesser the amount of moisture content, better the quality of fuel.
Volatile matter: The moisture free coal sample is taken in a crucible, covered with a lid and placed in muffle furnace (electric furnace) at 950°C for 7 minutes and then remove the crucible from the oven and cooled first in air, then cooled in a desiccator and weighed again. Loss in weight is due to presence of volatile matter in coal sample.

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

Low quantity of volatile matter, better the quality of a coal.
Ash: The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700-750°C for an hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed again. The process of heating, cooling and weighing are repeated until a constant weight is not obtained. The residue is reported as ash on percentage-basis.

$$\% \text{ of ash} = \frac{\text{weight of residue left}}{\text{weight of dry coal taken}} \times 100$$

Ash is non-combustible substance which reduces the calorific value of a coal. Therefore, low quantity of ash contents, better the quality of a coal.

Fixed carbon: The fixed carbon percentage is determined by following equation

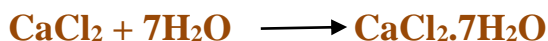**% of fixed carbon = 100 − (% of moisture + % of volatile matter + % of ash)**
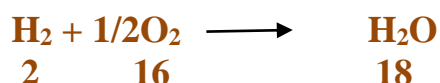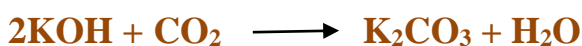
Greater the calorific value, higher the % of fixed carbon.

Ultimate analysis:

Ultimate analysis is involving the measurement of C, H, N, S, and O.

Carbon and hydrogen: In a combustion apparatus, about 1-2 gram of coal sample is burnt in a current of oxygen to convert C and H into CO_2 and H_2O respectively. The gaseous products CO_2 and H_2O are absorbed in KOH and $CaCl_2$ tubes of known weights, respectively. The increase in weights of these (KOH and $CaCl_2$) are then determined.
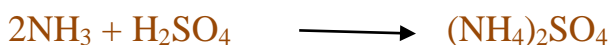
Calculation:

$$C + O_2 \longrightarrow CO_2$$
12   32   44

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

$$H_2 + 1/2O_2 \longrightarrow H_2O$$
2   16   18

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

$$\textbf{% of carbon} = \frac{\textbf{Increase in weight of KOH} \times 12}{\textbf{weight of coal sample taken} \times 44} \times \textbf{100}$$

$$\textbf{% of hydrogen} = \frac{\textbf{Increase in weight of CaCl2} \times 2}{\textbf{weight of coal sample taken} \times 18} \times \textbf{100}$$

Nitrogen: In Kjeldahl's flask add accurately weighed powdered coal and heated with concentrated H_2SO_4 and K_2SO_4 as a catalyst. The solution becomes clear when all the nitrogen is converted into ammonium sulphate then it is treated with excess of NaOH which convert ammonium sulphate into ammonia; the liberated ammonia is distilled over and absorbed in a known volume of standard (N/10) H_2SO_4 solution. From the volume of H_2SO_4 used by liberated ammonia, the percentage of Nitrogen in coal, calculated as follows:

$$N_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{NaOH} 2Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The volume of unused H_2SO_4 is then determined by titrating against standard NaOH solution (N/10)

Calculation:

The amount of H_2SO_4 required to neutralize ammonia evolve from coal is calculated as follows:

$$\text{Amount of acid} = \text{N/10 } V_1 - \text{N/10 } V_2$$
$$= 0.1 \ (V_1 - V_2) \text{ mili equivalents}$$
$$= \frac{0.1 \ (V_1 - V_2)}{1000} \text{ equivalents}$$

Thus,

$$\text{Weight of N} = \frac{0.1 \ (V_1 - V_2)}{1000} \times 14$$

V_1 = Volume of standard H_2SO_4 (N/10) solution
V_2 = Volume of standard NaOH (N/10) solution
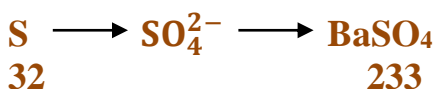Thus,

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

$$= \frac{0.1 \frac{(V_1 - V_2)}{1000}}{1} \times 14 \times 100$$

$$\% \text{ of nitrogen} = 0.1 \ (V_1 - V_2) \times 1.4$$

Sulphur: A known amount of coal sample is burnt in bomb calorimeter in presence of oxygen. After that, sulphur present in coal is converted into SO_2 and SO_3. The ash obtained from the bomb calorimeter, is extracted with dil. HCl. The washings (acid extracts) are treated with Barium chloride solution and the sulphates are precipitate as Barium sulphate. This precipitate is filtered, washed, dried and heated to obtain constant weight.

Calculation:

$$\underset{32}{S} \longrightarrow SO_4^{2-} \longrightarrow \underset{233}{BaSO_4}$$

$$\frac{\text{weight of sulphur}}{\text{weight of BaSO4}} = \frac{\text{atomic weight of sulphur}}{\text{molecular weight of BaSO4}}$$

$$\text{Weight of sulphur} = \frac{32}{233} \times \text{weight of BaSO}_4$$

Thus,

$$\% \text{ of sulphur} = \frac{\text{weight of BaSO4 obtained} \times 32}{\text{weight of coal taken in bomb calorimeter} \times 233} \times 100$$

Ash: Percentage of ash calculated by method given in proximate analysis.

Oxygen: It is calculated by subtracting the sum of total % of carbon, hydrogen, nitrogen, sulphur and ash from 100.

Calculation:

% of oxygen = 100 − [% carbon + % hydrogen + % nitrogen + % sulphur + % ash]

Biogas

It is formed by the bacterial degradation of biomass under anaerobic condition (airtight digesters). Biogas mainly contains methane (50-70%), carbon dioxide and trace amount of water, sulfur and hydrogen sulphide.

Biogas generation

The biogas generated by anaerobic digestion of organic waste (animal waste, plant residue, crops) in biogas plant, mainly involve three steps: hydrolysis, acid formation and gas production.

Hydrolysis: In this step, macromolecule like fats, proteins, carbohydrates are broken down through hydrolysis into fatty acids, amino acids and sugars respectively.

Acid formation: in this step, fatty acids, amino acids and sugars are fermented by acid producing bacteria under anaerobic condition into acetic acid, carbon dioxide and hydrogen.

Gas production: In this step, methanogenic bacteria produce methane either by fermenting acetic acid to form methane and carbon dioxide or by reduction of carbon dioxide into methane.
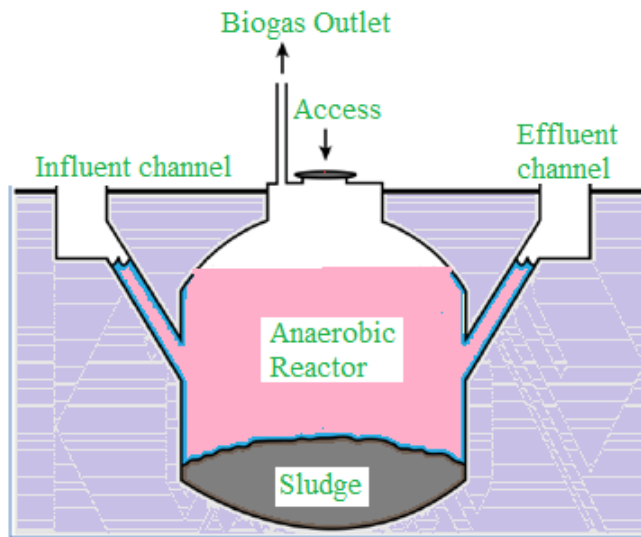
Advantage of biogas

i)   Produce organic waste
ii)   Burn without smoke
iii) Renewable
iv)   Help to reduce waste.

Disadvantage of biogas

i)   Methane is health hazardous.
ii)   Not efficient like fossil fuel.