Chapter-V
Energy Sources

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Syllabus of Engineering Chemistry (Theory)

Module No	Module Description	Hrs.
5	**Energy sources:** Fuels-Definition. Calorific value - Definition of LCV, HCV. Measurement of calorific value using bomb and Boy's calorimeter – problem solving. Coal analysis-proximate and ultimate analysis and significance. Stoichiometric combustion reactions of C, CH_4 etc. Calculation of minimum quantity of air by volume and by weight-Numerical problems. Knocking and chemical structure, octane number and cetane number and their importance; Alternate fuels and Fuel additives. Biodiesel-synthesis, advantages and commercial applications.	8

Text Books / Reference Books

1) O. G. Palanna, Engineering Chemistry, Tata McGraw Hill Education

2) Jain P. C. and Monica Jain, Engineering Chemistry, Dhanpat Rai Publishing Company Ltd.

3) Shashi Chawala, Chemistry, Dhanpat Rai & Co. New Delhi

4) Dara S. S., Umare S. S., Engineering Chemistry, S. Chand & Company Ltd.

Fuel

A fuel can be defined as any combustible substance which during combustion gives large amount of industrially or domestically useful heat.

A chemical fuel can be defined as any combustible substance containing "Carbon" as the main constituent which during combustion gives large amount of industrially or domestically useful heat.

Classification of Fuel

Fuel can be classified:

a) On the basis of their occurrence
b) On the basis of physical state of aggregation

On the basis of their occurrence
a) Natural or Primary Fuels: Fuels which are found in nature are called Natural Fuel. For e.g.- Wood, Coal, Petrol, Natural Gas.
b) Artificial or Secondary Fuels: Fuels which are prepared from artificial fuels are called Artificial Fuels.
For e.g.- Coke, Charcoal, Kerosene oil, Coal gas, Petrol.

On the basis of physical state
On the basis of physical state fuels are of three types i.e Solid, Liquid and Gas.
Solid Fuel: Charcoal, Coal, Wood, Coal.
Liquid Fuel: Petrol, Kerosene, Diesel.
Gaseous Fuel: Natural Gas (Methane), Bio Gas, Water Gas, Oil Gas.

Characteristics of a good Fuel

High Calorific Value:
Calorific value is the total quantity of heat liberated from the combustion of unit mass of fuel in air/oxygen. A good fuel should have high calorific value.

Moderate ignition temperature:
Low ignition temperature can cause fire hazard during storage and transportation of fuel. On the other hand fuel with high ignition temperature is safe for storage, handling & transportation but there will be difficulty in the ignition of the fuel. So a good fuel should have moderate ignition temperature.

Low moisture content:
The moisture present in the fuel reduces the heating value so, a good fuel should have low moisture content.

Low non combustible matter content:
The non combustible matter (Ash, Clinker) present in the fuel reduces the heating value so, a good fuel should have low non combustible content.

Moderate rate of combustion:
If the rate of combustion is low then a part of heat liberated may be radiated instead of raising the temperature hence high temperature may not be attained. On the other hand high rate of combustion may lead to abrupt combustion. So in order to have constant heat supply a good fuel should have moderate rate of combustion.

No harmless combustion product:
Fuel should not produce combustion products (like CO, SO_2, H_2S) which may be harmful to the atmosphere.

Low Cost
Easy to transport
Low storage cost

Calorific Value

The total quantity of heat liberated from the combustion of unit mass (or unit volume) of the fuel in air/oxygen.

Unit of Heat

Calorie: It is defined as the total amount of heat required to raise the temperature of 1 gm of water through 1° C.

Kilocalorie: It is defined as the total amount of heat required to raise the temperature of 1 Kg of water through 1° C.

1 Kcal = 1000 cal

British Thermal Unit (B.Th.U.): It is defined as the total amount of heat required to raise the temperature of 1 pound of water through 1° F.

Centigrade Heat Unit (C.H.U.): It is defined as the total amount of heat required to raise the temperature of 1 pound of water through 1° C.

Relationship between Units of Heat

1 Kcal = 3.968 B.Th.U. = 2.2 C.H.U

Higher Calorific Value (HCV) / Gross Calorific Value (GCV)

It is the total amount of heat liberated when unit mass or unit volume of fuel has been burnt completely and the products of combustion are cooled to room temperature.

Hydrogen is present in all most all the fuels & when the calorific value of the fuel is determined experimentally, hydrogen is converted into steam. If the product of combustion are condensed to the room temperature, the latent heat of condensation of steam also gets included in the measured heat, which is then called Gross Calorific Value or Higher Calorific Value.

Lower Calorific Value (LCV) / Net Calorific Value (NCV)

It is the net heat produced when unit mass or unit volume of fuel has been burnt completely and the products of combustion are allowed to escape.

In actual use of any fuel, the water vapour and moisture etc. escape as such along with hot combustion gases. Since they are not condensed. Hence a lesser amount of heat is available.

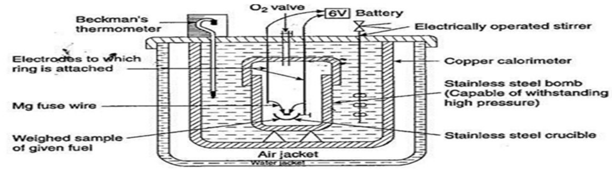
LCV = HCV – Latent heat of water vapour formed
(1 part by mass of hydrogen produces 9 part by mass of water)
LCV = HCV – 9 x Mass of Hydrogen x Latent Heat of steam

LCV = HCV – 0.09 * H * 587

Latent heat of steam = 587 Cal/gm or Kcal/Kg or 1060 B.Th.U/Ib of water vapour formed at room temperature (15° C)

Determination of Calorific Value by Bomb Calorimeter

Principal:
A known mass of the fuel is burnt and the quantity of heat produced is absorbed by water & measured, then the quantity of heat produced by burning unit mass of fuel is calculated.



Construction:

Bomb colorimeter consist of a stainless steel bomb in which the combustion of fuel takes place. It has two stainless steel electrodes connected with a 6V battery and a oxygen inlet valve.

To one of the electrode a small ring is attached where a stainless steel crucible is kept and a fuse wire of Magnesium is connected to both the electrode. A cotton thread is tied at one end of the fuse wire while other end remain in contact with fuel in the stainless crucible.

The bomb is kept in a copper calorimeter having known quantity of water. The copper calorimeter is surrounded by air-jacket and water-jacket to prevent loss of heat due to radiation.

The copper calorimeter is provided with an electrical stirrer and a Beckmann's thermometer.

Working:

1 gm of fuel is taken in the stainless steel crucible, the crucible is supported over the ring. A Magnesium fuse wire is connected to both the electrodes & a cotton thread is tied at the one end of fuse wire while other end remain in contact with the fuel in the crucible.

The bomb is kept in copper calorimeter having known quantity of water. Initial temperature of water is noted **(T_1° C).**

The ignition of fuel is initiated by passing high voltage across the fuse wire & a cotton thread of known mass & length is tied at one end of fuse wire while other end remain in contact with fuel in stainless steel crucible through 6V battery.

Short circuit triggers the combustion of fuel. The fuel sample burns and heat is liberated which is transferred to water. Stirring is continued and maximum temperature attained is noted **(T_2° C)**

Calculation:

HCV of Fuel (L) = $(W+w)(T_2-T_1)$/weight of fuel
(cal/gm or Kcal/kg)

LCV of Fuel (L) = HCV – 0.09 * %H * Latent heat of steam

LCV of Fuel (L) = HCV – 0.09 * %H * 587 (calories)

Corrections: For more accurate results following corrections are made.

i) Fuse wire corrections: Heat liberated & measured includes heat given by the ignition of fuse wire due to short circuit. Hence it should be deducted.

ii) Acid corrections: Fuel containing Sulphur, Nitrogen are oxidised under high pressure. Formation of acid is exothermic reaction so, measured heat also includes the heat given out during acid formation. Hence it should be deducted.

iii) Cotton Thread corrections: Cotton thread is used for the ignition of fuel, so its burning also generates heat & it should be deducted.

iv) Cooling corrections: Time taken to cool the water in calorimeter from maximum temperature to room temperature is noted. From the rate of cooling (dT/minute) and actual time taken for cooling (t min.) the cooling correction of (dT*t) is added to the rise in temperature.

HCV / GCV =

$$\frac{(W+w)[(T2-T1)+Cooling\ correction]-[Fuse\ wire\ correction+Acid\ Correction+Cotton\ Thread\ Correction]}{Weight\ of\ Fuel}$$

(cal/gm or Kcal/kg)

Calculation of GCV & LCV by Dulong's Formula using Ultimate Analysis data for Coal

GCV =
1/100 [8080 %C + 34500 (%H- %O/8) + 2240% S] (cal/gm)

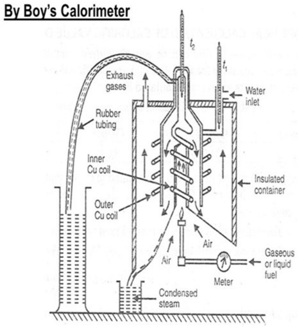
LCV = GCV – 0.09 * H * 587 (cal/gm)

<u>**Numerical: Annexure-1**</u>

Determination of Calorific Value by Boy's Calorimeter

The calorific value of gaseous or volatile liquid fuels is measured by Boy's Calorimeter.

By Boy's Calorimeter



Principle
The principal is to burn the gas at a constant rate in a vessel & the entire amount of heat produced is absorbed by water which is also flowing at constant rate.

From the volume of gas burnt, the volume of water collected and mean rise in temperature of water, the calorific value of gaseous fuel can be calculated.

Construction & Working:
The Boy's calorimeter consist of a burner situated in chimney which is the centre of the annual vessel.

The lower portion has a tank where the water condensate from the product of combustion is collected & removed through side tube.

The product of combustion moves upwards to the chimney and deflected downward by water cooled head. The gas is again deflected upward and passed out through number of holes in the lid of calorimeter.

The water flows from outer coil to the inner coil and the temperature of inlet and outlet water are measured with different thermometers.

The difference in inlet & outlet water, amount of water condensed from the products of combustion, atmospheric pressure & gas pressure are recorded.

The temperature of effluent gas, ambient air and the inlet gas are recorded.

Calculation:

HCV of Fuel (L) = W * (T_2-T_1)/volume of gas burnt (cal/gm or Kcal/kg)

LCV of Fuel = GCV – m/V (cal/gm or Kcal/kg)

V = Volume of gas burnt
m = Weight of steam condensate
W = Weight of cooling water passed in time 't'

Coal

Coal is a fossil fuel found under the earth crust commonly known as coal beds or coal seams. It is formed from the dead plants and animals by a process called coalification.

Dead plants and animals are first converted into peat which in turn is converted into lignite, after that bituminous coal and then anthracite.

Coal is classified on the basis of % of carbon which is known as “Rank of Coal”.

S.No.	Coal	% Carbon	Rank
1	Peat	57	Low
2	Lignite	67	⇩
3	Bituminous Coal	83	
4	Anthracite	93	High

Analysis of Coal

The analysis of coal done to determine the coal’s energy value. Coal’s heating value is a important factor for deciding the usage of coal.

Analysis of coal done by two methods:

a) Proximate Analysis
b) Ultimate Analysis (Elemental Analysis)

Proximate Analysis of Coal

Proximate analysis gives information about moisture content, Volatile content, ash content, sulphur content and Fixed carbon.

Moisture Content:
Moisture Content quenches the fire and it evaporates during the burning of coal & takes the liberated heat in the form of latent heat evaporation & reduces the effective calorific value.

Determination of Moisture Content:

The weight of empty crucible is taken and 1 gm of coal sample is taken in it (W_1 gm).

The crucible is kept in a oven at 105-110° C for a period of 60 min. The crucible is then withdrawn from the oven & kept in a desiccator for cooling. After cooling weight of the crucible is again taken (W_2 gm).

% Moisture Content =
$(W_1\text{-}W_2)$*100/Weight of coal sample

% Volatile Content:

The volatile matter may be combustible gases (like H_2, CO, CH_4 & other lower hydrocarbons) and non-combustible gases (like CO_2 & N_2).

The presence of volatile matter is undesirable since they don’t add to the heating value. Coal with high volatile content burns with long flame, high smoke & low calorific value.

Determination of Volatile Content:

The moisture free coal sample is kept in the muffel furnace at 925+/-20° C for 7 min. The crucible is taken out & air cooled inside the desiccator and weighed (W_3 gm).

% Volatile Content =
$(W_1\text{-}W_3)$*100/Weight of coal sample

% Ash Content:

Ash is a non-combustible & useless which is left behind when all the combustible substance is burnt off & reduces the calorific value

% Ash Content =
Weight of Ash formed *100/Weight of coal sample

% Fixed Content:

After the determination of moisture, volatile content and ash content the remaining matter is Fixed Carbon. Higher % of Fixed carbon, greater is the calorific value.

% Fixed Carbon =
100 - %(moisture content + volatile content + ash content)

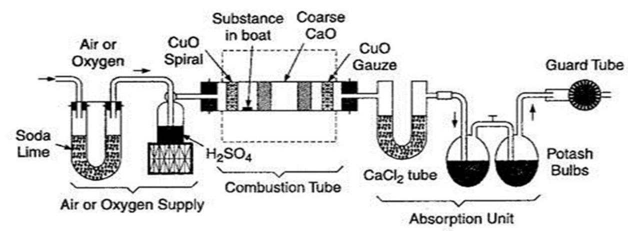
Numerical on Proximate Analysis

Ultimate/Elemental Analysis of Coal

Determination of Carbon & Hydrogen:

% of carbon is the basis for the classification of coal, higher the %C better is the quality of coal.

% of hydrogen is associated with the volatile matter and hence it affects the usability of coal, lower the %H better is the quality of coal.



A known quantity of coal (about 1-2 gm) is burnt in the current of dry oxygen when carbon and hydrogen in coal are oxidised to CO_2 & H_2O respectively.

A gaseous product of combustion are passed through $CaCl_2$ tube and potash bulbs.

The $CaCl_2$ tube contains weighted amount of anhydrous $CaCl_2$ absorbs water.
$CaCl_2 + 7\ H_2O \longrightarrow CaCl_2.7.H_2O$

The Potash tube contains weighted amount of KOH absorbs CO_2.
$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$

$C + O_2 \longrightarrow CO_2$
$H_2 + ½\ O_2 \longrightarrow K_2CO_3 + H_2O$

$$\frac{Weight\ of\ C}{Increase\ in\ weight\ of\ KOH} = \frac{Atomic\ weight\ of\ C}{Mol.Weight\ of\ CO_2}$$

$$\%\ C = \frac{Weight\ of\ C\ *100}{Weight\ of\ CO_2}$$

$$\%C = \frac{Increase\ in\ weight\ of\ KOH\ *Atomic\ weight\ of\ C\ *100}{Weight\ of\ coal\ *Mol.Weight\ of\ CO_2}$$

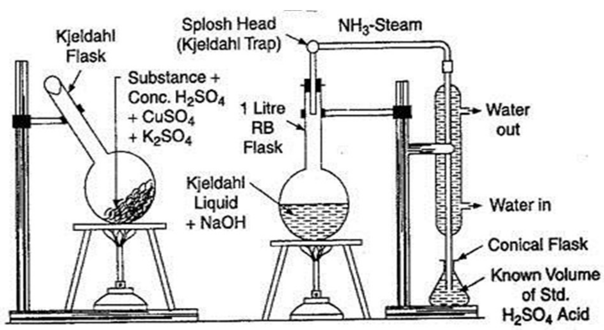
$$\%C = \frac{Increase\ in\ weight\ of\ KOH\ *12*100}{Weight\ of\ coal\ *44}$$

Similarly

$$\%H = \frac{Increase\ in\ weight\ of\ CaCl2\ *2*100}{Weight\ of\ coal\ *Mol.Weitht\ of\ H2O\ (18)}$$

Determination of Nitrogen:

Nitrogen is an inert and non-combustible gas & hence is presence is undesirable. Thus a good quality of coal should have very less/no Nitrogen content.



A known quantity of powdered coal (**about 1 gm**) is heated with H_2SO_4 along with K_2SO_4 and $CuSO_4$ in Kjeldahl's flask.

When a clear solution is obtained i.e. whole nitrogen is converted into $(NH_4)_2SO_4$ then it is treated with excess of NaOH to liberate NH_3.

The NH_3 produced is distilled over & absorbed in a known volume (V_1) of 0.1 N H_2SO_4 solution.

$N_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2\,H_2O$

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

The unused H_2SO_4 is determined by titrating against 0.1 N NaOH solution. Let V_2 ml of 0.1 N NaOH was required to neutralize excess acid.

Amount of H_2SO_4 used to neutralize liberate NH_3 =

$$\frac{0.1\,(V1 - V2)}{1000} \text{ equivalent}$$

Weight of N = $$\frac{0.1\,(V1 - V2) * 14}{1000}$$

% N = $$\frac{\text{Weight of N} * 100}{\text{Weight of Coal sample taken}}$$

$$\%\,N = 0.1\,(V_1 - V_2) * 1.4$$

Determination of Sulphur:

Sulphur increases the calorific value, on oxidation it produces harmful and corrosive SO_2 and SO_3. Oxides of sulphur is harmful for the atmosphere. Sulphur is present to an extent of 0.5 - 3%. Presence of sulphur is undesirable in coal.

A known amount of coal (**W1gm**) is burnt completely in bomb calorimeter in the current of oxygen, by which sulphur is oxidised to sulphates.

The ash from the bomb calorimeter is extracted with dil. HCl. The acid extracted is treated with $BaCl_2$ to precipitate sulphate as $BaSO_4$.

The $BaSO_4$ is filtered, washed, dried and heated to constant weight.

$S + O_2 \longrightarrow SO_4^{2-} \longrightarrow BaSO_4$

32   233

$$\frac{\text{Weight of } S}{\text{Weight of } BaSO_4} = \frac{\text{Atomic weight of } S}{\text{Mol.Weight of } BaSO_4}$$

Let the weight of $BaSO_4$is W2 gm.
Weight of S = 32 * W2 / 233

% S =
Weight of Sulphur * 100
____
Weight of Coal sample taken in Bomb calorimeter

% S =
W2 * 32 * 100
____
W1 * 233

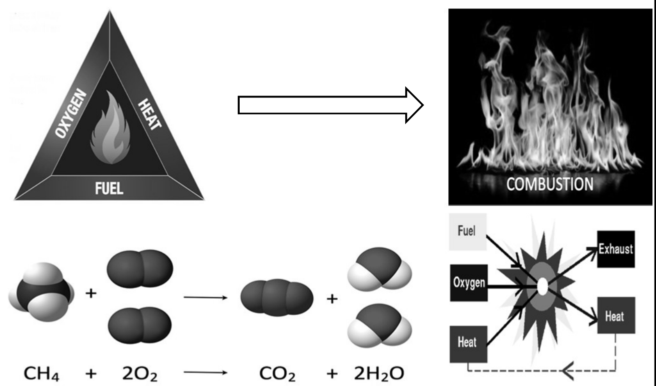
Determination of Oxygen:

Oxygen is present in combined form with hydrogen in coal and thus hydrogen available for combustion is lesser than the actual one.

High Oxygen content coals have high moisture & low calorific value. Thus a good quality coal should have low % of oxygen.

% Oxygen= 100 - % (C + H + N + S + Ash)

Combustion



Types of Combustion:

The combustion is of three types-

Rapid Combustion
Spontaneous Combustion
Explosion

Rapid Combustion: Combustion in which a substance burns rapidly and produces heat & light with the help of external heat. For e.g.- Burning of LPG

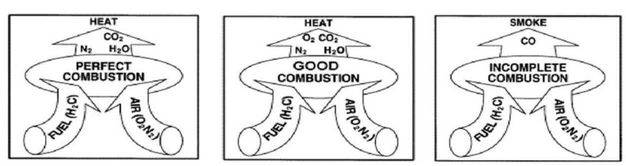
Spontaneous Combustion: Combustion in which a substance burns spontaneously and produces heat & light without the help of external heat. For e.g.- Phosphorous burns spontaneously at RT.

Explosion: Combustion in which a substance burns suddenly and produces heat, light and sound with the help of heat/pressure. For e.g.- Explosion of Crackers on applying heat/pressure.

Objective of Combustion:

The objective of good combustion is to release all of the heat in the fuel. This can be done by controlling the "three T's" of combustion i.e.

(1) **Temperature** high enough to ignite and maintain ignition of the fuel
(2) **Turbulence** or intimate mixing of the fuel and oxygen,
(3) **Time** sufficient for complete combustion.



Too much, or too little fuel with the available combustion air may result in unburned fuel and carbon monoxide generation.

A very specific amount of oxygen is required for perfect combustion & some additional/excess air is required to ensure the complete combustion.

Basic Stoichiometry

In general a fuel may contain Carbon, Hydrogen, Oxygen, Nitrogen & Sulphur. During combustion these elements combine with oxygen.

If the % of Carbon, Hydrogen, Oxygen, Nitrogen & Sulphur is known the quantity of oxygen/air required for combustion can be calculated.

Quantity of oxygen required for combustion of Carbon

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

"x" Kg of Carbon requires $\longrightarrow \frac{32 * x}{12}$ or 2.67 * C Kg of Oxygen

Quantity of oxygen required for combustion of Hydrogen

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

"y" Kg of Carbon requires $\longrightarrow \frac{16 * y}{2}$ or 8 * H Kg of Oxygen

Quantity of oxygen required for combustion of Sulphur

$$S + O_2 \longrightarrow SO_2$$
32Kg 32 Kg 64 Kg

"z" Kg of Carbon requires $\longrightarrow \frac{32 * z}{32}$ or 1 * S Kg of Oxygen

Quantity of oxygen required for combustion of 1 Kg of Fuel = (2.67 * C + 8 * H + S) Kg

If oxygen is already present in the fuel then this should be reduced.
Quantity of O_2 required =
(Total oxygen required - O_2 present in the fuel)

Minimum Quantity of O_2 or Theoretical amount of O_2 required for complete combustion
= (2.67 * C + 8 * H + S - O) Kg

Air contains 23% by weight hence minimum Quantity of air (Theoretical Air) required for complete combustion = $\frac{100}{23}$ * (2.67 * C + 8 * H + S - O) Kg

1 Kg of O_2 is supplied by $\frac{100}{23}$ * 1 = 4.35 Kg of air

Minimum weight of air needed for complete combustion = $\frac{100*}{23}$ **Net weight of O_2 gm**

% Excess Air = $\frac{(\text{Actual Air} - \text{Theoretical Air})}{\text{Theoretical Air}}$ * 100

If Composition is given by Volume

Air contains 21% by volume hence minimum Quantity of air (Theoretical Air) required for complete combustion =
$\frac{100}{21}$ * (2.67 * C + 8 * H + S - O) m^3

1 m^3 of O_2 is supplied by $\frac{100}{21}$ * 1 = 4.76 m^3 of air

Non combustible substances like Nitrogen, Ash, CO_2 etc. don't require any oxygen for combustion.

Conversion Factor for volume into weight = 28.94/22.4 gm

<u>Numerical: Annexure-2</u>

Problem-1

A sample of coal was found to have the following % composition C = 75%, H = 5.2%, O = 12.1%, N = 3.2%, & ash = 4.5%. (1) Calculate the minimum amount of air necessary for complete combustion of 1 kg of coal. (2) Also calculate the HCV & LCV of the coal sample.

Composition (%)	Composition in 1 kg of coal	Combustion Reaction	Weight of O_2 needed for combustion of 1 kg of coal
C = 75%	0.75	$C + O_2 \longrightarrow CO_2$	32*0.75/12 = 2 kg
H = 5.2%	0.052	$H_2 + ½ O_2 \longrightarrow H_2O$	16*0.052/2 = 0.416 kg
O = 12.1%	0.121	No Reaction	-
N = 3.2%	0.032	No Reaction	-
ASH = 4.5%	0.045	No Reaction	-
		Total O_2 needed	2.416

Net O_2 required = Total O_2 needed – O_2 present
= 2.416 – 0.121 = 2.295 kg

Minimum weight of air required for combustion of 1 kg of coal = $\frac{100 * \text{Net } O_2}{23}$
= 100 * 2.295/23 = 9.9782 kg

Dulong's Formula

GCV =
1/100 [8080 %C + 34500 (%H- %O/8) + 2240% S] (kcal/kg)
= 1/100 [8080 * 75 + 34500 (5.2- %12.1/8) + 2240 * 0]

= 7332.1875 kcal/kg

LCV = GCV – 0.09 * H * 587 (kcal/kg)

= 7332.1875 – 0.09 * 5.2 * 587

= 7057.47 kcal/kg

Problem-2

A gas used in an I.C. engine had the following composition by volume, H_2 = 45%, CH_4 = 36%, CO = 15%, N_2 = 4%. Find the volume of air required for combustion of 1m³ of the gas.

Composition (%)	Composition in 1 m³ of fuel	Combustion Reaction	Weight of O_2 needed for combustion of 1 kg of coal
H_2 = 45%	0.45	$H_2 + ½ O_2 \longrightarrow H_2O$	½ * 0.45 = 0.22 m³
CH_4 = 36%	0.36	$CH_4 + 2 O_2 \longrightarrow$ CO2 + H_2O	2 * 0.36 = 0.7 m³
CO = 15%	0.15	$CO + ½ O_2 \longrightarrow$ CO2	½ * 0.15 = 0.07 m³
N_2 = 4%	0.04	No Reaction	-
		Total O_2 needed	1.02 m³

Net O_2 required = 1.02 m³

Minimum volume of air required for combustion of 1 m^3 of fuel = 100 * Net O_2 / 21

= 100 * 1.02/21 = 4.85 m^3

Problem-3

The composition of petrol by weight was found to be C = 84% & H = 16%, Calculate

1) **Min. air required for complete combustion of 1kg of petrol.**
2) **% composition by weight of dry products of combustion corresponding to min. air/kg of petrol burnt.**
3) **Calorific value of fuel.**