The Bombay Salesian Society's

Don Bosco Institute of Technology, Mumbai

(An Autonomous Institute Affiliated to the University of Mumbai)

Dept. of Basic Sciences & Humanities

Course Code: 25FE1BSC03

Notes on Engineering Chemistry

(AY 2025-26)

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Module 5: Fuels and Energy Storage Technologies

5.1 Solid Fuels: Concept of Calorific Value and its Significance. Introduction to Proximate and Ultimate Analysis. Numerical On Calorific Value and Proximate Analysis
5.2 Numerical on Combustion Analysis of Solid Fuel.
5.3 Liquid Fuels: Octane Number, Cetane Number, Knocking and Anti-Knocking Agents, Unleaded Petrol and Oxygenates.
5.4 Use of Catalytic converter. Bio diesel-Definition, Properties and Uses.
5.5 Introduction to Lithium-Ion Batteries, Lithium-Polymer Batteries, their Advantages and Applications.
Self-Learning Topics: Fuel - Definition, Types and Characteristics of Good Fuel, Hydrogen as a Fuel – Advantages, Limitations

Learning Outcomes

- Define calorific value, octane number, cetane number, knocking, biodiesel, and battery types.
- List components of proximate and ultimate analysis.
- Identify the parts and functions of catalytic converters and lithium-based batteries.
- Explain the significance of calorific value in fuel efficiency.
- Describe the role of anti-knocking agents and oxygenates in fuel performance.
- Illustrate the working principles of catalytic converters and lithium-ion/lithium-polymer batteries.
- Discuss the environmental benefits of unleaded petrol and biodiesel.
- Solve numerical problems related to calorific value, proximate analysis, and combustion of solid fuels.
- Use fuel specifications to determine suitability for engine types.
- Demonstrate the use of biodiesel in conventional diesel engines.
- Differentiate between proximate and ultimate analysis methods.
- Analyze the effects of fuel additives on engine performance and pollution.
- Contrast lithium-ion and lithium-polymer batteries in terms of safety, cost, and performance.
- Assess the quality of fuels using analytical data.
- Judge the effectiveness of catalytic converters in reducing vehicular emissions.
- Evaluate the environmental impact of unleaded petrol, biodiesel, and battery technologies.
- Critique the use of anti-knocking agents and oxygenates in modern fuel systems.
- Propose a fuel blend that optimizes engine performance and minimizes emissions.
- Develop a strategy for integrating biodiesel into public transport systems.

5.1 Fuels : Definition, Types and Characteristics of Good Fuel,

A fuel may be regarded as **any combustible substance, which may be burnt to supply heat for practical applications without the formation of excessively objectionable byproducts.** During the process of combustion of a fuel like coal, the atoms of carbon, hydrogen etc combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the '**rearrangement of valence electrons**', in these atoms, resulting in the formation of new compounds (like CO_2, H_2O etc.).

Fuel	+	O_2	$\longrightarrow$	Products	+	Heat
more heat energy content				lesser heat energy content		

$$C + O_2 \longrightarrow CO_2 + 97.6 \text{ Kcal}$$

Types of Fuels:

Principally the fuels have been classified into three categories as,

1. Solid fuels, 2. Liquid fuels and 3. Gaseous fuels.

Each of them has been further sub-divide into two categories as-

a) Natural fuels and b) Artificial fuels.

Characteristics of a good fuel:

A good fuel should possess the following characteristics: -

1. High calorific value.
2. Moderate ignition temperature.
3. Moderate velocity of combustion.
4. Low contents of non-combustible matter
5. Non-toxic products of combustion.
6. Low contents of moisture.
7. Low cost.
8. Cleanliness in use and economy in labors.

- **A good fuel must not have too low nor too high but a moderate ignition temperature so that it will neither be dangerous for storage or transportation nor will require any additional heat to be supplied for its combustion.**
- **As such a good fuel must have a moderate velocity of combustion, so that the amount of heat produced may be used satisfactorily, for the desired purpose.**
- **The lesser the non – combustible matter the better is the fuel. Actually a good fuel should be as far as possible free form non – combustible matter.**

5.1.1 Calorific value:

It is the most important property because efficiency of a fuel is judged by its calorific value. It is **"the amount of heat liberated during the complete combustion of unit weight / volume of the fuel or it is the amount of heat obtainable by the complete combustion of unit quantity of fuel".**

The higher the calorific value the higher is the amount of heat obtainable from the fuel. So, a good fuel must have as higher calorific value.

Units of calorific value: - Calorific value is an important property. It is the capacity of fuel to supply heat. The unit of calorific value depends upon the nature of fuel.
In case of solid and liquid fuels: Since solids and liquids are measured in terms of their mass their calorific value as expressed in MKS or SI system as Kcal/Kg. **(The quantity of heat in kilocalories produced by the complete combustion of one kilogram of fuel when the products of its combustion are cooled down to 15°C. It is expressed as Kcal/ kg.)** (In C.G.S. system it is expressed as cal/gm)

5.1.2 High and Low Calorific Values:

The calorific value of a fuel can be considered in two ways:

a) High calorific value or Gross calorific value

Hydrogen is present in almost all fuels and when the fuel burns, hydrogen present in the fuel is converted into steam. Now when the products of combustion are cooled down to 60^0F or 15°C, the steam gets condensed into water and the latent heat is evolved on condensing the steam. This latent heat of condensation of steam so liberated also gets included in the total heat and as a result more amount of heat is available.

The gross calorific value is defined as **"the total amount of heat produced when a unit mass of fuel is burnt completely and the products of combustion are cooled down to room temperature usually 60^0F or 15^0C".**

b) Lower calorific value or Net calorific value

In actual practice the water is not condensed but escapes into the atmosphere along with other hot combustion gases and as a result lesser amount of heat is available.

The net or lower calorific value is defined as "**the net amount of heat produced when a unit mass of fuel is burnt completely and the products of combustion are allowed to escape into the atmosphere".**

5.1.3 Dulong's Formula:

For calculating Gross or High calorific value from the chemical composition of fuel in SI system is

$$\boxed{\text{H.C.V} = 1/100\ [8{,}080C + 34{,}500\ (H - O/8) + 2240\ S]\ \text{Kcal/kg}}$$

where C, H, O & S are the percentage of carbon, hydrogen, oxygen & sulphur in the fuel respectively.

Note: The calorific value of fuel can be approximately computed by noting the amounts of the constituents of the fuel. The oxygen if present in the fuel is assumed to be present in combined form with hydrogen as water.

For calculating Net or lower calorific value

= Gross calorific value - latent heat of water vapour formed.

= Gross calorific value - (weight of hydrogen per unit weight of fuel x 9 x latent heat of steam)

= Gross calorific value - H / 100 x 9 x 587

$$\boxed{\textbf{LCV} = \textbf{HCV} - \textbf{0.09 H x 587 Kcal/kg}}$$

where H = % of hydrogen in the fuel under consideration.

Problems based on Dulong's formula.

HCV	= 1/100 [8080C +34500 (H-O/8) + 2240 S] Kcal/kg
LCV	= [HCV – 9/100 H x 587] Kcal/kg

1) The ultimate analysis of a coal gave the following results: C = 84%, S = 1.5%, N = 0.6%, H = 5.5% & O = 8.4%. Calculate the gross & net calorific value of the coal using Dulong's formula.

Solution

Given: C = 84%, H = 5.5%, O =8.4%, & S = 1.5%

Gross calorific value GCV = 1/100[8080 C + 34500 (H- O/8) + 2240 S]

= 1/100[8080 x 84 + 34500 (5.5 – 8.4/8) + 2240 x1.5]

GCV = 8356.05 kcal/kg

Net calorific value NCV = [GCV - 0.09Hx 587]

= 8356 - 0.09x 5.5 x 587

= 8356 - 290.56

N CV = 8065.44 kcal/kg

2) A sample of coal was found to have the following percentage composition. C = 75%, H = 5.2%, O = 12.1%, N = 3.2%, & Ash 4.5% Calculate the higher calorific value & lower calorific value of coal sample.

Ans: -

HCV = 7332 Kcal/kg, LCV = 7057 Kcal/kg

3) A sample of coal contains C = 76%, O =16.2%, H = 5%, N = 1.5% , S = 0.3% Ash = 1.0% Calculate the higher & lower calorific value of the coal

Ans :-

GCV = 7173.89kcal/kg , NCV = 6909.74kcal/kg

4) A coal is having the following composition by weight C = 90%, O = 0.3%, S = 0.5%, N = 0.5%, ash = 2.5%. Net calorific value was found to be 8925.28 kcal / kg . Calculate the % H , and gross calorific value.

Answer :

% H=5.66, GCV = 9222.96 kcal/kg

Review Questions:

1) Write a short note on characteristics of a good fuel.
2) Define/Differentiate high calorific value and low calorific value.
3) What do you understand by the term Calorific value of a fuel? How is it determined by Dulong's formula?

5.1.4 Solid Fuels: Introduction

Solid natural fuels are wood, peat, lignite, bituminous coal, anthracite coal etc. and the most important artificial fuels are coke and charcoal, which are derived from natural coal.

Coal:

Coal is a complex carbonaceous material. Its origin in nature is due to gradual decomposition of vast deposits of wood and other vegetable matter, buried underneath the earth and slowly changed under the influence of heat and pressure and in limited supply of air. The process of transformation of plant into coal takes millions of years and is accomplished by bacteria, heat and pressure.

Coal is generally classified by what is known as "rank" which is based on the degree of transformation of the original plant material to carbon**. The ranks of coals, from those with the least carbon to those with the most carbon, are lignite, sub-bituminous, bituminous and anthracite.**

Analysis of Coal:

For deciding the utility of coal for a particular purpose, it is analyzed. Principally there are two types of analysis as –

a) **Proximate Analysis**
b) **Ultimate Analysis**

5.1.5 Proximate Analysis :- It deals with the determination of –

1. Moisture, 2. Volatile Matter, 3. Ash and 4. Fixed Carbon.

Determination of Moisture:-

Presence of moisture in the coal lowers its calorific value. Hence determination of moisture contents is important. It is carried out as below –

Procedure:-

a) About one gm of a powdered sample coal is weighed in a clean and dry silica crucible with lid.

b) The crucible, after removing the lid, is placed inside the electric hot – air oven maintained at 105 to 110 ºC.
c) The crucible is allowed to remain in the oven for about an hour.
d) After one hour it is transferred to a desiccator by means of a pair of tongs and is allowed to remain there till it acquires the room temperature.
e) When the crucible with its contents attains the room temperature it is taken out of the desiccators and weighed along with lid.
f) The process of heating followed by cooling to room temperature and weighing is continued till the constant weight is obtained.

During the process of heating the crucible in the electric oven to a temperature in the range of 105 to 110ºC, the moisture associated with the coal gets vaporized.

Thus,

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

Determination of Volatile Matter :

Presence of the volatile matter leads lowering of calorific value. Determination of it involves the following procedure.

Procedure :-

a) The dried sample of powdered moisture free coal is placed in empty and dry pre – weighed crucible covered with a lid.
b) The crucible is then transferred to a muffle furnace, which is maintained at a temperature of about 925±20 ºC for nearly seven minutes.
c) The crucible after seven minutes is taken out and allowed to remain in air till it attains room temperature. It is then placed in a desiccator for some time to allow any moisture that may get associated with it during cooling.
d) The crucible along with its contents is then weighed to know the loss in weight corresponding to the amount of volatile matter evaporated.
e) The process of heating followed by cooling and weighing is continued till constant weight is obtained.

$$\boxed{\%\text{ of volatile matter} = \frac{\text{Loss in weight at } 950 \pm 20\ ^{o}\text{C}}{\text{weight of coal sample}} \times 100}$$

Determination of Ash: - Presence of ash leads to formation of clinkers, which are bad conductor of heat and create the problems of its disposal. The fuel is then not clean in use and economic in labor.

Procedure:

a) The crucible with contents, but without lid, after the determination of volatile matter is then placed again in the muffle furnace maintained at the temperature in the range of 725 – 750 ºC for nearly one hour. Herein the coal burns to form ash.

b) The crucible along with its contents (ash) is then transferred to a desiccator and allowed to attain room temperature.
c) It is then out and weighed to know the weight of ash formed.
d) The procedure of heating followed by cooling and weighing is continued till the constant weight is obtained.

During the process of heating the coal burns to form ash, which the ultimate product of combustion. Its determination is important in the selection of a proper quality of coal for a specific purpose, because the coal forming large amount of ash affects the calorific value and hence the net quantity of heat obtainable is less.

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

Determination of Fixed Carbon :-

The percentage of fixed carbon in the given sample of coal is calculated by subtracting the sum of percentage moisture and percentage volatile matter and percentage ash from 100.

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

5.1.6 Proximate Analysis Parameters and Their Significance

- **Moisture Content**
    - High moisture reduces the **calorific value** of coal as part of the energy is wasted in evaporating water.
    - It **delays ignition** and makes coal difficult to burn efficiently.
    - Moist coal tends to promote **storage and handling problems** However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".
    - Excess moisture reduces the **efficiency of furnaces, boilers, and gasifiers**.
    - Hence, **lower moisture content indicates better coal quality**.
- **Volatile Matter**
    - Represents the portion of coal released as gas/vapors (other than moisture) when coal is heated without air. Volatile matter consists of both combustible gases—such as methane, hydrogen, carbon monoxide, and other hydrocarbons—and non-combustible gases like carbon dioxide
    - High volatile matter leads to **smoky flames, incomplete combustion, and soot deposition**, which causes air pollution.
    - Coals with **too low volatile matter** are difficult to ignite and burn.
    - Optimum volatile matter is desirable depending on application:
        - **Low volatile coal** → metallurgical uses (coke making).
        - **Moderate volatile coal** → thermal power generation.
    - Excessive volatile matter lowers efficiency and increases **emission of unburnt hydrocarbons**.

- **Ash Content**
    - Ash is the **non-combustible residue** left after burning coal.
    - High ash reduces **calorific value** and increases **handling, disposal, and transportation costs**.
    - Causes **clinker formation** in furnaces, obstructing airflow and reducing combustion efficiency.
    - Excessive ash leads to **erosion and scaling** in furnaces.
    - Ideal coal has **low ash content** for efficient use and reduced maintenance.
- **Fixed Carbon**
    - Represents the **solid combustible portion** of coal left after removal of moisture, volatile matter, and ash.
    - Higher fixed carbon → **higher calorific value** and **longer burning time**.
    - Indicates the **degree of maturity (rank) of coal**.
    - Fixed carbon is crucial in **coke making, metallurgy, and high-temperature applications**.
    - Coals with higher fixed carbon provide **steady heat and efficient combustion**.

Problems on proximate analysis:

1) 1 gm of coal sample on heating at 110^0C for 1 hour produced a residue 0.850 gm and this residue on heating at 950^0C for 7 mins. in absence of air, left 0.720 gm mass which on combustion left 0.1 gm of non-combustible matter. Calculate the results of proximate analysis.

Solution: -

Mass of coal sample = 1 gm
Mass of moisture = 1.0 – 0.850 = 0.150 gm
Mass of volatile matter = 0.850 – 0.720 = 0.130 gm
Mass of ash (non-combustible matter) = 0.1 gm

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

$$= \frac{(1.0 - 0.850) \times 100}{1}$$

$$= 15\%$$

$$\boxed{\%\text{ of volatile matter} = \frac{\text{Loss in weight at } 950 \pm 20\ ^oC}{\text{weight of coal sample}} \times 100}$$

$$= \frac{(0.850 - 0.720) \times 100}{1}$$

$$= 13\%$$

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

$$= \frac{0.1}{1} \times 100$$

$$= 10\%$$

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

= 100- (15+13+10)

= 62 %

2) A coal sample was analyzed as follows: Exactly 2.500gm was weighed into silica crucible. After heating for one hour at 110^{o}C, the residue weighted 2.415gm. The crucible next covered with lid of strongly heated for 7 mins. At 950 $\pm$ 20^{o}C. The residue weighed 1.528gm. The crucible was then heated without cover, until a constant weight is obtained. The last residue was found to weight 0.245 gm. Calculate the results of proximate analysis.

Ans:

%Moisture = 3.40% , %Volatile matter = 35.48%, %Ash = 9.80%, %Fixed carbon = 51.32%

3) An air-dried sample of coal weighing 2.9 gm whose weight after losing volatile matter was 1.96 gm. If it contains 4.5% moisture find the percentage of volatile matter in it.

Ans:

% volatile matter = 27.91%

5.1.7 Ultimate Analysis:-

Constituents Measured

Ultimate analysis gives exact elemental composition of coal (C, H, N, S, O), essential for energy calculations, pollution assessment, and industrial use.

Key Elements Affecting Coal Quality

- **Carbon and Hydrogen:**
  Higher carbon and hydrogen content improves coal's calorific value and quality. Carbon also reduces the required size of the combustion chamber. Hydrogen, mostly found in volatile matter, influences coal's application. Carbon percentage increases with coal rank—from lignite to anthracite—and serves as a basis for classification.
- **Nitrogen:**
  Has no calorific value and is undesirable in coal. Good quality coal should contain minimal nitrogen.
- **Sulphur:**
  Though it adds to heating value, sulphur forms corrosive and polluting oxides (SO_2, SO_3) upon combustion. Typically present at 0.5–3%, it originates from minerals like

iron pyrites and gypsum. Sulphur is especially harmful in coal used for coke production in steelmaking.

- **Oxygen:**
  Reduces calorific value and coking power. High oxygen content indicates more moisture and less usable hydrogen. A 1% increase in oxygen lowers calorific value by ~1.7%, making low

5.1.8 Significance of Ultimate Analysis:

- Helps in calculating **theoretical air required for complete combustion**.
- Determines **calorific value** more accurately than proximate analysis.
- Useful in **designing furnaces, boilers, and combustion chambers**.
- Assists in **selecting suitable coal** for metallurgical, power generation, and chemical industries.
- Important for assessing **environmental impact** (pollutant gases like SO_2, NOx).
- Essential in **industrial quality control and economic assessment** of coal.

Review Questions:

1) What are proximate & ultimate analyses of coal? Discuss their significance.
2) Describe the method to estimate the following in a coal sample.
    a) percentage of moisture
    b) percentage of ash
    c) percentage of volatile matter.

5.2 Combustion Analysis Numerical Problems:

Combustion is an exothermic chemical reaction in which heat and light are liberated and temperature increases considerably.

Example :-

C (s) 1 mole + O_2 (g) 1mole → CO_2 (g) 1mole ↑ + 97kcal

or

12kg C (s) + 32kg O_2 (g) → 44kg CO_2 (g) ↑ + 97kcal

The most commonly involved combustion reaction is :

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

$$S + O_2 \longrightarrow SO_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

$$2C_2H_2 + 5O2 \longrightarrow 10\ CO2 + 2H_2O$$

Nitrogen, ash and carbon dioxide, if any, present in the fuel or air are incombustible matters and hence they do not take part during combustion reaction.

The total amount of oxygen required by the fuel can be given by sum of the amount of oxygen required by individual constituents present in the fuel.

Some important formulae & hints to solve problems on calculation of quantity of air required for combustion of fuel.

1) First write the appropriate chemical reaction with oxygen and find their relation between the elements or compound on weight or volume basis.
2) Calculate the oxygen required on the basis of unit quantity of fuel.
3) Calculate the total oxygen, which is already present in the fuel.
4) The oxygen calculated should be converted into air by knowing that air contains 23 part by weight of oxygen or 21 parts by volume of Oxygen .
5) The average molecular weight of air is 28.94 gm
6) Calculation for quantity of air required for combustion of coal.

a) Weight of air needed = $\left\{ \frac{32C}{12} + \frac{16H}{2} + \frac{32S}{32} - O \right\} \times \frac{100}{23}$

("O" is oxygen present in fuel)

$$= \left\{ 2.67 \times C + 8 \times H + S \right\} \times 100/23$$

b) Volume of air required = (No. of mol. of air) x 22.4 litres at STP

$$= \frac{\text{wt. of air needed in gm}}{28.94} \times 22.4 \text{ litre at STP}$$

$$= \frac{\text{wt. of air needed in kg}}{28.94} \times 22.4 \text{ m}^3 \text{ at STP}$$

Problems on Combustion Analysis:

1) Calculate volume of air required for complete combustion of 1kg of coal containing C = 60% , H = 7%, O = 8%, N = 5% & moisture = 13.8% remaining being ash.
{Mol. wt. of air = 28.949g}

Solution :-

Elements	% by weight per kg of coal
C	0.6
H	0.07
O	0.08
N	0.05
moisture	0.138

weight of O_2 required per kg = { 32C/12 + 16H/2 – O}

= {2.66(0.6) + 8 X 0.07 – 0.08}

= 2.08 kg

wt. of air per kg fuel = wt. of O_2 required per kg X 100/23

= 2.08 X100/23

wt. of air per kg fuel = 9.04 kg.

volume of air required = (No. of mol. of air) X 22.4 lit. at STP

$$= \frac{\text{wt. of air needed in g X 22.4 lit at STP}}{28.949}$$

$$= \frac{22.4 \text{ X } 9.026}{28.949} = 6.99 \text{ m}^3$$

Therefore, volume of air required per m^3 of fuel for complete combustion = 6.99 m^3

2) A coal sample was found to contain the following constituents:
Carbon=81%, Hydrogen =6%, Oxygen=6%, Suphur = 1%, Nitrogen =2% and other remaining ash. Calculate minimum weight of air required for compete combustion of 1 of coal kg Solution:

Constituents	% by wt	Wt of each per kg of fuel
C	81	81/100=0.81
H	6	6/100=0.06
S	1	1/100=0.01
O	6	6/100=0.06
N	2	does not contribute
ash	4	does not contribute

Weight of oxygen= [2.67 C + 8H + S – O] kg

=[2.67x0.81) + 8x(0.06) + 0.01 – 0.06] kg

=2.59 kg

Amount of air required $=\frac{100}{23}$[Weight of Oxygen] kg

$=\frac{100}{23}$[2.59] kg

=11.26kg

5.3 Liquid Fuel: Introduction

Liquid fuels, particularly crude oil, are highly valued for their convenience and economic benefits in domestic and industrial applications. Petroleum is a dark, viscous liquid found deep within the earth, comprising a complex mixture of hydrocarbons (paraffins, cycloparaffins, olefins, aromatics) and small amounts of organic compounds containing oxygen, nitrogen, and sulfur.

Petroleum is vital for modern development, serving as the primary fuel for various engines (automobiles, aircraft, locomotives, ships). It also yields lubricating oils that enhance machine life and efficiency, and is a source for everyday products like paints, cosmetics, and shampoos. Furthermore, it provides asphalt for roads, paraffin wax for candles, and waterproofing agents.

5.3.1 Fuel performance in internal combustion engines-Petrol and Diesel

Petrol engine is a spark plug engine. Knocking is the abnormal combustion in an internal combustion (IC) engine, producing a sharp metallic noise due to the spontaneous ignition of the last unburnt fuel-air mixture. This causes loss of energy, reduced efficiency, and potential engine damage.

Causes of Knocking

- Occurs when the fuel-air mixture burns too quickly (detonation).
- Depends on hydrocarbon structure, temperature, and compression ratio (V1/V2).
- Higher compression ratio increases efficiency but also increases knocking tendency.

Normal Combustion vs Knocking:

Feature	**Normal Combustion**	**Knocking (Detonation)**
Initiation	Ignited at spark plug at optimized cycle moment	Unburnt mixture auto-ignites ahead of flame front
Flame Propagation	Smooth, controlled flame travels across the cylinder	Sudden, rapid explosion of end-gas
Pressure Pattern	Gradual pressure rise; peak occurs just past TDC	Abrupt high local pressure; creates shock waves
Sound and Vibration	Quiet operation, minimal metallic noise	Metallic "knock" or "ping," noticeable vibration
Efficiency and Damage	High efficiency, protects engine components	Reduced efficiency, damages pistons/cylinder walls
Cause	Proper fuel structure, timing, mixture, compression ratio	High temperature, pressure, poor-quality fuel, high compression ratio
Flame Front Speed	Regular, depends on air–fuel ratio and turbulence	Very fast, up to 25x normal flame speed

Compression Ratio

Compression ratio (CR) is defined as:

$$CR = \frac{\text{Total volume when piston at bottom dead center (V1)}}{\text{Volume at top dead center (V2)}}$$

Compression Ratio

As higher compression ratio increases efficiency but also increases knocking risk with low-octane fuel.

Thus, knocking is due to the spontaneous ignition of the last unburnt portion of the charge giving a detonating shock wave. The tendency to knock depends upon the nature and structure of hydrocarbons present in the gasoline.

The tendency to knocking decreases in the following order.

Straight chain Paraffin → Branched chain Paraffin → Olefins → Cyclo paraffins → Aromatics

knocks the most (low octane number) → knocks the least (high octane number)

A good fuel is that which has the minimum tendency to knock. It has been found that the straight hydrocarbons such as n-heptane (C_7H_{16}), knocks very badly. On the other hand, a liquid such as iso- octane (C_8H_{18}) burns very smoothly without producing any knock or in other words it has higher antiknocking property.

The knocking tendency of an unknown fuel is rated relative to the knocking property obtained with a fuel of known rating used under exactly the same conditions.

5.3.2 Octane Scale

Therefore, **octane number scale has been formed in which iso-octane (2,2,4-trimethyl pentane) is rated 100 octane i.e. it has antiknocking property as cent percent and n-heptane rated as zero.i.e. it has antiknocking property (octane number) as '0'**. Thus if two hydrocarbons such as iso-octane and n-heptane are mixed in all proportions a series of fuels, having knocking property of octane numbers from '0 to 100' are obtained. Such mixtures of iso-octane and n-heptane are taken as standard and the knocking property of gasoline or other fuel is compared with them.

Octane Number:

Octane number is the measure of antiknocking property of petrol. Octane number is defined as percentage of iso-octane in mixture of iso-octane and n-heptane that knocks with same intensity as petrol fuel being tested.

Antiknocking Agents:

- Added to gasoline to raise octane rating and reduce knocking.

- Tetraethyl lead (TEL) was widely used: 0.4 g/L could increase octane number by 6–7.
- TEL works by inhibiting free radical chain reactions during combustion.
- Ethylene dibromide was added to remove harmful lead deposits as volatile lead bromide.
- Banned from 1975 due to environmental and catalytic converter issues.

5.3.3 Unleaded Petrol (Gasoline):

Tetra ethyl lead (TEL) is added to petrol to increase octane number of the fuel and to improve engine efficiency. With the introduction of catalytic converters, unleaded petrol was introduced in 1995.

Practically zero quantity of lead is present in the unleaded petrol supplied in India. Unleaded petrol is supplied in India so as to reduce the undesirable lead emissions as well as to enable the use of catalytic converters in the vehicle

The octane number of unleaded petrol is maintained

- by highly efficient refining process or
- by addition of certain aromatic compounds like benzene, toluene, xylene etc.. or
- by addition of certain compounds known as oxygenates such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), ethanol etc..

What Are Oxygenates?

Oxygenates are organic compounds that contain oxygen and are blended into gasoline to improve combustion efficiency and reduce harmful emissions. They are primarily used to:

- Increase the **octane rating** of fuel
- Promote **cleaner burning**
- Reduce **carbon monoxide** and **unburned hydrocarbon emissions**

They are especially important in **unleaded petrol**, which lacks tetraethyl lead—a traditional octane booster now phased out due to toxicity.

Both MTBE and ethanol have low hydroxyl radical reaction rates and low vapour pressures which favours these oxygenates to be used in unleaded petrol.

5.3.4 Cetane number :

Cetane number is one of the most widely known parameters of diesel fuel. Knocking characteristics of a diesel fuel are expressed in terms of cetane number.

A diesel engine is a compression-Ignition engine. The high-temperature, high-pressure air created in the cylinder as the piston nears the end of the compression stroke ignites the fuel. (Fuel in gasoline engines is ignited by a spark plug.)

The cetane *number* is a measure of ease with which diesel fuel is ignited during the compression stroke

When injected into the combustion chamber of the cylinder, fuel must quickly mix with air then ignite with no other ignition source. **The time interval between the beginning of fuel injection and the beginning of combustion is called "ignition delay."** Higher cetane number fuels result in shorter ignition delay, providing improved combustion, lower combustion noise, easier cold starting, faster warm-up, less white smoke, and, in many engines, reduction in of some emissions.

Thus, the delay between the time the fuel is injected into the cylinder and ignition is expressed as a cetane number.

Cetane number is the percentage by volume of hexadecane (known as cetane) in a combustible mixture that contains cetane and alpha-methylnaphthalene whose ignition properties are similar or match with the fuel that is being tested. The one ignition property that is compared here is engine knock.

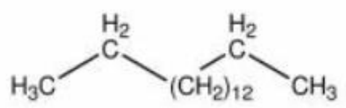
In order to grade the diesel fuels, a rating called cetane rating is employed, in which cetane numbers are assigned to diesel oil.

straight chain hydrocarbon > cycloparaffins > olefins > branched chain hydrocarbons > aromatics

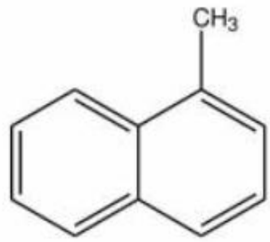
(High cetane number)
Least ignition delay

(Low cetane number)
Highest ignition delay

Cetane ($C_{16}H_{34}$) is a saturated hydrocarbon, which, ignites very quickly, and without delay, while **alpha-**methyl naphthalene ($C_{11}H_{10}$), an aromatic hydrocarbon, does not ignite quickly and thus a long ignition delay. Thus, a cetane number scale has been set up in which cetane is rated as '100' cetane and a-methyl naphthalene is rated as '0' cetane.



n-Hexadecane



Cetane ($C_{16}H_{34}$)
Cetane number =100

alpha-methyl naphthalene
Cetane number = 0

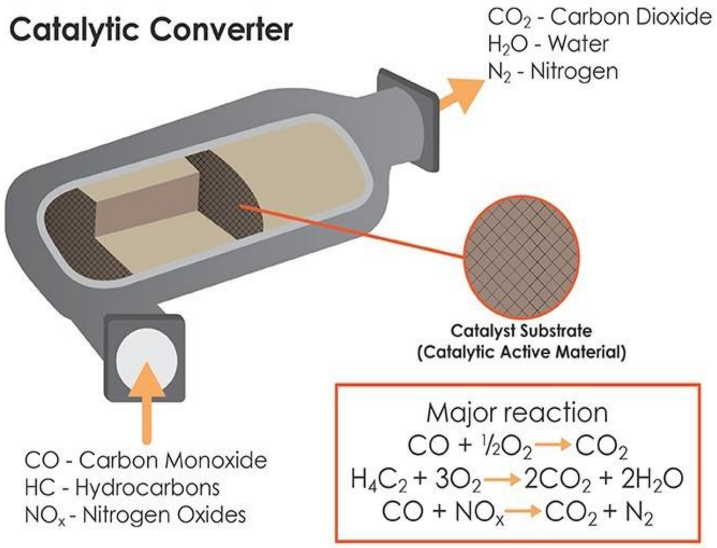
So cetane number of fuel is obtained by comparing the ignition quality by a mixture of cetane and **alpha-** methyl naphthalene

5.4.1 Catalytic Converters:

The vehicular exhaust produces harmful emissions of hydrocarbons, carbon monoxide and nitrogen oxides that are damaging to the atmosphere if released into the air.

A catalytic converter substantially reduces the amount of harmful pollutants by taking these gases and converting them into water vapour and less harmful gases via a series of chemical reactions.

It is fitted in the exhaust system of the internal combustion engines between the engine and the silencer of petrol driven vehicles. The catalytic converter consists of a ceramic or metallic honeycomb support coated with a metal catalyst such as platinum or palladium (noble metals). When the exhaust gases flow into the support channels and come in contact with the coated catalyst surface, the CO and HC (hydrocarbons) contents of the exhaust get catalytically converted into CO_2 and H_2O. The NOx emission also gets reduced under suitable conditions of engine operation.



5.4.2 Biodiesel : Green Fuel

Definition of a Biodiesel :

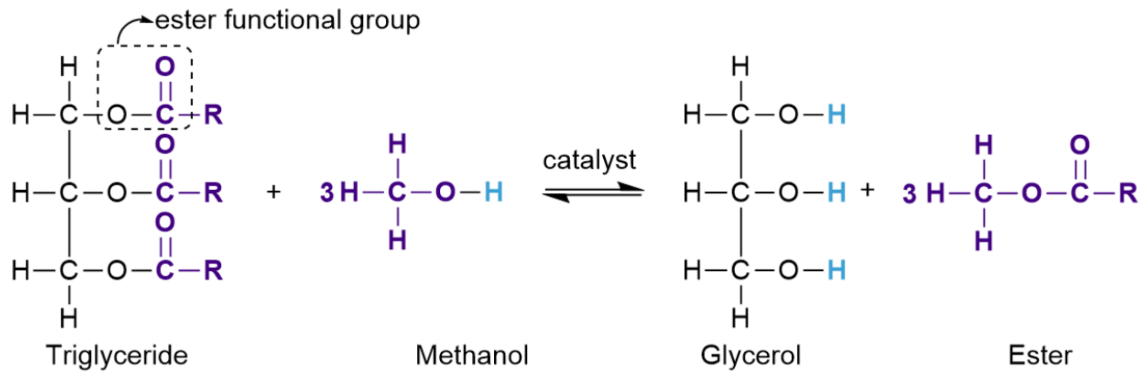
Biodiesel is mono-alkyl esters of fatty acids derived from vegetable oils or animal fats via a catalytic reaction called as transesterification.

Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form mono alkyl esters (biodiesel) and glycerol.

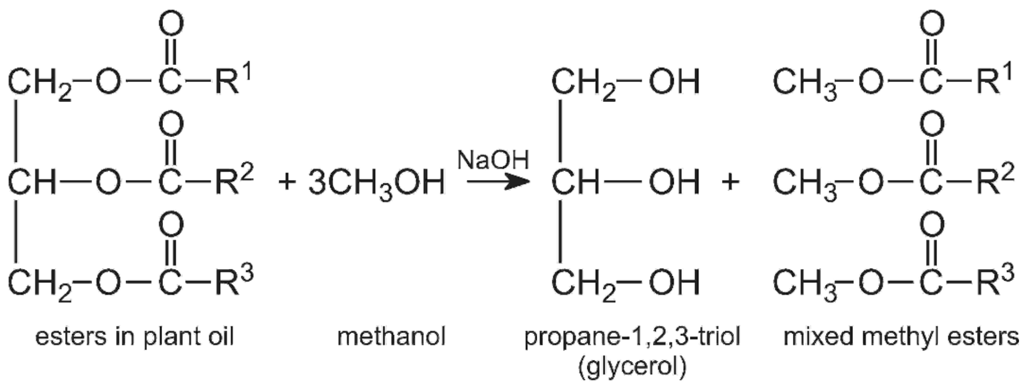
Biodiesel Synthesis:

1. The transesterification process involves reacting vegetable oils or animal fats with methanol (or ethanol) in the presence of a strong alkali catalyst, like sodium or potassium hydroxide. This reaction produces biodiesel (methyl or ethyl esters) and glycerol as a by-product.
2. To drive the reaction to completion, excess alcohol is used since the reaction is reversible. Potassium hydroxide is preferred for ethyl ester (biodiesel) production, while either sodium or potassium hydroxide can be used for methyl esters.

3. After the reaction, the biodiesel and glycerol separate, with glycerol settling as the heavier layer. Glycerol can be sold or purified for use in other industries, like pharmaceuticals and cosmetics.
4. This process is efficient, requiring low temperatures and pressures, with a conversion yield of about 98%.
5. Biodiesel can be made from various feedstocks, including vegetable oils (e.g., corn, canola, palm, soy, and Jatropha oil), restaurant waste oils (frying oils), animal fats (e.g., beef tallow, pork lard), and grease from restaurant traps etc.



Catalyst-NaOH/KOH



Properties , Advantages and Uses of Biodiesel:

1. Biodiesel is a **renewable fuel** made from animal fats and vegetable oils, unlike fossil diesel.
2. It is **carbon neutral**, as the CO_2 absorbed by the crops equals the CO2 released during combustion.
3. It is **biodegradable and non-toxic**, posing less risk in case of spills.
4. With a **higher flash point (150°C),** biodiesel is safer than fossil diesel.
5. Biodiesel has **a higher cetane rating**, leading to more efficient combustion.
6. It can be used in **pure form (B100) or blended with fossil** diesel in existing engines, with little or no modifications.
7. Biodiesel improves engine lubrication and extends engine life, being virtually sulfur-free.
8. Used in **diesel engines** for cars, trucks, buses, and tractors.

9. Compatible with existing diesel infrastructure (can be used as B100 or blended like B20, B5).

Review Questions:

1) Define biodiesel and explain the role of transesterification in its synthesis.
2) Which alcohols are commonly used in biodiesel production and why is excess alcohol required?
3) Why is biodiesel considered carbon neutral?
4) Compare the flash point of biodiesel with fossil diesel and state its significance.
5) How does biodiesel improve engine performance and life compared to fossil diesel?
6) Explain the environmental advantages of using biodiesel over conventional diesel.

5.5.1 Lithium-ion (Li-ion) Battery Chemistry:

- **Electrolyte:**
  - A liquid organic electrolyte (typically lithium salts such as $LiPF_6$ dissolved in organic solvents like ethylene carbonate and dimethyl carbonate).
- **Electrodes:**
  - **Cathode (positive):** Usually made from lithium metal oxides ($LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, NMC, etc.).
  - **Anode (negative):** Typically graphite (carbon), sometimes silicon–graphite composites.
- **Separator:**
  - A porous polymer film soaked with liquid electrolyte, preventing short-circuits while allowing Li^+ ion transport.
- **Working Principle:**
  - During charging: Li^+ ions move from cathode → anode and are stored between graphite layers.
  - During discharging: Li^+ ions move back from anode → cathode, releasing electrical energy.

Features:

- High energy density
- Longer cycle life
- Stable but sensitive to overcharging/overheating (risk of thermal runaway).

Applications

- Electric vehicles
- Smartphones
- Laptops
- Power tools
- Renewable energy storage systems

Review Questions: Lithium-ion (Li-ion) Battery

1) Name at least three common cathode materials used in Li-ion batteries.
2) Describe the role of the separator in a Li-ion battery.

3) Explain the movement of lithium ions during charging and discharging.
4) Why does Li-ion have high energy density compared to other rechargeable batteries?
5) What are the major safety concerns associated with Li-ion batteries?
6) Mention three common applications of Li-ion batteries.

5.5.2 Lithium Polymer (Li-Po) Battery Chemistry

- **Electrolyte:**
  - A solid, gel-like polymer electrolyte (e.g., polyacrylonitrile, polyethylene oxide, or a gelled polymer with lithium salts).
- **Electrodes:**
  - Same materials as Li-ion (cathode: lithium metal oxides, anode: graphite).
- **Separator:**
  - Solid/gel polymer film acts as both separator and electrolyte.
- **Working Principle:**
  - Identical ion movement to Li-ion, but ions travel through a polymer medium rather than a liquid electrolyte.
- **Features:**
  - Flexible, lightweight, and can be made into thin or custom shapes.
  - Lower energy density than Li-ion.
  - Safer (less leakage, reduced explosion risk).
  - Used widely in drones, RC devices, smartphones, and wearables.

Review Questions: Lithium Polymer Battery.

1) What is the main difference between the electrolyte of Li-ion and Li-Po batteries?
2) Which electrode materials are used in Li-Po batteries?
3) How does the polymer electrolyte act as both separator and electrolyte?
4) Explain why Li-Po batteries are considered safer than Li-ion batteries.
5) Compare the energy density of Li-ion and Li-Po batteries.
6) Mention three common applications of Lithium Polymer batteries.

SELF STUDY

Hydrogen as a Fuel: Self Study

Economic Advantages (Pros)

- Energy Independence – Hydrogen can be produced locally from water, natural gas, or biomass, reducing reliance on imports.
- Job Creation & Industry Growth – Expanding hydrogen infrastructure creates employment in manufacturing, engineering, and logistics.
- Market Diversification – Hydrogen can be used in transport, heavy industry, electricity storage, and shipping.
- Long-Term Cost Reduction Potential – Costs of green hydrogen are expected to fall with technological advances and economies of scale.
- Environmental Cost Savings – Reduced healthcare and climate costs due to hydrogen's clean byproducts.

Economic Challenges (Cons)

- High Production Costs – Green hydrogen currently costs more than fossil fuels.
- Infrastructure Costs – Refueling stations, pipelines, and storage require heavy investment.
- Energy Inefficiency – Hydrogen production, storage, and transport waste more energy compared to direct electrification.
- Market Uncertainty – Competing clean technologies may outpace hydrogen adoption.

- Price Volatility – Hydrogen tied to fossil fuel prices may fluctuate until renewables dominate.

Economic Outlook

Short Term (Now–2030): Expensive, limited to niche applications.
Medium Term (2030–2040): Costs expected to decline as renewables and electrolyzers scale.
Long Term (2040+): Potential to become a global commodity if production and infrastructure challenges are solved.

Issues with Hydrogen as a fuel:

High cost of green hydrogen production	According to Columbia Business School, grey hydrogen (from fossil fuels) costs ~$1–3/kg, while green hydrogen may cost $4–12/kg in current conditions
Infrastructure and capital cost barriers	Building hydrogen storage, transportation pipelines, refueling stations, compression, etc., requires major capital investment. Retrofitting existing energy/fuel infrastructure for hydrogen compatibility can raise costs by ~20–30%. In a working paper, financing costs / capital costs are shown to be a key constraint in developing countries.
Limited infrastructure/ distribution challenges	Hydrogen fueling stations are scarce; vehicles cannot easily be refueled at home. Distribution and storage (compression, liquefaction) are complex and expensive processes.
Dependence on energy inputs and efficiency losses	Hydrogen is not a primary energy source but an energy carrier, which means energy is spent in production, storage, and transport. Electrolysis efficiency (water → H_2 + O_2) is 55–80 %, meaning losses exist.
Sector-specific economic viability/ carbon abatement costs	A recent analysis shows that, at current delivered prices, using green hydrogen as a decarbonization route is often prohibitively expensive. For many sectors, carbon abatement costs with green H_2 are estimated between **US$ 500–1,250 / tCO_2**. Unless storage and distribution costs fall, use of green hydrogen may remain limited to sectors already using hydrogen (e.g., ammonia, steel) even if production cost falls to $2/kg H_2.

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MCQs on Oxygenates, Cetane Number, Catalytic Converters & Biodiesel

Q1. Oxygenates are primarily added to gasoline to:
a) Reduce octane rating
b) Increase knocking in engines
c) Improve combustion efficiency and reduce harmful emissions
d) Increase lead content in fuel
Answer: c) Improve combustion efficiency and reduce harmful emissions

Q2. Which of the following is an oxygenate commonly used in unleaded petrol?
a) Benzene
b) Ethanol
c) Toluene
d) Naphthalene
Answer: b) Ethanol

Q3. Cetane number is related to:
a) Octane rating of petrol
b) Ignition quality of diesel fuel
c) Amount of oxygen in biodiesel
d) Engine lubrication property
Answer: b) Ignition quality of diesel fuel

Q4. A high cetane number fuel results in:
a) Longer ignition delay
b) Shorter ignition delay
c) Lower combustion efficiency
d) More engine knocking
Answer: b) Shorter ignition delay

Q5. In the cetane number scale, the reference fuel cetane ($C_{16}H_{34}$) is given a rating of:
a) 0
b) 50
c) 75
d) 100
Answer: d) 100

Q6. Catalytic converters in vehicles use which of the following metals as catalysts?
a) Iron and Nickel
b) Platinum and Palladium
c) Copper and Zinc
d) Sodium and Potassium
Answer: b) Platinum and Palladium

Q7. Catalytic converters mainly reduce emissions of:
a) CO, HC, and NO_x
b) SO_2 and H_2S
c) CO_2 and H_2O
d) Methane and Oxygen
Answer: a) CO, HC, and NO_x

Q8. Biodiesel is produced by which chemical reaction?
a) Polymerization
b) Hydrogenation
c) Transesterification
d) Oxidation
Answer: c) Transesterification

Q9. Which of the following is a by-product of biodiesel production?
a) Carbon monoxide
b) Ethanol
c) Glycerol
d) Propane
Answer: c) Glycerol

Q10. Which of the following is NOT an advantage of biodiesel?
a) It is renewable and biodegradable
b) It has a higher flash point than fossil diesel

c) It reduces sulfur emissions
d) It increases dependence on fossil fuels
Answer: d) It increases dependence on fossil fuels

Q11. The ignition delay in a diesel engine refers to:
a) Time between fuel injection and piston movement
b) Time between fuel injection and start of combustion
c) Time between piston movement and spark plug firing
d) Time between exhaust release and intake stroke
Answer: b) Time between fuel injection and start of combustion

Q12. Which property of oxygenates like MTBE and ethanol makes them suitable for use in unleaded petrol?
a) High sulfur content
b) Low vapour pressure and low hydroxyl radical reaction rates
c) High aromatic content
d) Low boiling point
Answer: b) Low vapour pressure and low hydroxyl radical reaction rates

Q13. Which of the following statements about biodiesel is FALSE?
a) Biodiesel can be used in existing diesel engines without major modifications
b) Biodiesel production involves transesterification of oils/fats
c) Biodiesel is more toxic and less biodegradable than fossil diesel
d) Glycerol is a by-product of biodiesel production
Answer: c) Biodiesel is more toxic and less biodegradable than fossil diesel

Q14. The main environmental benefit of using biodiesel is:
a) Increased engine knocking
b) Higher greenhouse gas emissions
c) Carbon neutrality due to CO_2 absorption during crop growth
d) Higher sulfur oxide emissions
Answer: c) Carbon neutrality due to CO_2 absorption during crop growth

Q15. Which emission is reduced by **both** catalytic converters and biodiesel usage?
a) Sulfur oxides (SOx)
b) Carbon monoxide (CO)
c) Methane (CH_4)
d) Carbon dioxide (CO_2)
Answer: b) Carbon monoxide (CO)

Additional Practice Problems:

1) Calculate the Net Calorific Value of coal sample containing C= 68%, H =12%, O=8%,S = 4%, N = 6%, ash = 2%.
Ans: HCV=9379 Kcal/Kg, LCV=8745.04 Kcal/Kg

2) A sample of coal contains C = 60%, O = 33%, H = 6% , S = 0.05%, N = 0.3% Ash = 0.2%. Calculate the gross calorific value of coal.
Ans: GCV = 5495.9 Kcal/Kg and NCV = 5179.52 Kcal/Kg

3) 4 g of coal was heated at 110 degree Celsius for an hour when it left behind the mass of 3.75 g. This when heated at 950 degree Celsius for 7 minutes gave mass of 3.35 g. This upon further heating at 750 degree Celsius in air for an hour left behind residue of constant mass of 0.150g Calculate the results of proximate analysis.
Ans: Moisture=6.25%, Volatile Matter=10%, Ash=3.75%, Fixed Carbon=80%

4) A sample of coal was analyzed for content of moisture, volatile matter and ash from the following data, calculate the fixed carbon in the sample.
   a) Weight of coal taken = 2.5 gms,
   b) Weight of coal after heating at 110 ºC = 2.365gms
   c) Weight of coal after heating crucible at 950 ºC covered = 1.165gms
   d) Constant weight obtained at the end of analysis = 0.460gm.

Ans: Moisture = 5.4%, Volatile matter = 48%, Ash = 18.4%, Fixed carbon = 28.2%

5) Calculate the minimum weight and volume of air required for the complete combustion of 1kg of fuel containing C = 80 %, H = 6 %, O = 8 %, S = 1.5 %, H_2O = 1.0 %, N = 1.5 % and ash= rest. Given : Molecular weight of air = 28.94 gm.
Ans: Weight of air required = 11.0913 kg
Volume of air required = 8.5848 m^3

6) A sample of coal was found to contain the following constituents C = 72%, O = 8% , S = 1% , H = 14% , N = 1% and Ash = 4%. Calculate the minimum amount of air required for the complete combustion of 5 kg of coal.
Ans: Weight of air required = 64.617 kg