

APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 1



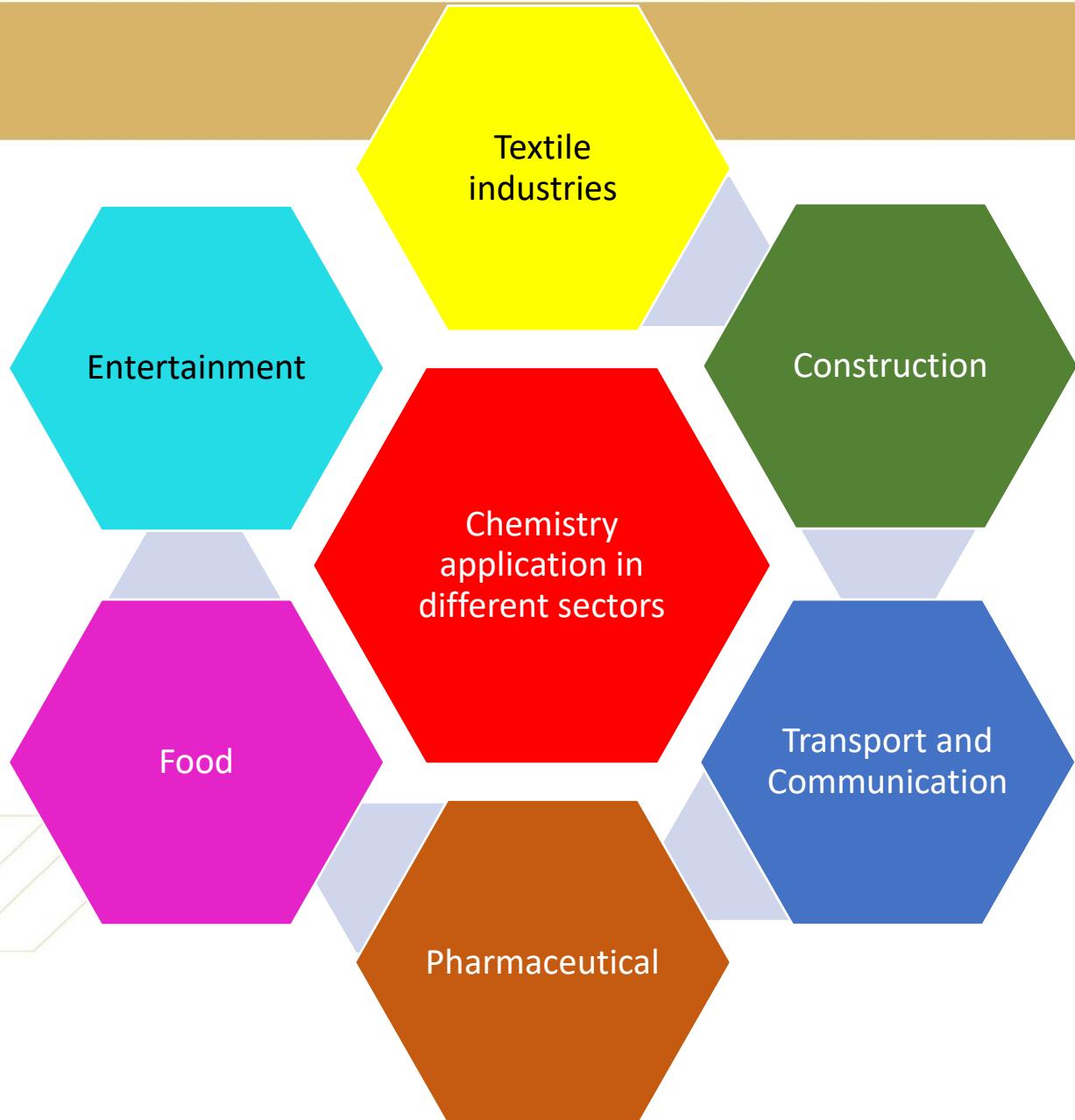
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My Education

- **B.Sc (H) Chemistry and M.Sc Chemistry** – Hansraj College, Delhi University
- **Ph.D in Chemistry** – Department of Chemistry, Delhi University
- **Research Interests-** Material Science, Wastewater Treatment, Adsorption
- **Research papers:** [Mudita Nagpal's Research Papers \(Google scholar\)](#)

Why are we studying Chemistry?



Chemistry plays an important role in various sectors globally

Understanding the industrial process is essential for better opportunities

Course Outcomes (CO's)

- CO1: Ability to use fuels and perform energy conversion calculations
- CO2: Understand the phase rule and its applications. Also, to understand the properties and industrial applications of polymers.
- CO3: Ability to analyse water and use technologies to purify it.
- CO4: Understand the chemical aspects of corrosion and its prevention. Also, to understand the basics of Green Chemistry and Nano-chemistry.

Unit 1: Fuels

What is a fuel?

- A fuel is a substance that produces useful energy through combustion

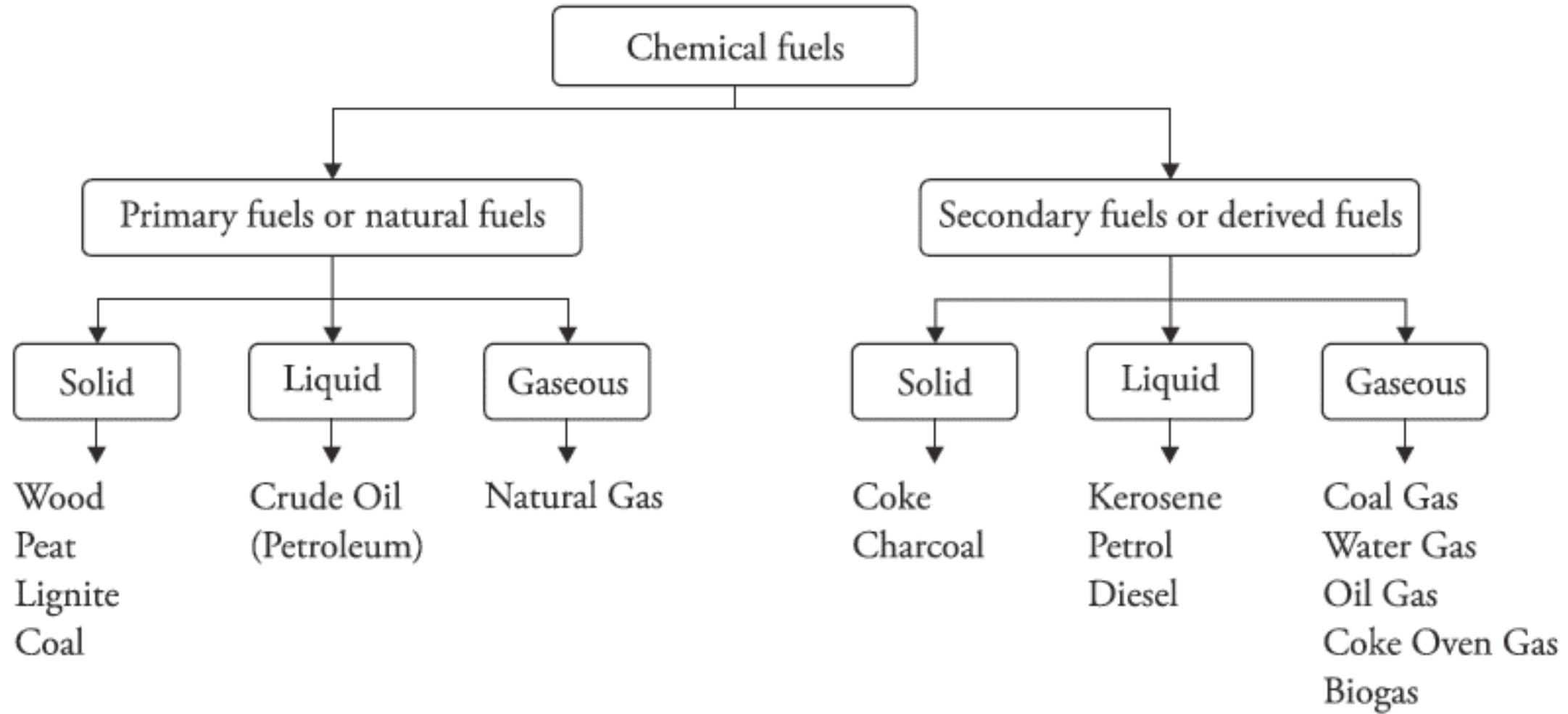


Useful industrially and
domestically

- During combustion, carbon, hydrogen, sulphur and phosphorus that are present in the fuel combine with oxygen and release energy.



Classification of fuels



Characteristics of a good fuel

★ ✓ High Calorific value

Calorific Value: The total amount of heat liberated when a unit mass or volume of fuel is burnt completely.

★✓ Moderate ignition temperature

Ignition temperature: The lowest temperature to which the fuel must be preheated so it starts burning smoothly

★✓ Low moisture content

★✓ Low non-combustible matter content

★✓ Harmless combustion products

★✓ Low cost and easy to transport

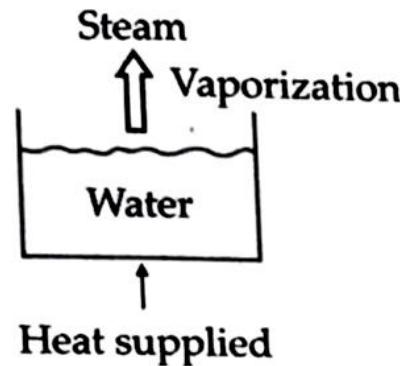
★✓ Combustion should be controllable

Fuel Characteristics	Solid Fuels	Liquid Fuels	Gaseous Fuels
Cost	Cheap	More costly than solid fuel	Costly
Storage	Convenient to store	Should be stored in closed containers	Must be stored in leak-proof voluminous storage tanks
Risk of fire hazards	Least	Greater	Very High
Combustion rate and control	Combustion is slow but it cannot be controlled easily	Combustion takes place readily and can easily be controlled or stopped	Combustion is fast and can be controlled and stopped easily
Ash	Ash is produced and its disposal is a big problem.	No ash problem	No ash problem
Smoke	Smoke is produced	Clean burning but fuels with high carbon and aromatic contents may produce smoke	Smoke is not produced
Thermal Efficiency	low thermal efficiency	thermal efficiency is higher than solid fuels	thermal efficiency is the highest
Calorific value	Lowest	Higher than solids	Highest

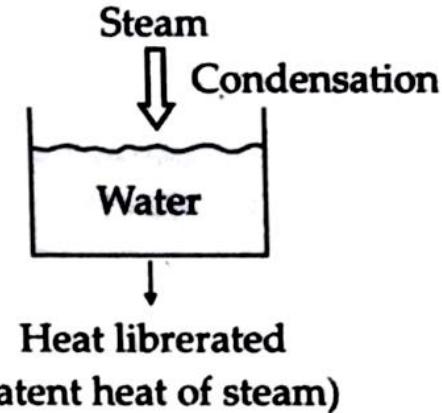
Calorific values

- Higher or Gross Calorific Value

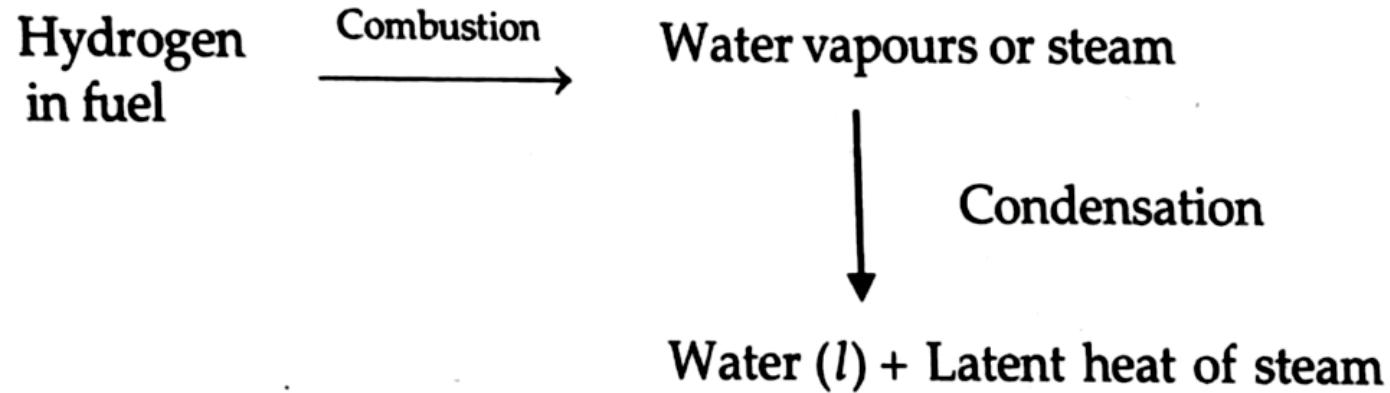
Total amount of heat produced when a unit quantity (mass/volume) of fuel is burnt completely, and the products of combustion are cooled to room temperature.



Heat is required for converting water into steam.



Heat is liberated as steam is condensed to water.



~~Heat liberated as a result of condensation of steam into water is known as Latent heat of condensation of steam .~~

HCV = Heat liberated from combustion of fuel + latent heat condensation of steam

- Lower or net calorific value (LCV)

Heat produced when a unit quantity (mass/volume) of a fuel is burnt completely and the hot combustion products are allowed to escape.

LCV = HCV – Latent heat of water vapour formed.

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Lecture 2



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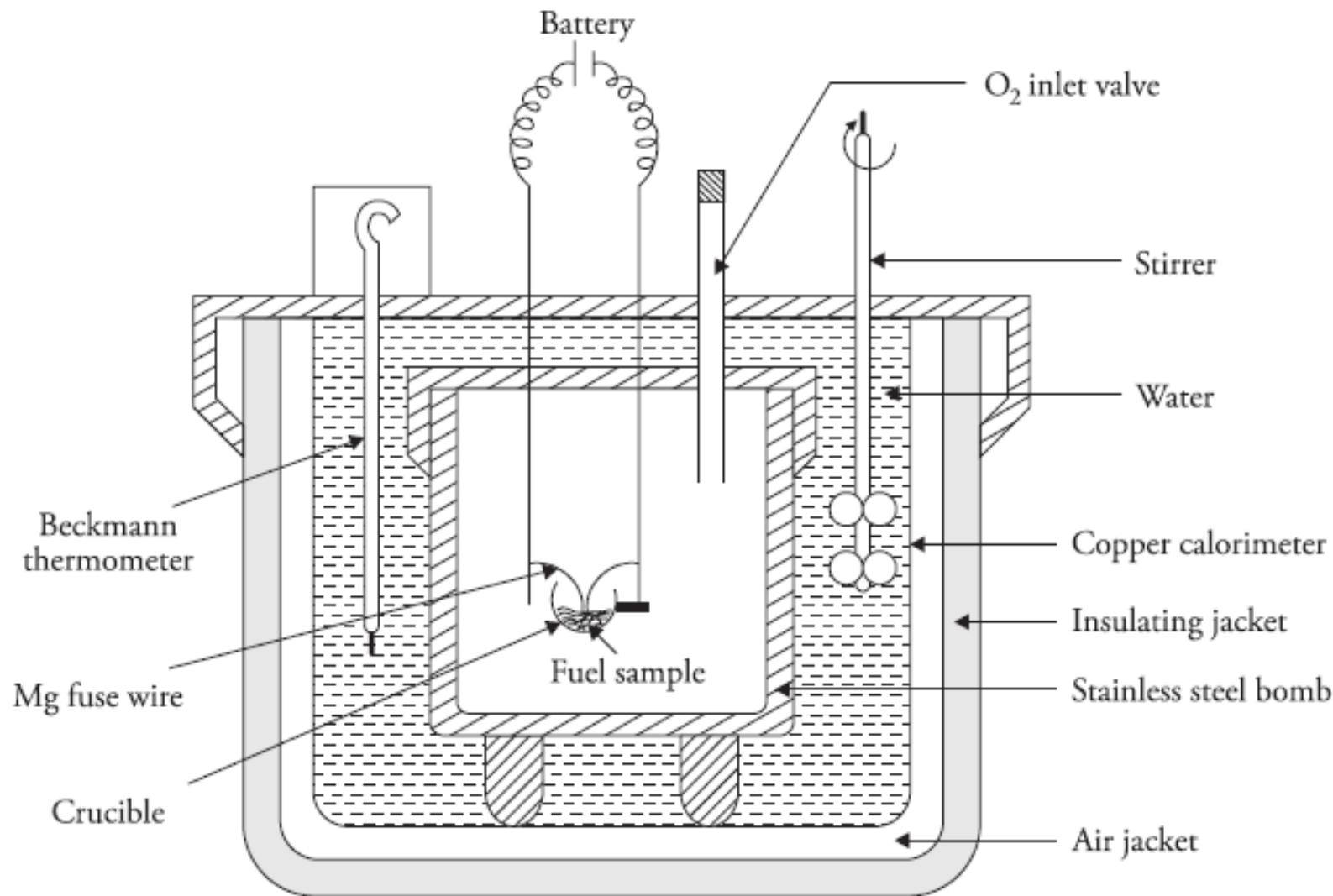


Determination of calorific value by Bomb Calorimeter

PRINCIPLE

- A known amount of fuel is burnt in excess of oxygen and the heat liberated is absorbed in a known amount of water.
- This heat liberated is measured by noting the change in temperature.
- Heat liberated by fuel = Heat absorbed by water and the calorimeter.

Bomb Calorimeter



Calculations

Let

- Weight of fuel sample taken = x g
- Weight of water in the calorimeter = W g
- Water equivalent of calorimeter, stirrer, thermometer, bomb etc = w g
- Initial temperature of water in the calorimeter = t_1 °C
- Final temperature of water in the calorimeter = t_2 °C
- Higher calorific value of fuel = H calorie / g
- Heat liberated by burning of fuel = $x \times H$
- Heat gained by water = $W \times T \times$ specific heat of water = $W (t_2 - t_1) \times 1$ cal
- Heat gained by calorimeter = $w (t_2 - t_1)$
- Total heat gained = $W (t_2 - t_1) + w (t_2 - t_1)$
 $= (W + w) (t_2 - t_1)$

- According to the principle,

★ Heat liberated by the fuel = Heat absorbed by water and calorimeter.

$$x \times H = (W + w) (t_2 - t_1)$$

$$H = [(W+w) (t_2-t_1)]/x$$

Higher calorific value of fuel (HCV)

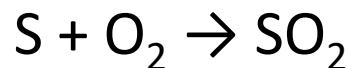
- Lower calorific value (LCV)

$$LCV = HCV - 0.09 \text{ Hydrogen} \times 587 \text{ cal/g or kcal/kg}$$

(Latent heat of condensation of steam = 587 kcal/kg)

Corrections

- **Fuse wire correction (FWC):** Heat liberated by the ignition of Mg fuse wire
- **Acid Correction (AC):** During combustion, sulphur and nitrogen present in the fuel get oxidized to H_2SO_4 and HNO_3 , respectively:



Exothermic process

- **Cooling correction (CC):** Loss of heat due to radiation
- **Cotton thread correction (CTC):** Heat liberated due to burning of thread used for igniting the fuel

➤ Heat liberated = Heat absorbed

$$xH + (AC + FWC + CTC) = (W+w) [(t_2 - t_1) + CC]$$

★ Gross calorific value (GCV) =

$$\frac{\left(\text{Weight of water} + \text{Water equivalent of calorimeter} \right) \left(\text{Rise in temperature} + \text{Cooling correction} \right) - \left(\text{Acid correction} + \text{Fuse wire correction} + \text{Cotton thread correction} \right)}{\text{Weight of fuel}}$$

Numericals for class

1. A 0.80 g sample of solid fuel was completely combusted in the excess of oxygen using bomb calorimeter. The rise in temperature of water in calorimeter was 2.5°C. Calculate the high calorific value of the fuel, if water taken in calorimeter is 2000g and water equivalent of calorimeter is 2200 g. Also calculate the low calorific value. (Given: % Hydrogen in fuel = 2.2)

Solution:

Weight of water taken in calorimeter = $W=2000$ g,

Water equivalent of calorimeter = 2200 g.

Rise in temperature - $T_2-T_1=2.5^\circ\text{C}$,

Weight of solid fuel combusted in the excess of oxygen using bomb calorimeter = $x = 0.8$ g

Let, The high calorific value of the fuel = HCV

$$\text{HCV} = [(2000+2200) (2.5)]/0.8$$

Let, The low calorific value of the fuel - LCV

$$\text{LCV}=\text{HCV}-0.09 \text{ H} \times 587$$

$$\text{LCV}=13125-0.09 \times 2.2 \times 587$$

$$=13008.0 \text{ cal/g.}$$

2.The following data is obtained in a bomb calorimeter experiment:

Weight of crucible = 3.649 gms;

Water equivalent of calorimeter = 570 gms;

Observed rise in the temperature = 2.3 °C;

Acid correction = 62.6 cal;

Cotton thread correction = 1.6 calories.

Weight of (crucible+fuel) = 4.678 gms

Water taken in the calorimeter = 2200 g

Cooling correction = 0.047 °C

Fuse wire correction = 3.8 cal

Cotton thread correction = 1.6 calories

Calculate the gross calorific value of the fuel sample. If the fuel contain 6.5% H, determine the net calorific value.

Solution. Weight of fuel = $4.678 - 3.649 = 1.029$ gms.

Gross calorific value (GCV) =

$$\frac{\left(\text{Weight of water} + \text{Water equivalent of calorimeter} \right) \left(\frac{\text{Rise in temperature}}{2.3} + \frac{\text{Cooling correction}}{0.047} \right) - \left(\frac{\text{Acid correction}}{62.6} + \frac{\text{Fuse wire correction}}{3.8} + \frac{\text{Cotton thread correction}}{1.6} \right)}{\text{Weight of fuel}}$$

$$\begin{aligned}\text{Gross calorific value (GCV)} &= \frac{(2200 + 570)(2.3 + 0.047) - (62.6 + 3.8 + 1.6)}{1.029} \\ &= \frac{2770 \times 2.347 - 68}{1.029} \\ &= \frac{6433.19}{1.029} = 6251.88 \text{ cal/gm}\end{aligned}$$

$$\begin{aligned}\text{Net calorific value (NCV)} &= [\text{GCV} - (0.09 \times \% \text{H} \times 587)] \text{ cal/gm} \\ &= [6251.88 - 0.09 \times 6.5 \times 587] \text{ cal/gm} \\ &= [6251.88 - 343.395] \text{ cal/gm} = 5908.48 \text{ cal/gm.}\end{aligned}$$

Homework questions

1. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water increased from 26.5 °C to 29.2 °C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g, respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific values.
2. A coal sample contains C = 92%, H = 5% and ash = 3%. When this coal sample was tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained

Wt of coal burnt = 0.95 g

Wt of water taken = 700 g

Water equivalent of bomb and calorimeter = 2000 g

Rise in temperature = 2.48 °C

Fuse wire correction = 10.0 cal

Acid correction = 60.0 cal

Cooling correction = 0.02 °C

Calculate the gross and net calorific value of the coal sample in cal/g. Assume the latent heat of condensation of steam as 580 cal/g.

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APPLIED CHEMISTRY

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Lecture 3



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Boy's Calorimeter - Measuring calorific value of gaseous and volatile liquid fuels

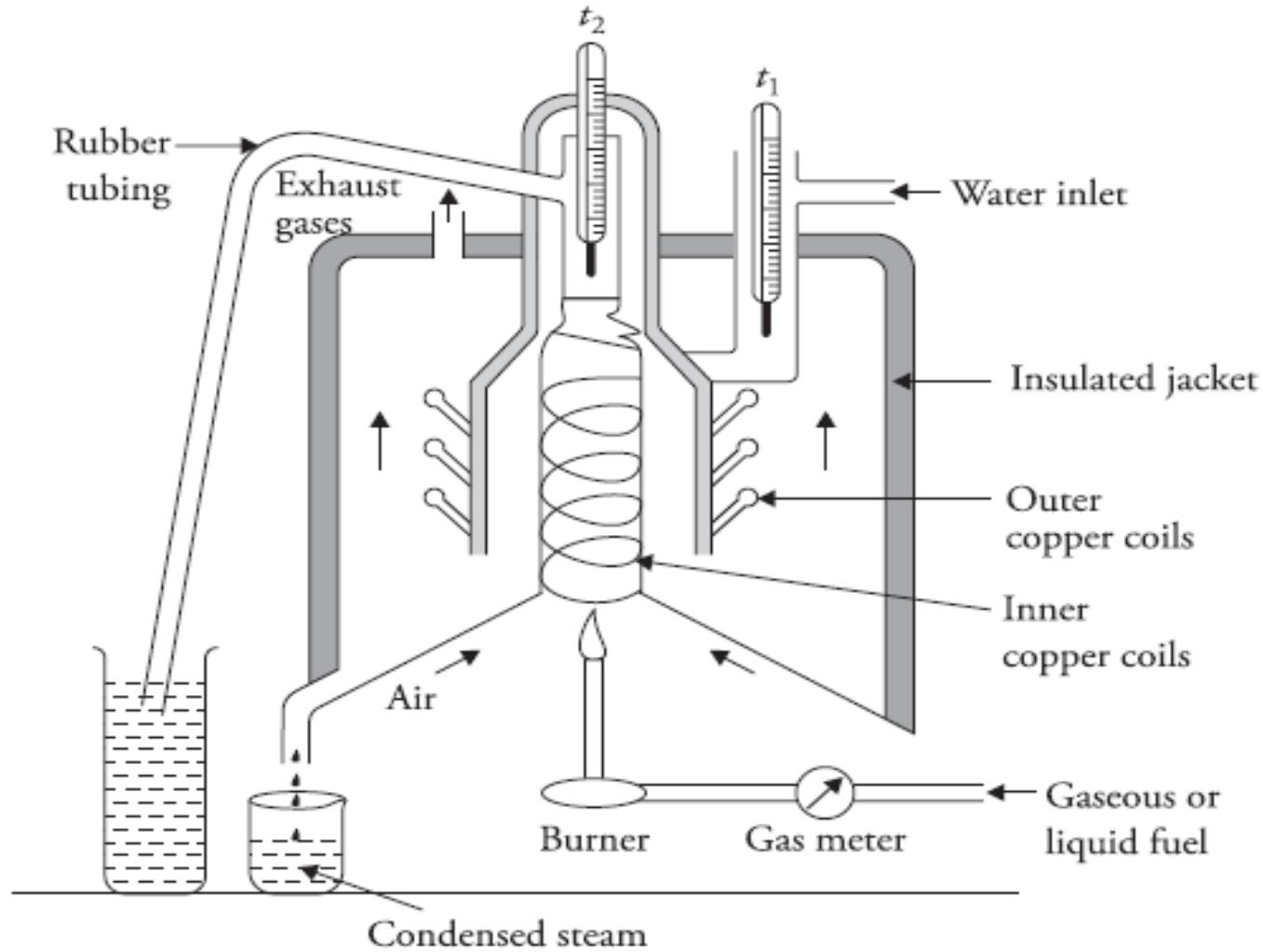
PRINCIPLE

- A known volume of gas is burnt at a constant rate in a combustion chamber in the presence of excess air and the heat liberated is absorbed in a known amount of water.

- This heat liberated is measured by noting the change in temperature.

- Heat liberated by fuel = Heat absorbed by circulating water

Boy's Calorimeter



Components of the Boy's Calorimeter

1. **Gas Burner:** used for the combustion of a known volume of gas at a known pressure.
1. **Combustion Chamber:** The combustion chamber or chimney has copper tubes coiled inside and outside the combustion chamber. Water circulates in these coils.
2. **Thermometers** Two thermometers t_1 and t_2 measure the temperatures of the incoming and outgoing water.
3. **A graduated beaker** is placed at the bottom to collect the condensed steam produced during combustion.

Calculations

- The volume of gaseous fuel burnt at a given temperature and pressure = $V \text{ m}^3$
- Weight of water circulated through the coils in time $t = W \text{ g}$
- Temperature of inlet water = $t_1 \text{ }^\circ\text{C}$
- Temperature of outlet water = $t_2 \text{ }^\circ\text{C}$
- Weight of steam condensed in time t in a graduated cylinder = $m \text{ kg.}$

Let GCV of the fuel = H

Heat produced by the combustion of fuel = $V \times H$

Heat absorbed by circulating water = $W (t_2 - t_1)$

Assuming no loss of heat,

$$V \times H = W (t_2 - t_1)$$

$$\text{HCV or GCV} = [W (t_2 - t_1)]/V$$

Weight of steam condensed in a certain time t by the combustion of $V \text{ m}^3$ of the fuel = $m \text{ kg}$

Mass of H_2O condensed per m^3 of the fuel = $m/V \text{ kg}$

Latent heat of steam = 587 kcal/kg

Latent heat of steam per m^3 of the fuel = $(m/V) * 587 \text{ kcal}$

$$\text{NCV or LCV} = \left[H - \frac{m \times 587}{V} \right] \text{ kcal/m}^3$$

Numerical in class

1. The following data were obtained in a Boy's calorimeter experiment:

- Volume of gas used = 0.1 m^3 at STP
- Wt of water heated = 25 kg
- Temperature of inlet water = 20°C
- Temperature of outlet water = 33°C
- Weight of steam condensed = 0.025 kg

Calculate the higher and lower calorific value per m^3 at STP. Take the heat liberated in condensing water vapours and cooling the condensate as 580 kcal/kg.

Solution

Here,

$$V = 0.1 \text{ m}^3; W = 25 \text{ kg}; T_2 = 33^\circ\text{C}; T_1 = 20^\circ\text{C}; m = 0.025 \text{ kg.}$$

$$\text{Therefore, HCV(H)} = \frac{W(T_2 - T_1)}{V} = \frac{25(33 - 20)}{0.1 \text{ m}^3} = 3250 \text{ kcal/m}^3.$$

$$\text{And LCV} = \text{HCV} - (m/V) \times 580$$

$$= 3250 \text{ kcal/m}^3 - [(0.025 \text{ kg}/0.1 \text{ m}^3) \times 580 \text{ kcal/kg}].$$

$$= 3250 \text{ kcal/m}^3 - 145 \text{ kcal/m}^3 = 3105 \text{ kcal/m}^3.$$

Homework question

1. During the determination of calorific value of a gaseous fuel by Boy's calorimeter, the following results were recorded:

Volume of gaseous fuels burnt at NTP = 0.098 m^3

Weight of water used for cooling the combustion products = 50 kg

Weight of steam condensed = 0.051 kg

Temperature of inlet water = $26.1 \text{ }^\circ\text{C}$

Temperature of outlet water = $46.5 \text{ }^\circ\text{C}$

Latent heat of condensation of steam = 587 kcal/kg

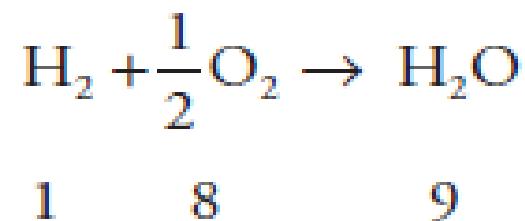
Determine the gross and net calorific values.

Theoretical calculation of calorific value using Dulong formula

- Dulong's assumed that the heat evolved comes from the combustion of carbon, hydrogen and sulphur present in the fuel, and the calorific value of the fuel is the sum of the calorific values of these constituents.

Constituent	Higher calorific value
C	8080 kcal/kg
H	34500 kcal/kg
S	2240 kcal/kg

- **Fixed hydrogen:** hydrogen in combined form not available for combustion
- Amount of hydrogen available for combustion = Total mass of hydrogen–hydrogen combined with oxygen.



If the fuel contains O mass of oxygen then

$$\text{Fixed hydrogen} = \frac{1}{8} * \text{O} = \text{Mass of oxygen in fuel}/8$$

$$\text{Amount of hydrogen available for combustion} = (\text{H} - \text{O}/8)$$

Dulong's formula for calculating calorific value:

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

Here C, H, O and S are percentages of carbon, hydrogen, oxygen and sulphur in fuel.

$$\text{Net calorific value (LCV)} = \left(HCV - \frac{9H}{100} \times 587 \right) \text{ kcal/kg}$$

$$(HCV - 0.09 H \times 587) \text{ kcal/kg}$$

(Latent heat of steam = 587 kcal/kg).

Class Numerical

Calculate the gross and net calorific values of coal having the following composition:

Carbon = 85%; hydrogen = 8%; sulphur = 1%; nitrogen = 2%; ash = 4%

Latent heat of steam = 587 cal/g.

Solution

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

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

$$= 100 - (85 + 8 + 1 + 2 + 4) = 0$$

$$= \frac{1}{100} \left[8080 \times 85 + 34500 \left(8 - \frac{0}{8} \right) + 2240 \times 1 \right] \text{kcal/kg}$$

$$= \frac{1}{100} [686,800 + 276,000 + 2240] \text{ kcal/kg}$$

$$= \frac{1}{100} [965040] \text{ kcal/kg} = 9650.4 \text{ kcal/kg}$$

$$\text{LCV} = (\text{HCV} - 0.09 H \times 587) \text{ kcal/kg} = 9227.76 \text{ kcal/kg.}$$

Homework questions

1. A sample of coal has the following composition:

Carbon = 83%; hydrogen = 7.5%; sulphur = 1.5%; nitrogen = 0.6%; oxygen = 8.4%

Find the gross calorific value using Dulong formula.



2. Calculate the gross and net calorific value of coal having the following composition

Carbon = 80%; hydrogen = 7%; sulphur = 3.5%; nitrogen = 2.1%; ash = 4.4%

Latent heat of steam = 587 kcal/kg.



Ans 1 = 8965.25 Kcal/kg

Ans 2 = HCV = 8828.02 Kcal/kg LCV = 8458.21 Kcal/kg

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APPLIED CHEMISTRY

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Lecture 4+5



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Solid Fuels: Coal

- Coal is produced when the plant and animal debris are subjected to conditions of high temperature and pressure over millions of years → **Fossil Fuel**
- **Coalification is a two stage process**

STAGE 1: Biochemical Coalification (Conversion of plant material into peat by microorganisms)

STAGE 2: Transformation with high T, Pressure and long time

- Progressive transformation of wood

Wood → Peat → Lignite → Bituminous → Anthracite



C content, hardness and calorific value increasing

Volatile matter, moisture content decreasing

Percentage composition of solid fuels

Fuel	Moisture of air dried sample at 40 °C (%)	C (%)	H (%)	N (%)	O (%)	Calorific value (kcal/kg)
Wood	25	50.0	6.0	0.5	43.5	4000–4500
Peat	25	57.0	5.7	2.0	35.3	4125–5400
Lignite	20	67.0	5.0	1.5	26.5	6500–7100
Sub-bituminous coal	11	77.0	5.0	1.8	16.2	7000–7500
Bituminous coal	4	83.0	5.0	2.0	10.0	8000–8500
Semi-bituminous coal	1	90.0	4.5	1.5	4.0	8350–8500
Anthracite	1.5	93.3	3.0	0.7	3.0	8650–8700

Coal Analysis

- **PROXIMATE ANALYSIS**

1. Moisture Content

High moisture content is undesirable because:

- ❖ Reduces the calorific value and increases the transportation cost.
- ❖ Quenches fire in the furnace
- ❖ Heat is wasted in evaporating the moisture during combustion.

Determination: Loss of weight of coal when heated at 105 °C in a crucible for 1 hour

Weight of sample = W g

Weight of sample after heating for 1 h = W₁ g

$$\% \text{ Moisture} = \frac{(W - W_1)}{W} \times 100$$

2. Volatile matter

- ❖ May be combustible gases such as H₂, CO, CH₄ and other hydrocarbons or non-combustible gases such as CO₂ and N₂
 - ❖ Presence of non-combustible gases is undesirable since they do not add to the heat value and escape unburnt
 - ❖ Coal containing high percentage of volatile matter burns with a long flame and high smoke and has low calorific value.
-
- **Determination:** heating a known weight of moisture-free coal in a silica crucible covered with a vented lid at 950 ± 20 °C for 7 minutes in a muffle furnace, cooled and weighed again

Weight of sample after removal of volatile matter = W₂ g

Weight of volatile matter = (W₁ – W₂) g

$$\% \text{ Volatile matter} = \frac{(W_1 - W_2) \times 100}{W}$$

3. Ash

- ❖ Non-combustible, useless matter that is left behind when all the combustible substances have burnt off from coal.
- ❖ High percentage of ash is undesirable as it reduces the calorific value of the fuel.
- ❖ Presence of ash increases the transporting, handling and storage cost.
- **Determination:** Residue obtained after heating the coal obtained after removal of moisture and volatile matter at 700 ± 50 °C for half an hour without a lid in muffle furnace.
- Let the weight of ash formed = W_3 g.

$$\% \text{ ash} = \frac{W_3}{W} \times 100$$

4. Fixed carbon

- Material remaining after determination of moisture, volatile matter and ash content.
- Higher the percentage of fixed carbon, greater is the calorific value and better is the quality of coal
- **Percentage of fixed carbon = $100 - \text{percentage of (moisture + volatile matter + ash)}$.**

Problem 1

A sample of coal was analysed as follows. Exactly 2.5 g was weighed into a silica crucible. After heating for an hour at 110 °C, the residue weighed 2.415 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at 950 ± 20 °C. The residue weighed 1.528 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245 g. Calculate the percentage of moisture, volatile matter, ash and fixed carbon in the coal sample.

Solution 1

(i) Percentage of moisture

Weight of coal sample taken = 2.5 g

Weight after heating at 110 °C = 2.415 g

Loss of weight = weight of moisture = 2.500 – 2.415 = 0.085 g

$$\begin{aligned}\% \text{ moisture} &= \frac{\text{weight of moisture}}{\text{weight of coal taken}} \times 100 \\ &= \frac{0.085}{2.500} \times 100 = 3.4\%\end{aligned}$$

% moisture = 3.4%

(ii) Percentage of volatile matter

Weight of residue after heating at 950 °C = 1.528 g

Loss of weight = weight of volatile matter = 2.415 – 1.528 = 0.887 g.

$$\begin{aligned}\% \text{ volatile matter} &= \frac{\text{weight of volatile matter}}{\text{weight of coal sample taken}} \times 100 \\ &= \frac{0.887}{2.500} \times 100 = 35.48\%\end{aligned}$$

% volatile matter = 35.48%

(iii) Percentage of ash

$$\begin{aligned}\frac{\text{weight of residue left}}{\text{weight of coal sample taken}} \times 100 \\ \frac{0.245}{2.5} \times 100 = 9.8\%\end{aligned}$$

% ash = 9.8%

(iv) Percentage of fixed carbon = 100 – percentage of (moisture + volatile matter + ash)

$$\begin{aligned}&= 100 - (3.4 + 35.48 + 9.8) \\ &= 100 - 48.68 = 51.32\%\end{aligned}$$

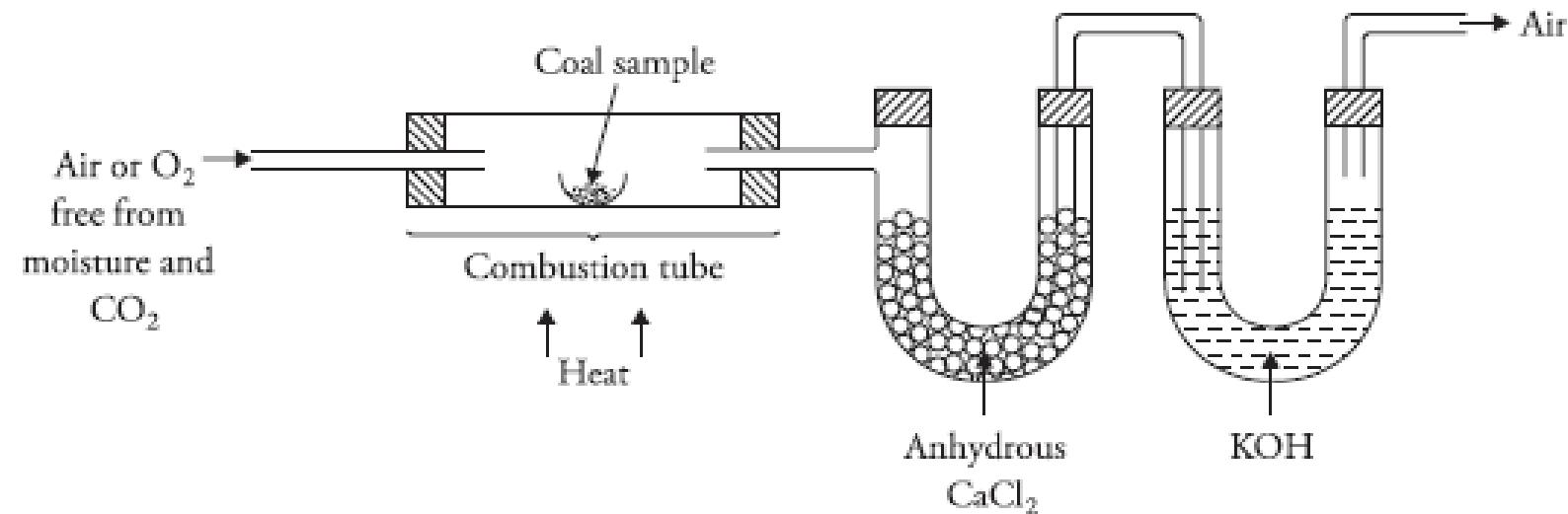
% fixed carbon = 51.32%

• ULTIMATE ANALYSIS

1. Determination of C and H

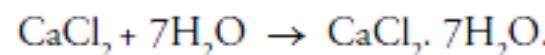
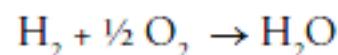
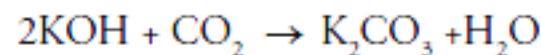
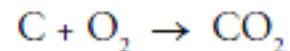
- ❖ Calorific value of a fuel is directly related to the carbon content; hence, greater the percentage of carbon, greater is the calorific value of the fuel.
- ❖ High percentage of hydrogen also increases the calorific value of coal. However, hydrogen is mostly associated with volatile matter and affects the use to which coal is put.

Determination:



Calculation:

- Carbon and hydrogen present in the fuel is converted to CO_2 and H_2O , respectively. These are then absorbed by previously weighed tubes containing KOH and anhydrous CaCl_2 .



Let the weight of coal sample taken = x g.

Increase in weight of KOH tube = y g.

Increase in weight of CaCl_2 tube = z g.

Now,

44 g of CO_2 contains 12 g of C.

y g of CO_2 contains $\frac{12}{44} \times y$ g of C.

Percentage of carbon = $\frac{12}{44} \times \frac{y}{x} \times 100$

or percentage of carbon = $\frac{12}{44} \times \frac{\text{Increase in weight of KOH tube}}{\text{weight of coal sample taken}} \times 100$

18 g of H_2O contains 2 g of H

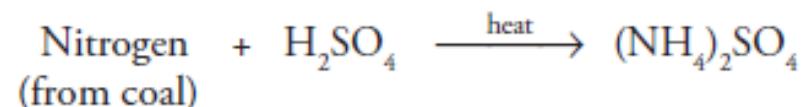
z g of H_2O contains $\frac{2 \times z}{18}$ g of H

Percentage of hydrogen = $\frac{2}{18} \times \frac{z}{x} \times 100$

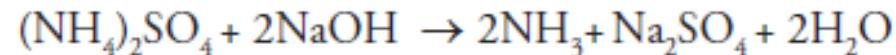
Percentage of hydrogen = $\frac{2}{18} \times \frac{\text{Increase in weight of CaCl}_2 \text{ tube}}{\text{Weight of coal sample taken}} \times 100$

2. Determination of Nitrogen : Kjehldahl's method

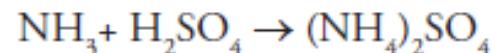
- Nitrogen is an inert and incombustible gas with no calorific value, its presence in fuel is undesirable.
- **DETERMINATION:** 4 step process
- **Step 1:** 1 gm of accurately weighed powdered coal is heated with conc. H_2SO_4 along with K_2SO_4 and CuSO_4 in a long-necked flask.



Step 2: The contents are then transferred into a round bottom flask and the solution is heated with excess of NaOH to liberate NH_3 .



- **Step 3:** The NH_3 thus liberated is absorbed in a known volume (V_1) of a standard H_2SO_4 solution (N/10).



- **Step 4:** The volume of unused H_2SO_4 is determined by titrating against standard NaOH solution (N/10). Let V_2 mL be the amount of 0.1 N NaOH used to neutralize the excess acid.

Calculation:

Amount of H_2SO_4 used to neutralize the ammonia evolved

$$= 0.1 \text{ N} \times V_1 - 0.1 \text{ N} \times V_2$$

$$= 0.1(V_1 - V_2) \text{ milli equivalents}$$

$$= \frac{0.1(V_1 - V_2)}{1000} \text{ equivalents}$$

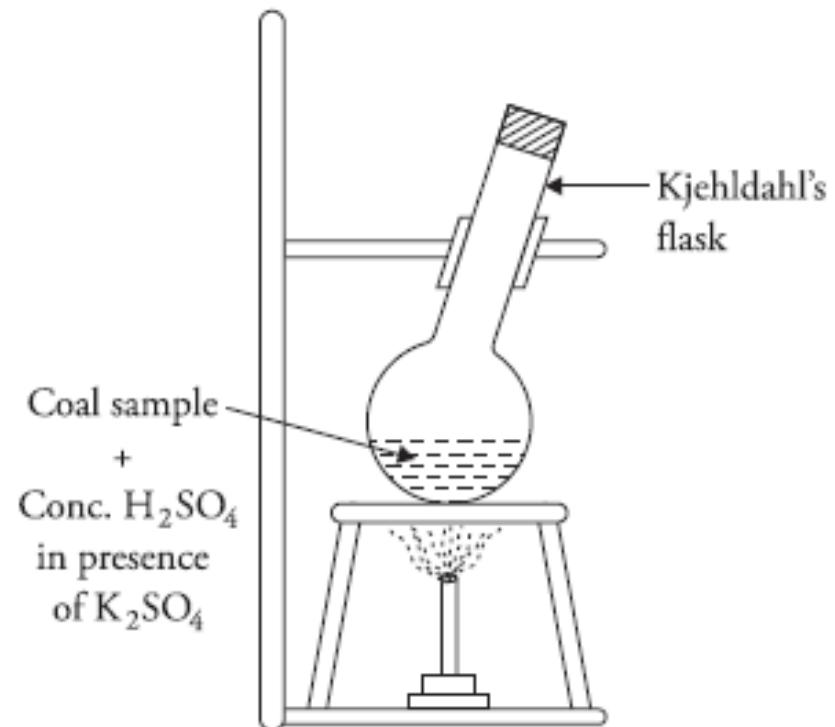
Equivalents of H_2SO_4 used = Equivalent of NH_3 formed

Normal (1N solution of NH_3 means 1 g equivalent NH_3 dissolved in 1 liter water)

\therefore 1000 mL contains 17 g $\text{NH}_3 \equiv 14$ g nitrogen.

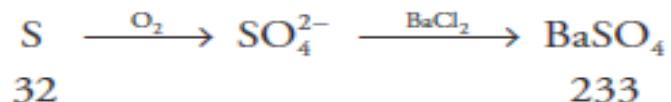
$$\text{Weight of } N = \frac{0.1(V_1 - V_2)}{1000} \times 14$$

$$\% \text{ Nitrogen} = \frac{1.4 \times \text{Normality of } \text{H}_2\text{SO}_4 \times \text{Volume of } \text{H}_2\text{SO}_4 \text{ used}}{\text{Weight of coal sample taken}}$$



3. Determination of Sulphur

- Sulphur increases the calorific value of fuel, yet its presence is undesirable because it gets oxidised to SO_2 and SO_3 , which causes environmental pollution.
- **Determination:** A known amount of coal is burnt completely in a bomb calorimeter in a current of oxygen. Sulphur in the coal is oxidised to sulphates.



Let the weight of coal sample = W g

Weight of $\text{BaSO}_4 = x$ g

$\therefore 233$ g of $\text{BaSO}_4 = 32$ g of S

$$\therefore x \text{ g of } \text{BaSO}_4 = \frac{32}{233} \times x$$

$$\% \text{ S} = \frac{32}{233} \times \frac{x}{W} \times 100$$

or $\% \text{ S} = \frac{32}{233} \times \frac{\text{Weight of } \text{BaSO}_4}{\text{Weight of coal taken}} \times 100$.

3. Determination of Oxygen

- Oxygen is present in coal in combined form. It is present in association with hydrogen; hence, it reduces the hydrogen available for combustion.
- High oxygen-containing coals have high inherent moisture and hence low calorific values.
- Calorific value decreases about 1.7% for every 1% increase in oxygen
- A good-quality coal should have low percentage of oxygen.

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

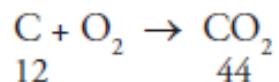
Numericals in class

1. 0.25 g of a sample of coal was analysed by combustion method. The increase in weights of CaCl_2 tube and the potash bulbs at the end of the operation was found to be 0.15 g and 0.55 g, respectively. Calculate the percentage of carbon and hydrogen in the coal.

Solution

Weight of CO_2 (increase in weight of KOH bulb) = 0.55 g.

Weight of H_2O (increase in weight of CaCl_2 tubes) = 0.15 g.



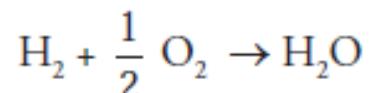
44 g CO_2 contains carbon = 12 g

$$0.55 \text{ g } \text{CO}_2 \text{ contains carbon} = \frac{12}{44} \times 0.55 \text{ g}$$

$$\begin{aligned} \text{Percentage of carbon} &= \frac{12 \times \text{weight of carbondioxide}}{44 \times \text{weight of coal sample taken}} \times 100 \\ &= \frac{12}{44} \times \frac{0.55}{0.25} \times 100 = 60\% \end{aligned}$$

Percentage of carbon = 60%.

To calculate the percentage of hydrogen,



18 g H_2O contains hydrogen = 2 g

$$0.15 \text{ g } \text{H}_2\text{O} \text{ contains hydrogen} = \frac{2}{18} \times 0.15$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{0.15}{0.25} \times 100 = 6.67\%$$

Percentage of hydrogen = 6.67%

2. 1.0 g of a coal sample was used in a bomb calorimeter for the determination of calorific value. Calorific value of coal was found to be 8800 cal/g. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with BaCl_2 solution and a precipitate of BaSO_4 was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.08 g. Calculate the percentage of sulphur in the coal sample.

Solution

$$\begin{aligned}\text{Percentage of sulphur} &= \frac{\text{weight of } \text{BaSO}_4 \text{ ppt obtained} \times 32 \times 100}{233 \times \text{weight of coal sample taken}} \\ &= \frac{0.08 \times 32 \times 100}{233 \times 1} = 1.0987\%\end{aligned}$$

Percentage of sulphur = 1.0987%

3.

1.56 g of a coal sample was Kjehldahlised and NH_3 gas thus evolved was absorbed in 50 mL of 0.1 N H_2SO_4 . After absorption, the excess (residual) acid required 6.25 mL of 0.1 N NaOH for exact neutralisation. Calculate the percentage of nitrogen in the coal sample.



Solution

Weight of coal sample taken = 1.56 g

Since 6.25 mL of 0.1N NaOH is used for neutralisation, excess acid

$$= 6.25 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4$$

Therefore, volume of H_2SO_4 used to neutralise NH_3 evolved

$$= 50 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4 - 6.25 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$= (50 - 6.25) \times 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$= 43.75 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$\text{Percentage of nitrogen} = \frac{\text{Volume of } \text{H}_2\text{SO}_4 \text{ used} \times \text{normality of } \text{H}_2\text{SO}_4 \times 1.4}{1.56} = 3.926\%$$

$$\frac{43.75 \times 0.1 \times 1.4}{1.56} = 3.926$$

$$\text{Percentage of nitrogen} = 3.926\%$$

Homework questions

1. 0.26 g of a sample of coal analysed by combustion gave 0.039 g of water and 0.245 g of carbon dioxide. Calculate the percentage of carbon and hydrogen in the coal.
2. 0.1 g of a sample of coal was used in a bomb calorimeter for the determination of calorific value. The ash formed was extracted with acid and the acid extract was heated with BaCl_2 solution and a precipitate of BaSO_4 was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.01 g. Calculate the percentage of sulphur in the coal sample. [Ans % sulphur = 1.3734%]
3. 3.12 g of the coal sample was Kjehldahlised and NH_3 gas was absorbed in 50 mL of 0.1N H_2SO_4 . After absorption, the excess (residual) acid required 12.5 mL of 0.1 N NaOH for exact neutralisation. Determine the percentage of nitrogen in the coal sample.

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APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 6



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Carbonisation of coal

- **Coke:** When coal is heated to a high temperature in the absence of air, it loses volatile matter and gets converted into a white, dense, lustrous, strong, porous and coherent mass, which is richer in carbon content than the original fuel.
- **Carbonization of coal:** The process of converting coal into coke in the absence of air

Process of carbonization

Bituminous Coal



Moisture and occluded gases are driven off



H_2O , H_2S , some low molecular weight alkenes and alkanes are evolved

↓ 350 °C



Decomposition of coal accompanied by the evolution of gases and elimination of tarry vapours takes place

↓ 400 °C

Caking coal becomes soft and plastic

↓ 700 °C

Hydrogen is evolved

↓ 800 °C



Gases evolved from the plastic mass and expand to give foam-like appearance

↓ > 800 °C

Coke is formed by solidification of this foam-like mass

Coals

Caking Coals: Coals that soften and form a plastic mass around 400C that swells to a much larger volume than the original sample and resolidifies into a porous solid.

Non-caking coals : They do not produce a porous solid on cooling

Coking coals: When this porous solid is quenched, it results in the formation of a strong residue called coke. If the coke formed is hard, porous and strong, then the coal is coking coal. Eg. Bituminous coal

Non-coking coals

Eg. Anthracite, sub-bituminous, lignite

Types of carbonisation

S.No	Characteristic	Low-temperature carbonisation	High-temperature carbonisation
1	Carbonisation temperature	About 500–700 °C	900–1200 °C
2	Yield	75–80%	65–75%
3	Volatile matter content in coke	5–15%	1–3%
4	Mechanical strength of coke	Poor	Good
5	Hardness	Soft coke	Hard coke
6	Use of coke	For domestic purposes	For metallurgical purposes
7	Smoke produced on burning	Smokeless	Smoky
8	Yield of by-product gas	Lower (130–150 m ³ /ton of coal carbonised)	Higher (about 370–480 m ³ /ton of coal carbonised)
9	Calorific value of by-product gas	6500–9500 kcal/m ³	5000–6000 kcal/m ³
10	Percentage of straight chain hydrocarbon in by-products (tar and gas)	Higher	Lower
11	Percentage of aromatics in the by-products	Lower	Higher

Metallurgical Coke

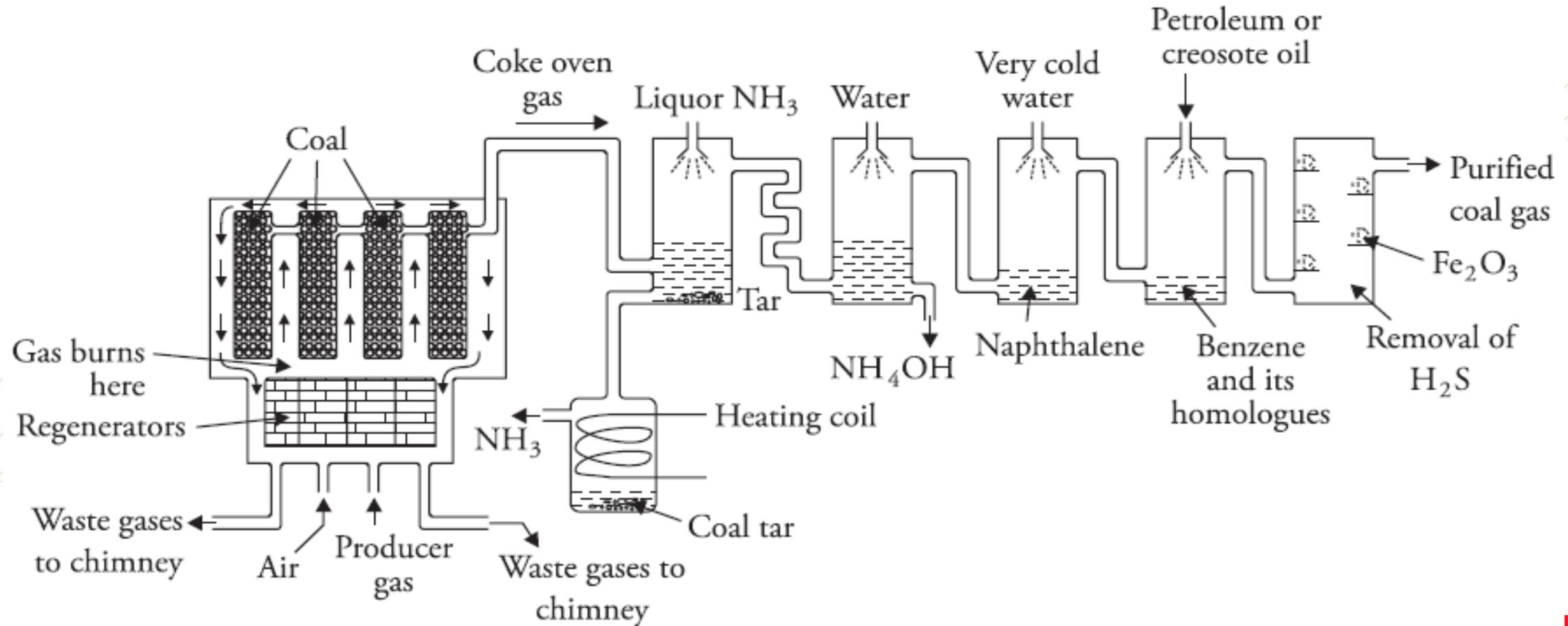
- Coke is used as a heat source and reducing agent in metallurgy.

- **Properties of a good metallurgical coke.**

- **Purity:** The moisture, ash, sulphur and phosphorus contents should be very low
- **Porosity:** Coal should be porous so that oxygen can come in contact with carbon, which ensures complete combustion
- **Strength:** Coke should be compact, hard and strong enough to withstand high pressure
- **Size:** Metallurgical coke should be of medium size – neither too big nor too small.
- **Combustibility:** Coke should burn easily but at the same time it should not be very reactive.
- **Calorific Value:** The calorific value of coke should be high.
- **Cost:** It should be cheap and easily available.
- **Calorific intensity:** The calorific intensity of coke should be high enough to melt the metal.

Manufacture of metallurgical coke

Otto Hofmann's oven or by-product oven or chamber oven method



Recovery of by-products

The gas coming out of the oven is known as 'coke oven gas' and is mainly composed of ammonia, H_2S , naphthalene, benzene, tar, moisture.

- **RECOVERY**

- ***Recovery of tar:*** The gases from the coke oven are passed through a tower in which liquor ammonia is sprayed. Tar and dust get collected in a tank below and ammonia is recovered using heating coils in the tank.
- ***Recovery of ammonia:*** The gases now enter another tower where water is sprayed. Ammonia goes into the solution as NH_4OH .
- ***Recovery of naphthalene:*** The gases then pass to a cooling tower where water at low temperature is sprayed. Naphthalene gets condensed which is then collected.
- ***Recovery of benzene:*** The gases then pass through a scrubber, where petroleum is sprinkled, resulting in the condensation of benzene and its homologues.
- ***Recovery of H_2S :*** The gases then enter a purifying chamber packed with moist Fe_2O_3 . Here H_2S is retained.

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Lecture 7



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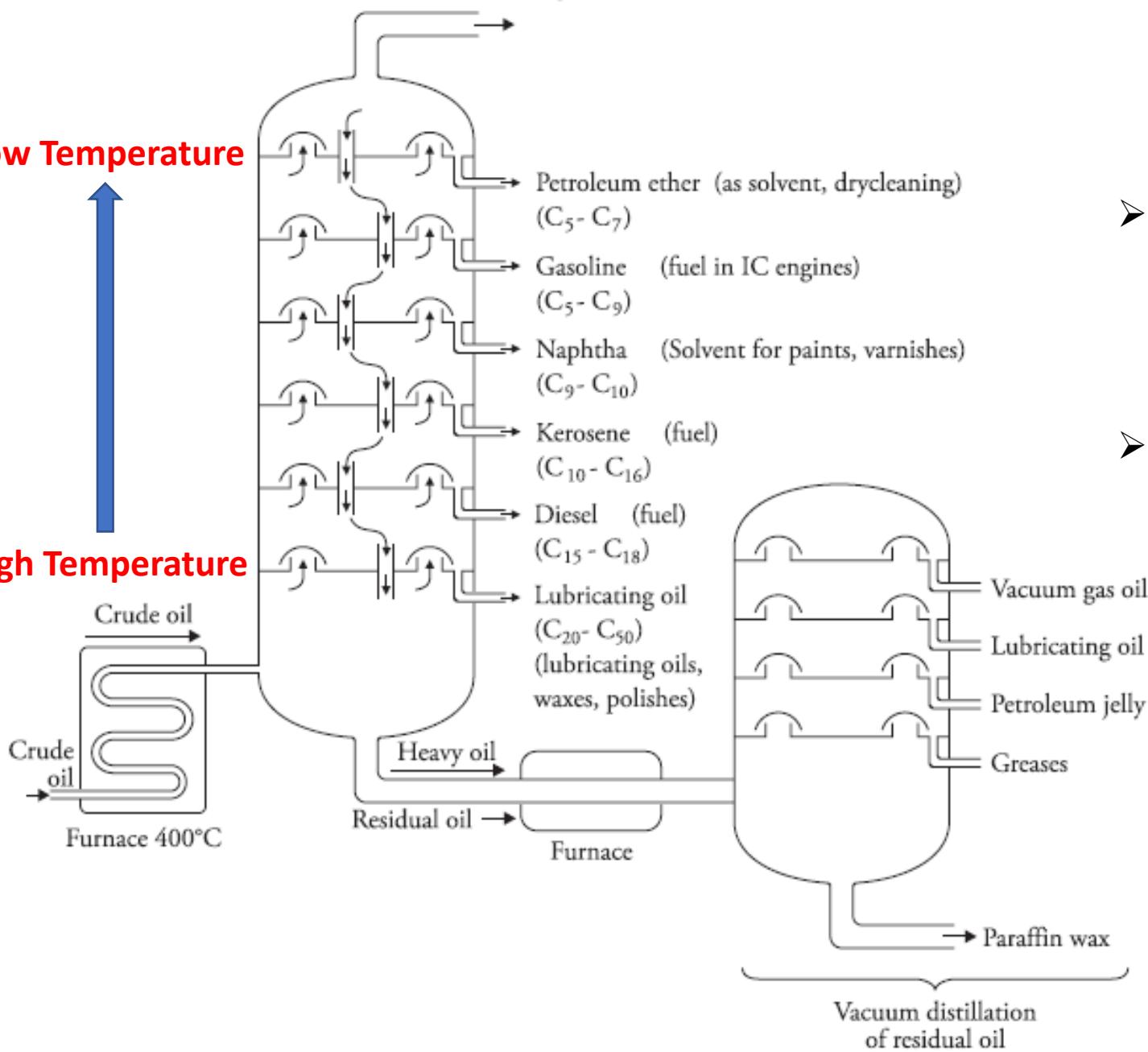
Liquid Fuels: Petroleum

- Single largest source of liquid fuels is petroleum or crude oil (**petroleum means rock oil. Latin-Petra means rock; oleum means oil**) is a dark, greenish-brown viscous oil found deep inside the earth's crust
- It is a **mixture of hydrocarbons such as straight chain paraffins, cycloparaffins, olefins and aromatics** along with small amount of organic compounds containing oxygen, nitrogen and sulphur
- **Classification of Petroleum**
 - **Paraffinic base petroleum:** It is mainly composed of straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amounts of naphthenes/cycloalkanes and aromatic hydrocarbons.
 - **Naphthenic base petroleum:** It contains mainly cycloparaffins or naphthenes along with smaller amount of paraffins and aromatic hydrocarbons.
 - **Mixed base petroleum:** It contains both paraffins and asphaltic hydrocarbons.

Refining of Petroleum

- Refining is the process of removing unwanted impurities and separating petroleum into useful fractions with different boiling ranges
- Steps in petroleum refining:
 - Separation of water (demulsification): The crude oil from the well is an extremely stable emulsion of oil and salt water. The demulsification is achieved by Cotrell's process.
 - Removal of harmful impurities: NaCl and MgCl₂ corrode the refining equipments. These are removed by modern techniques like electrical desalting and dehydration.
 - Fractional Distillation

Low Temperature



➤ Long chain hydrocarbons: High boiling point



Condense first at bottom of tower

➤ Small Chain hydrocarbons: Low boiling point



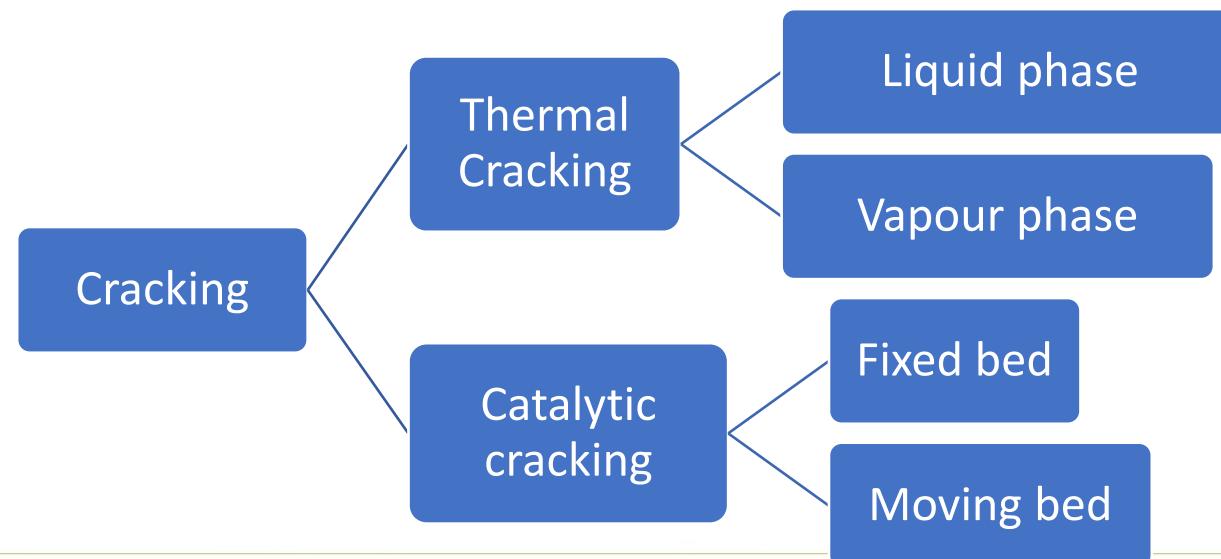
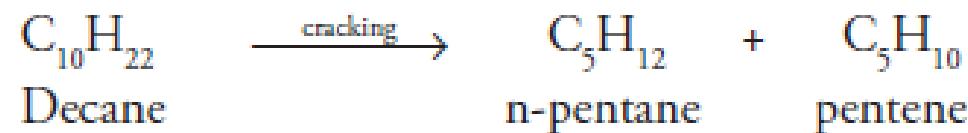
Condense later at top of tower

Major fractions obtained by the distillation of crude oil

S.No.	Fraction's name	Boiling temperature	Approximate composition in terms of hydrocarbons containing C atoms	Uses
1	Uncondensed gases	Below 30 °C	C ₁ –C ₄	Used as domestic fuel (LPG)
2	Petroleum ether	30–70 °C	C ₅ –C ₇	Solvent for fats, essential oils, used in dry cleaning
3	Gasoline or petrol or motor spirit	70–120 °C	C ₅ –C ₉	As a motor fuel for IC engines, as a solvent and in dry cleaning
4	Naphtha or solvent spirit	120–180 °C	C ₉ –C ₁₀	As a solvent for paints and varnishes and in dry cleaning
5	Kerosene oil	180–250 °C	C ₁₀ –C ₁₆	Fuel for stoves, jet engine fuel and for preparing oil gas used in laboratories
6	Diesel oil	250–320 °C	C ₁₅ –C ₁₈	Diesel engine fuel
7	Heavy oil Heavy oil on vacuum distillation gives i. Lubricating oil ii. Petroleum jelly (vaseline) iii. Greases iv. Paraffin wax	320–400 °C – – – –	C ₁₇ –C ₃₀ C ₁₇ –C ₂₀ – C ₂₀ –C ₂₈	Fuel for ships, in metallurgical furnaces and in conversion to gasoline by cracking As lubricants Used in cosmetics and medicines In candles, boot polishes, wax paper, etc.
8	Residue: It may be either i. Asphalt (if the crude oil is asphaltic) ii. Petroleum coke	> 400 °C	C ₃₀ and above	Used for water proofing of roofs and for road making As a fuel in moulding electrode rods for cells

Cracking

- Gasoline is in maximum demand because of its use as fuel in the automobile industry. Hence, there is a need to convert the middle oil and heavy oil fractions into a more useful fraction gasoline.
- **Cracking:** Process of converting high-molecular-weight bigger hydrocarbons into low-molecular-weight smaller hydrocarbons by the application of heat, with or without a catalyst.



Thermal Cracking

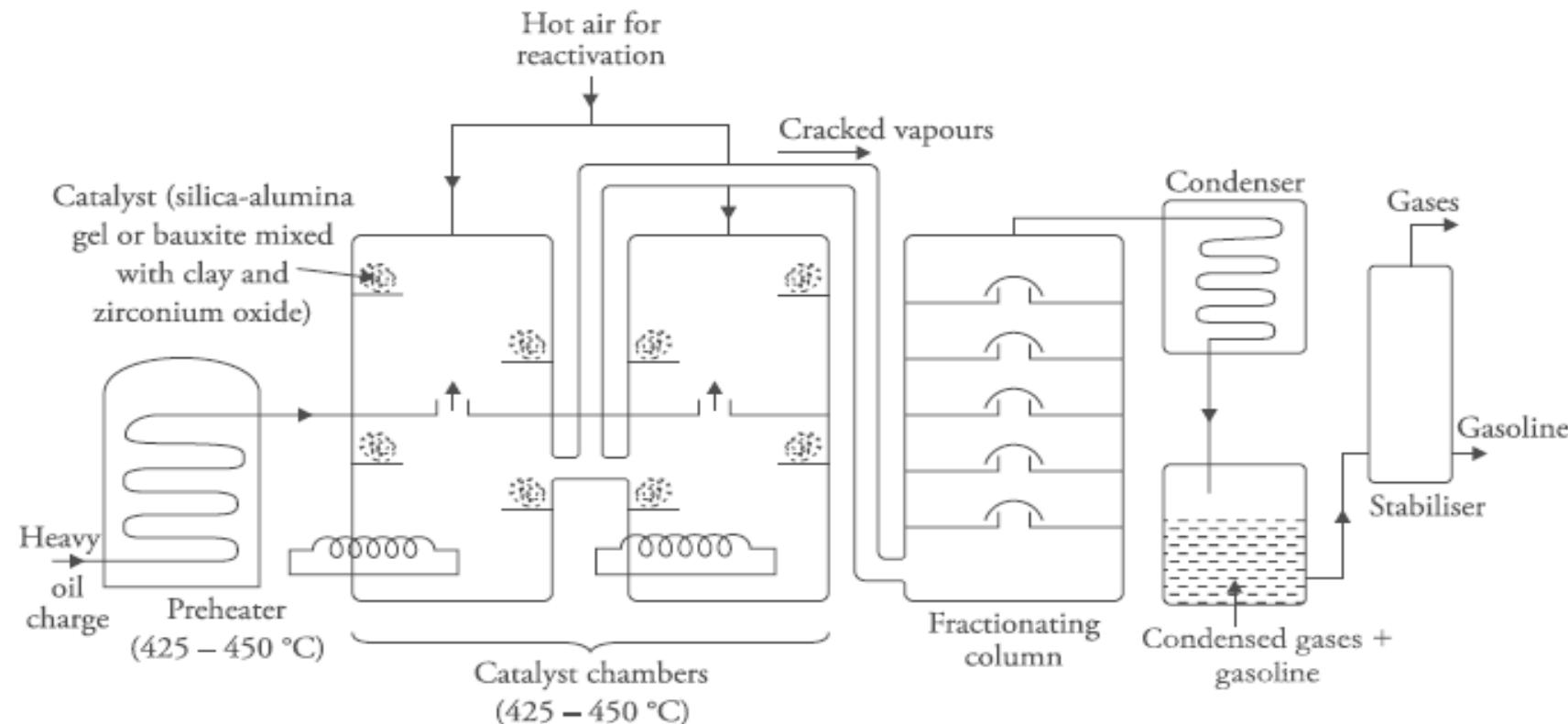
- When the heavy oils are subjected to high temperature (to break C-C bonds) and pressure (to prevent vaporization of cracked residues) in the absence of catalyst, the bigger hydrocarbons breakdown to give smaller molecules of paraffins, olefins and some hydrogen.

Characteristic	Liquid phase thermal cracking	Vapour phase thermal cracking
Cracking Temperature	475 – 530 °C	600–650 °C
Pressure	100 kg/cm ²	10–20 kg/cm ²
Time Required	More time	Less time
Octane Rating of petrol	65–70	Greater than 70
Type of oil used	Any heavy oil can be cracked	Oil should be readily vapourised

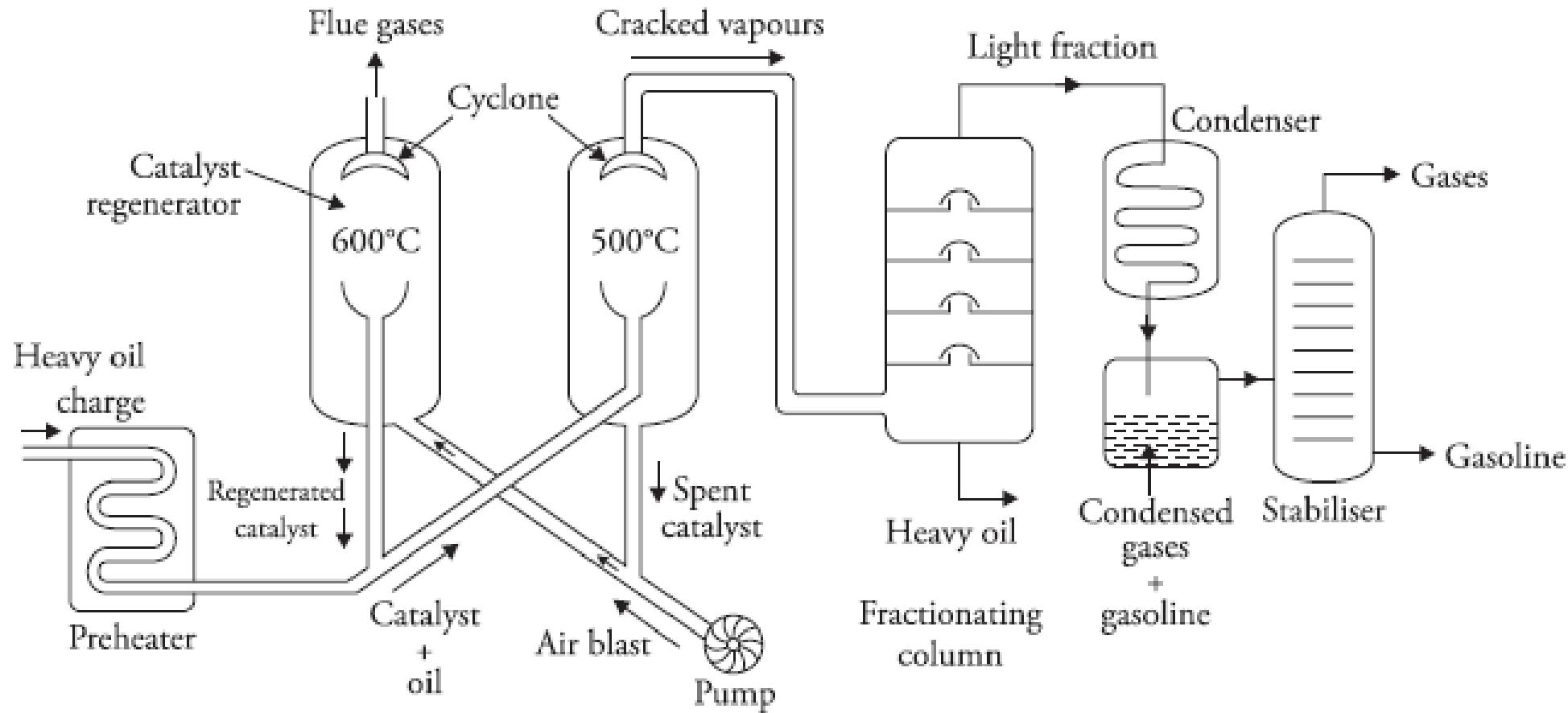
Catalytic Cracking

- Carried out in the presence of a catalyst at a much lower temperature and pressure.
- The catalyst used is usually a mixture of silica and alumina (hydrated aluminium silicate) or zeolites in the form of beads or pellets

1. Fixed bed catalytic cracking



2. Moving bed catalytic cracking/ fluidised bed catalytic cracking



Advantages of catalytic cracking over thermal cracking

- The yield of gasoline is higher. About 70% of the raw material by weight is converted into gasoline.
- Production cost is low as high temperatures and pressures are not needed
- No external fuel is required for cracking since the heat required is obtained by burning the carbon deposited on the catalyst itself during regeneration
- Process can be controlled to obtain desired products.
- The process is faster.
- Action of catalysts is selective, hence cracking of only high-boiling hydrocarbons takes place.
- Quality of gasoline produced is better because:
 - The product contains very little amount of undesirable sulphur as the major portion of it escapes out as H_2S during cracking.
 - The gasoline obtained by cracking contains low percentage of olefins and higher percentage of isoparaffin and aromatic hydrocarbons. This increases the antiknock properties of gasoline.

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Lecture 8



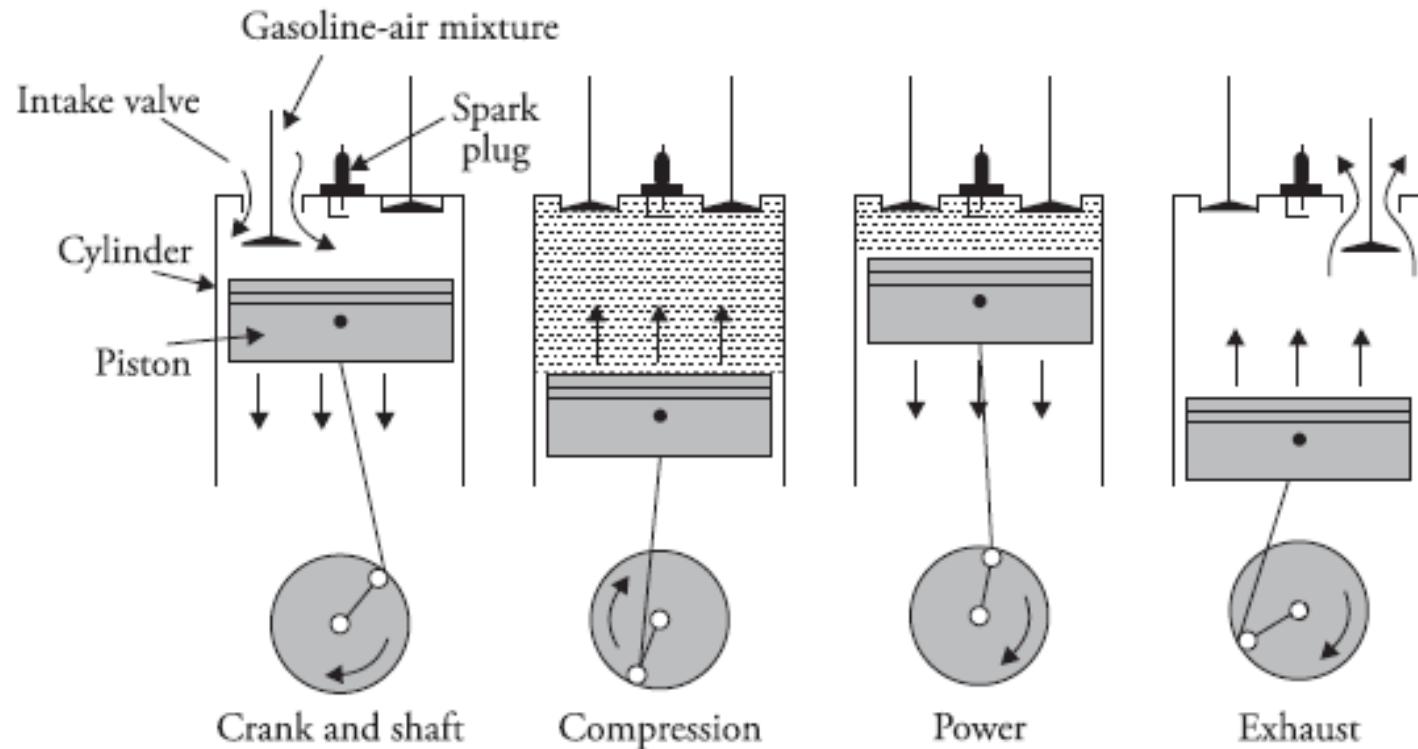
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Knocking

- It is defined as the **metallic sound similar to rattling of hammer** produced in internal combustion engine due to immature ignition of fuel air mixture.
- In a **petrol engine** the whole process comprises of four strokes:
 - **Suction stroke:** The downward moving piston sucks a mixture of air and petrol vapours in the carburetor into the cylinder
 - **Compression stroke:** The piston moves up, compressing the gas mixture.
 - **Power stroke:** Just before the piston reaches the top centre of the cylinder a spark from the spark plug ignites the gas mixture. The hot gases produced due to combustion increase the pressure and push the piston down.
 - **Exhaust stroke:** This is the last stroke in which the piston rises up and expels the exhaust gases from the cylinder
- The cycle then repeats itself

A four-stroke, spark-ignition engine



Compression Ratio: The ratio of initial gaseous volume in the cylinder at the end of suction stroke to final volume at compression stroke



Indicates the extent of compression of fuel-air mixture by the piston

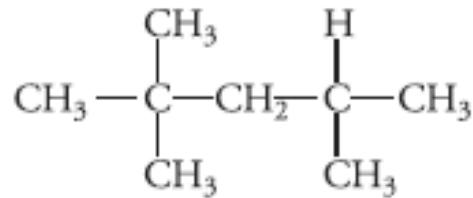
- If the compression ratio exceeds a certain limit, the fuel-air mixture may get heated to a temperature greater than its ignition temperature and spontaneous combustion of the fuel occurs even before sparking. This is called **pre-ignition**
- As a result of pre-ignition, the unburned fuel air mixture gets heated to such an extent that some of the hydrocarbons reach their ignition temperature and ignite all at once – explosively causing a metallic sound called **knocking**

Chemical Structure and knocking

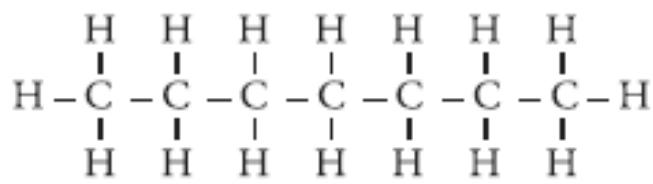
- With normal paraffins/alkanes, the knocking increases with increase in length of the hydrocarbon chain.
 n-butane < n-pentane < n-hexane < n-heptane
- Knocking decreases with the increase in the number of double bonds and rings (cyclic structure)
- Knocking decreases as the branching in carbon chain increases
 n-heptane > 2-methylhexane > 2, 2-dimethylpentane
- Aromatics such as benzene and toluene have very high antiknock properties
- Overall knocking order**

Straight chain paraffins > branched chain paraffins (i.e., isoparaffins) > olefins > cycloparaffins (i.e., naphthalenes) > aromatics.

Octane Rating



Isooctane
2,2,4-trimethylpentane
(Octane number 100)



n-heptane
(Octane number 0)

Isooctane has high resistance to knocking and is assigned an antiknock value of 100

n-heptane knocks very badly and is assigned an antiknock value of zero

- **Octane Number:** The percentage of isoctane in a mixture of isoctane and n-heptane, which has the same knocking characteristics as that of the fuel under examination, under same set of conditions.
- A fuel with octane number 80 is one which has the same combustion characteristics as a 80:20 mixture of isoctane and n-heptane

• Fuel Structure and Octane rating

Straight chain paraffins

Branched chain paraffins

Olefins

Cycloparaffins

Aromatics

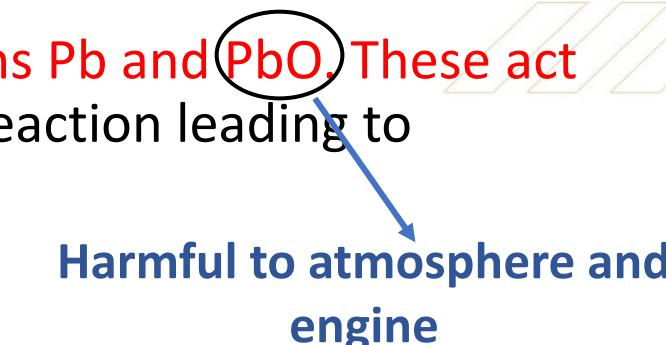


- Knocking tendency decreases as we move downwards
- Antiknocking property of fuel increases as we move downwards
- Octane number of fuel increases as we move downwards

Fuel	N-hexane	cyclohexane	Benzene
Octane Number	26	77	100+

Antiknocking agents

- The antiknock properties of gasoline are usually increased by adding tetraethyl lead (TEL) $Pb(C_2H_5)_4$ and the process is called 'doping'.
- TEL is a colourless liquid with a sweet odour but it is highly poisonous
- Gasoline containing TEL is coloured with 2% red dye to indicate its poisonous nature.
- Knocking is a free radical mechanism. During combustion $Pb(C_2H_5)_4$ forms Pb and PbO . These act as free radical chain inhibitors and hence the propagation of the chain reaction leading to knocking does not take place.


Harmful to atmosphere and engine
- **Solution** → Ethylene dibromide ($C_2H_4Br_2$) is also added, so that lead formed is converted into lead bromide, which is volatile and escapes into the atmosphere.
- $Pb + C_2H_4Br_2 \rightarrow PbBr_2 + CH_2=CH_2$

Diesel Engine Fuels

- The combustion cycle has four strokes
- ***Suction stroke:*** In this the air is drawn into the cylinder.
- ***Compression stroke:*** Here, the air is compressed to a pressure of 30–50 kg/cm². Compression leads to rise in temperature to about 500 °C.
- ***Power stroke*** Towards the end of compression stroke, that is, when the piston reaches its top centre, the diesel oil is injected in the form of fine droplets into the very hot compressed air. The fine particles of fuel absorb heat from the compressed air (at about 500 °C) and ignite. The pressure of the gases evolved during the ignition/combustion pushes the piston downwards.
- ***Exhaust stroke*** This is the last stage of the cycle. In this the expulsion of hot gases from the cylinder takes place.

 In a diesel engine, the fuel is ignited not by a spark as in petrol engine, but by the application of heat and pressure.

Knocking in diesel engine

- The combustion of fuel in the diesel engine is not spontaneous. **The interval between the start of fuel injection and its ignition is termed as ignition delay or induction delay.**
- This ignition delay is due to the time taken for the vaporization of the individual droplets and raising the vapour to its ignition temperature.
- **Diesel Knocking:** When a fuel has long induction lag a portion of the injected fuel gets accumulated in the cylinder even before ignition and when ignition takes place, the accumulated fuel burns violently leading to sudden increase in temperature and pressure.
- The diesel should have a spontaneous ignition temperature less than the temperature produced by compression to minimize ignition delay.
- Diesel engine fuels consist of straight chain hydrocarbons with minimum amount of branched chain and aromatic hydrocarbons.(IN CONTRAST TO GASOLINE)

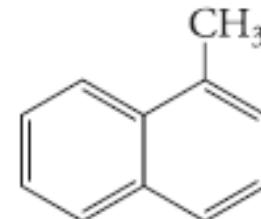
Cetane rating / Cetane number

- It is a measure of ignition quality of a diesel fuel / It is the measure of the ease with which the fuel will ignite under compression.



or
n-hexadecane
(Cetane no. = 100)

Very short ignition delay as compared to any diesel fuel and is assigned an arbitrary value of 100.



α -methylnaphthalene
(Cetane no =0)

long ignition delay compared to any other diesel fuel and hence is assigned a value of 0 (zero).

- Cetane number:** the percentage of cetane (n-hexadecane) in a mixture of cetane and - methylnaphthalene, which will have the same ignition characteristics as the fuel under test, under the same conditions.
- Ignition quality order among the constituents of diesel engine fuels in order of decreasing cetane number is:

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

- High cetane number fuels eliminate diesel knock
- Hydrocarbons which are poor gasoline fuels are quite good diesel fuels.
- The cetane number of a diesel fuel can be raised by addition of small quantity of certain ‘preignition dopes’ such as ethylnitrite, isoamyl nitrite, acetone peroxide, etc.



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Lecture 9+10



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Combustion of fuel

➤ Calculation of air required for the combustion of solid and liquid fuels

- The elements generally present in the fuel are carbon, hydrogen, oxygen, nitrogen and sulphur. During combustion of the fuel these elements combine with oxygen.
- Let the weight of carbon, hydrogen, oxygen, and sulphur in one kg of the fuel be C kg, H kg, O kg and S kg, respectively
- The quantity of oxygen required for the combustion of C kg of carbon, H kg of hydrogen, S kg of sulphur can be calculated

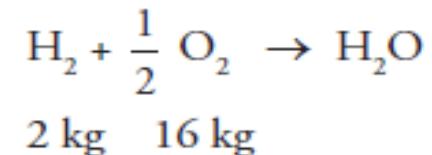
→ Combustion of carbon



12 kg of carbon requires 32 kg of oxygen.

C kg of carbon requires $\frac{32}{12} \times C$ kg or 2.67 C kg of oxygen.

→ Combustion of hydrogen



2 kg of hydrogen requires 16 kg of oxygen.

H kg of hydrogen requires $\frac{16}{2} \times H$ kg or 8 H kg of oxygen

→ Combustion of sulphur



32 kg of sulphur requires 32 kg of oxygen.

S kg of sulphur requires $\frac{32}{32} \times S$ kg or 1 S kg of oxygen.

- The total quantity of oxygen required for the combustion of 1 kg fuel will be = $(2.67C + 8H + S)$ Kg
- If oxygen is already present in the fuel, the quantity of oxygen to be supplied from air = $(2.67 C + 8 H + S - O)$ kg
- Minimum quantity of O_2 required for the complete combustion of 1 kg of a fuel = = $(2.67 C + 8 H + S - O)$ kg
- As air contains 23% oxygen by weight; hence, minimum weight of air required for combustion

$$= (2.67 C + 8 H + S - O) \frac{100}{23} \text{ kg.}$$

Calculation of volume of oxygen or air required

- **METHOD 1**

- Average mass of 1 mole air = 28.94 g
- 1 mol of any gas at STP (0 °C and 760 mm pressure) occupies 22.4 L,
- Let the weight of air required = x kg
- According to Avogadro's law, 28.94 g air occupies 22.4 L OR 28.94 kg of air occupies 22.4 m³
- x kg of air occupies $(22.4 \times x)/28.94$ m³ volume
(Since, 1 m³ = 1000 L and 1 kg = 1000 g)



METHOD 2 → Ideal gas equation

$$PV = \frac{W}{M} \times RT$$

where,

P = pressure of gas in atmosphere;

V = volume of gas

R = gas constant;

T = temperature in K

W = mass of gas;

M = molecular mass of the gas.

Note:1.

Composition of air	% oxygen	% nitrogen
By volume	21	79
By weight	23	77

Thus, 1 kg of oxygen is supplied by $1 \times \frac{100}{23} = 4.35$ kg of air.

1 m³ of oxygen is supplied by $1 \times \frac{100}{21} = 4.76$ m³ of air.

2. Combustion seldom takes place efficiently with minimum weight of oxygen or air. An excess of air has to be supplied for proper combustion.

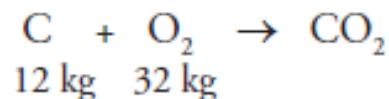
$$\% \text{ Excess air} = \frac{\text{Actual air used} - \text{Minimum weight of air required}}{\text{Minimum weight of air required}} \times 100$$

Class Numericals

1. Calculate the weight and volume of air required for the combustion of 3 kg of carbon.

Solution

Combustion reaction



Weight of oxygen required to burn 12 kg C = 32 kg

Weight of oxygen required to burn 3 kg $C = \frac{32}{12} \times 3 = 8 \text{ kg}$

As, air contains 23% oxygen by weight

Therefore, weight of air required = $8 \times \frac{100}{23} = 34.783 \text{ kg} = 34783 \text{ g}$

Volume of air required

as, 1 mole of any gas at STP occupies 22.4 L

Therefore, volume occupied by 1 mole air = 28.94 g air = 22.4 L

(molecular weight of air = 28.94 g)

$$\begin{aligned} \text{Volume occupied by } 34783 \text{ g of air} &= \frac{22.4}{28.94} \times 34783 \\ &= 26.92 \times 10^3 \text{ L} = 26.92 \text{ m}^3 \\ &\quad (\text{Since } 1 \text{ L} = 10^3 \text{ m}^3) \end{aligned}$$

2. A sample of coal was found to have the following composition by weight

$C = 75\%$; $H = 5.2\%$; $O = 12.1\%$; $N = 3.2\%$ and ash = 4.5%

Calculate (i) minimum amount of O_2 and air necessary for complete combustion of 1 kg of coal; (ii) weight of air required if 40% excess air is supplied.

3. A given sample of petrol contains $H = 15.4\%$ and $C = 84.6\%$. Calculate the minimum volume of O_2 required for the combustion of this sample.

Solution 2

Constituent	Amount per kg of the coal sample	Combustion reaction	Weight of O ₂ required
C	0.75 kg	C + O ₂ → CO ₂	$0.75 \times \frac{32}{12} = 2 \text{ kg}$
H	0.052 kg	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	$0.052 \times \frac{16}{2} = 0.416 \text{ kg}$
O	0.121 kg	-	-
N	0.032 kg	-	-
Ash	0.045 kg	-	-
	-	-	Total O ₂ required = 2.416 kg

$$\begin{aligned}\text{O}_2 \text{ required from air} &= \text{Total O}_2 \text{ required} - \text{O}_2 \text{ in fuel} \\ &= 2.416 \text{ kg} - 0.121 \text{ kg} = 2.295 \text{ kg}\end{aligned}$$

$$\text{Minimum weight of air required} = 2.295 \times \frac{100}{23} = 9.978 \text{ kg.}$$

$$\text{Weight of excess air} = 9.978 \times \frac{40}{100} = 3.9912 \text{ kg}$$

$$\text{Total air supplied} = 9.978 + 3.9912 = 13.969 \text{ kg.}$$

Solution 3

Constituent	Amount in 1 kg of petrol	Combustion reaction	Weight of O ₂ required(kg)
H	0.154 kg	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	$0.154 \times \frac{16}{2} = 1.232 \text{ kg}$
C	0.846 kg	C + O ₂ → CO ₂	$0.846 \times \frac{32}{12} = 2.256 \text{ kg}$
			Total O ₂ reqd = 3.488 kg

Weight of O₂ required for combustion of 1 kg fuel = 3.488 kg
= 3488 g.

Since 1 mole = 32 g of O₂ at NTP occupies 22.4 L

$$\begin{aligned}\text{Therefore } 3488 \text{ g of O}_2 \text{ at NTP occupies} &= \frac{22.4}{32} \times 3488 \\ &= 2441.6 \text{ L} \\ &= 2.441 \text{ m}^3\end{aligned}$$

(Since 1000 L = 1 m³)

Homework Questions

1. Calculate the mass of air needed for the complete combustion of 5 kg of coal containing C = 80%; H = 15%, O = rest (71.369 kg)

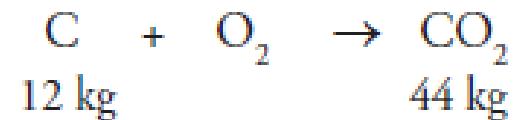
2. A sample of coal was found to contain: C = 80%; H = 5.0%; N= 2%; O = 1.0% and remaining ash.
 - i. Calculate the amount of air required for complete combustion of 1 kg of coal sample.
 - ii. If 45% excess air is supplied, estimate the weight of air supplied
(Air = 10.9708 kg, 15.9 kg)

Calculation of quantity of flue gases

- The gases coming out after combustion CO_2 , SO_2 , CO , O_2 , N_2 are called flue gases.
- The water vapours formed condense as the gases cool down while the ash is excluded as it does not take part in combustion.

➤ Calculation of the flue gases when minimum amount of air is supplied

- All the O_2 of air will be used in combustion of carbon and sulphur while N_2 in air remains unreacted.
- Let 1 kg of fuel contain C kg of carbon and S kg of sulphur.



12 kg of carbon on combustion gives 44 kg of carbon dioxide.

Therefore, C kg of carbon gives $\frac{44}{12} \times C \text{ kg of CO}_2$.



32 kg of sulphur on combustion gives 64 kg of sulphur dioxide.

S kg of sulphur gives $\frac{64}{32} \times S$ kg or 2 S kg of SO₂.

Weight of N₂ = $\frac{77}{100} \times$ weight of air supplied + weight of N₂ per kg of fuel.

Total weight of dry flue gases formed by the combustion of 1 kg of fuel =

Weight of CO₂ + weight of SO₂ + weight of N₂

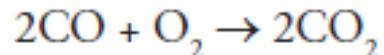
➤ Calculation of the flue gases when excess of air is supplied

- CO₂ and SO₂ are calculated as mentioned above.
- N₂ in flue gas = N₂ of total air supplied + N₂ present in the fuel.
- When excess air is supplied the flue gas will contain O₂ of excess air.
- Hence, the total weight of flue gas per kg of the fuel (when excess air is supplied) = weight of CO₂ + weight of SO₂ + weight of N₂ + weight of O₂ in excess air

Combustion of gaseous fuel

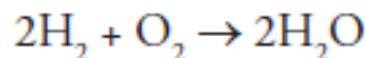
- CO, H₂ and hydrocarbons such as CH₄, C₂H₆, etc. are the main constituents of common gaseous fuels.

Combustion of carbon monoxide



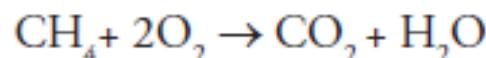
Thus, 2 volume of CO combine with 1 volume of O₂ to give 2 volume of CO₂

Combustion of H₂

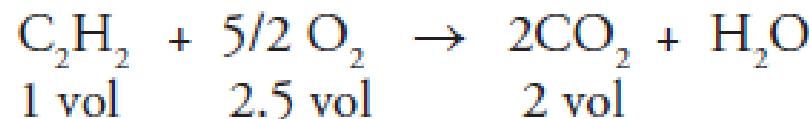
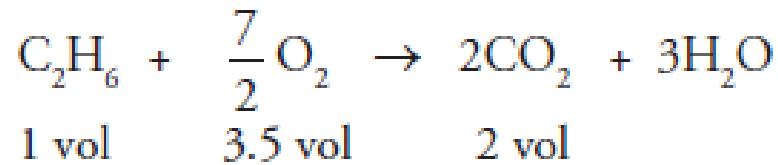


Here 2 volumes of H₂ combines with 1 volume of O₂

Combustion of CH₄



1 volume of methane reacts with 2 volumes of O₂



- The other constituents such as CO_2 and N_2 do not require any oxygen
- If the fuel already contains oxygen then that amount is subtracted from the total O_2 required.

Class Numericals

1. A fuel is found to contain C = 90%; H = 6.0%; S = 2.5%; O = 1.0% and ash = 0.5%. Calculate the amount of air required for complete combustion of 1 kg of fuel. If 25% excess air is used for combustion, calculate the total air supplied and the percentage composition of the dry products of combustion.
2. A gas used in internal combustion 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 the combustion of 1 m^3 of the gas.
3. A gaseous fuel has the following composition by volume – CH_4 = 4.0%; CO = 26%; CO_2 = 10%; H_2 = 10%; N_2 = 50%. If 20% excess air is supplied calculate the volume of air supplied and the % composition of dry flue gases.

• Solution 1

Constituent	Amount per kg of the coal sample	Combustion reaction	Weight of O ₂ required	Weight of dry flue gas
C	0.90 kg	C + O ₂ → CO ₂	$0.90 \times \frac{32}{12} = 2.4 \text{ kg}$	$0.90 \times \frac{44}{12} = 3.3 \text{ kg}$
H	0.06 kg	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$0.06 \times \frac{16}{2} = 0.48 \text{ kg}$	H ₂ O does not constitute dry flue gas
S	0.025 kg	S + O ₂ → SO ₂	$0.025 \times \frac{32}{32} = 0.025 \text{ kg}$	$0.025 \times \frac{64}{32} = 0.05 \text{ kg}$
O	0.01 kg	—	—	—
Ash	0.005 kg	—	—	—
		—	Total O ₂ required = 2.4 + 0.48 + 0.025 kg = 2.905 kg	

O_2 required from air = Total O_2 required – O_2 in fuel

$$= 2.905 - 0.01 = 2.895 \text{ kg}$$

Minimum weight of air required for combustion

$$2.895 \times \frac{100}{23} = 12.587 \text{ kg}$$

According to the question 25% excess air is supplied

$$\text{Excess air} = 12.587 \times \frac{25}{100} = 3.147 \text{ kg}$$

$$\begin{aligned}\text{Total air supplied} &= 12.587 \text{ kg} + 3.147 \text{ kg} \\ &= 15.734 \text{ kg}\end{aligned}$$

Calculation of dry products in the flue gases

The flue gases contains CO_2 , SO_2 , O_2 from excess air and N_2 from the total air supplied.

Weight of CO_2 = 3.3 kg

Weight of SO_2 = 0.05 kg

$$\text{Weight of } O_2 = 3.147 \times \frac{23}{100} = 0.724 \text{ kg}$$

$$\text{Weight of } N_2 = 15.734 \times \frac{77}{100} = 12.115 \text{ kg}$$

$$\begin{aligned}\text{Total weight of flue gases} &= 3.3 + 0.05 + 0.724 + 12.115 \\ &= 16.189 \text{ kg}\end{aligned}$$

Percentage composition of dry flue gases

$$\% CO_2 = \frac{3.3}{16.189} \times 100 = 20.38\%$$

$$\% SO_2 = \frac{0.05}{16.189} \times 100 = 0.309\%$$

$$\% O_2 = \frac{0.724}{16.189} \times 100 = 4.47\%$$

$$\% N_2 = \frac{12.115}{16.189} \times 100 = 74.835\%$$

Solution 2

Constituent	Amount in 1m ³ of the fuel	Combustion reaction	Volume of O ₂ required(m ³)
H ₂	0.45 m ³	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	45 × 0.5 = 0.225
CH ₄	0.36 m ³	CH ₄ + 2 O ₂ → CO ₂ + 2H ₂ O	0.36 × 2 = 0.72
CO	0.15 m ³	CO + $\frac{1}{2}$ O ₂ → CO ₂	0.15 × 0.5 = 0.075
N ₂	0.04 m ³		
			Total = 1.020

$$\text{Therefore volume of air required per m}^3 \text{ of the gas} = 1.020 \text{ m}^3 \times \frac{100}{21}$$
$$= 4.857 \text{ m}^3$$

Solution 3

Constituents	Volume in 1 m ³ of gas	Combustion Reaction	O ₂ required (in m ³)	Volume of dry flue gases(m ³)
CH ₄	0.04 m ³	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.04 × 2 = 0.08 m ³	CO ₂ = 0.04 × 1 = 0.04 m ³
CO	0.26 m ³	CO + $\frac{1}{2}$ O ₂ → CO ₂	0.26 × $\frac{1}{2}$ = 0.13 m ³	CO ₂ = 0.26 × 1 = 0.26 m ³
H ₂	0.10 m ³	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	0.10 × $\frac{1}{2}$ = 0.05 m ³	
CO ₂	0.10 m ³	–	–	CO ₂ = 0.10 m ³
N ₂	0.50 m ³	–	–	0.50 m ³ + N ₂ in total air supplied
			Volume of O ₂ required = 0.260 m ³	Total CO ₂ in flue gas = 0.40 m ³

$$\text{Minimum volume of air required} = 0.260 \times \frac{100}{21} = 1.238 \text{ m}^3$$

$$\text{Excess air} = 1.238 \times \frac{20}{100} = 0.2476 \text{ m}^3$$

$$\text{Total air supplied} = 1.238 \text{ m}^3 + 0.2476 \text{ m}^3 = 1.4856 \text{ m}^3$$

Calculation of volume of dry flue gases

The flue gas contains CO₂, O₂ from excess air and N₂ of fuel + N₂ of total air supplied.

$$\text{CO}_2 = 0.40 \text{ m}^3$$

$$\text{O}_2 = 0.2476 \times \frac{21}{100} = 0.052 \text{ m}^3$$

$$\text{N}_2 = 0.50 \text{ m}^3 (\text{of fuel gas}) + 1.4856 \times \frac{79}{100} \text{ (from total air supplied)}$$

$$\text{N}_2 = 0.50 + 1.1174 = 1.674 \text{ m}^3.$$

$$\text{Total volume of dry flue gases} = (0.40 + 0.052 + 1.674) \text{ m}^3 = 2.126 \text{ m}^3$$

$$\% \text{ CO}_2 = \frac{0.40}{2.126} \times 100 = 18.81\%$$

$$\% \text{ O}_2 = \frac{0.052}{2.126} \times 100 = 2.446\%$$

$$\% \text{ N}_2 = \frac{1.674}{2.126} \times 100 = 78.74\%$$

Homework questions

1. Calculate the volume of air required for the complete combustion of 1 m³ of gaseous fuel having the composition CO = 46%; CH₄ = 10%; H₂ = 40%; C₂H₂ = 2.0%; N₂ = 1.0% and remaining being CO₂. (3.238 m³)
2. A gaseous fuel has the following composition by volume – CH₄ = 6%; CO = 22%; O₂ = 4%; CO₂ = 4%; H₂ = 20%; N₂ = 44%. 20% excess air is used. Find the weight of air actually supplied per m³ of this gas. Molecular weight of air = 28.97. (2143.107 g)
3. A sample of coal was found to contain: C = 80%; H = 5.0%; N = 2%; O = 1.0% and remaining ash.
 - i. Calculate the amount of air required for complete combustion of 1 kg of coal sample.
 - ii. If 45% excess air is supplied, estimate the percentage composition of the dry products of combustion.

(Air = 10.9708 kg; % CO₂ = 17.976%; N₂ = 75.067%; O₂ = 6.956%)

Assignment 2

Describe the production process, composition and applications of the following gaseous fuels

1. Natural gas
2. CNG
3. LPG
4. Coal gas
5. Oil gas
6. Producer gas
7. Water gas



Combustion Numericals

1. Calculate the minimum amount of air required for complete combustion of 100 kg of the fuel containing C = 80%, H₂ = 6%; O₂ = 5%; S = 2% and rest N₂ by weight.
2. The percentage composition of a sample of bituminous coal was found to be as under: C = 75.4%, H = 4.5%, O = 12.5%, N = 3.1%, S = 1.4%. The rest being ash, calculate the minimum weight of air necessary for complete combustion of 1 kg of coal and percentage composition of the dry products by combustion by weight.
3. Calculate the minimum weight of air required for the complete combustion of 1kg coal having the following percentage composition by weight. C = 90%, H₂ = 3.5%, O₂ = 3%, S = 0.5%, N₂ = 0.5% and ash = 1.5%. Calculate the percentage composition by weight of the dry products of the combustion.
4. Calculate the volume of air required for complete combustion of 1 m³ of a gaseous fuel having the composition: CO = 46%, CH₄ = 10%; H₂ = 40%, C₂H₂ = 2%, N₂ = 1% and the remaining being CO₂.
5. The percentage analysis by volume of producer gas is –H₂ = 19.4, CO = 20.5, N₂ = 50.1, CH₄ = 4.2, CO₂ = 6.0. Calculate the weight of air required and the percentage of dry product obtained if 30% excess air is supplied for combustion.

THANK YOU

