

# FUELS AND LUBRICANTS

## FUELS

### 4.1 INTRODUCTION

[May 19]

- Fuels are the sources of heat energy. Fuels are the substances containing carbon as a main constituent and other elements or atoms, which on combustion (reaction with oxygen) produce heat energy that can be utilized economically for domestic and industrial purposes. Fuels are generally made up of carbon and hydrocarbon, but may also contain elements like sulphur, oxygen, nitrogen etc.
- This definition does not include nuclear fuel because it cannot be used easily by a common man.
- Fuel + Oxygen  $\longrightarrow$  Combustion product/s + Heat
- The calorific value of the fuel is defined as the amount of heat generated when unit mass of fuel is completely combusted. The units of calorific value are kcal/kg, cal/g, British Thermal Unit (B.Th.U.) and Centigrade Heat Unit (C.H.U.).
- During the combustion, depending upon whether the combustion product of hydrogen, i.e.,  $H_2O$  is condensed or allowed to escape, calorific value is of two types – (i) Higher or Gross calorific value (HCV or GCV) and (ii) Lower or Net calorific value (LCV or NCV).
- Gross calorific value is defined as the amount of heat generated, when a unit mass or volume of the fuel is completely burnt and the products of the combustion are cooled down to room temperature ( $18^\circ C$ ).
- Net calorific value is defined as the amount of heat generated, when a unit mass or volume of the fuel is completely burnt and the products of the combustion are allowed to escape.

### 4.2 CLASSIFICATION OF FUEL

[Oct., Dec. 17, May 18, 19, Dec. 18]

Fuels are classified on the basis of occurrence and physical state.

#### 1. On the Basis of Occurrence:

- Natural or Primary: Occurs naturally. E.g. Wood, Dung, Crude oil, Natural gas.
- Derived or Secondary: Derived from natural fuels. E.g. Coke, Charcoal, Petrol, Kerosene, Biogas.

#### 2. On the Basis of Physical State:

- Solid: E.g. Wood, Dung, Coke, Charcoal.
- Liquid: E.g. Crude oil, Petrol, Kerosene.
- Gaseous: E.g. Natural gas, Biogas.

### 4.3 CALORIFIC VALUE

The most important property of a fuel is its calorific value. It is defined as:

"The amount of heat energy liberated when unit mass of a solid or non-volatile liquid fuel or unit volume of the gaseous fuel is completely burnt in the presence of oxygen at STP".

**Units of Calorific Value:** The units of calorific value in different systems are as follows:

**Table 4.1 : Units of Calorific Value**

System	Solid Fuel/Liquid Fuel	Gaseous Fuel
CGS	cal/gm	cal/lit
MKS	kcal/kg	kcal/m <sup>3</sup>
SI	J/kg	J/m <sup>3</sup>

The interrelations among different units of calorific value are:

$$1 \text{ cal/gm} = 1 \text{ kcal/kg}$$

$$= 4.187 \text{ kJ/kg. (for solid and liquid fuels)}$$

$$1 \text{ kcal/m}^3 = 4.187 \text{ kJ/m}^3 \\ (\text{for gaseous fuels at STP})$$

#### 4.3.1 Types of Calorific Values

- Main chemical composition of fossil fuels is carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S) along with a small amount of ash (i.e. inorganic components).
- Carbon is the main constituent responsible for heat generation as its oxidation liberates large amounts of energy i.e.  $C + O_2 \rightarrow CO_2 + Energy$ .
- When fuel is burnt,  $CO_2$ ,  $H_2O$ ,  $SO_2$ ,  $SO_3$ ,  $NO_2$ ,  $NO_3$  etc. gases are produced as byproducts. These are called as combustion products.
- Sometimes if the combustion products are condensed then latent heat of condensation is liberated which is additional to that of heat liberated during actual condensation.
- So depending on whether the combustion products are condensed or not, calorific values of fuels are of two types.

**1. Higher or Gross Calorific Value (GCV):**

- "It is the amount of heat liberated when unit mass of a solid or non-volatile liquid fuel or unit volume of gaseous fuels are burnt in the presence of sufficient oxygen or air and the combustion products are allowed to cool at room temperature."
- During the cooling of combustion product, water vapour which is a combustion product gets converted to liquid water and latent heat of condensation is liberated. This is additional to the actual heat generated by combustion of carbon.

$\therefore$  Total heat generated =

$$\left[ \text{Heat generated due to combustion of fuel} \right] + \left[ \text{Heat liberated due to condensation of water vapour} \right]$$

$\therefore$  Gross calorific value =

$$\left[ \text{Heat generated by combustion} \right] + \left[ \begin{array}{l} \text{Heat liberated by condensation of} \\ \text{water i.e. latent heat of condensation} \end{array} \right]$$

- The latent heat of condensation of other combustion products such as  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$  is not considered because they cannot be condensed easily.

**2. Lower or Net Calorific Value (NCV):**

- "It is the amount of heat liberated when unit mass of a solid or non-volatile liquid fuel or unit volume of gaseous fuel is completely burnt in the presence of sufficient oxygen or air and combustion products are allowed to escape as soon as they are formed".
- Since combustion products are allowed to escape, there is no question of their condensation.
- Latent heat of condensation of combustion products does not contribute to the calorific value measurements.
- Heat liberated is only due to the combustion of the constituents of fuel. Hence, this is also called as lower calorific value.

$$\therefore \text{GCV} = \text{NCV} + L$$

where,  $L$  = Latent heat of condensation of water

$$L = \frac{9 \times \% H \times 587}{100}$$

$$\text{or } L = 0.09 \times H \times 587 \text{ cal/g or kcal/kg}$$

$$\therefore \text{GCV} = \text{NCV} + 0.09 \times H \times 587 \text{ cal/g or kcal/kg}$$

**4.4 ESSENTIAL PROPERTIES OF FUEL**

The essential properties of fuel are given below:

- Calorific value
- Ignition temperature
- Flame temperature
- Flash and Fire point
- Aniline point
- Knocking
- Specific gravity
- Cloud and Pour point
- Viscosity
- Coke number

**4.5 CHARACTERISTICS OF GOOD FUEL**

[Oct., Dec. 17, May 18, 19, Dec. 18]

The characteristics of good fuel are listed.

- The calorific value should be high since it indicates the amount of heat generated by the combustion of fuel.
- The moisture content should be low as moisture lowers the calorific value.
- The ash content should be low as ash being the non-combustible matter lowers the calorific value.
- It should have moderate ignition temperature, i.e., the lowest temperature at which fuel starts burning. If it is too low, then it is dangerous to store and transport fuel safely. If it is too high, then it may cause difficulty in initial ignition of fuel.
- It should have moderate velocity of combustion. If it is too low, then higher temperature cannot be achieved. If it is too high, then the heat generated may get wasted before utilization.
- Its combustion should be easily controllable.
- On combustion, it should not produce harmful and pollution creating products.
- It should not produce smoke during combustion.
- It should be easily available and at affordable cost.
- It should be easy to transport and store.
- In case of solid fuel, the size of the particles should be uniform.

**4.6 DETERMINATION OF CALORIFIC VALUE OF FUELS**

- The experimental determination of calorific values is done by using apparatus called as 'calorimeters'.
- As it is known, the rate of ignition, ignition temperature, amount of air/oxygen required for combustion differ for solid, liquid and gaseous fuels.

- So the design of calorimeters is different for different types of fuels.
- for solid fuels (such as coal, starch, wood) and non-volatile or low volatile liquid fuels (alcohols, petrol, diesel). Bomb calorimeter is used.
- For gaseous fuels (LPG, CNG), Boy's calorimeter is used.

#### 4.6.1 Bomb Calorimeter [Calorific values of Solid or Non-volatile Liquid Fuels]

##### Principle:

- "A known quantity of fuel is combusted in the calorimeter and the heat generated is allowed to absorb by known quantity of water. From rise in temperature of water, the calorific value of the combusted fuel can be determined by using the law of conservation of energy."
- It is difficult to make the design of calorimeter in such a way that the heat liberated is only absorbed by water.
- Some part of generated heat is always absorbed by calorimeter accessories such as Bomb pot, stirrer etc.
- In order to account for heat absorbed by these accessories, the water equivalent of the calorimeter should be taken into consideration.

##### Construction:

- Fig. 4.1 shows the schematic diagram of Bomb calorimeter.
- The Bomb calorimeter contains outermost water jacket to make the system 'isolated' from the surrounding.
- Inside the water jacket, there is a copper calorimeter.
- The copper calorimeter is a removable part in water jacket and screw fitted during the experiment.
- Inside the copper calorimeter, there is most important apparatus called as Bomb pot where actually the combustion of the fuel takes place.
- The space between the copper calorimeter and the Bomb pot is filled with known quantity of water.

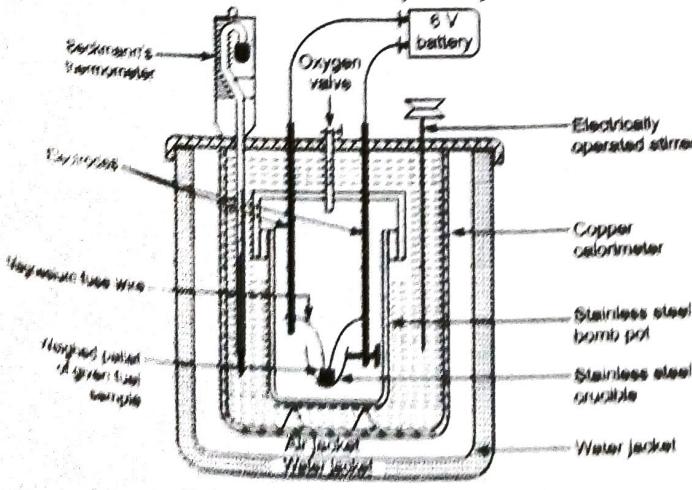


Fig. 4.1 : Bomb calorimeter

- In this space, the calorimeter accessories such as Beckmann's thermometer, stirrer are also fitted.
- Inside the Bomb pot, there is a crucible which holds the fuel.
- Two metallic electrodes are inserted inside the Bomb pot. The fuel in the crucible is brought in contact with electrodes with the help of magnesium fuse wires.
- These electrodes are attached to 6 V DC battery to start the combustion.
- As combustion takes place in the presence of oxygen/air, there is also an arrangement made so that oxygen can enter the Bomb pot through oxygen valve.

##### Working:

- A known quantity of fuel ( $x$  gm) is kept in the crucible and the known quantity of water ( $W$ ) is filled in the copper calorimeter.
- The calorimeter is fitted into the outer water jacket and screw fitted.
- The electrodes are brought in contact with the fuel with the help of fuse wires.
- The stirring of the water is started and initial temperature (i.e. temperature before combustion of fuel) is recorded with the help of thermometer ( $T_1$ ).
- The oxygen is pumped into the Bomb pot and its pressure is maintained at the pressure of 25 atmospheres.
- The desired current is passed through the battery for 3-4 sec that generates a spark so that the fuse wires are burnt.
- Since fuse wires are in contact with the fuel, the ignition of the fuel starts and the heat is liberated.
- This heat flows out of Bomb pot and is absorbed by the water present in the calorimeter.
- The absorption of heat is made uniform by stirring the water continuously.
- The temperature of the water starts rising and the maximum temperature observed is recorded i.e. final temperature ( $T_2$ ).
- The water equivalent of the calorimeter ( $w$ ) is determined in a separate experiment using a standard fuel (e.g. Benzoic acid) whose calorific value is already known.

##### Calculations:

Let

$x$  = Mass of fuel burnt (gm)

$W$  = Mass of water in the calorimeter (gm)

w = Water equivalent of calorimeter, stirrer, thermometer and Bomb pot assembly (gm)

$T_1$  = Initial temperature of water before combustion of fuel ( $^{\circ}\text{C}$ )

$T_2$  = Maximum temperature reached by water after combustion ( $^{\circ}\text{C}$ )

S = Specific heat of water (cal/g/ $^{\circ}\text{C}$ )

GCV = Gross calorific value of fuel (cal/g)

NCV = Net calorific value of the fuel (cal/g)

L = Latent heat of water

From the principle of conservation of energy,

Total heat generated by combustion of fuel =

Heat absorbed by water + Heat absorbed by the calorimeter apparatus

$$\times \cdot \text{GCV} = [S \cdot W (T_2 - T_1) + S \cdot w (T_2 - T_1)]$$

$$\therefore \times \cdot \text{GCV} = (W + w) \cdot S \cdot (T_2 - T_1)$$

Since S = Specific heat or heat capacity of water at constant pressure is 1 cal/g/ $^{\circ}\text{C}$ .

$$\therefore \text{GCV} = \frac{(W + w) \cdot (T_2 - T_1)}{x} \quad (\text{cal/g}) \quad (S = 1 \text{ cal/g}/^{\circ}\text{C})$$

$$\therefore \text{GCV} = \frac{(W + w) (T_2 - T_1)}{x} \text{ cal/g}$$

$$\text{or} \quad \text{GCV} = \frac{4.184 (W + w) (T_2 - T_1)}{x} \text{ J/g}$$

$$\text{as} \quad S = 4. \text{ J/g}/^{\circ}\text{C} \quad \dots (1)$$

We know that,

$$\text{GCV} = \text{NCV} + L$$

$$\text{NCV} = \text{GCV} - L$$

$$\text{NCV} = \frac{(W + w) (T_2 - T_1)}{x} - \frac{9 \times \% \text{ H} \times 587}{100} \text{ cal/g}$$

In this way, GCV and NCV of a solid or non-volatile liquid fuels are determined using Bomb calorimeter apparatus.

From the Bomb calorimeter experiment, GCV of fuels can be obtained. But this value has to be corrected by applying correction because rise in temperature of the water has other contributions also.

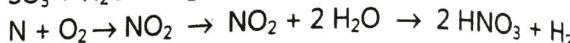
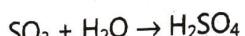
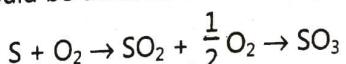
#### (i) Fuse Wire Correction:

The heat liberated, as measured by Bomb experiment, includes the heat given out by ignition of the fuse wire. This heat, however small should be deducted from the gross heat liberated.

#### (ii) Acid Correction:

Fuels contain sulphur and nitrogen and produce  $\text{SO}_2$  and  $\text{NO}_2$ . Water present in the calorimeter and formed during combustion dissolves these gases and produce  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ .

These reactions are exothermic and produce heat which should be deducted from the gross heat liberated.



#### (iii) Cooling Correction:

Time taken to cool the water in the calorimeter from maximum temperature to room temperature is noted. From the rate of cooling ( $dt/\text{min}$ ) and the time of cooling ( $t \text{ min.}$ ), the cooling correction of  $dt \times t$  is to be added to the rise in temperature.

After applying all the above corrections, the gross calorific value is given by

$$\text{GCV} = \frac{(W + w) (t_2 - t_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse wire correction})}{\text{Mass of fuel}}$$

The latent heat of steam is 587 cal/gm or 2.54 J/kg. If 'H' is the percentage of hydrogen in fuel, the net calorific value can be calculated by the following equation.

$$\text{N.C.V.} = \text{G.C.V.} - \frac{9 \times H \times \text{latent heat of condensation of water vapour}}{100}$$

$$= \text{G.C.V.} - 0.09 \times H \times 587 \text{ cal/gm (kcal/kg)}$$

#### 4.6.2 Boy's Calorimeter [Calorific Values of Gaseous and Volatile Liquid Fuels]

##### Principle:

- "The heat liberated by combustion of known volume of fuel is allowed to be absorbed by known quantity of water circulating in the calorimeter."
- From rise in temperature of water and amount of steam condensate collected, the calorific value of gaseous and volatile liquid fuels can be determined".

**Construction:** Fig. 4.2 shows the schematic diagram of a Boy's calorimeter.

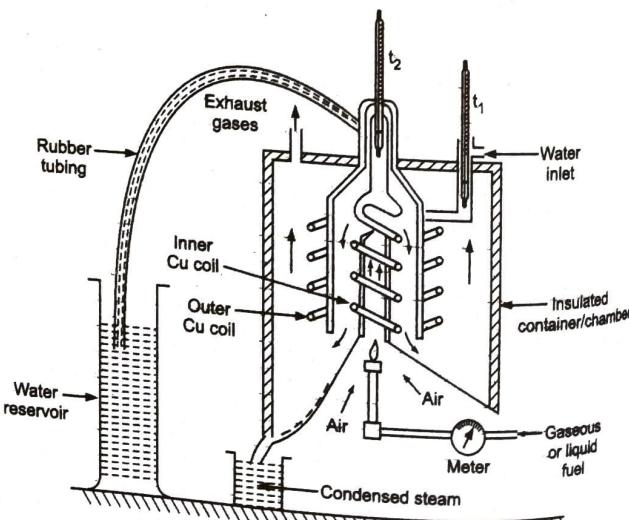


Fig. 4.2 : Boy's calorimeter

- Boy's calorimeter consists of a gas burner connected to gaseous fuel reservoir and fuel enters the burner at constant pressure.

- The gas burner is surrounded by a hood whose inner surface and outer surface has hollow tube through which known quantity of water can be circulated during the experiment.
- The copper tube winding is done in such a way that the water circulates on the outer surface first, enters the inner surface of the hood from bottom and after circulating in the inner surface of the hood, goes out of the calorimeter as shown in Fig. 4.2.
- Two thermometers  $T_1$  and  $T_2$  are provided at the inlet and outlet of the circulating water to record the initial and final temperatures of water.
- The hood, burner and the circulating water is made an 'isolated' system by fitting them in an insulated container/chamber.
- There is also an arrangement to collect the condensed steam.
- The heated water that comes out of the inner copper tubing is collected in a water reservoir.

**Working:**

- Initially, water inlet and outlet are opened and the rate of flow of water entering the calorimeter is regulated and maintained at constant rate.
- The temperature of water (before combustion) is recorded as  $T_1$  at inlet.
- Then the gas burner is started and the pressure of the gas entering the burner is maintained at 3-4 L/min.
- The heat generated by burning of the gas is absorbed by circulating water and its temperature rises.
- After sometime of burning of gas, the final temperature of water at the outlet is recorded as  $T_2$ .
- During this burning period, the mass of steam condensed is collected and recorded.

**Calculation:**

$V$  = Volume of gas burnt at S.T.P. in time 't'

$W$  = Weight of circulating water

$T_1$  = Temperature of water at inlet

$T_2$  = Temperature of water at outlet

$m$  = Mass of steam condensate collected

$L$  = Gross calorific value

and

$S$  = Specific heat of water

By law of conservation of energy,

Total heat produced by fuel combustion

= Heat absorbed by circulating water

$VL = W(T_2 - T_1) \times S$

$$\therefore L = \frac{W(T_2 - T_1)}{V} \text{ cal/g as } S = 1 \text{ cal/g/}^{\circ}\text{C}$$

or  $L = \frac{4.184 \times W(T_2 - T_1)}{V} \text{ J/g}$

as  $S = 4.184 \text{ J/g/}^{\circ}\text{C}$   
Net calorific value  $N$ ,

$N = L - \text{Latent heat of steam generated per cubic metre of fuel burnt}$

$N = \left[ L - \frac{m \times 587}{V} \right] \text{ kcal/m}^3$

**SOLVED EXAMPLES**

**Example 4.1:** 0.72 g of a fuel contains 80% carbon, when burnt in a Bomb calorimeter, increased the temperature of water from  $27.3^{\circ}\text{C}$  to  $29.1^{\circ}\text{C}$ . If the calorimeter contains 250 g of water and its water equivalent is 150 g, calculate GCV of the fuel.

(2 M) (May 05)

**Solution: Given:** Weight of fuel = 0.72 g,  $T_2 = 29.1^{\circ}\text{C}$ ,  $T_1 = 27.3^{\circ}\text{C}$

$$W = 250 \text{ g, } w = 150 \text{ g}$$

$$\text{GCV} = \frac{(W + w)(T_2 - T_1)}{\text{Weight of fuel}}$$

$$= \frac{250 + 150(29.1 - 27.3)}{0.72}$$

$$= [1000 \text{ cal/g or kcal/kg}]$$

**Example 4.2:** 1.6 g of coal sample in Kjeldahl's experiment liberated ammonia which was absorbed in 50 ml 0.5 N sulphuric acid. The resultant solution required 14 ml of 0.1 N NaOH for complete neutralization of  $\text{H}_2\text{SO}_4$  in back titration. The reading for blank titration was 25 ml. Find percent of N in coal.

**Solution: Given:** Weight of coal = 1.6 g,  $V_1 = 50 \text{ ml}$ , Conc. of  $\text{H}_2\text{SO}_4 = 0.5 \text{ N}$

After neutralization,

Volume of NaOH = 14 ml, Conc. of NaOH = 0.1 N

Reading for blank titration = 25 ml. % N in coal.

$$\% \text{ N} = \frac{(\text{Blank} - \text{Back}) \times \text{Conc. of acid} \times 1.4}{\text{Weight of coal}}$$

$$= \frac{(25 - 14) \times 0.1 \times 1.4}{1.6}$$

$$\boxed{\% \text{ N} = 0.95\%}$$

**Example 4.3:** 1.2 g of coal sample was heated in silica crucible in an electric oven at  $110^{\circ}\text{C}$  for 1 hr. The residue weighed 1.16 g.

The crucible was ignited to a constant weight of 0.09 g. In another experiment, 1.2 g of sample was heated in a silica crucible covered with vented lid at  $950^{\circ}\text{C}$  for 7 mins. After cooling the residue weighed 0.80 g. Calculate percent fixed carbon and GCV using Goutel formula. ( $G = 116$ ).

## ENGINEERING CHEMISTRY (BATU)

(4.6)

**Solution: Given:** (i) For % M,

$$\begin{aligned} \text{Weight of coal} &= 1.2 \text{ g}, \quad \text{Weight of residue after heating} \\ &= 1.16 \text{ g} \end{aligned}$$

(ii) For ash content,

$$\text{Weight of ash} = 0.09 \text{ g}$$

(iii) For % V<sub>m</sub>,

$$\text{Weight of coal} = 1.2 \text{ g}, \quad \text{Weight of residue} = 0.8 \text{ g}$$

(iv) Also calculate % FC and GCV.

$$G = 116$$

$$\begin{aligned} \text{(i)} \% M &= \frac{\text{Weight of coal} - \text{Weight of residue}}{\text{Weight of coal}} \times 100 \\ &= \frac{1.2 - 1.16}{1.2} \times 100 \end{aligned}$$

$$\% M = 3.3\%$$

$$\begin{aligned} \text{(ii)} \% \text{ Ash} &= \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 \\ &= \frac{0.09}{1.2} \times 100 \end{aligned}$$

$$\% \text{ Ash} = 7.5\%$$

$$\begin{aligned} \text{(iii)} \% V_m &= \frac{\text{Weight of coal} - \text{Weight of residue}}{\text{Weight of coal}} \times 100 \\ &= \frac{1.2 - 0.8}{1.2} \times 100 \end{aligned}$$

$$\% V_m = 33.3\%$$

$$\begin{aligned} \text{(iv)} \% FC &= 100 - (\% M + \% V_m + \% \text{ Ash}) \\ &= 100 - (3.3 + 33.3 + 7.5) \\ &= 55.9\% \end{aligned}$$

Now, using Gothal formula,

$$\begin{aligned} \text{(v)} GCV &= 82 \times \% FC + G \times V_m \\ &= 82 \times 55.9 + 116 \times 33.3 \text{ cal/g} \\ &= 8446.6 \text{ cal/g} \\ &= 8.446 \text{ kcal/g} \end{aligned}$$

## 4.7 SOLID FUEL – COAL

Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter under favourable conditions. It mainly consists of C, H, N and O along with non-combustible inorganic matter.

## 4.7.1 Various Types of Coal

[May, Dec. 17]

Coal is classified on the basis of carbon content present in it. It is obtained from the coalification of the wood. The composition of wood is C = 50%, H = 6%, N = 0.5%, O = 43.5%. The calorific value of wood is 4000-4500 kcal/kg.

The evolution of coal occurs as follows:

Wood → Peat → Lignite → Bituminous → Anthracite

The details of each coal are given in the Table 4.2 below:

Table 4.2 : Details of Coal

Type of Coal	General Description and Uses	Composition (Air-dried)	Calorific Value	Occurrence in India
Peat	<ul style="list-style-type: none"> <li>(i) Brown fibrous jelly-like mass.</li> <li>(ii) Uneconomical fuel as contains 80-90% water, needs 1-2 months air-drying for free burning.</li> </ul>	C = 57%, H = 5.7%, N = 2%, O = 35.3%	4125-5400 kcal/kg	Nilgiri Hills
Lignite	<ul style="list-style-type: none"> <li>(i) Soft, brown coloured, compact in texture.</li> <li>(ii) Contains 20-60% moisture, on air-drying breaks up into small pieces. Burns with long smoky flame.</li> <li>(iii) Use in manufacture of producer gas.</li> </ul>	C = 67%, H = 5%, N = 1.5%, O = 26.5%	6500-7100 kcal/kg	Assam, Rajasthan and Madras

Type of Coal	General Description and Uses	Composition (Air-dried)	Calorific Value	Occurrence in India
<b>Bituminous – It is Further Sub-Classified as Follows:</b>				
1. Sub-bituminous	(i) Black in colour, more homogeneous and smooth in nature. (ii) On exposure in air, crumble into small pieces. (iii) Non-caking coals.	C = 77%, H = 5%, N = 1.8%, O = 16.2%	7000-7500 kcal/kg	
2. Bituminous	(i) Banded in appearance. (ii) Use for making metallurgical coke, coal gas, for steam raising and domestic heating.	C = 83%, H = 5%, N = 2%, O = 10%	8000-8500 kcal/kg	Bihar, Bengal, Madhya Pradesh and Orissa
3. Semi-bituminous	(i) Used for coke manufacture.	C = 90%, H = 4.5%, N = 1.5%, O = 4%	8500-8600 kcal/kg	
Anthracite	(i) Hardest, quite dense and lustrous in appearance. (ii) Burn without smoke, give intense local heating. (iii) Possess no caking power. (iv) Used for steam raising, house hold purposes and in metallurgical processes.	C = 93.3%, H = 3%, N = 0.7%, O = 3%	8650-8700 kcal/kg	Kashmir and eastern Himalayas

## 4.8 ANALYSIS OF COAL

The coal is analysed for the determination of parameters which influence its calorific value. The two important analysis to evaluate the quality of coal are Proximate analysis and Ultimate analysis.

### 4.8.1 Proximate Analysis

[Dec. 17, 18]

It involves the determination of % moisture, % volatile matter, % ash and % fixed carbon.

**1. % Moisture Determination:** A known weight of powdered and air dried coal sample ( $m$ ) is taken in a previously weighed crucible. The crucible is then kept in an electric oven at  $105\text{-}110^\circ\text{C}$  for 1 hour. After 1 hour, the crucible is taken out and cooled in a desiccator. The crucible is weighed and the process is repeated till a constant weight is obtained. The weight of coal sample is calculated ( $m_1$ ). Weight of moisture in the coal sample can be calculated as loss in weight of coal due to moisture ( $m - m_1$ ).

$$\therefore \% \text{ Moisture} = \frac{\text{Weight of moisture}}{\text{Weight of coal (air dried)}} \times 100$$

$$\therefore \% \text{ Moisture} = \frac{m - m_1}{m} \times 100$$

**Significance:** Moisture lowers the calorific value of coal since considerable amount of heat is required to drive off the moisture during combustion of fuel. Also, moisture increases the weight of the coal and hence the transportation cost rises. Hence, a good coal should contain less amount of moisture.

**2. % Volatile Matter Determination:** It can be carried out by starting with either moisture free coal or air dried coal.

**(i) Starting with Moisture Free Coal :** The moisture free coal ( $m_1$ ) in a crucible is kept at  $925 \pm 25^\circ\text{C}$  for 7 minutes in a muffle furnace with vented lid. After 7 minutes, the crucible is taken out and cooled in a desiccator. The crucible is weighed and the process is repeated till a constant weight is obtained. The weight of coal sample is calculated ( $m_2$ ). Weight of volatile matter in the coal sample can be calculated as loss in weight of coal due to volatile matter ( $m_1 - m_2$ ).

$$\% \text{ Volatile matter} = \frac{\text{Weight of volatile matter}}{\text{Weight of coal (air dried)}} \times 100$$

$$\% \text{ Volatile matter} = \frac{m_1 - m_2}{m} \times 100$$

**(ii) Starting with Air Dried Coal :** A known weight of powdered and air dried coal sample ( $m$ ) is taken in a previously weighed crucible. The crucible is then kept at  $925 \pm 25^\circ\text{C}$  for 7 minutes in a muffle furnace with vented lid. After 7 minutes, the crucible is taken out and cooled in a desiccator. The crucible is weighed and the process is repeated till a constant weight is obtained. The weight of coal sample is calculated ( $m_3$ ). Weight of volatile matter in the coal sample can be calculated as loss in weight of coal due to volatile matter ( $m - m_3$ ). Weight of volatile matter and moisture can be calculated as loss in weight of coal due to moisture and volatile matter.

$$\% \text{ Volatile matter} = \frac{\text{Weight of volatile matter and moisture}}{\text{Weight of coal (air dried)}} \times 100 - \% \text{ Moisture}$$

$$\% \text{ Volatile matter} = \frac{m - m_3}{m} \times 100 - \% \text{ Moisture}$$

**Significance :** Volatile matter is the material that escapes unburnt during combustion of fuel. Thus, volatile matter lowers the calorific value of fuel. Fuel with high volatile matter burns with a long flame giving high smoke. Therefore, furnace providing larger combustion space is required in such cases. Hence, a good coal should contain less amount of volatile matter.

On the other hand, in coal gas manufacture and carbonization plants where main aim is the by-product recovery, fuel with high volatile content is desirable.

**3. % Ash (Non-Combustible Matter) Determination:** A known weight of coal sample is taken in a previously weighed crucible. The crucible is then kept at  $700 \pm 50^\circ\text{C}$  for half an hour in a muffle furnace without lid. After half an hour, the crucible is taken out and cooled in a desiccator. The crucible is weighed and the process is repeated till a constant weight is obtained. Weight of residue remained is calculated.

$$\% \text{ Ash} = \frac{\text{Weight of residue}}{\text{Weight of coal (air dried)}} \times 100$$

**Significance:** Since ash is the non-combustible matter present in the fuel, it lowers the calorific value of coal. Hence, a good coal should possess low ash content.

**4. % Fixed Carbon Determination:** It is the combustible matter in the sample calculated by subtracting the moisture, volatile matter and ash from the sample.

$$\% \text{ Fixed carbon} = 100 - (\% \text{ Moisture} + \% \text{ Volatile matter} + \% \text{ Ash})$$

**Significance:** During combustion, fixed carbon present in the fuel burns in the solid state. Thus, it increases the calorific value of coal. Hence, a good coal should possess high fixed carbon percent. The information regarding percentage of fixed carbon is useful for designing the furnace and firebox.

#### 4.8.2 Ultimate Analysis

[May 18, 19]

**1. Determination of % Carbon and % Hydrogen by Combustion Method :** (Fig. 4.3) A known weight of coal sample is burnt in presence of oxygen in a combustion tube. Carbon and hydrogen from coal are converted to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively and are allowed to pass through previously weighed KOH tube/bulb and  $\text{CaCl}_2$  tube respectively. The increase in weight of KOH tube/bulb and  $\text{CaCl}_2$  tube is calculated which is used to determine % carbon and % hydrogen in the coal sample.

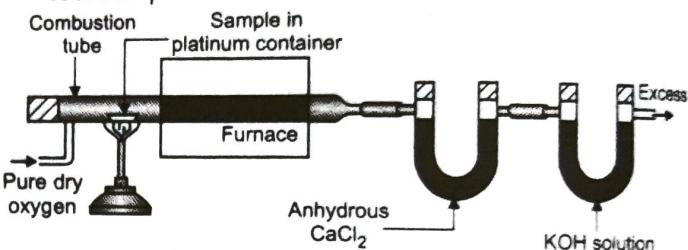


Fig. 4.3: Combustion method

$$\% \text{ C} = \text{Increase in weight of KOH bulb} \times \frac{12}{44} \times \frac{100}{\text{Weight of coal sample taken}}$$

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

Increase in weight of KOH bulb = Weight of  $\text{CO}_2$  formed

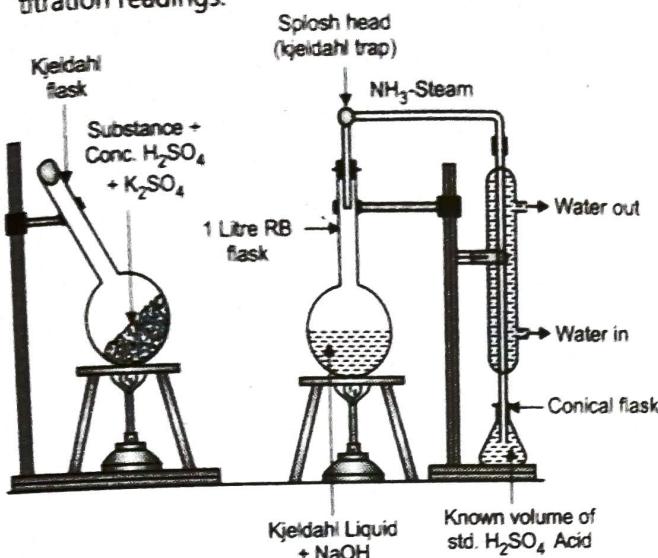
Increase in weight of  $\text{CaCl}_2$  tube = Weight of  $\text{H}_2\text{O}$  formed

**Significance:** More the amount of carbon and hydrogen, more is the calorific value of coal. Hence, a good coal should have higher amount of carbon and hydrogen. Hydrogen is generally associated with volatile matter, thus influencing the use of coal.

#### 2. Determination of % Nitrogen by Kjeldahl's Method:

(Fig. 4.4) A known weight of coal sample is heated with  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  in a Kjeldahl's flask. Nitrogen from coal is converted to  $\text{NH}_4\text{SO}_4$  salt. The contents are made alkaline where  $\text{NH}_4\text{SO}_4$  is converted to  $\text{NH}_3$  and passed through a known volume of standard acid. Initially, the same volume of acid is titrated against a standard base (Blank titration reading). The unreacted acid leftover after the neutralization with ammonia is titrated against the same standard base (Back titration reading). The acid consumed for neutralising the

ammonia is equivalent to the Blank minus Back titration readings.



**Fig. 4.4 : Kjeldahl's method**

$$\% \text{ N} = \frac{\text{Volume of acid consumed in neutralizing NH}_3}{\text{Weight of coal taken}} \times \frac{\text{Normality of acid}}{1.4}$$

Volume of acid consumed in neutralizing  $\text{NH}_3$   
= Blank titration reading – Back titration reading

**Significance:** Nitrogen does not contribute to the calorific value. Hence, its presence in the coal is undesirable.

**3. Determination of % Sulphur by  $\text{BaSO}_4$  Method:** A known weight of coal sample is used to determine the calorific value in Bomb calorimeter experiment. The washings obtained in the experiment contain S in the form of sulphate. The washings are treated with  $\text{BaCl}_2$  where sulphate is converted to  $\text{BaSO}_4$  precipitate. From the weight of  $\text{BaSO}_4$  precipitate, % sulphur is determined.

$$\% \text{ S} = \frac{\text{Weight of BaSO}_4 \text{ obtained}}{233} \times \frac{100}{\text{Weight of coal sample taken}}$$

**Significance:** Even though sulphur contributes to the calorific value of coal, oxides of sulphur are corrosive in nature, mainly in presence of moisture. Moreover, they lead to atmospheric pollution.

**4. Determination of % Ash:** As determined in proximate analysis.

**Significance:** Same as discussed in proximate analysis.

**5. Determination of % Oxygen:** It is determined by subtracting percentages of carbon, hydrogen, sulphur and ash from 100.

$$\% \text{ Oxygen} = 100 - (\% \text{ Carbon} + \% \text{ Hydrogen} + \% \text{ Sulphur} + \% \text{ Ash})$$

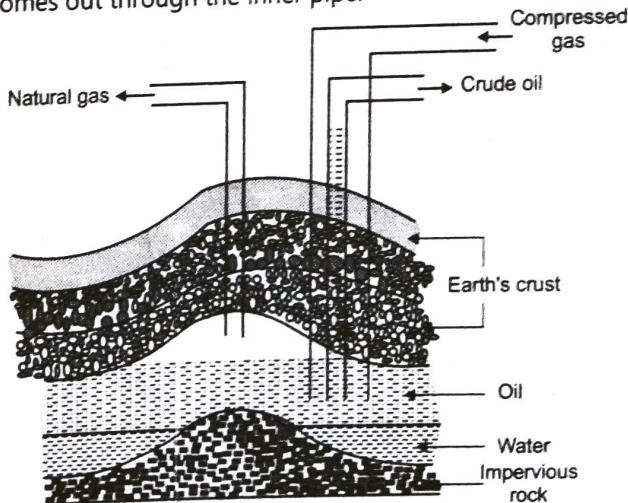
**Significance:** Oxygen is present in the coal in the form of moisture. Thus, it decreases the calorific value of coal. Hence, a good coal should have low moisture content.

## 4.9 LIQUID FUEL

- This includes petroleum products, tar, alcohols and colloidal fuels. The hydrogenation of coal also produces liquid fuel.
- Crude oil is the main source of liquid fuel. It comprises of different types of cyclic, straight chain and aromatic hydrocarbons with small amount of organic compounds containing O, N, S and traces of metallic constituents. The average composition of crude oil consists of carbon 80-87%, hydrogen 11-15%, sulphur 0.1-3.5%, oxygen 0.1-0.9% and nitrogen 0.4-0.9%.
- Crude oil has been originated due to partial decomposition of marine animals and vegetable organisms buried under the earth. The buried matter gets affected by radioactive substances or anaerobic bacteria under high temperature and high pressure.

### 4.9.1 Mining of Crude Oil

Crude oil is a dark coloured viscous liquid present deep in earth's crust above water and below natural gas. It is obtained by drilling the holes into the earth's crust and sinking the pipes upto the oil-bearing rocks. The hydrostatic pressure exerted by the natural gas forces oil to come out to the surface. However, when the pressure becomes too low, it needs to be mechanically pumped by means of air-lift pump. It consists of two coaxial pipes which are sunk into the oil bed (Fig. 4.5). The compressed air or water jet is forced through the outer pipe and the oil comes out through the inner pipe.



**Fig. 4.5: Mining of petroleum**

### 4.9.2 Refining of Petroleum

The crude oil obtained through mining process contains water in the form of suspension and other impurities. Hence, initially it needs to be demulsified and impurities are removed. It is then fractionated in order to obtain the

specific products. The complete process is known as refining of petroleum. The steps are discussed below:

**1. Separation of Water or Demulsification:** The crude oil is present in the form of stable emulsion with water. The emulsion gets stabilized because of presence of naturally occurring emulsifying agents (such as sodium salts of naphthenic acid) and the static energy on the dispersed particles. To separate oil from emulsion, demulsification of crude oil is carried out by mechanical, thermal, chemical, thermochemical and electrical methods.

The electrical method is an extensively used method which involves placing the emulsified oil between two charged electrodes. The high voltage applied destroys the emulsion films. Water droplets coalesce to form larger drops which separate out from the oil. The process is called Cottrell's process.

## 2. Removal of Harmful Impurities:

- Removal of sulphur compounds:** The oil is treated with copper oxide and the solid copper sulphide formed is filtered off.
- Removal of NaCl and MgCl<sub>2</sub>:** The presence of NaCl and MgCl<sub>2</sub> can generate scales in the heating pipes and corrode the refining equipment. Hence, they are removed by electrical desalting and dehydration methods.

**3. Fractional Distillation:** It involves the combination of distillation and rectification. The process is carried out continuously in a specially designed fractionating tower made of steel. The tower is provided with a number of horizontal trays for the separation of fractions (Fig. 4.6).

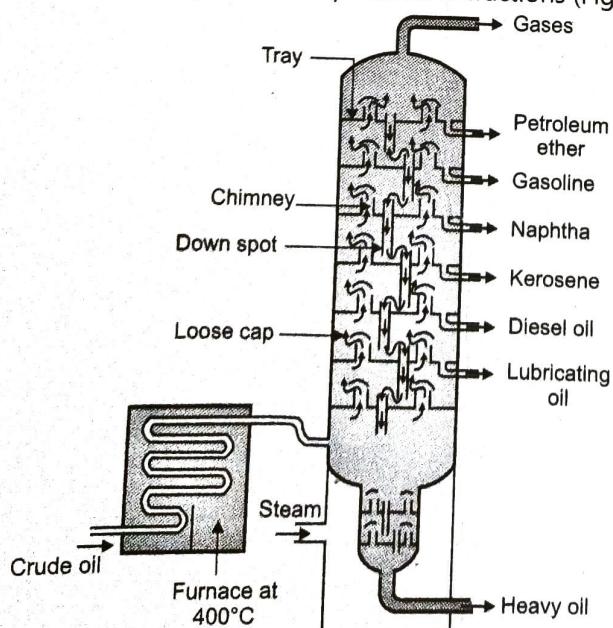


Fig. 4.6: Refining of petroleum

The crude oil is preheated in a furnace at about 400°C. The hot vapours are allowed to rise up the tower. The vapours get cooled and condensed in the respective trays. The fractionation takes place according to the boiling range. The highest boiling fraction condenses at the bottom and the lowest fraction at the top. The fractions are collected through the outlets. The various fractions, their boiling ranges, composition and uses are given in Table 4.3.

Table 4.3: Fractions by Distillation of Crude Oil

Sr. No.	Name of Fraction	Boiling Range	Approximate Composition in Terms of Hydrocarbon Containing C atoms	Uses
1.	Uncondensed gas	Below 30°C	C <sub>1</sub> – C <sub>4</sub>	As domestic or industrial fuel under the name Liquefied Petroleum Gas or L.P.G.
2.	Petroleum ether	30 – 70°C	C <sub>5</sub> – C <sub>7</sub>	As a solvent.
3.	Gasoline or Petrol	40 – 120°C	C <sub>5</sub> – C <sub>9</sub>	As motor fuel, solvent and in dry cleaning.
4.	Naphtha	120 – 180°C	C <sub>9</sub> – C <sub>10</sub>	As a solvent and in dry cleaning.
5.	Kerosene oil	180 – 250°C	C <sub>10</sub> – C <sub>16</sub>	As an illuminant, jet engine fuel and for preparing laboratory gas.
6.	Diesel oil	250 – 320°C	C <sub>10</sub> – C <sub>18</sub>	Diesel engine fuel.
7.	Heavy oil	320 – 400°C	C <sub>17</sub> – C <sub>30</sub>	For getting gasoline by cracking process.
Heavy oil on refractionation gives:				
(i)	Lubricating oil	-	-	As a lubricant.
(ii)	Petroleum jelly or Vaseline	-	-	As a lubricant, in cosmetics and medicines.

Conti...

	(iii) Grease	-	-	As a lubricant.
	(iv) Paraffin wax	-	-	In candles, boot polishes, wax paper, tarpolin cloth etc.
8.	Residue	Above 400°C	C <sub>30</sub> and above	
Residue may be either Asphalt or Petroleum coke				
	(i) Asphalt	Above 400°C	C <sub>30</sub> and above	Water proofing of roofs and road making.
	(ii) Petroleum coke	Above 400°C	C <sub>30</sub> and above	As a fuel and in moulding arc light rods.

## 4.10 GASEOUS FUELS

- Liquefied petroleum gas, also called LPG, GPL, LP Gas, liquid petroleum gas or simply propane or butane, is a flammable mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles.
- LPG is prepared by refining petroleum or "wet" natural gas, and is almost entirely derived from fossil fuel sources, being manufactured during the refining of petroleum (crude oil), or extracted from petroleum or natural gas streams as they emerge from the ground. Burning LPG releases CO<sub>2</sub>, an important greenhouse gas, contributing to global warming. LPG does, however, release less CO<sub>2</sub> per unit of energy than does coal or oil.
- Compressed natural gas (CNG) is made by compressing natural gas to less than 1% of the volume it occupies at standard atmospheric pressure. Principal constituents of natural gas are methane and ethane, but most gases contain varying amounts of heavier hydrocarbons that are normally removed by processing. After recovery of the heavier hydrocarbons, the remaining gas, known as lean gas, is returned to the pipeline system. Natural gas is drawn from pipeline system for compression and distribution as CNG. Predominantly methane is available in the lean gas, hence CNG contains mostly methane (normally not less than 85%). It is stored and distributed in hard containers at a pressure of 200–248 bar (2900–3600 psi), usually in cylindrical or spherical shapes.
- Compressed natural gas (CNG) is a fossil fuel substitute for gasoline (petrol), diesel fuel, or propane/LPG. Although its combustion does produce greenhouse

gases, it is a more environmentally clean alternative to those fuels and it is much safer than other fuels in the event of a spill (natural gas is lighter than air and disperses quickly when released).

**Example 4.4:** 3.5 g of air dried coal sample was kept in an electric oven for 1 hour at 110°C. The weight reduced to 3.325 g. Further it was kept in a muffle furnace in a crucible with vented lid at 950 ± 25°C for exactly 7 minutes. The weight of coal reduced to 3.02 g. It was then burnt in a furnace at 750°C for half an hour. The residue weighed 0.40 g. Report the proximate analysis results.

**Solution:**

(i) To find % Moisture,

$$\text{Weight of coal (air dried)} = 3.5 \text{ g}$$

$$\text{Weight of coal after losing moisture} = 3.325 \text{ g}$$

$$\text{Weight of moisture} = 3.5 - 3.325 = 0.175 \text{ g}$$

$$\begin{aligned} \text{\% Moisture} &= \frac{\text{Weight of moisture}}{\text{Weight of coal (air dried)}} \times 100 \\ &= \frac{0.175}{3.5} \times 100 \end{aligned}$$

$$\therefore \% \text{ Moisture} = 5.00$$

(ii) To find % Volatile matter,

$$\text{Weight of coal after losing volatile matter} = 3.02 \text{ g}$$

$$\text{Weight of volatile matter} = 3.325 - 3.02 = 0.305 \text{ g}$$

$$\begin{aligned} \text{\% Volatile matter} &= \frac{\text{Weight of volatile matter}}{\text{Weight of coal (air dried)}} \times 100 \\ &= \frac{0.305}{3.5} \times 100 \end{aligned}$$

$$\therefore \% \text{ Volatile matter} = 8.71$$

(iii) To find % Ash,

$$\text{Weight of residue after burning} = 0.4 \text{ g}$$

$$\begin{aligned} \text{\% Ash} &= \frac{\text{Weight of residue}}{\text{Weight of coal (air dried)}} \times 100 \\ &= \frac{0.4}{3.5} \times 100 \end{aligned}$$

$$\therefore \% \text{ Ash} = 11.43$$

(iv) To find % Fixed carbon,

$$\begin{aligned} \text{\% Fixed carbon} &= 100 - (\text{\% Moisture} + \text{\% Volatile matter} + \text{\% Ash}) \\ &= 100 - (5.00 + 8.71 + 11.43) \end{aligned}$$

$$\therefore \% \text{ Fixed carbon} = 74.86$$

The proximate analysis results are,

$$(i) \% \text{ Moisture} = 5.0$$

$$(ii) \% \text{ Volatile matter} = 8.71$$

$$(iii) \% \text{ Ash} = 11.43$$

$$(iv) \% \text{ Fixed carbon} = 74.86$$

**Example 4.5:** 3.2 g of coal sample was taken for carbon and hydrogen determination by combustion method. The increase in weight of tube containing anhydrous  $\text{CaCl}_2$  was 2.7 g and increase in weight of bulb containing KOH solution was 5.48 g. Calculate percentage of carbon and hydrogen in the coal sample. If the coal sample contains only C, H and O, calculate percentage of oxygen.

**Solution:**

$$\text{Weight of coal sample taken} = 3.2 \text{ g}$$

$$\text{Increase in weight of } \text{CaCl}_2 \text{ tube} = 2.7 \text{ g}$$

$$\text{Increase in weight of KOH bulb} = 5.48 \text{ g}$$

(i) To find percentage of Carbon,

$$\% \text{C} = \frac{\text{Increase in weight of KOH bulb}}{12} \times \frac{12}{44} \times \frac{100}{\text{Weight of coal sample taken}}$$

$$= 5.48 \times \frac{12}{44} \times \frac{100}{3.2}$$

$$\therefore \% \text{C} = 46.70$$

(ii) To find percentage of Hydrogen,

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

$$= 2.7 \times \frac{2}{18} \times \frac{100}{3.2}$$

$$\therefore \% \text{H} = 9.38$$

(iii) To find percentage of Oxygen,

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

$$= 100 - (46.70 + 9.38 + 0 + 0 + 0)$$

$$\therefore \% \text{O} = 43.92$$

**Example 4.6:** 4.0 g of coal was heated in Kjeldahl's flask and ammonia evolved was absorbed in 45 mL of 0.5N  $\text{H}_2\text{SO}_4$ . After absorption, the excess acid required 20.5 mL of 0.5N KOH for neutralization. 3.5 g of coal in quantitative analysis gave 0.55 g  $\text{BaSO}_4$ . Calculate % N and % S.

**Solution:**

(i) To calculate percentage of Nitrogen,

$$\text{Weight of coal} = 4.0 \text{ g}$$

$$\text{Blank reading} = 45 \text{ mL}$$

$$\text{Normality of } \text{H}_2\text{SO}_4 = 0.5 \text{ N}$$

$$\text{Back reading} = 20.5 \text{ mL}$$

$$\text{Normality of KOH} = 0.5 \text{ N}$$

$$\% \text{N} = \frac{(\text{Blank} - \text{Back}) \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}$$

$$= \frac{(45 - 20.5) \times 0.5 \times 1.4}{4}$$

$$\therefore \% \text{N} = 4.29$$

(ii) To calculate percentage of Sulphur,

$$\text{Weight of coal} = 3.5 \text{ g}$$

$$\text{Weight of } \text{BaSO}_4 \text{ obtained} = 0.55 \text{ g}$$

$$\% \text{S} = \frac{\text{Weight of } \text{BaSO}_4 \text{ obtained}}{\text{Weight of coal sample taken}} \times \frac{32}{32} \times \frac{100}{100}$$

$$= 0.55 \times \frac{32}{233} \times \frac{100}{3.5}$$

$$\therefore \% \text{S} = 2.16$$

**Note:** For more solved numericals and practice problems refer 'Numericals in Engineering Chemistry, Sameera Rege & Geetanjali Gokhale-Ashtekar (Nirali Prakashan)'

## LUBRICANTS

### 4.11 INTRODUCTION

- The word lubricate comes from the latin word lubricus, which means slippery. The old concept of lubrication was slipperiness and a lubricant was considered as a substance which promotes the slipping of one body over another. When one solid surface moves over another solid surface there is resistance offered to motion due to friction. If the two solid surfaces were clean and smooth, this frictional resistance which is mainly due to molecular attraction, would be large. Thus, when one solid moves over another solid there is wear of surface and loss of energy which turns into heat. Both these effects are undesirable.
- In reality however, even the best polished surface when observed under high magnification is rough, having peaks and valleys of various heights and depths. The highest peaks are called asperities (Fig. 4.7 (a)). When two surfaces are over each other, the asperities of upper surface touch the asperities of lower surface. Thus, the surfaces make contact at these points only and the areas other than the asperities are apart (Fig. 4.7 (b)).

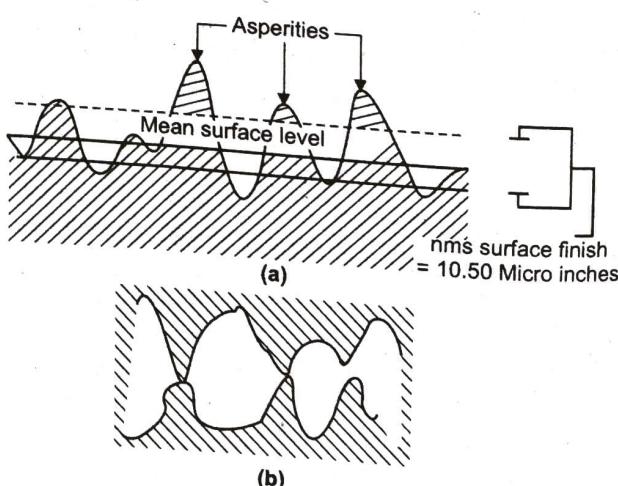


Fig. 4.7: Surface roughness and intimacy of contact

- Any substance introduced between two moving / sliding surfaces which gets adsorbed in between surfaces, thus reducing the frictional resistance between them is known as lubricant and the mechanism of reduction in friction and wear is known as lubrication.
- The lubricant pushes into the peaks and valleys of moving surfaces and prevents two surfaces from touching each other thus decreasing friction and reducing wear and tear.

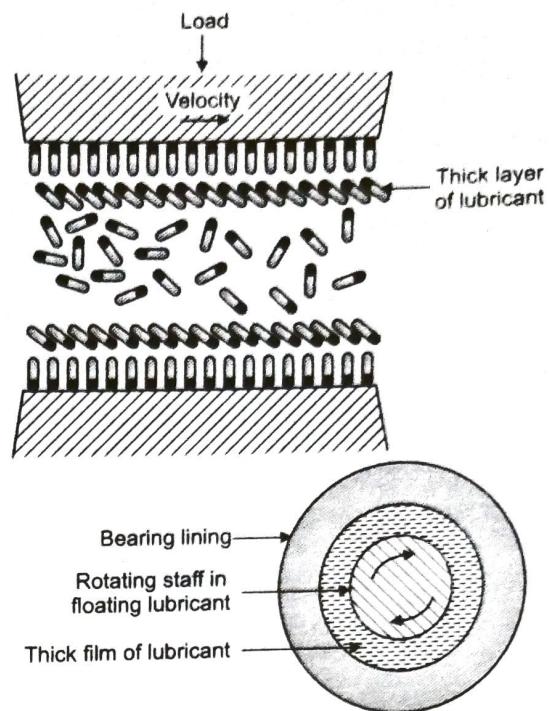
Apart from decreasing friction and reducing wear and tear, a lubricant performs several other functions:

- Acts as a coolant by distributing the heat of friction generated by rubbing surfaces. Thus, metal expansion by localized heating of metal and resultant deformation and damage of metal gets avoided.
- In internal combustion engines, the lubricant does the work of fuel gasket/ sealant between piston and cylinder wall at the compression rings and prevents leakage of gases at high pressure in the combustion chamber, thus minimizing the power loss.
- It stops the entry of moisture, dust and dirt between moving surfaces and thus prevents corrosion of metal.
- Acts as a cleansing agent and as a scavenger to wash off and carry solids produced due to combustion or wear.
- It acts as a hydraulic fluid in aircrafts for other mechanisms.

## 4.12 TYPES OF LUBRICATION

### 4.12.1 Thick Film Lubrication [Dec. 17, 18, May 18]

- It is also called as Fluid or Hydrodynamic lubrication. This mechanism of lubrication is applicable at low load and fair speed. The moving/ sliding surfaces are separated from each other by a thick volume of the lubricant (at least  $1000 \text{ A}^\circ$ ) with minimum viscosity under the working parameters.
- If the viscosity of the lubricant chosen is high, there will be an internal resistance between the layers of the lubricant. Hence, lubricant of minimum viscosity is desirable.
- Hydrodynamic lubrication exists when the moving surfaces are separated by the pressure generated from the continuous unbroken layer of lubricant. The pressure thus generated is proportional to the thickness of the lubricating fluid. Hence, a thick film of lubricant is required which is used to avoid the surface contact between the moving/ sliding parts of the metal surfaces and also fill up the peaks and valleys on the surfaces, thereby reducing friction and wear.

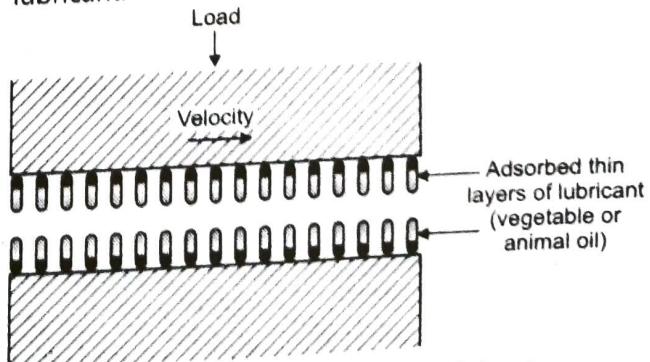


**Fig. 4.8 : Fluid Film/ Thick film/ Hydrodynamic Lubrication**

- Hydrocarbon oils satisfy the requirements to be used for thick film lubrication. In order to maintain the required viscosity in all seasons, they are blended with certain additives. Delicate instruments, light machines like watches, clocks, guns, sewing machines, scientific instruments require this type of lubrication.

### 4.12.2 Thin Film Lubrication [Dec. 17, 18, May 18]

- It is also called as Boundary lubrication. This mechanism of lubrication is applicable whenever a continuous film cannot persist and surface to surface contact occurs due to (i) high load (ii) low speed (iii) shaft starts moving from rest (iv) viscosity of the lubricant is too low. The moving/ sliding surfaces are separated from each other by a thin film of the lubricant.



**Fig. 4.9: Boundary/ Thin film lubrication**

- In boundary lubrication, a thin lubricant film gets adsorbed on both the moving surfaces by physical or chemical or by both forces. The adherence of this

boundary film formed depends on the oiliness of the lubricant. The next layer is a fluid film of lubricant which carries the load and is continuously sheared. In case the fluid film is squeezed out for some reason, then boundary layer protects the metal surfaces.

- Vegetable and animal oils, as well as their soaps possessing the property of adsorption satisfy the requirements to be used for thin film lubrication. Internal combustion engines require this type of lubrication.

#### 4.12.3 Extreme Pressure Lubrication

[May 18]

- This mechanism of lubrication is applicable when the moving/ sliding surfaces are under very high speed and pressure. The moving/ sliding surfaces are separated from each other by a thin film of the mineral oil.
- The high friction developed due to the high speed causes localized temperature rise, which does not allow the lubricant to stick on and may deform or decompose or vaporize. Hence, extreme pressure additives are added to mineral oils to form durable films on the metal surface which withstand the high pressure and temperature. If these durable films are broken under certain circumstances, they are instantly replaced with the same film.
- Extreme pressure additives are organic compounds containing sulphur, phosphorous, chlorine which react with metal surface at high temperatures to form metallic sulphide, phosphide or chloride. Extreme pressure additives are usually used in applications such as gearboxes, wire drawing.

#### 4.13 CLASSIFICATION OF LUBRICANTS

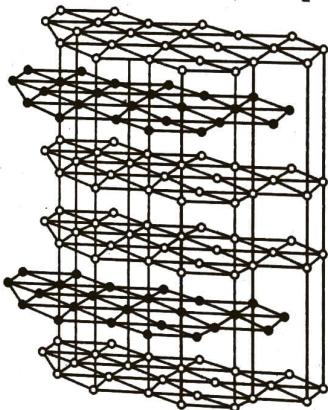
[May 19]

- Lubricants are classified as Solid, Semi-solid, Liquid and Emulsions.
- A. Solid Lubricants:** These solid state lubricants are used in
  - > Machines used at high load and low speed.
  - > Machines where a semi-solid or liquid lubricant cannot be used due to high temperature and pressure.
  - > Inaccessible parts of machines which need lubrication.
- They are used only in special cases (as mentioned above) as many of them may damage delicate machine parts due to presence of grains or particles.
- The most widely used are graphite, allotrope of carbon (powder/ colloidal form) and molybdenum disulphide -  $\text{MoS}_2$  (powder form), both having laminar layer lattice structure and used at high temperature and extreme pressure (Fig. 4.10).

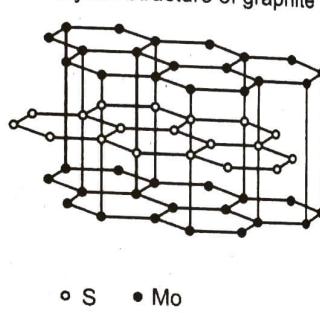
• Graphite has  $\text{sp}^2$  hybridized carbon atoms, which are arranged in regular hexagons in flat parallel layers. Each atom is linked by equidistant covalent bonds to three other atoms, however the fourth bond length is more than double. Consequently there is no strong bonding between layers and easy sliding becomes possible giving lubricating property. Graphite preparation is made into dispersion, with water named as 'Aquadag' and with oil named as 'Oil dag'. Aquadag is used in processes where a lubricant free from oil is needed (e.g. Food processing). Oil dag is used in internal combustion engines.

- Molybdenum disulphide consists of a layer of molybdenum atoms which is sandwiched between two layers of sulphur atoms. There is a weak force of attraction between these two layers which gives easy sliding and hence the lubricating property.  $\text{MoS}_2$  preparations are available commercially as 'Molykotes'.

Crystal structure of  $\text{MoS}_2$



Crystal structure of graphite



○ S   ● Mo

Fig. 4.10: Crystal structure of  $\text{MoS}_2$  and Graphite

- The other solid lubricants used besides graphite and molybdenum disulphide are talc, mica, french chalk, boron nitride etc.

#### B. Semi-Solid Lubricants (Grease and Vaseline):

These semi-solid lubricants are used in

- > Machines used at high load and low speed.
- > Conditions where spilling or spurting oil is undesirable on finished products like textile, paper and food as they are designed to stay in position.
- > Conditions where oil cannot hold position due to bad seal or intermediate operation.
- > Condition where bearing has to be sealed against the entry of dirt, water and dust.

Generally, grease is prepared by dispersing a gelling agent (soap/ mixture of soaps) in a lubricating oil (petroleum product/ synthetic oil). The gelling agents are soaps of fatty acid, which gives stiffness to the mixture.

**Functions of Gelling Agent are :**

- Acts as thickener
- Gives ability to stick on metal surface

- Determines working temperature range depending on its constituents.
- Greases are classified depending on the soap used in their manufacture as in Table 4.4.

**Table 4.4: Classification of Greases**

Sr. No.	Types of Grease (w.r.t. soap)	Properties	Uses
1.	Sodium soap grease	Slightly soluble in water, used in dry conditions	High temperature lubrication in ball bearings
2.	Calcium soap grease	Water resistant, stable upto 70°C, cheapest	Lubrication of water pumps
3.	Lithium soap grease	Resistant to water and heat, expensive	Lubrication of engines, for use at low temperatures
4.	Barium soap grease	Water resistant, good adhesiveness	Lubrication of automotives
5.	Aluminium soap grease	Highly adhesive, water resistant, expensive	Lubrication of chains and oscillating surfaces
6.	Axle grease (resin grease) (talc and mica added as fillers)	Water resistant, very cheap	Lubrication of less delicate instruments under high load and low speed

**Greases have below Limitations :**

- They tend to separate into oil and soap on storage.
- Due to repeated use, oil in the grease volatizes off.

**C. Liquid Lubricants:** They are classified as,

**1. Animal and Vegetable Oils:** These oils were commonly used as lubricants before the discovery of petroleum industry. They possess good oiliness, hence adhere to the surfaces strongly. However, the disadvantage is that they undergo oxidation easily, get thickened to form gummy and acidic products which corrodes the machinery. Also, they are costly. Examples of vegetable oils are olive oil, castor oil, cotton-seed oil, rape seed oil etc.

Examples of animal oils are whale oil, tallow oil, lard oil etc.

**2. Mineral Oil:** They are obtained from the fractional distillation of crude oil. Compared to animal and vegetable oils, they are cheaper and stable under working conditions. They possess poor oiliness than animal and vegetable oils. Examples of mineral oil are fractions of petroleum oil such as alkanes, cycloalkanes.

**3. Blended Oils:** As a single lubricant oil cannot fulfil the requirements of lubrication, additives are added to

overcome the limitations of a single lubricant. The oils thus made are called as blended / compounded oils.

**The Additives Used are as Follows :**

- Oiliness carriers, when added improves the oiliness of the blend. Examples – vegetable oils such as coconut oil, castor oil and fatty acids.
- Anti-oxidants, when added retards the oxidation of oils. Examples – phenols, amines, organic sulphides.
- Viscosity index improvers, when added increases the viscosity and reduces the rate of change of viscosity with temperature. Examples – hexanol, long chain polymers.
- Pour point depressants, when added lower the pour point of the blend and prevents the separation of wax from oil. Examples – wax alkylated naphthalene and phenol.
- Corrosion inhibitors, when added prevents the contact between metal surface and corrosive substances. Examples – organometallic compounds.
- Extreme pressure additives, when added get adsorbed on metal surface and react chemically to form a surface layer to protect the metal. Examples – chlorinated hydrocarbons, sulfurized fats.

- Antifoam additives, when added avoid formation of stable foam. Examples – silicone polymers, glycerols.
- 4. Synthetic Oils:** These are liquids neither found naturally nor produced directly during the manufacturing processes of petroleum industry. They are synthesized for specific uses when operations at extreme conditions are unsatisfactory even with special additives. They must possess following characteristics :
- Non flammable
  - High flash point
  - High thermal stability at high operating conditions
  - High viscosity index
  - Chemical stability

**Example :** Lubricants synthesized for aviation industry, silicones, fluorocarbons.

## 4.14 PROPERTIES OF LUBRICANTS

[May 17]

Various properties of lubricants are explained below :

### 1. Physical Properties

- Viscosity and Viscosity Index
- Surface tension
- Oiliness
- Flash point and fire point

### 2. Chemical Properties

- Acid value
- Emulsification
- Saponification value

## 4.15 PHYSICAL PROPERTIES

**1. Viscosity and Viscosity Index:** Viscosity is the property by which a liquid or fluid (oil) offers resistance to its own flow.

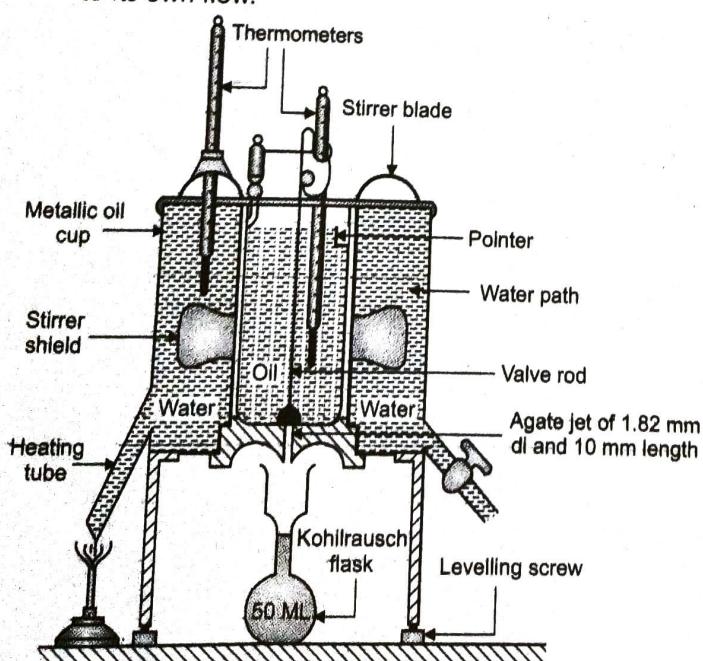


Fig. 4.11: Redwood Viscometer No.1

Viscosity Index (VI) is the rate at which viscosity of lubricant changes with temperature. If the viscosity of an oil drops rapidly with increase in temperature, it has a low viscosity index. If the viscosity of an oil is only slightly affected by increase in temperature, it has a high viscosity index.

A good lubricant should have low viscosity and high viscosity index.

The viscosity can be measured with a Redwood viscometer (Fig. 4.11) or Saybolt viscometer.

**2. Surface Tension:** Surface tension is an inward force experienced per unit area by the liquid at its surface. Because of the higher attraction within the liquid molecules than the attraction of the liquid molecules with the air at liquid-air interfaces, a tension is developed on the surface due to imbalanced forces, which is the surface tension.

$$\text{Unit} = \text{N/m}^2$$

A good lubricant should have low surface tension so that it should spread over a large area or surface.

**3. Oiliness:** Oiliness is the property of a lubricant which determines the ability of the oil to stick on the surface of moving machine parts under pressure. Lubricants used in boundary or thin lubrication conditions must possess this quality of oiliness or lubricity to lower the coefficient of friction of the oil between the rubbing surfaces.

A good lubricant should have good oiliness. There is no perfect method to determine the absolute oiliness, only relative oiliness is considered while choosing an oil for a given job.

**4. Flash Point and Fire Point:** Flash Point is the minimum temperature at which liquid gives off vapours that will ignite for a moment when a small flame is brought near it.

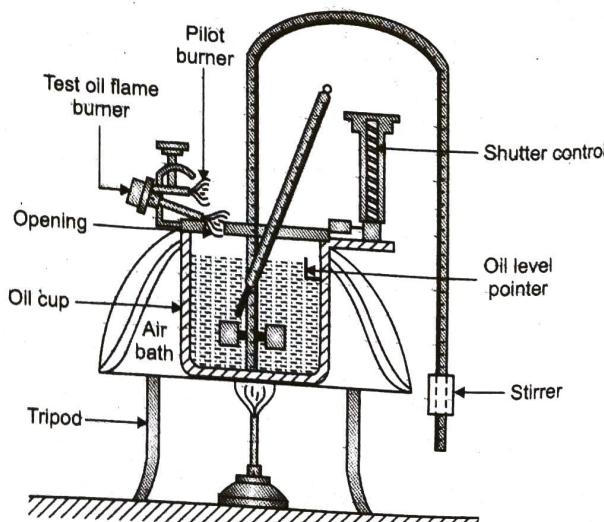


Fig. 4.12: Pensky-Marten's flash point apparatus

Fire Point is the minimum temperature at which vapours of the oil burn continuously for at least 5 seconds when a small flame is brought near it.

A good lubricant should possess flash and fire point higher than the working temperature of the machine thereby avoiding the fire hazards and ensuring safety.

The flash point and fire point can be measured with a Pensky-Marten's Flash Point Apparatus (Fig. 4.12).

**5. Cloud Point and Pour Point:** Cloud Point is the temperature at which oil becomes cloudy or hazy in appearance.

Pour Point is the temperature at which oil ceases to flow or pour.

A good lubricant must have low cloud and pour point or else it may solidify at working temperature causing jamming of machine parts.

The cloud point and pour point can be measured with a Cloud and Pour Point Apparatus (Fig. 4.13).

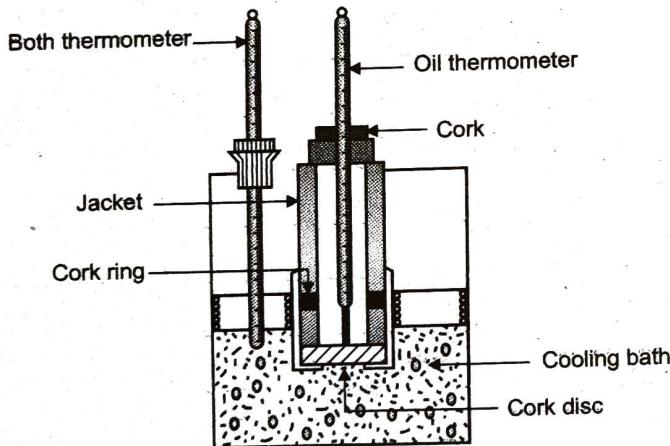


Fig. 4.13: Cloud and Pour Point Apparatus

#### 4.16 CHEMICAL PROPERTIES OF LUBRICANTS

**1. Acid Value:** Acid value is the number of milligrams of potassium hydroxide required to neutralize free fatty acids present in one gram of oil.

$$\text{Unit} = \text{mg of KOH/g}$$

A good lubricant should have low acid value. A high acid value indicates presence of free acid and should be taken as an indicator of oxidation of the oil which may lead to gum and sludge formation besides corrosion.

#### Calculation of Acid value:

On titration of 'W' g of oil (dissolved in ethanol) with x N KOH using phenolphthalein indicator, let the burette reading be V mL.

Now, 1000 mL 1 N KOH  $\equiv$  56 g of KOH

(Equivalent weight of KOH = 56)

$$\therefore 1 \text{ mL 1 N KOH} \equiv 56 \text{ mg of KOH}$$

$$\therefore V \text{ mL } x \text{ N KOH} = (V \times x \times 56) \text{ mg of KOH}$$

$$\text{Thus, } W \text{ g oil} = (V \times x \times 56) \text{ mg of KOH}$$

$$\therefore 1 \text{ g oil} = \frac{V \times x \times 56}{W} \text{ mg of KOH}$$

$$\therefore \text{Acid value} = \frac{\text{Volume of KOH consumed} \times \text{Normality of KOH} \times 56}{\text{Weight of oil}}$$

**Note:** If acid value of oil is more than 0.1 mg of KOH/g, oil cannot be used as a lubricant.

**2. Emulsification:** Emulsification is the property of the lubricant by which it gets mixed with water and forms emulsion (Pure oil and water separate into two layers when mixed. But if oil shows presence of dust, metal particles, acid/ alkali, the rate of separation of two layers decreases and emulsion is formed). Emulsions have a tendency to collect dirt particles which can cause abrasions and they also form sludge which clogs oilines. Hence, it is necessary that a lubricating oil should quickly break away from the emulsion, if an emulsion is formed. This property of the oil to separate out from an emulsion is known as 'demulsification number' and is determined by counting the time required in seconds for the given volume of an oil to separate out distinctly from an equal volume of condensed steam under standard conditions.

A good lubricating oil must have low demulsification number; means the oil separates out from the emulsion quickly.

**3. Saponification Value:** Saponification value (SV) is the number of milligrams of potassium hydroxide required to saponify one gram of oil. Saponification is hydrolysis of an oil with KOH to give glycerol and K-salt of free fatty acid.

$$\text{Unit} = \text{mg of KOH/g}$$

A good lubricant should have low saponification value. Moreover, it predicts the stability of a lubricant in aqueous/alkaline medium.

### Calculation of Saponification Value:

Saponification value is calculated by refluxing a known quantity of the oil sample ( $W$  g) with a known excess of alcoholic KOH added ( $Y$  mL of  $N_1$  normality) for about two hours. The oil gets saponified to produce glycerol and potassium salt of free fatty acids. The unreacted alcoholic KOH is then titrated against acid (HCl) solution having  $N_2$  normality, using phenolphthalein indicator (Back titration reading). The known excess alcoholic KOH used ( $Y$  mL of  $N_1$  normality) is titrated against  $N_2$  normal acid (HCl) solution using phenolphthalein indicator (Blank titration reading). The HCl volume equivalent to the alcoholic KOH consumed for saponifying the oil is calculated as  $V_2$  mL, i.e., (Blank – Back) titration readings. As  $N_1$ ,  $N_2$ ,  $V_2$  are known, the KOH volume  $V_1$  mL consumed in saponification is calculated from

$$N_1 V_1 = N_2 V_2$$

(KOH) (HCl)

$$1000 \text{ mL } 1 \text{ N KOH} = 56 \text{ g of KOH}$$

(Equivalent weight of KOH = 56)

$$\therefore 1 \text{ mL } 1 \text{ N KOH} = 56 \text{ mg of KOH}$$

$$\therefore V_1 \text{ mL } N_1 \text{ KOH} = (V_1 \times N_1 \times 56) \text{ mg of KOH}$$

$\therefore (V_1 \times N_1 \times 56)$  mg KOH is required to saponify  $W$  g of oil

$$\therefore \text{Saponification value} = \frac{\text{Volume of KOH consumed} \times \text{Normality of KOH} \times 56}{\text{Weight of oil}}$$

$$\text{Saponification value} = \frac{(\text{Blank} - \text{Back}) \times \text{Normality of KOH} \times 56}{\text{Weight of oil}}$$

**Example 4.7:** A spent oil was analysed for its acid value. 9 mL of the oil required 4.7 mL of 0.08 N KOH. Find its acid value. State whether the spent oil can still be useful for lubrication. (Density of oil = 0.89 g/cm<sup>3</sup>).

### Solution:

$$\text{Volume of oil} = 9 \text{ mL}$$

$$\text{Normality of KOH} = 0.08 \text{ N}$$

$$\text{Volume of KOH} = 4.7 \text{ mL}$$

$$\text{Acid value} = \frac{\text{Volume of KOH} \times \text{Normality of KOH} \times 56}{\text{Weight of oil}}$$

$$\text{Density} = \frac{\text{Mass (Weight)}}{\text{Volume}}$$

$$\therefore \text{Weight} = \text{Density} \times \text{Volume}$$

$$\therefore \text{Weight of spent oil} = 0.89 \times 9$$

$$= 8.01 \text{ g}$$

Substituting for weight in the formula of Acid value,

$$\text{Acid value} = \frac{4.7 \times 0.08 \times 56}{8.01}$$

$$\therefore \text{Acid value} = 2.628 \text{ mg of KOH/g}$$

Since acid value is more than 0.1, oil cannot be used as a lubricant.

**Example 4.8:** 5.2 g of vegetable oil was saponified with excess of 0.3 N alcoholic KOH. The mixture required 17 mL of 0.3 N HCl while blank titration required 48 mL of same HCl. Find the saponification value of the oil.

### Solution:

$$\text{Weight of oil} = 5.2 \text{ g}$$

$$\text{Normality of KOH} = 0.3 \text{ N}$$

$$\text{Blank reading} = 48 \text{ mL}$$

$$\text{Back reading} = 17 \text{ mL}$$

$$\text{Normality of HCl} = 0.3 \text{ N}$$

$$\text{Saponification value} = \frac{\text{Volume of KOH consumed} \times \text{Normality of KOH} \times 56}{\text{Weight of oil}}$$

$$\text{Saponification value} = \frac{(\text{Blank} - \text{Back}) \times \text{Normality of KOH} \times 56}{\text{Weight of oil}}$$

$$\text{Saponification value} = \frac{(48 - 17) \times 0.3 \times 56}{5.2}$$

$$\therefore \text{Saponification value of oil} = 100.15 \text{ mg of KOH/g}$$

**Note:** For more solved numericals and practice problems refer 'Numericals in Engineering Chemistry' Sameera Rege & Geetanjali Gokhale-Ashtekar (Nirali Prakashan)'

### SUMMARY

- Fuels are the sources of energy. They produce heat on combustion.
- The calorific value of the fuel is defined as the amount of heat generated when unit mass of fuel is

- completely combusted. There are two types High/Gross calorific value and Low/ Net calorific value.
- The units of calorific value are kcal/kg, cal/g, British Thermal Unit (B.Th.U.) and Centigrade Heat Unit (C.H.U.).
  - Fuels are classified as solid (e.g. Coal), liquid (e.g. Diesel, Petrol) and gaseous (e.g. CNG, LPG) fuels.
  - The two important analysis to evaluate the quality of coal are Proximate analysis and Ultimate analysis.
  - Any substance introduced between two moving/sliding surfaces which gets adsorbed in between surfaces, thus reducing the frictional resistance between them is known as lubricant.
  - Lubricants are classified as Solid Lubricants, Semi-solid Lubricants, Liquid Lubricants.
  - There are three types of lubrication mechanisms: Thick Film, Thin Film and Extreme Pressure Lubrication.

**EXERCISE**

- What are fuels and what are the good characteristics of fuel?
- Explain the Proximate analysis of coal.
- Explain the Ultimate analysis of coal.
- Discuss the method for calculating the % N by Kjeldahl's Method and % S by BaSO<sub>4</sub> method.
- Discuss the method for calculating the % C and % H by combustion method.
- How is mining of crude oil done?
- Discuss the steps in reforming of crude oil.
- Write a short note on LPG or CNG.
- What are lubricants? Explain the mechanism of :
  - Thick film lubrication
  - Thin film lubrication.
  - Extreme pressure lubrication.
- What are lubricants and list their functions.

- Explain the terms Acid value and Saponification value of oil. Give their significance.
- What are blended oils? Name any four additives and give their function.
- Define the following terms and give the significance.
  - Viscosity and Viscosity Index
  - Surface Tension
  - Oiliness
  - Flash Point and Fire Point
  - Cloud Point and Pour Point
  - Emulsification

**UNIVERSITY QUESTIONS****May 2017**

- What are fuels? How they are classified? State characteristics of a good fuel. [5]
- What is coal? Give the classification of coal. [5]
- Write various physical properties of lubricants. [5]

**December 2017**

- Give the classification of fuels and explain characteristics of good fuel. [6]
- Discuss the Proximate analysis of coal with its significance. [6]
- Explain Thick film and Thin film lubrication with suitable examples. [6]

**May 2018**

- What are the types of fuels and characteristics of good fuel? [6]
- Describe the process of determination of % of C, H and N in the coal. [6]
- How can you differentiate between Thick film and Extreme pressure lubrication with examples? [6]

**December 2018**

1. What are the types of fuels and characteristics of good fuel? [6]
2. Explain in detail the Proximate Analysis of Coal. [6]
3. Describe the Thick film and extreme pressure lubrication with examples? [6]
4. Explain synthesis, physical-chemical properties and uses of Pyridine. [6]

**May 2019**

1. What are Fuels? How they are classified? State characteristics of a good fuel.
2. Describe in brief types of lubricants.
3. Explain how the percentage of Nitrogen and Sulphur in coal can be estimated.

