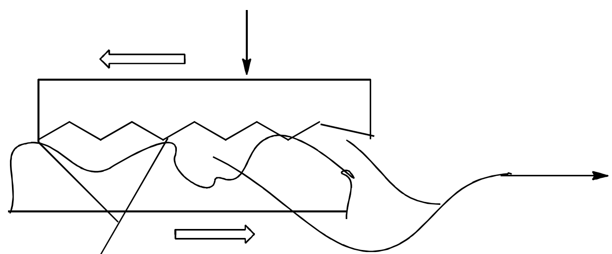
UNIT–V: LUBRICANTS AND FUEL CHEMISTRY

Lubricants: Definition, functions of lubricants, mechanism of lubrication, classification of lubricants, properties of lubricants – viscosity and viscosity index, flash and fire point, cloud and pour point, Aniline point, neutralization number and mechanical strength.

All metal surfaces, no matter how smooth they are, show many irregularities in the form of peaks (asperities) and valleys. When two metal surfaces are pressed over each other, a real contact between these surfaces occurs only at a limited number of asperities. Thus the real contact is very low when compare to total surfaces. Even under low pressure at asperities may cause deformation in soft metals. In these cases two types of frictions can be observed, during the rubbing of one material over another. They are i) Slidingfriction ii) Rolling friction



i) Sliding friction: If two materials of different hardness slide over one another, the peaks of the softer metal get broken more easily than the peaks of the harder materials and there is a chance for interlocking of the surface irregularities.
ii) Rolling friction can be observed when a loaded sphere or cylinder rolls over a flat surface of the other body.

The coefficient of rolling friction is very low when compare to coefficient of sliding friction, which makes lubrication is necessary in case of sliding.

A **coefficient of friction** is a value that shows the relationship between the force of friction between two objects and the normal force between the objects.

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other, as result a resistance is offered to their moment. This resistant is called as **friction**.

This friction is an undesirable process that results in (i) wear and tear of the surfaces of the moving parts (ii) loss of enormous energy as heat dissipation (iii) lowers the efficiency of the moving parts and (iv) damage of machine parts as seizure etc.

The ill-effects of the friction can be minimized by using a suitable substance, known as lubricants, which forms a thin layer in between the moving parts.

A **lubricant** is a substance introduced to reduce friction between moving/sliding/rolling surfaces. The property of reducing friction by using lubricant is known as **lubrication**.

A good lubricant possesses the following characteristics**:**

- High boiling point
- Low freezing point
- High viscosity index
- Thermal stability

- Hydraulic Stability
- Durability
- Corrosion prevention
- High resistance to oxidation

Functions of lubricant:

The important functions of a lubricant are

i) It prevents the direct contact between the rubbing surfaces, as a results it reduces surface deformation.

ii) It acts as coolant and prevents the chance for seizure of moving surfaces.

iii) It reduces waste of energy, so that efficiency of machine is enhanced.

iv) It avoids or reduces unsmooth relative motions of the moving/sliding parts.

v) It reduces the maintenance and running cost of the machine.

vi) It increase the efficiency of the moving parts

vii) It prevent the expansion of metal due to local frictional heat

viii) It minimize the possibility of corrosion

How Do Lubricants Reduce Friction?

Lubricants reduce friction by adding a smooth layer between two solid layers. This provides protection from damage to the solid layers. Lubricants can be used in many situations where friction is a problem.

Mechanism of Lubrication

Considering the nature of motion between moving or sliding surfaces, there are different types of mechanisms by which the lubrication is done. They are:

(i) Thick-film lubrication <u>or</u> Fluid-film <u>or</u> hydrodynamic lubrication

(ii) Thin film <u>or</u> boundary lubrication

(iii) Extreme pressure lubrication.

(i) Thick-film lubrication <u>or</u> Fluid-film <u>or</u> Hydrodynamic lubrication

In this type of lubrication, lubricant forms a thick layer of a fluid-film in-between the sliding/ moving metal surfaces and covers the irregularities on them, so that there is no direct contact between the material surfaces. The moving or sliding surfaces are separated from each other by a thick-film at least 1000 A^0. As a result the direct surface to surface contact and welding of junctions rarely occurs. This prevents the deformation. At this stage, the resistance to movement of sliding/ moving parts is only due to internal resistance between the particles of the lubricant moving over each other. So the lubricants having low viscosity are used in this lubrication, it is because to avoid internal frictional resistance of the lubricant molecules.

Hydrodynamic lubrication is said to exist when the moving surfaces are separated by the pressure of a continuous unbroken film or layer of lubrication. In this type of lubrication, the load is taken completely by the oil film (oil layer).

The basis of hydrodynamic lubrication is the formation of an oil layer. When the normal bearing rotates, it creates oil taper between the two surfaces, and the pressure build up with the oil film supports the load. *Hydrocarbon oils* are considered to be satisfactory lubrication for fluid film lubrication. Hydrodynamic lubrication depends on the relative speed between the surfaces, oil viscosity, load, and clearance between the moving or sliding surfaces.

The thick-film lubricant / Hydrodynamic lubrication should satisfy the following conditions.

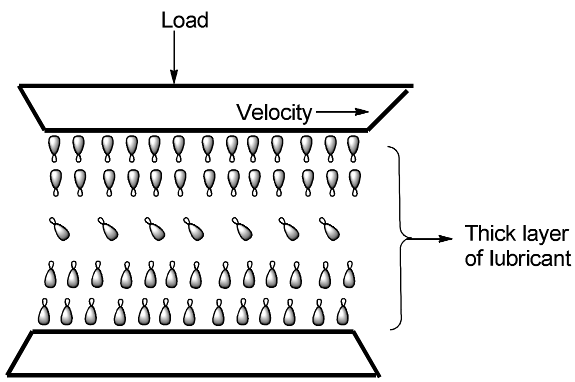
a) Should have the minimum viscosity.

b) It should remain in place and separate the surfaces. In such a case the *coefficient of friction* is in between **0.001 to 0.03.**

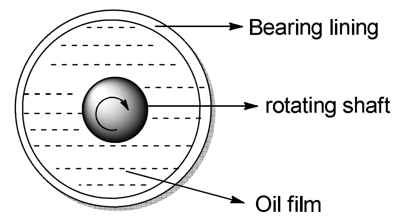
Application of hydrodynamic lubrication / thick film lubrication

- Delicate instruments & scientific instruments.

Ex: Light machines like watches, clocks, guns, sewing machines.



Thick layer of lubrication



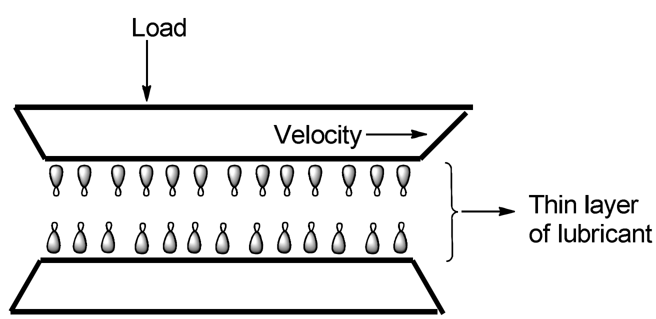
Hydrodynamic lubrication

(ii) Thin Film Lubrication <u>or</u> Boundary Lubrication

Boundary lubrication happens when

a) A shaft starts moving from rest. b) The speed is very low.

c) The load is very high. d) Viscosity of the lubricant is too low.



Clearly, boundary lubrication exists when the operating condition is not possible to establish a full fluid condition, particularly at low relative speeds between the moving or sliding surfaces. Here thick film of lubricant cannot be maintained between the moving surfaces but the lubricants are adsorbed physically / chemically on the metal surfaces. Under such conditions, the space between the moving / sliding surface is lubricated with oil as a thin layer. This adsorbed oil layer avoids direct metal to metal contact and further the applied load is carried by the layer of the adsorbed lubricant on the metal surface. The oil film thickness may be reduced to such a degree that metal to metal contact occurs between the moving surfaces. The oil film thickness is so small that oiliness becomes predominant for boundary lubrication. In such a case the coefficient of friction is in between **0.05** to **0.15.**The effectiveness of boundary lubrication depends on the oiliness of the lubricant. Oiliness is the ability of a lubricant to stick on to the surface.

Vegetable/Animal oils are considered to be satisfactory lubrication for Boundary lubrication. Ex: Oleic acid ($C_{17}H_{33}COOH$), Steric acid ($C_{17}H_{35}COOH$) either physically adsorbed to metal surface or react chemically at the metal surfaces and forms a thin film like a protective layer that resembles a molecular shag (carpet), which acts as lubricant.

Examples for boundary lubrication**:**

- Rollers, Gears, Tractors, Railway track joint
- Bearings, Diesel Engines, Cams
- Piston rings and cylinder liner .

(iii) Extreme Pressure Lubrication

When the moving or sliding surfaces are under very high pressure and speed, a high local temperature is attained. Under such condition, liquid lubricant fails to stick to the moving parts and may decompose and even vaporize. To meet this extreme pressure condition, special additives are added to the minerals oils known as *extreme pressure additives*. These special types of lubricants are called as “extreme pressure lubricants.”

These *extreme pressure additives* are organic compounds having active radicals or groups such as chlorine, sulphur, and phosphorus. These compounds react with metal surfaces at very high temperature, pressure to form metallic chlorides, sulphide or phosphides. The formed new surface film is more durable, and capable of withstanding high loads and high temperature.

For example iron chlorides and iron sulphide can withstand up to 650 ^{o}C and 1100 ^{o}C respectively. In this way the extreme pressure lubricants serves as good lubricants under extreme pressure and extreme temperature conditions.

Difference between fluid film lubrication & boundary lubrication

Thick-film lubrication or Fluid film lubrication	**Thin Film Lubrication or Boundary lubrication**
These are used in the machines working under light load & high speed	These are used in the machines working under heavy load & low speed
Lubricants having low viscosity are used in this lubrication.	Lubricants having high viscosity are used In this lubrication
The thickness of lubricating oil film is more than 1000 A^0	The thickness of lubricating oil film is less than 1000A^0(~100 A^0)
Coefficient of friction is in between 0.001 to 0.03.	Coefficient of friction is in between 0.05 to 0.15.
The thick-film lubricating oil does not adsorb on metallic surfaces. i.e. They work as such.	The thin film of lubricating oil is adsorbed by physical or chemical forces at the metallic surface
The load applied is sufficient to keep apart the moving surface	The load applied is carried by the layers of adsorbed lubricants
For example: Watches, clocks, gums, sewing machines	For example: Rollers, Gears, Tractors, Railway track joint

CLASSIFICATION OF LUBRICANTS

Based on their physical state the lubricants are broadly divided into *three* types.

(I) Liquid Lubricants or lubricating oils

(II) Semi-Solid lubricants or greases

(III) Solid lubricants

(I)<u>**Liquid lubricants**</u>:

- Liquid lubricants reduce friction and wear between two moving or sliding metallic surfaces by providing a continuous fluid film in between them.
- They act as a cooling medium, a sealing agent, and corrosion preventers.
- Further they show thermal stability, and oxidation resistant
- Liquid lubricants are classified into many types, depending on the type of base oil used

a) Vegetable oil and animal oil b) Mineral oil (or) petroleum oil

c) Blended oil d) Synthetic Lubricants

a) *Vegetable oil and animal oil*:

(i) Before the advent of petroleum industry, oils of the vegetable and animal origins were most commonly used lubricants because of their high oiliness.

(ii) But there usage is limited due to following reasons. They i) are costly ii) undergo oxidation easily leads to formation of gummy material iii) easily hydrolyze iv) decompose at high temperature.

(iii) However, they are used as blending agents with other lubricating oils to increase their oiliness.

Oil category	Source	Application
<u>Vegetable Oil</u> i) Castor oil ii) Olive oil iii) Palm oil	 Castor seeds Olive seeds Palm fruits	▪ To withstand high speed and low pressure ▪ In watches and scientific instrument
<u>Animal Oil</u> i) Whale oil ii) Lard oil	 Whales Pig	• Light machinery lubricant • Ordinary machinery lubricant

b) *Mineral or Petroleum oils*:

Mineral oils that are used as lubricants are obtained by fractional distillation of petroleum. During fractional distillation the carbon chains with 12 to 50 carbon atoms collected separately and they can use as lubricants. Greater the carbon chain, greater the viscosity.

	Category	Carbon atoms	Use as lubricants
i	Light oil	12-20	Transformers, refrigerators, spindles
ii	Medium oil	21-30	Compressor, light machinery
iii	Heavy oil	31-40	Internal combustion engines, gear oil, heavy machinery
iv	Residue	41-50	Engines works at high lode

Asphalt (sticky, black and viscous liquid)

The mineral oils are mostly used as lubricants; because they are i) cheap ii) available in abundance iii) stable under working conditions.

However, these mineral oils as such cannot be used as lubricants, because, they contain wax, asphalt and other oxidizing compounds. So they have to be thoroughly purified before being used as lubricants. But on purification these lubricants loses some of the essential properties.

c) ***Blended oils <u>or</u> doped oil <u>or</u> compound oil*:**

The property of mineral oils can be enhanced or regenerated by adding external additives. So these are called as Blended oils.

(i) *Oiliness-carriers*: the substance added to improve oiliness of lubricant.
Eg. Animal oil (oleic acid, stearic acid) and vegetable oil (coconut oil, castor oil)

(ii) *Extreme pressure additives*: under high pressure a thick film of oil is difficult to maintain. The organic compounds with chlorides, sulphides and phosphide compounds are used as extreme pressure additives. These compounds react with metal and forms metal chlorides, metal sulphides and metal phosphides respectively. And they tolerate extreme pressure and temperature.

(iii) *Viscosity index additives*: High molecular weight compounds like hexanol, polyisobutylenes prevent thickening at lower temperature and thinning at higher temperature.

(iv) *Thickeners*: The compounds with molecular weight between 300 and 3000 (polystyrene and polyestyersetc.) are added to lubricants to increase their viscosity.

(v) *Anti-oxidants*: For retarding the oxidation in internal combustion engines, turbines etc. eg; phenols and aromatic amino compounds.

(vi) *Corrosion inhibitors*: Organic compound of antimony and phosphorus prevents the corrosion of bearings.

(vii) *Deposit inhibitors*: due to internal combustion engine or imperfect combustion there is chance for the deposition of carbon particles. Salts of phenols and carboxylic acids are used as deposit inhibitors.

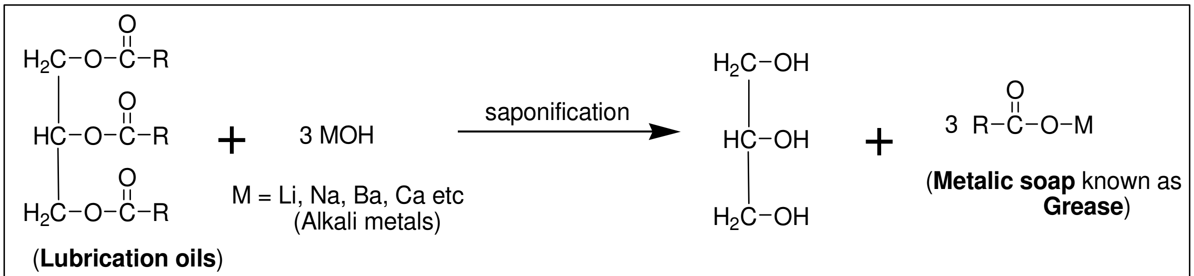
d) ***Synthetic oils*:**

- Eg: Silicons (Si-O-Si) and polyglycol-ether (C-O-C). These lubricants work at various temperature ranges.
- The synthetic lubricants are developed to use under harsh conditions those existing in aircraft engines. In which the same lubricant has to work in the temperature range of -50 to -250 ^{o}C during takeoff and during landing the temperature stands in between 120 to 150 ^{o}C.
- Further, these synthetic oils used in rocket motors and atomic energy plants, furnace doors etc.
- Synthetic oils show following characteristic i) non-inflammable ii) high thermal stability iii) high viscosity-index iv) chemically stable.

(II)Semi-solids lubricants or Greases:

- The lubrication oils on treating with alkali gives a metallic soap called as Semi-solids lubricant. This process is called as 'saponification'.

- After, saponification hot lubricating oil is added to Semi-solids and stirred continuously to get greases.
- Additives are added to semi solid lubricant to improve its quality of Semi-solids.



Main function of Semi-solids lubricants:

i) they act as thickeners
ii) sticks to the surface of metals
iii) water and oxidation resistant

Further, the chemical nature of the metallic soap decides its property and applications.

Example	Property	Application
lithium soap	water resistant	Works at low temp (15 ^{0}C)
Sodium soap	slightly water soluble and Can with stand up to 175 ^{0}C	ball bearings
Calcium Soap	water resistant	engines working at low speed and high loads
Barium soap	water resistant but somewhat toxic	in automobiles
Aluminum soap	Water resistant, good adhesive property	in heavy duty engines, wire ropes

When the greases are used?

i) When oils are not enough to work as lubricants
ii) In bearing and gears works at high temperature
iii) Where bearing need to be sealed against entry of dust or moisture etc.
iv) Frequent use of lubricants can be avoided.

(III) Solid lubricants: Eg- graphite, molybdeniumdisulphide (MoS_2), mica (mineral silicates) etc

At normal temperature they are solid in nature. They are used when

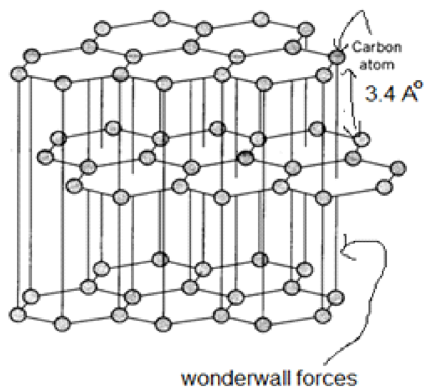
(a) The lubricating oils and semi-solid lubricants fail to work effectively.
(b) The operating temp and load is too high.
(c) Combustible lubricants must be avoided.

- *Graphite*is most widely used solid lubricant; due to its soapy touch, non-inflammable non-oxidized and thermal stability (up to 400 ^{0}C).
  i) The graphite is used in powdered or suspension form.
  ii) When the graphite is dispersed in oil, it is called as oil-dag and when it is dispersed in water, it is called as aqua-dag.

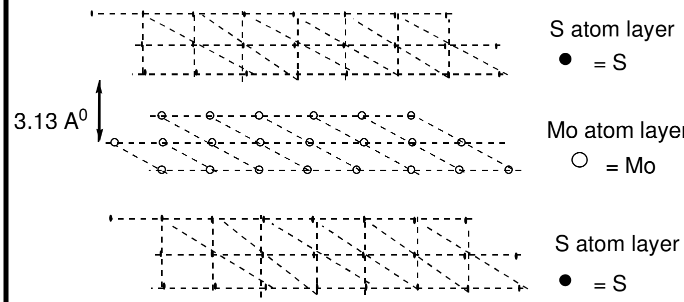
  Oil-dag is used in internal combustion engines. (Where it forms a film between the piston rings and the cylinder and gives tight-fit contact)

Aqua-dagis used in air compressors, railway track-joints.

- *Graphite-greases*: Graphite is mixed with greases to form graphite-greases which can use at high temperature.
- *Molybdenium disulphide* (MoS_2)(mp.1185 °C). Possesses very low coefficient of friction and is stable at very high temp. MoS_2 can also use in powdered or suspension form. Its fine powder sprinkled on surfaces sliding at high velocities. It is also used along with solvents and greases.



Layer structure of Graphite



Sand witch-like structure of MoS_2

PROPERTIES OF LUBRICATING OILS

A large number of lubricants are available now a days and their specific application depends on the properties of the lubricant. Some of the important properties of lubricants are

a) Viscosity & Viscosity-Index **b)** flash point & fire point **c)** cloud point & pour point

d) Aniline point **e)** neutralization number **f)** mechanical strength

***Viscosity &* Viscosity-Index**:

- Viscosity is the most important property of lubricant. Viscosity describes the flow behavior of a fluid. This indicates the resistance of a liquid to flow.
- Viscosity defined as "The internal resistance offered by the fluid to the movement of one layer of fluid over an adjacent layer.
- In general liquids move like a series of parallel layers. When a series of parallel layers moving one above the other; any two layers moves with different velocity due to internal friction.
- Consider two layers of a liquid separated by a distance '**d**' and moving with relative velocity difference '**v**'. Then force per unit area '**F**' required to maintain the velocity differences is given by

$$\mathrm{F} = \frac{n\mathrm{v}}{d}$$ Where '***n***' is eta. Called as *viscosity coefficient*

- Viscosity is measured in terms of *viscosity coefficient*. The unit of viscosity is Poise.

  The *viscosity coefficient* is defined as "force per unit area required to maintain a unit velocity gradient between two parallel layers".

Applications based on Viscosity **or** Significance of Viscosity:

- The lubricants with *low Viscosity* are applied for bearings subjected to high speed, low temperature and low pressure (sewing machines, Watches)
- The lubricants with *high Viscosity* are applied for bearings subjected to low speed, high temperature and high pressure (heavy trucks).

If viscosity is low, this results to:

- Loss of oil film causing excessive wear
- Increased mechanical friction causing excessive energy consumption and Heat generation due to mechanical friction

If viscosity is very high, this can cause:

- More stickiness results excessive fluid friction. This leads to
  - Excess energy consumption to overcome fluid friction.
  - Excessive heat generation resulting in lubricant oxidation leads to sludge formation

Effect of temperature on viscosity:

- At particular temperature, higher the flow rate, lesser is the viscosity of the oil.
- Viscosity of a lubricant oil decreases with increase of temperature and consequently it becomes thinner. On the other hand the Viscosity of a liquid increases with decrease of temperature and consequently it becomes thicker. However, the viscosity of good quality lubricant should not change much with change in temperature.
- In order to maintain the viscosity of the oil in all seasons of the year, ordinary hydrocarbon lubricants are blended with selected long chain polymers.
- **The rate at which the viscosity of oil changes with temperature is measured by an arbitrary scale, known as Viscosity-Index (V.I.).** The viscosity index is a unit less number.
- Higher the level of the viscosity index, the lower the variation in viscosity at temperature changes.
- The viscosity index is different for different lubricants.
- In general the Viscosity-Index of lubricating oils are improved by using external additives. Normally these additives are external organic polymers (viscosity modifiers), which are sensitive to temperature.
  a) At low temperature, an external organic polymer is less soluble in lubricant oil and does not impact the fluid viscosity.
  b) At high temp, external organic polymers are highly soluble in lubricant oil and as a result, the viscosity of the lubricant oil unchanged.

Effect of molecular structure **&** molecular weight of the lubricating oil on viscosity:

- The molecular structure of the lubricating oil has the direct influence on the viscosity and Viscosity-Index.
  a) Molecules of linear strictures possessing free rotation, thus shows low viscosity.

b) The molecule with short side chains/branches exhibits high viscosity. It is because the side chains prevent the alignment of the neighboring molecules due to the greater intermolecular forces of attraction.

c) In general lubricant with high molecular weight shows high boiling point and high viscosity.

Measurement of viscosity of lubricating oil:

i) The instrument used for measuring the viscosity is known as viscometer.

ii) There are many types of viscometers are available. Ex: a) Ostwald's Viscometer b) Redwood Viscometer etc.

iii) *General Principle*: In any viscometer, a fixed volume of the liquid is allowed to flow, from a given height, through a standard capillary tube under its own weight and the time of flow in seconds is noted. The time in seconds is proportional to the viscosity of that liquid.

Flash point & Fire point:

- *Flash point* of lubricating oil is defined as "the lowest temperature at which the lubricating oil gives enough vapors to ignite for a moment, when a tiny flame is brought near to it".
- *Fire point* of lubricating oil is defined as "the lowest temperature at which the vapors of lubricating oils burn continuously at least for 5 sec. when a tiny flame is brought near to it".
- A good lubricant should have flash-point at least above the temperature at which it is to be used and in general, the fire points are 5 to 40 °C higher than its flash points.
- Flash point & Fire point are usually measured by 'Pensky-Martens flash point' apparatus.

Fire point > Flash point > Operating temperature

Cloud point & Pour point:

- When lubricating oil is cooled slowly, the temperature at which it becomes cloudy in appearance is called its Cloud point and the temperature at which lubricating oil ceases to flow or pour is called as Pour point.
- Cloud point and Pour point of a lubricant indicates the suitability of lubricants in cold conditions.
- Pour point indicates flow characteristic at low temperature.
- Lubricant used in the machine working at low temperature should possess low pour point chance. Otherwise solidification of lubricant cause jamming of machine.
- Pour Point depends on the wax content of the oil. The presence of wax in lubricant enhances the Pour point property of a lubricant.
- The Pour point of lubricant is determined by using 'Pour point apparatus'.

Pour point < cloud point < Operating temperature

For ex: -80 °C -60 °C -40 °C

Aniline Point:

- It is defined as "the lowest temperature at which equal volumes of aniline and lubricating oil are completely miscible".

- Aniline point represents the aromatic content of the given oil sample. Low Aniline Point means oil has high aromatic content which attacks rubber seals. In other words higher Aniline point means low % of aromatic hydrocarbons i.e. they contains ‘higher percentage of paraffinic hydrocarbons.
- Aromatic hydrocarbons have a greater tendency to dissolve rubber, hence oils with a low aromatic content in lubricating oil is desirable
- Thus Aniline Point is used as an indication of possible deterioration of rubber sealing etc.

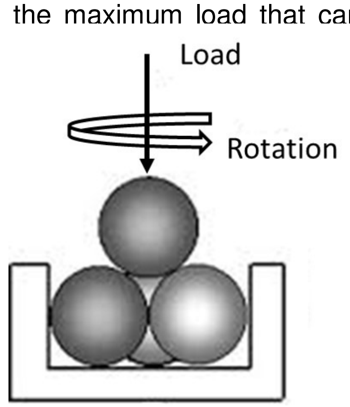
$\boxed{\textbf{Aniline point > Operating temperature}}$

Neutralization number: (Acid number)

- It is defined as the number of milli grams of KOH required to neutralize free acids in 1 g of lubricating oil.
- A lubricating oil should possess an acid values less than 0.1%.
- The values higher than 0.1% shows that the oil has been oxidized, which leads to corrosion of machine parts in addition to gum and sludge formation.

Mechanical strength:

- The stability of lubricant under the condition of very high pressure is determined by mechanical tests.
- One of such test is ‘Four-balls extreme-pressure lubricant test’ for estimation of the mechanical strength of lubricant.
- The lubricant under-test is poured in a machine contain four balls. The lower three balls are stationary; while the upper ball is rotated. The pressure is gradually increased on the balls. If the lubricant is satisfactory under the given pressure, the ball bearing after the test comes out clean. When the load is progressively increased and if the liberated heat causes the weld the balls together, the lubricant is said to have failed completely. Thus this test helps to determine the maximum load that can be carried safely by a lubricant.



Fuel chemistry

Fuels: Classification of fuels, calorific value, numerical problems; Liquid fuels, cracking of oils (Thermal and Fixed-bed catalytic cracking), Synthetic petrol: Fischer-Tropsch method and Bergius process. Eco friendly fuels-Types, significances.

Introduction:

- Any substance used to produce energy is called Fuel.
- Fuel is a combustible substance, containing carbon as main constituent.
- Fuel on proper burning/combustion gives large amount of heat.

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

- In the process of combustion, the chemical energy of fuel is converted into heat energy. During combustion the atoms of carbon, hydrogen, sulphur etc. present in fuel combines with oxygen with the simultaneous liberation of heat at a rapid rate. Combustion is a chemical process in which fuel reacts rapidly with oxygen and gives heat
- The liberated energy is due to the rearrangement of valency electrons in carbon, hydrogen atoms of fuel resulting in the formation of CO_2, H_2O etc.
- Fuel can be used for domestic and industrial purposes.
- Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, oil gas etc are some of the fuels.
- The main fuels are coal and petroleum oils. These fuels available from earth's crust. So these are generally called as 'fossil fuels'.
- **D**ifference between burning and combustion **-** All combustions are not burning but all burnings are combustion.... the basic difference is that combustion is heating and no flames are produced whereas in burning most of the energy is converted to light energy and this results in less heat energy as compared to combustion.

Classification of fuels / Types of fuels

Chemical Fuels are broadly classified in two ways**:**

(a) According to the mode of their procurement – natural and manufactured.

(b) According to the physical state in which they exist in nature – solid, liquid and gaseous

Primary fuels**:** Fuels which occur in nature as such are called primary fuels.

Secondary fuels: fuels which are derived from the primary fuels are called secondary fuels.

Chemical Fuels

- **Primary (or) Natural**
  - **Solid**: Wood, lignite, coal, dung, peat
  - Liquid: Crude oil
  - **Gaseous**: Natural gas
- **Secondary (or) Derived**
  - Solid: Coke, Charcoal, coal briquette
  - **Liquid**: synthetic diesel, petrol, kerosene, LPG, Tar
  - **Gaseous**: water gas, producer gas, coal gas, bio gas

Briquette: Agricultural wastes are converted into solid bricks, which is used as fuel

Liquid fuels:

- **Liquid fuels** are combustible *or* energy-generating molecules that can be used to create mechanical energy by producing kinetic energy.
- Most of the liquid fuels are derived from fossil fuels. However, several types liquid fuels are available now, but important are hydro carbon fuel (for automotive uses), ethanol, and biodiesel. However, the liquid fuels can be classified as follows: (a) Natural or crude oil, and (b) Artificial or manufactured oils.
- Many liquid fuels play a primary role in transportation and the economy.

Characteristics properties *of Liquid fuels*:

- They are with highly inflammable nature
- They take the shape of their container.
- They are volatile in nature and fumes of liquid fuels are flammable.

Advantages of Liquid fuels

(a) They possess higher calorific value per unit mass than solid fuels.
(b) They burn without dust, ash, clinkers, etc.
(c) Their firing is easier and also fire can be controlled easily by stopping liquid fuel supply.
(d) They are easy to transport through pipes.
(e) They can be stored indefinitely without any loss.
(f) They are clean in use and economic to handle.
(g) Loss of heat in chimney is very low due to greater cleanliness.
(h) They require less excess air for complete combustion.
(i) They require less furnace space for combustion.
(j) Can be used as a fuel in internal combustion engines

Disadvantages of Liquid fuels

a) The cost of liquid fuel is relatively much higher as compared to solid fuel.
b) Special storage tanks are required for storing liquid fuels, which are expensive.
c) There is a greater risk of fire hazards, particularly, in case of highly inflammable and volatile liquid fuels.
d) For efficient burning of liquid fuels, specially constructed burners and spraying apparatus are required.
e) They give bad odour.

Cracking of oils

- The decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight is known as cracking.

$$\underset{\substack{\text{Decane} \\ \text{bp } 174\ ^{o}\text{C}}}{C_{10}H_{22}} \xrightarrow{\text{Cracking}} \underbrace{\underset{\text{n-pentane}}{C_5H_{12}} + \underset{\text{pentene}}{C_5H_{10}}}_{\text{bp } =36\ ^{o}\text{C}}$$

Of all the fractions obtained by fractionation of petroleum, gasoline has the largest demand as a motor fuel, but the yield of this fraction is only 20% of the crude. Also the quality of so called 'Straight-run' gasoline is not high, so it has to properly blend with additives. Moreover there is a surplus of heavier petroleum fractions. To overcome these difficulties, the middle and heavy fractions are cracked to get petrol. The petrol made by cracking has far better characteristics (as for as the internal combustion engine is concerned) than `straight-run' petrol.

- The main purpose of this cracking process is to produce a synthetic petroleum substitute (C_5-C_9), typically from heavy oils (C_{17}-C_{30}).
- Cracking is of two types ***a)*** Thermal cracking ***b)*** Catalytic cracking

(1) <u>Thermal cracking</u>:

The heavy oils (C_{17}-C_{30})are subjected to high temperature and pressure, to break down the bigger hydrocarbon molecules to get smaller molecules (C_5-C_9) and some hydrogen. This process may be carried out either in 'liquid-phase' or 'vapour-phase'.

(a) Liquid-phase thermal cracking**:**

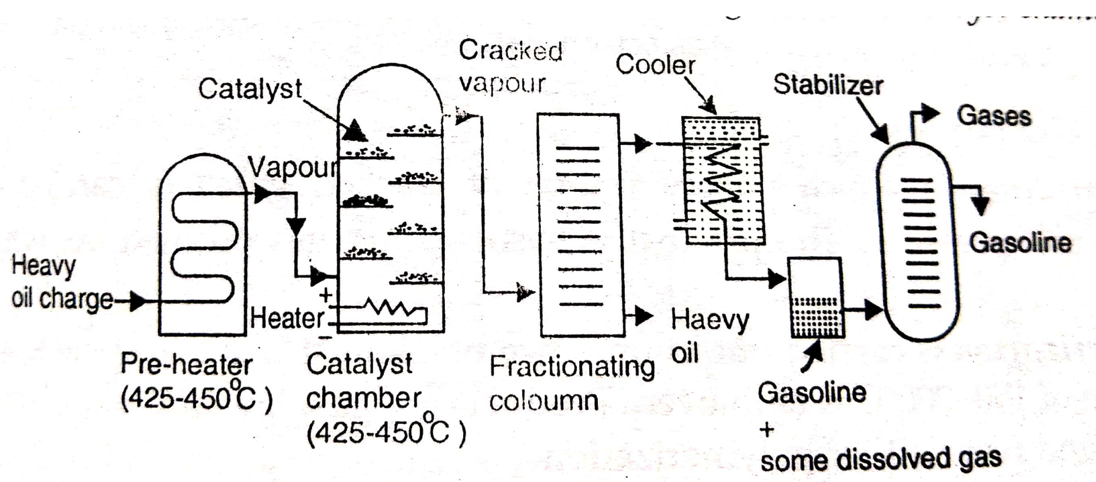
The heavy oil or gas oil stock is cracked at a suitable temperature of 475-530°C and under pressure of 100 kg/cm^2. The cracked products are then separated in a fractionating column. The yield is 50-60% and octane rating of the petrol produced is 65-70.

(b) Vapour-phase thermal cracking**:**

The cracking oil is first vaporized and then cracked at about 600-650°C and under a low pressure of 10-20 kg/cm^2. Petrol obtained from vapour-phase cracking has better anti-knock properties, but poorer stability than petrol from liquid-phase cracking.

This process is suitable only for those oils, which may be readily vaporized. It requires less time than the liquid-phase method.

(2) <u>Fixed-bed catalytic cracking</u>:



The oil vapours are heated in a pre-heater to cracking temperatures. (425-450°C) and then forced through a catalytic chamber (containing artificial clay mixed with zirconium oxide ZrO_2) maintained at 425-450 ^{0}C and 1.5 kg/cm^2 pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2-4% carbon is formed. The latter gets adsorbed on the catalyst bed. The vapours produced are then passed through a *fractionating column,* where heavy oil fractions condense. The vapors are then led through a *cooler,* where some of the gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a *'stabilizer,* where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of *black layer of carbon,* formed during cracking. This is *re-activated* by burning off the deposited carbon. *During the re-activation interval, the vapours are diverted through another catalyst chamber.*

Advantages of Catalytic cracking:

(1) The yield of petrol is higher.

(2) The quality of petrol produced is better.

(3) A much lower pressure (about 1.5 kg/cm^2) is needed in catalytic cracking.

(4)The product contains a very little amount of undesirable Sulphur, because a major portion of it escapes out as H2S gas, during cracking.

Synthetic petrol: (Non-petroleum fossil fuels)

- Petroleum produced by synthetic processes instead of from the natural (fossil) reserves.
- When petroleum is not easily available, chemical processes used to produce liquid fuels from coal or natural gas. Synthetic fuels from coal were strategically important during World War II for the German military.

- *Advantage of synthetic petrol*:

  i) Synthetic petroleum could be better than the naturally occurring product because it is pure from any of the non-beneficial properties found in conventional petroleum.

  ii) Improved viscosity at low temperatures. Mineral oils tend to include wax impurities which coagulate at lower temperatures.

  iii) Moreover it is sulphur free.

  iv) Improved Fuel Economy from 1.8% to up to 5% in fleet tests.

  v) Resistance to oil sludge problems (*i.e*. Superior protection against "ash" and other deposit formation in engine hot spots)

- *Disadvantage of synthetic petrol*:

  a) *More expensive*: The primary disadvantage of synthetic oils is that they cost significantly more than mineral oils

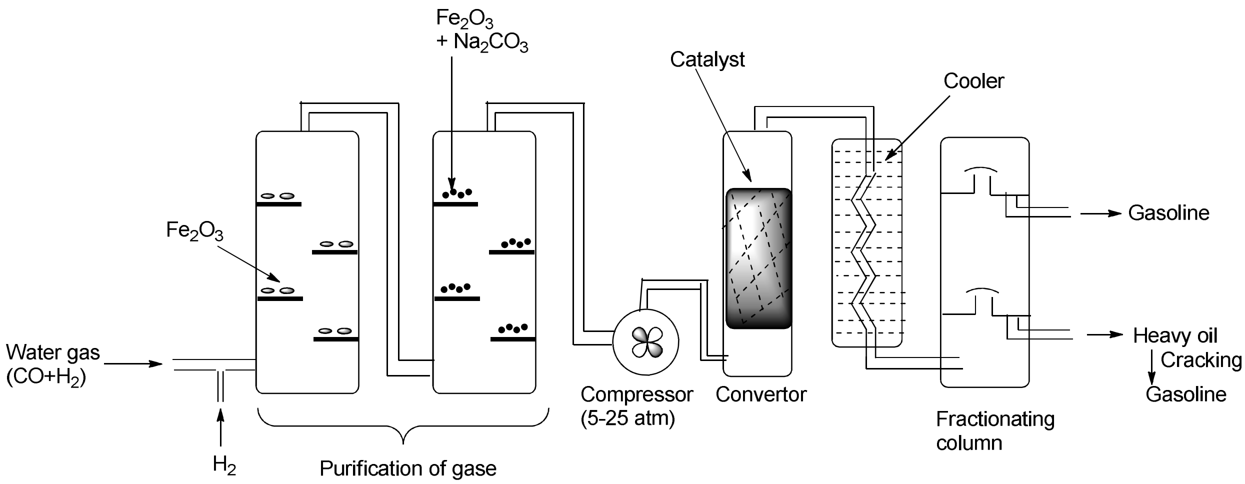
  b) *Limited applications*: Synthetic oils are only significant in high performance applications such as motor racing and aviation, or for general lubrication in extreme environments.

  c) *Decomposition*: Potential decomposition problems in certain chemical environments

- Synthetic petrol is best synthesized by a) **Fischer-Tropsch process** *b)***Bergius process**

a) <u>Fischer-Tropsch process</u> (*or*) <u>Fischer-Tropsch Synthesis</u> (*or*) <u>FT Synthesis</u>.

- *Principle:* In Fischer-Tropsch process, water gas ($CO+H_2$) and hydrogen, is converted into liquid hydrocarbons of various forms in presence of a catalyst.



Fisher-Tropsch synthesis

- Water gas is produced by passing steam over heated coke, may consist of some sulphur.
- Pure hydrogen is mixed with this raw water gas then subjected to purification by passing through Fe_2O_3 (to remove H_2S) and then into a mixture of Fe_2O_3 + Na_2CO_3 (to remove organic sulphur compounds).

$$Fe_2O_3 + H_2O + 3H_2S \longrightarrow Fe_2S_3 + 4H_2O$$

- The purified water gas is compressed to 5 to 25 atm and then passed over a catalytically activated convertor at about 200-300 ^oC. .
- The following chemical reactions take place in a convertor.

$$n\,CO + 2n\,H_2 \longrightarrow C_nH_{2n} + n\,H_2O$$

$$n\,CO + (2n+2)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O$$

- The above reaction is exothermic, so out coming hot gases mixture is passed through a cooler to obtained crude oil. The crude oil thus obtained is then fractionated to yield *i)* gasoline *ii)* high-boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.
- **<u>Convertor</u>:** Catalytically activated convertor contains a mixture of Cobalt, Thoria (Thorium dioxide ThO_2), Magnesia (MgO) and kieselguhr earth (ke) in 20**:**2**:**1**:**40 respectively.(Catalytically activated convertor contains a mixture of 100 parts of cobalt, 5 parts of Thoria (Thorium dioxide ThO2), 8 parts of magnesia (MgO) and 200 parts of kieselguhr earth (ke)(ke occurs naturally in Africa. it is a soft, white powder, consist of 80 to 90% silica, with 2 to 4% alumina and 0.5 to 2% iron oxide. <u>Use</u>: chiefly as a filter, catalyst)

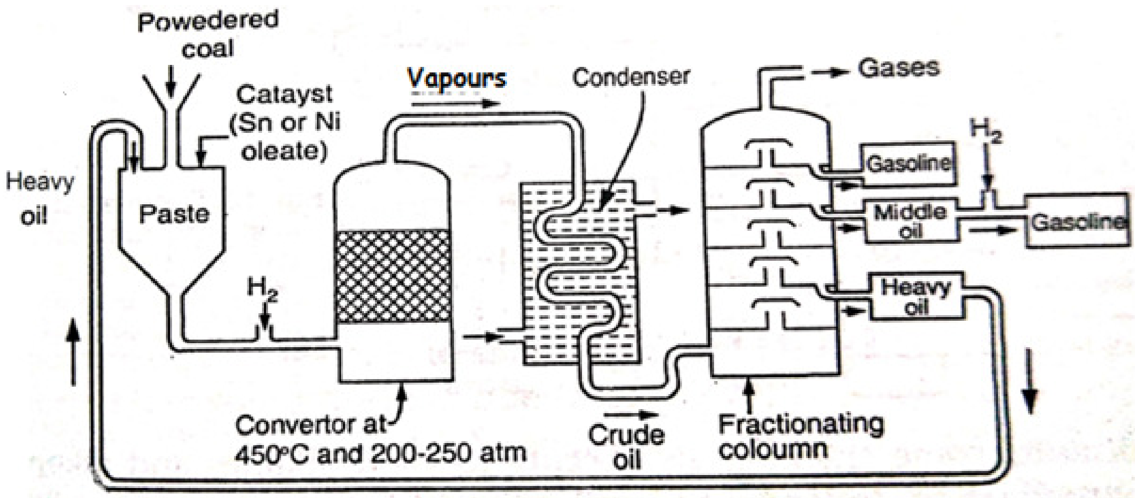
a) Bergius Process:

- The finely powdered coal made into a paste with heavy oil and then a catalyst (Sn or Ni-oleate) is incorporated.
- The whole mixture is heated with hydrogen at 450°C and under a pressure 200-250 atm for about 1½ hours, during which hydrogen combines with coal to form saturated

hydrocarbons, which decompose under same conditions to yield low-boiling hydrocarbons gases.

$$nC + (n - x + 1)H_2 \longrightarrow C_nH_{(2n-2x+2)}$$ (where x = Degrees of Un-saturation i.e Hydrogen deficiency)

- The issuing gases from the converter are passed into condenser, where a liquid resembling crude oil is obtained.
- The crude oil on fractional distillations gives (j) gasoline, (ii) middle oil, and (iii) heavy oil.
- The heavy oil is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapour-phase in presence of a solid catalyst to yields more gasoline.
- The overall yields of gasoline in this process are about 60% of the coal powder used.



Eco friendly fuels-Types, significances

<u>Eco friendly fuel **or** Green fuel, **or** bio-fuel</u>:

It is a type of fuel distilled from plants and animal materials, believed by some to be more environmentally friendly than the widely-used fossil fuels.

<u>The characteristics of eco-friendly fuels</u>: Include a significant achievement in reducing the environmental impact; Burns cleaner than fossil diesel and produces significantly fewer emissions. Almost sulphur-free and contains no aromatic compounds. Easier to ignite than fossil diesel

As of now there are five types of eco-friendly fuel are there. i) bioethanol, ii) biodiesel, iii) biogas, iv) compressed natural gas, v) hydrogen

1. Bioethanol

Bioethanol is a popular fuel used to improve air quality by limiting pollution and increase vehicle performance. This is one of the types of fuel that is made with fermentation process. Normally in this the agricultural waste materials are used as starting materials.

2. Biodiesel

Biodiesel is another one of the alternative fuels because it can be made with vegetable oil or animal fats i.e. edible oils. This is one of the types of fuel that can be used as alternative to diesel. Biodiesel is especially attractive in areas where people may be exposed to diesel exhaust. Biodiesel is comfortable, biodegradable, and lessens severe air pollutants such as particulates, carbon monoxide, hydrocarbons, and other air toxins. Biodiesel is meant to be utilized in standard diesel motors. Biodiesel can be used alone or stirred with petrodiesel.

3. Bio gas

- Biogas typically refers to a mixture of different gases produced by degradation of biological matter by anaerobic bacteria (absence of oxygen).
- The cheapest biogas is *gobar gas* which is produced by the anaerobic degradation of cattle dung.
- Biogas can also produce from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste.
- Composition of biogas (*gobar gas*) is CH_4 = 55%, CO_2 = 35%, H_2 = 7.4%, N_2 = 2.6% and traces of H_2S.
- Its calorific value is 1200 kcal/m^3
- The *gobar gas* is carried out in a 'gobar gas plant'.
- Uses of bio-gas**:**
  - *i)* As a domestic fuel
  - *ii)* As a fuel to run engine
  - *iii)* As an illuminant in villages
- Advantages of biogas**:**
  - It burns without smoke, thereby causing no pollution.
  - It does not contain any toxic gases
  - Calorific value is high
  - Cheapest gas fuel
  - It is clean and convenient fuel in use
- Limitations of biogas**:**
  - ✓ It is necessary to have the gas lamp or stove or burner within 10 meters of the plant.
  - ✓ Need special stoves/burners
  - ✓ It takes nearly 50-60 day to for the initial production of biogas from the plant for its use.

Reason for the use of animal dung in the biogas plant: It has found that 1Kg of dry cattle dung gives about 160 liters of gobar gas, which can supply 800 KJ of heat. On the other hand 1 kg of dry dung on direct burning gives only 100 KJ of heat.

4. CNG or compressed natural gas is a smoke-free gas and does not spread pollution, and thus used in our vehicles. Therefore, CNG is considered as an eco-friendly fuel. Natural gas is one of the most inexpensive aspects of energy vacant to the residential customer. Preparing food with natural gas can deliver many advantages, a natural gas automobile can be less costly to regulate than a similar conventionally fuelled vehicle relying on natural gas rates.

5. Hydrogen gas plays a significant role in developing the endurable machine in the World. Hydrogen and oxygen from air fed into a proton exchange membrane fuel cell create enough electricity to power an electric automobile without producing harmful emissions. The only derivative of a hydrogen energy cell is water.

Significances of Eco friendly fuels

1) Produce lower emissions and fewer toxic contaminants than gasoline and diesel vehicles.

2) Providing a better environment by decreasing greenhouse gases results the decrease in the radiated to the ground which leads to enable to decrease the rate of climate difference.

3) Reduces the carbon emissions, for example by using renewable energy

---

Calorific value: The energy of a fuel is measured in terms of calorific value.

"The total amount of heat liberated, when a unit mass or volume of the fuel on complete combustion under standard conditions" is known as calorific value.

It is of two categories based on the energy levels. i) HCV ii) LCV

***Higher Calorific Value (HCV)*or Gross Calorific Value - GCVor Higher Heating Value - HHV:**

"The total amount of heat released, when unit mass/volume of the fuel on combustion completely and the products of combustion cooled to 15 ^{0}C"

Normally, all the fuel contains hydrogen and when the calorific value of hydrogen determined experimentally, the hydrogen is converted into steam. If the combustion products are condensed to 15 ^{0}C, the latent heat of condensation of steam also included in the measured heat. Which is called as Higher or gross calorific value. The heat contained in water vapour must be recovered in the condensation process

$$\boxed{\text{HCV = CV of fuel + Latent heat of water vapour formed}} \text{ -----eq-1}$$

***Lower Calorific Value (LCV)* or Net Calorific Value - NCV, or Lower Heating Value - LHV):**

"The net amount of heat released, when unit mass/volume of the fuel on combustion completely and the products are permitted to escape"

$$\boxed{\text{LCV = CV of fuel}} \text{ -----eq-2}$$

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

On combining the eq-1 and 2

LCV = HCV – latent heat of water vapour formed

HCV – Mass of hydrogen x 9 x latent heat of steam

Since, 1 part by mass of hydrogen produces 9 parts by mass of water. The latent heat of steam is 587 Kcal/Kg of water vapour formed at 15^{0}C

Units of calorific value**:** LBS has been derived from a Roman word Libra, it is represented by 'lb' or 'lbs'. It is an international term used to define weight or mass of an object. Pound is a Latin word meaning 'a pound by weight'

- *For solid or liquid fuel* 'Calorie/gram (cal/g) **or** kilocalorie/Kg (Kcal/Kg) **or** B.Th.U/lb' lb = labs pound
- *For gases fuel* 'kilocalories/cubic meter (Kcal/m^3) **or** British Thermal unit/cubic feet (B.Th.U/ft^3)'

❖ Two types of calorimeters are used to determine the calorific value of fuels.

a) Bomb Calorimeter b) Boy's calorimeter

Bomb calorimeter is used to find the calorific value of solid fuels and nonvolatile liquid fuels

Boy's calorimeter is used to find the calorific value of gaseous fuel Units of heat: **1 pound = 0.45 Kg**

Calories: The amount of heat required to raise the temperature of one gram of water through 1 ^{0}C

Kilocalorie: The amount of heat required to raise the temperature of one kilogram of water through 1 ^{0}C

1 Kcal = 1000 Cal

British Thermal unit: (B.Th.u**)** The amount of heat required to raise the temperature of one pound (0.4535 g) of water through 1 ^{0}F

1 B.Th.U =252 Cal = 0.252 kcal

1 Kcal = 3.968 B.Th.u

Centigrade heat unit: (C.H.U) The amount of heat required to raise the temperature of one pound of water through 1 ^{0}C

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

Theoretical calculation of calorific value of a fuel:

The calorific values of fuel can be approximately computed by noting the amount of the constituents of the fuel. The HCV of some of the chief combustible constituents of fuels are

Constituent	Hydrogen	Carbon	Sulphur
HCV (kcal/kg)	34500	8080	2240

Dulong's formula gives the gross heating value of coal in terms of the weight fractions of carbon, hydrogen, oxygen, and sulfur from the ultimate analysis. In ultimate analysis a complete breakdown of coal into its chemical constituents is carried out by chemical process.

Dulong's formula for calorific value from the chemical composition of the fuel is

HCV = $\frac{1}{100}$ [8080 x C + 34500 [H – $\frac{O}{8}$] + 2240 x S] kcal/kg

Where C, H, O, S are the percentages of Carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula oxygen is assumed to be present in combination with hydrogen as water.

LCV = [HCV – $\frac{9}{100}$ H x 587] kcal/kg

= HCV – 0.09 H x 587] kcal/kg

This is based on fact that 1 part of H by mass gives 9 parts of H_2O and the latent heat of steam is 587 kcl/kg

Numerical problems based on calorific value:

Dulong's formula for calorific value from the chemical composition of the fuel is

$$HCV = \frac{1}{100} [8080 \times C + 34500 [H - \frac{O}{8}] + 2240 \times S] \quad kcal/kg$$

Where C, H, O, S are the percentages of Carbon, hydrogen, oxygen and sulphur in the fuel respectively.

LCV = HCV– 0.09 H x 587] kcal/kg

<u>Problem 1</u>. ***Calculate the gross and net calorific value of coal having the following compositions carbon = 85%, hydrogen = 8%, sulphur = 1%, nitrogen = 2%, ash = 4%. Latent heat of steam = 587 kcal/kg.*** *(by hart the Latent heat of steam)*

Gross calorific value (GCV) $= \frac{1}{100}$ [8080 x C + 34500 [H – $\frac{O}{8}$] + 2240 x S] kcal/kg

$= \frac{1}{100}$ [8080 x 85 + 34500 [8 – $\frac{O}{8}$] + 2240x 1] kcal/kg

$= \frac{1}{100}$ [686800 + 276000 + 2240] kcal/kg

= **9650.4 kcal/Kg**

Net calorific value (NCV) = (GCV — 0.09 H x 587) kcal/kg

= (9,650.4 — 0.09 x 8 x 587) kcal/kg = **9,227.8 kcal/kg.**

<u>Problem 2</u>. A coal has the following composition by weight: C = 90%; 0 = 3.0%; S = 0.5% ; N = 0.5% and ash = 2.5%. Net calorific value of the coal was found to be 8,490.5 kcal/kg. Calculate the percentage of hydrogen and higher calorific value of coal.

LCV = HCV – 0.09 H x 587] kcal/kg this can be on rewrite as

HCV = (LCV + 0.09 H x 587) kcal/kg

= (8,490.5 + 0.09 H x 587) kcal/kg

= (8,490.5 + 52.8 H) kcal/kg --------------------------- (i)

Also HCV = $\frac{1}{100}$ [8080 x 90 + 34500 [H – $\frac{3}{8}$] + 2240 x 0.5] kcal/kg

= [7,272 + 345 H —129.4 + 11.2] kcal/kg

= [7,754.8 + 345 H] kcal/kg ------------------------ (ii)

From (i) and (ii),

7,754.8 + 345 H= 8,490.5 + 52.8 H

292.2H = 8,490.5 — 7,154.8 =1,335.7

Percentage of H = 1,335.7/292.2 = 4.575% --------------- (iii)

Substitute (iii) in (i)

HCV = (8,490.5 + 52.8 x 4.575) kcal/kg

= (8,490.5 + 241.3) kcal/kg = **8,731.8 kcal/kg.**

Problem 3. Sample of coal has following composition by mass C = 70 %, O = 8 %,H = 10 %, N = 3 %, S = 2%, Ash = 7 %. Calculate H.C.V. and L.C.V. using Dulong formula

HCV = 1/100[8080 x C+34500(H—O/8) +2240 S]

= 1/100[8080 + 70+34500(10— 8/8) +2240 X 2]

= 1/100 [565600 + 34500 (10— 1) X 4480]

= 1/100 [565600 + 310500 + 4480]

= 1/100 [880580]

= 8805.80kcal/kg

LCV = [HCV- 9/100 H X 587] kcal/kg

= [8805.80-9/100 x 587] = [8805.80- 528.30]

= **8277.80 kcal/kg**

Problem 4. Calculate the higher and lower clorific values of a coal sample containing 84% carbon, 1.5% sulphur, 0.6% nitrogen, 5.5% hydrogen and 8.4% oxygen.

[Ans. (i) 8,356 kCal/kg; (ii) 8,066 kcal/kg]

Problem 5 Calculate the gross and net calorific value of a sample of coal having following composition: 85%, H = 9 %, 0 = 3.4 %, S = 4.2%, N = 11%, and ash = 2 %.

[Ans. (i) 9.920.4 kcal/kg ; (ii) 9444.9 kcal/kg]

Problem 6. A sample of coal has the following analysis: C = 83%, S =1.5%, N = 0.6%, H = 7.5% and 0 = 8.4%. Find the gross calorific value using Dulong Formula.

[Ans = 8965.25 kcal/ kg]

Problem 7. Calculate the gross and net calorific value of coal sample having the following composition: C = 80%, H = 7%, 0 = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

[Ans. GCV = 8,828 kcal/kg; NVC = 8,458 kcal/kg]

- ✓ This material gives you basic information
- ✓ Refer text book for more details