

# ENERGY

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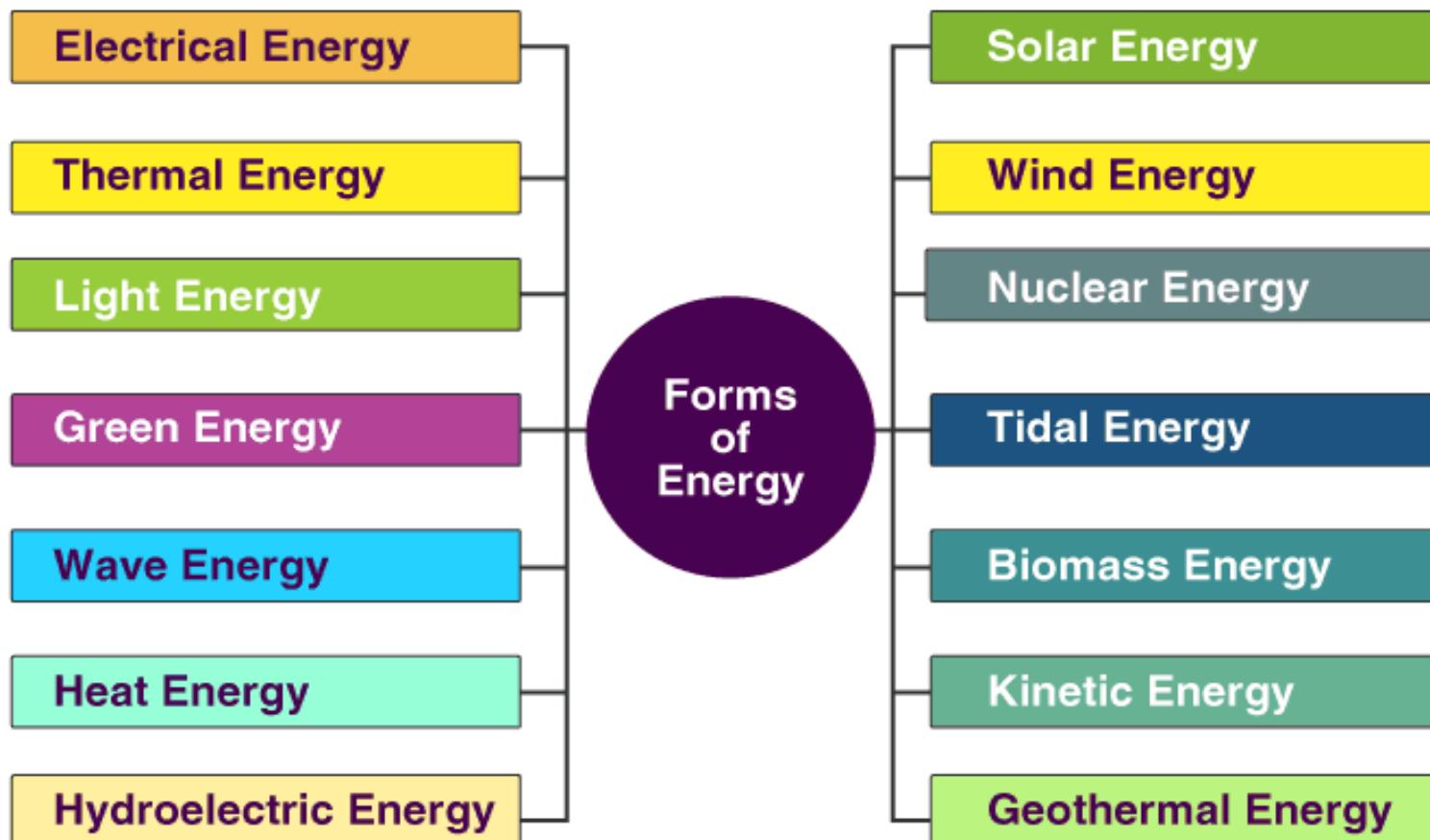
Modified by Dr. Druman Utekar

# Energy

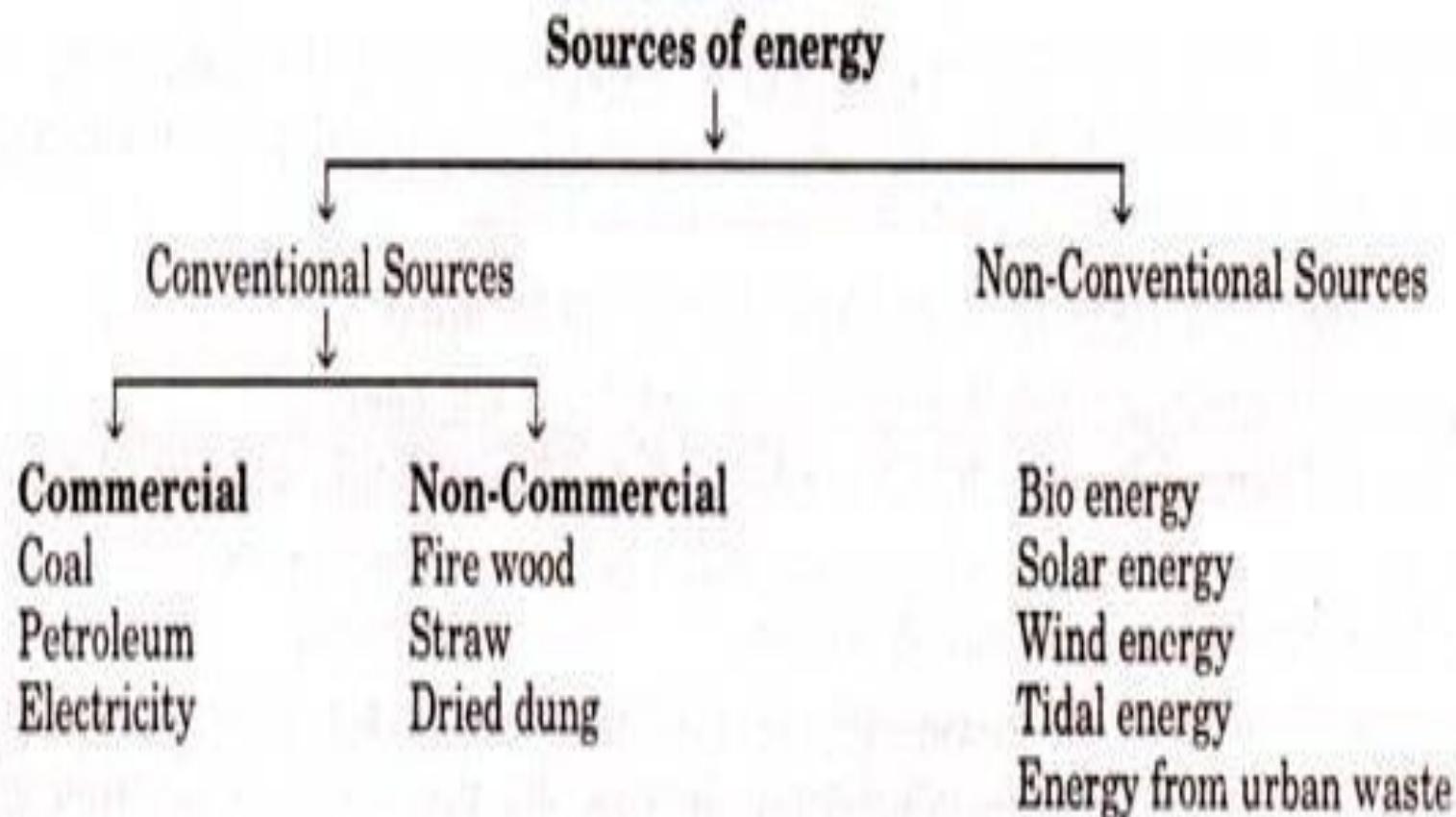
The sun, directly or indirectly, is the source of all the energy available on Earth. Energy is essential to life and all living organisms.

Energy is a conserved quantity and the law of conservation of energy states that energy can neither be created nor destroyed but can only be converted from one form to another. The SI unit of energy is Joule.

# Types of Energy



# Classification of Energy



# Distinction: Conventional (non-renewable) and nonconventional energy (renewable) sources.

<b>Renewable resources</b>	<b>Non-renewable resources</b>
Resources which can be renewed or can be reused are renewable resources.	Resources which cannot be renewed or reused once utilized are called non-renewable resources.
These include components like air, water, wind, sunlight etc.	These include components like fossil fuels, LPG gases.
They are sustainable resources.	They are exhaustible resources.
Their rate of renewal is greater than the rate of getting exhausted.	Their rate of renewal is slower than the rate of getting exhausted.
They are mostly environmental friendly and does not cause pollution.	They are the main cause of pollution.

# Solar Energy

The electromagnetic radiation from sun is commonly known as solar energy. These radiations are resulted from thermo nuclear fusion reaction on the surface of sun. All the radiation from the sun is not

in the same wavelength range. Almost 92% lie in the range of 315 nm to 1400nm. The estimated amount of solar flux reaching the atmosphere of earth is approximately 1400W/m<sup>2</sup>min. and that of heat

equivalent is  $2.68 \times 10^{24}$  J/Year. The eco system of earth utilizes about 0.2-0.5 % of total amount of solar energy received. It indicates clearly that large amount solar energy get wasted, which otherwise

can be immense use for satisfying needs of humans.

Advantage of solar energy:

1. It is non-polluting and non-depleting source of energy.
2. It is renewable source of energy.
3. It is available abundantly.

In spite of these advantages, the use of solar energy in large scale is still not in practice, due to following reasons,

1. Non availability of intense light in all areas throughout year
2. Difficulties faced in economic collection and conversion of solar energy into other forms of energy such as electricity.

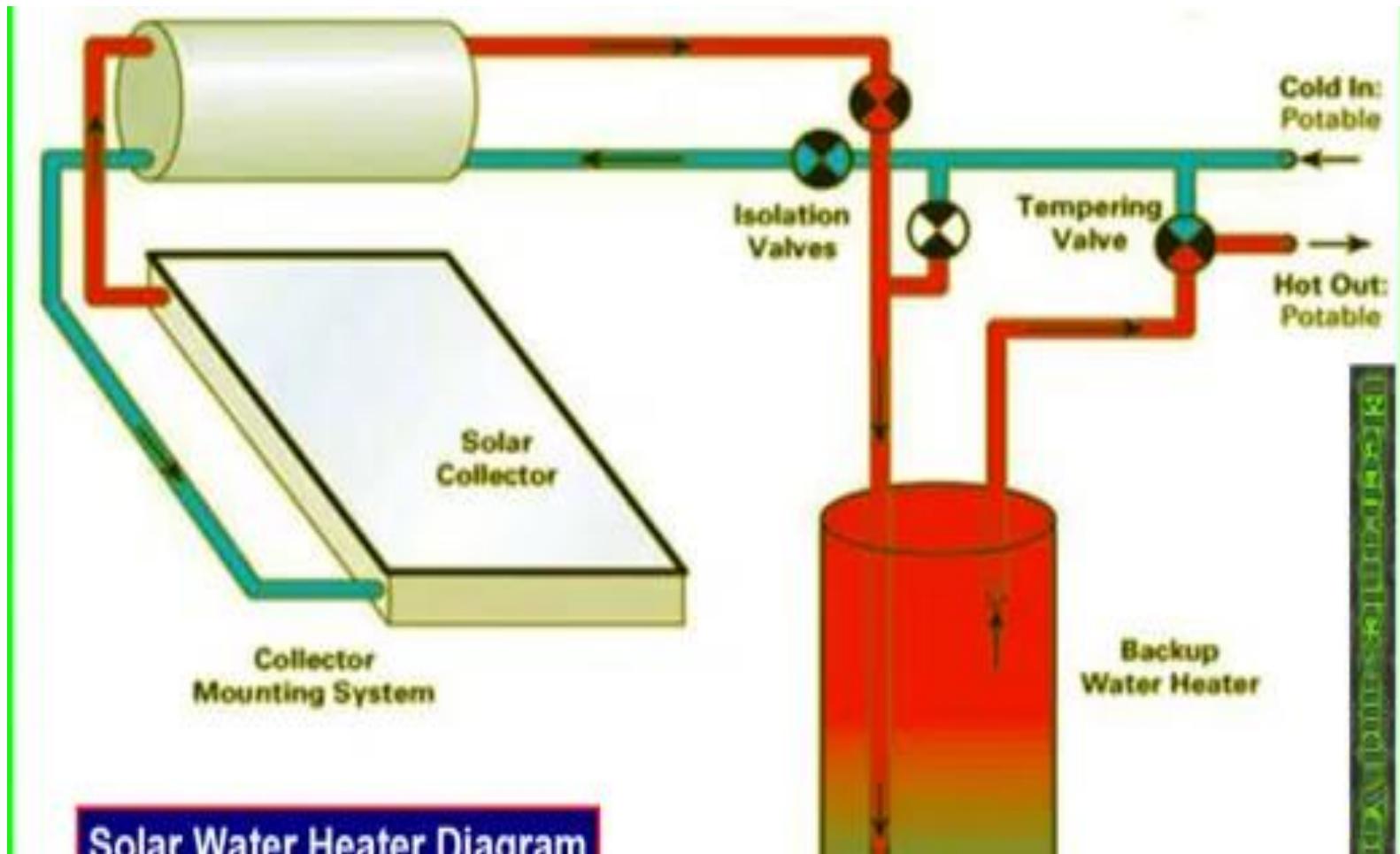
The solar energy has been successfully used in following purpose

- i) Heating: Used for water and space heating in colder countries.
- ii) Electricity: Using solar energy electric energy can be generated.

# Advantages and Disadvantages

Advantages	Disadvantages
Reduces consumption of fossil fuels.*	Currently, electricity from PV systems is more expensive than electricity produced from fossil fuel or nuclear power plants.
Reduces production of greenhouse gases.*	Expensive to buy.
Reduces production of various pollutants.*	Requires engineering expertise to design and install systems.
Good for remote applications: satellites, rural hospital equipment in developing countries, telecommunication equipment, etc.	Production of PV systems from single silicon crystals is technically challenging, and energy- and time-consuming.
Reduces the loss of electricity due to power line resistance (distribution losses) because it can be sited where the electricity is used.	Sunlight is not constant, so must get electricity from other sources at night or on cloudy days or store it (such as batteries, etc.)
Reduces water consumed in electrical generation processes by displacing electrical demand.	Sunlight is diffuse; PV would take much space to produce enough electricity to meet our current needs (an area ~one sixth the size of Arizona)
Does not contribute to thermal pollution of waterways.	* Once manufactured, PV systems produce no waste products. Manufacturing of almost any device uses some nonrenewable resources, consumes energy and produces waste products.
No hidden costs.	PV systems consume some nonrenewable resources if a system component needs repair or maintenance (such as batteries, inverter, etc.).
Can provide energy independence.	
PV cells last ~ 30 years.	
Uses a renewable energy source.	

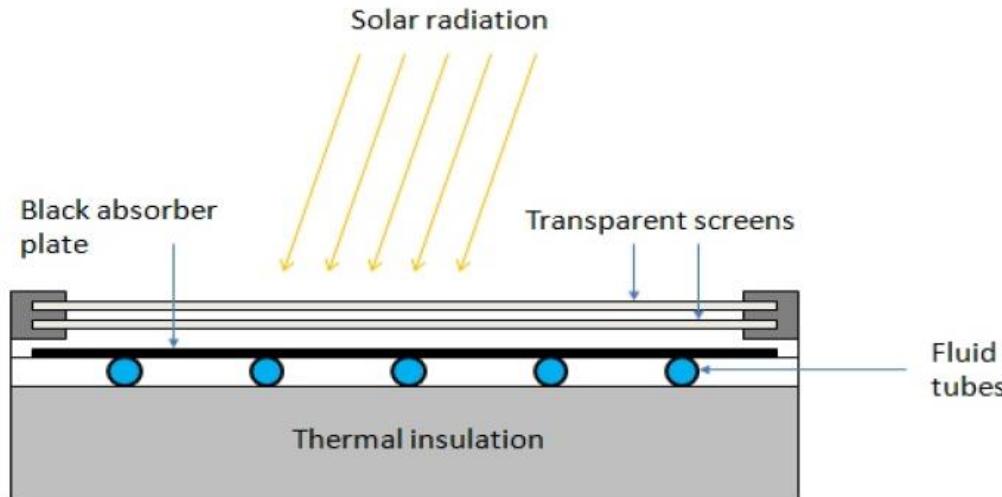
# Solar Water Heater



## **Flat Plate Collector:**

The device works on the principle of black body in which heat absorbing capacity and tendency of a black surface is utilized to achieve benefits for human.

Diagram:



## **Construction:**

These are the main components of a typical flat-plate solar collector:

- Black surface - absorbent of the incident solar energy
- Glazing cover - a transparent layer that transmits radiation to the absorber, but prevents radiative and convective heat loss from the surface
- Tubes containing heating fluid to transfer the heat from the collector
- Support structure to protect the components and hold them in place
- Insulation covering sides and bottom of the collector to reduce heat losses

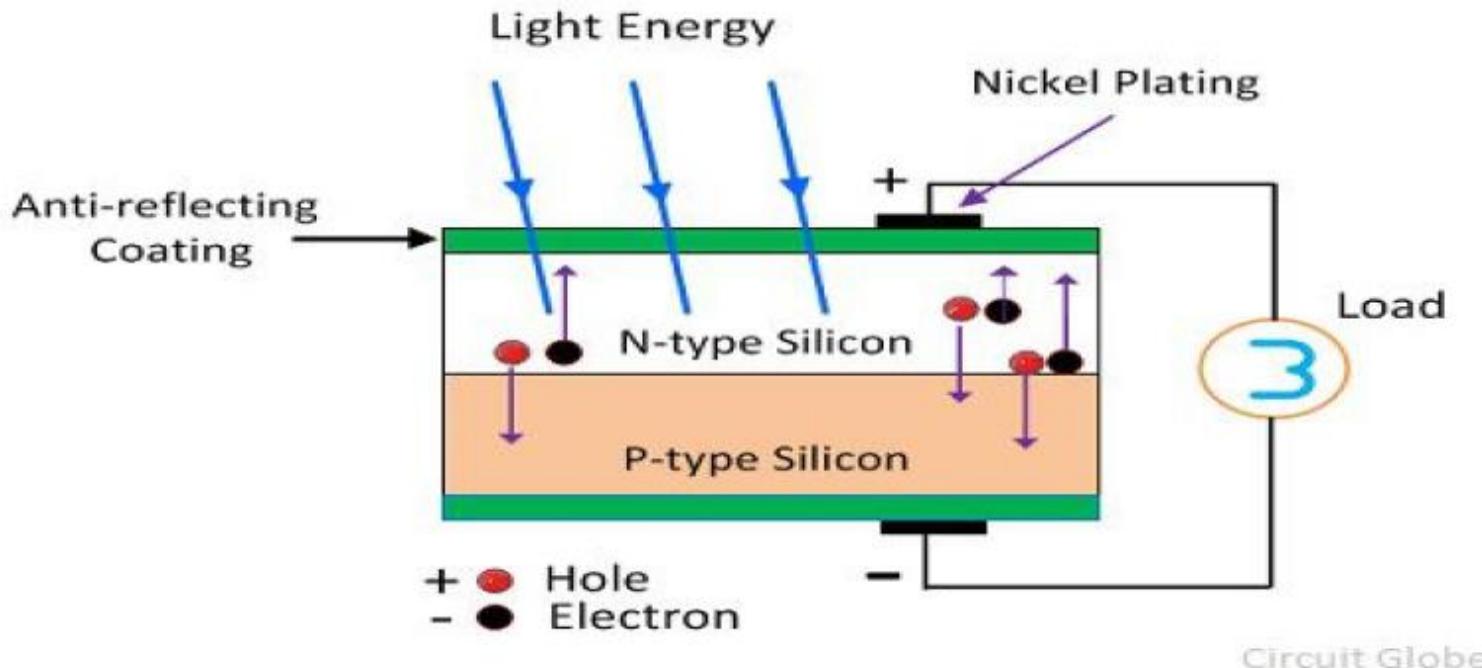
## **Application**

Some advantages of the flat-plate collectors are that they are:Easy to manufacture

- Low cost, Collect both beam and diffuse radiation
- Permanently fixed (no sophisticated positioning or tracking equipment is required)
- Little maintenance

# PHOTO VOTAIC CELL (SOLAR CELL)

A conventional solar cell structure is shown in figure:



Semiconductors like silicon has the capacity to absorb light and deliver a portion of the energy of the absorbed photons to carry charge carriers (electrons and hole). Thus solar cell is a semiconductor diode that has been designed carefully so that it can absorb the light energy efficiently and convert light energy from the sun into electrical energy.

**Construction:** A typical silicon photo voltaic cell composed of thin layer of phosphorus doped silicon (n-type) on top of boron doped (p-type) silicon. Hence these two layers form p-n junction. A metallic grid is the electrical contact of the diode and allows light to fall on the semiconductor between the grid lines. An anti-reflective layer between the grid lines increases the amount of light transmitted to semiconductor.

**Working:** of tiny energy packets called photon. When light radiation falls on the p-n junction diode,

photons are absorbed and electron-hole pairs are generated. The electrons are diffused and collected

at the n-type end and holes are diffused and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through

the external circuit. Thus photoelectric current is produced and available for use. The current output

of a cell depends on its efficiency and size and is proportional to the intensity of sun light striking the

surface of the cell. Therefore, photovoltaic cells are connected electrically in series or parallel circuits to produce higher voltages, currents and power levels. A number of solar cells electrically connected

to each other and mounted in a support structure or frame is called a photovoltaic module. A photovoltaic array is the complete power generating unit, consisting of any number of photovoltaic modules and panels.

# Advantages & Disadvantages

## Photovoltaic solar energy

### Advantages:

- environmentally friendly
- no noise, no moving parts
- no emissions
- no use of fuels and water
- minimal maintenance requirements
- long lifetime, up to 30 years
- electricity is generated wherever there is light, solar or artificial
- PV operates even in cloudy weather conditions
- modular “custom-made” energy can be sized for any application from watch to a multi-megawatt power plant

### Limitations:

- PV cannot operate without light
- high initial costs that overshadow the low maintenance costs and lack of fuel costs
- large area needed for large scale applications
- PV generates direct current special DC appliances or an inverter are needed
- in off-grid applications energy storage is needed

# Fuel cells

- H<sub>2</sub>-O<sub>2</sub> fuel cells-Self Study

# Fuels

- Fuels can be defined as substances which undergo combustion in the presence of air to produce a large amount of heat that can be used economically for domestic and industrial purpose.
- Examples, Wood, Coal, Kerosene, Petrol

# Classification of chemical fuels

- A) Based on the origin:
  - i) Primary or natural fuels
  - ii) Secondary or artificial or derived fuels
- B) Based on Physical State:
  - i) Solid Fuels
  - ii) Liquid Fuels
  - iii) Gaseous Fuels
- C) Based on Chemical Nature
  - i) Organic eg. Vegetable fuel, coal
  - ii) Inorganic eg. Iron Pyrites
  - iii) Nuclear Fuels eg. Uranium oxide

# Characteristic Properties of Fuels

- Fuels are characterized by testing certain physical and chemical properties.
  - i) Calorific Value should be as high as possible.
  - ii) Ignition temperature-Moderate
  - iii) Flame temperature should be as high as possible.
  - iv) Flash and Fire point should be as high as possible.
  - v) Aniline point should be low.
  - vi) Cloud and Pour point should be as low as possible.
  - vii) Viscosity should be adequate.
  - viii) Coke number should be as high as possible.
  - ix) Moisture content-as low as possible.
  - x) Volatile matter as low as possible.
  - xi) Ash content should be absent.
  - xii) Easy risk free transport should be possible.
  - xiii) Storage space-ideally fuel should occupy small space.
  - xiv) Air requirement- adequate
  - xv) Harmless products should be produced on combustion.

# Calorific Value

- Calorific value is defined as the number of parts of water which gets heated through  $1^{\circ}\text{C}$  by the heat evolved by the complete combustion of one unit weight of fuel( unit volume of gaseous fuels) under the conditions such as
  - i) Whole of heat evolved is absorbed by water.
  - ii) The products formed leave the system at atmospheric temperature and pressure.
- It is the most important property of fuel.

# Units of calorific value

## 1) B.T.U. (British Thermal Unit)

A British thermal unit may be defined as the heat required to raise the temperature of one pound of water from 60°F to 61°F.

## 2) K.C.U. (Kilogram Centigrade Unit)

The calorie, a unit of heat may be defined as, the heat required to raise the temperature of one Kg of water from 15°C to 16°C.

Correlation between BTU and KCU:

$$1\text{BTU} = 0.252\text{KCal} = 252\text{Cal}$$

$$1\text{KCal} = 3.968 \text{ BTU}$$

## 3) C.H.U. (Centigrade Heat Unit)

The calorific value can also be expressed as centigrade heat unit (C.H.U.), which is the amount of heat required to raise temperature of one pound of water through one degree centigrade.

## **1) High Calorific value (HCV) or Gross Calorific value (GCV):**

High calorific value may be defined as the total amount of heat produced when one unit of the fuel has been burnt completely and the products of combustion have been cooled to 16°C or 60°F.

## **2) Low calorific value( LCV) or Net Calorific value (NCV)**

Low calorific value may be defined as the net heat produced when unit mass or volume of fuel is completely burnt and products are allowed to escape.

$$\begin{aligned} \text{NCV or LCV} &= \text{GCV (HCV)} - \text{Latent Heat of water formed} \\ &= \text{GCV(HCV)} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of steam} \\ &= \text{GCV(HCV)} - 0.09 \times \%H \times 587 \end{aligned}$$

Because 1 part by weight of hydrogen produces 9 parts (1+8) by mass of water.

# Dulong Formula

- The calorific value of fuels is determined theoretically by Dulong formula or I.A. Davies formula.
- It is expressed as

$$Q = 1/100 [ 8080 \times C + 34500 \times (H - O/8) + 2240 \times S ]$$

Where, Q = Calorific value in KCU/Kg

C = % of carbon

H = % of hydrogen

O = % of oxygen

S = % of sulphur

Dulong formula for HCV & LCV

$$HCV = 1/100 [8080 \times C + 34500 \times (H - O/8) + 2240 \times S]$$

$$LCV = HCV - [9/100 \times \%H \times 587]$$

Experimentally calorific value of solid and liquid fuel is determined using Bomb Calorimeter.

- Numerical 1: A sample of coal contains C = 55%, O = 28%, H = 7%, S = 0.7%, N = 0.2%, Ash = 0.2%. Calculate the GCV and NCV.

Soln:

$$\begin{aligned} \text{GCV} &= 1/100[8080C + 34500(H-O/8) + 2240S] \\ &= 1/100 [8080 \times 55 + 34500(7-28/8) + 2240 \times 0.7] \\ &= 5667 \text{ Kcal/Kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{HCV} - 0.09 \times \% \text{ H} \times 587 \\ &= 5667 - 0.09 \times 7 \times 587 \\ &= 5297.19 \text{ Kcal/Kg} \end{aligned}$$

- Numerical 2: A sample of coal has following composition C = 70%, O = 8%, H = 10%, N = 3%, S = 2%, Ash = 7%. Calculate HCV and GCV.

- Numerical 3: A sample of coal contains C = 61%, O = 32%, S = 0.5%, N = 0.2% and Ash = 0.3%. If NCV of coal is 5313.02KCal/Kg. Calculate % H and GCV.

$$\text{GCV} = 1/100[8080C + 34500(H-O/8) + 2240S] \text{---i)}$$

$$\text{NCV} = \text{GCV} - 0.09 \times \% \text{ H} \times 587$$

$$\text{GCV} = \text{NCV} + 0.09 \times \% \text{ H} \times 587 \text{-----ii)}$$

$$1/100[8080C + 34500(H-O/8) + 2240S] = \text{NCV} + 0.09 \times \% \text{ H} \times 587$$

Numerical 3: A sample of coal contains C = 70% , O = 25%, S = 01%, N = 01% and Ash = 0-5%. If NCV of coal is 5200KCal/Kg. Calculate % H and GCV.

$$GCV = 80.80 \times 70 + 345(H - 25/8) + 22.40 \times 1 \text{----i)}$$

$$= 5656 + 345H - 1078.125 + 22.4$$

$$= 4600 + 345H$$

$$NCV = GCV - 0.09 \times \%H \times 587$$

$$GCV = 5200 + 0.09 \times \%H \times 587$$

$$= 5200 + 52.83H \text{-----ii)}$$

$$4600.275 + 345H = 5200 + 52.83H$$

$$345H - 52.83H = 5200 - 4600.275$$

$$292.17H = 599.725$$

$$H = 2.05\%$$

$$GCV = 5308.44 \text{Kcal/Kg}$$

# Coal

## Purpose of Analysis of Coal

- To decide price of coal
- To determine quality
- To specify use of coal for a particular purpose.
- To calculate theoretical calorific value of coal.
- To calculate air requirement for complete combustion of coal and design the furnace fire box suitably.

- Types of Analysis of Coal

- A) Proximate Analysis

- i) % Moisture
  - ii) % Volatile Matter
  - iii) % Ash
  - iv) Fixed Carbon

- B) Ultimate Analysis

- i) % Carbon and % Hydrogen
  - ii) % Nitrogen
  - iii) % Sulphur
  - iv) % Ash

# Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which

- a) % Moisture b) % VM c) % Ash d) % Fixed Carbon are found out.

## a) % Moisture

A known weight of powdered and air dried coal sample is taken in a crucible and it is placed in an oven for 1hr at 110°C. Then the coal is cooled in a desiccator and weighed out. If the initial weight of the coal is W gms and final weight is W1 gms.

Then the loss in weight (W-W1) corresponds to moisture in coal.

$$\% \text{ Moisture} = \frac{\text{Loss in weight} \times 100}{\text{Weight of coal sample}} = \frac{(W-W_1) \times 100}{W}$$

b) % Volatile Matter

Moisture free coal left in the crucible in first experiment W1 is covered with a lid loosely. Then it is heated at 925°C in a muffle furnace for 7min.

The crucible is taken out and cooled in a desiccator. Then it is weighed (W2 gms) .

$$\% \text{ Volatile matter} = \frac{\text{weight of volatile matter} \times 100}{\text{Weight of coal sample}} = \frac{(W_1 - W_2) \times 100}{W}$$

c) % Ash

The residual coal in the above experiments is heated and burnt in an open crucible at above 750°C for half hour.

The coal gets burnt. The ash left in crucible is cooled in a desiccator and weighed W3 gms.

$$\% \text{ Ash} = \frac{\text{weight of ash} \times 100}{\text{Weight of coal}} = \frac{W_3 \times 100}{W}$$

d) % Fixed Carbon:

It is found by calculations

$$\% \text{FC} = 100 - (\% \text{ moisture} + \% \text{ VM} + \% \text{ Ash})$$

## **Significance or Importance of proximate analysis**

### a) Moisture

It decreases calorific value of coal largely as it does not burn and takes away heat in the form of latent heat.

It increases ignition point of coal.

Hence a coal with lower moisture % is better quality.

### b) Volatile matter

It decreases calorific value of coal.

It elongates flame and decreases flame temperature.

It form smoke and pollute air.

However the coals containing 15-25% of VM on carbonization gives coke oven gas which is source of various organic aromatic chemicals.

Such coal have good coaking property and coke can be obtained from the coals.

Overall regarding burning of coal the coal with lesser VM is better quality coal.

### c) Ash

It reduces calorific value of coal as ash is non-burning part in coal.

Ash disposal is a problem.

Ash fuses to form clinker at high temperature obstructing the air supply of coal burning furnace.

Hence lesser the % ash better is the quality of coal.

### d) Fixed carbon

Carbon is the burning part in coal and higher the fixed carbon higher is calorific value.

Hence a good quality coal contains high fixed carbon percentage.

**Numerical 1:** A sample of coal was analysed for content of moisture, volatile matter & ash. From the following data, calculate the percentage of the above quantities.

- i) weight of coal taken = 2.5g
- ii) weight of coal after heating at 110°C = 2.365g
- iii) weight of coal after heating at covered crucible at 950°C = 1.165g
- iv) constant weight obtained at the end of the experiment = 0.460g

**Soln:**

a) % Moisture =  $\frac{(W-W_1) \times 100}{W} = \frac{(2.5-2.365) \times 100}{2.5} = 5.4\%$

b) % volatile Matter =  $\frac{(W_1-W_2) \times 100}{W} = \frac{(2.365-1.165) \times 100}{2.5} = 48\%$

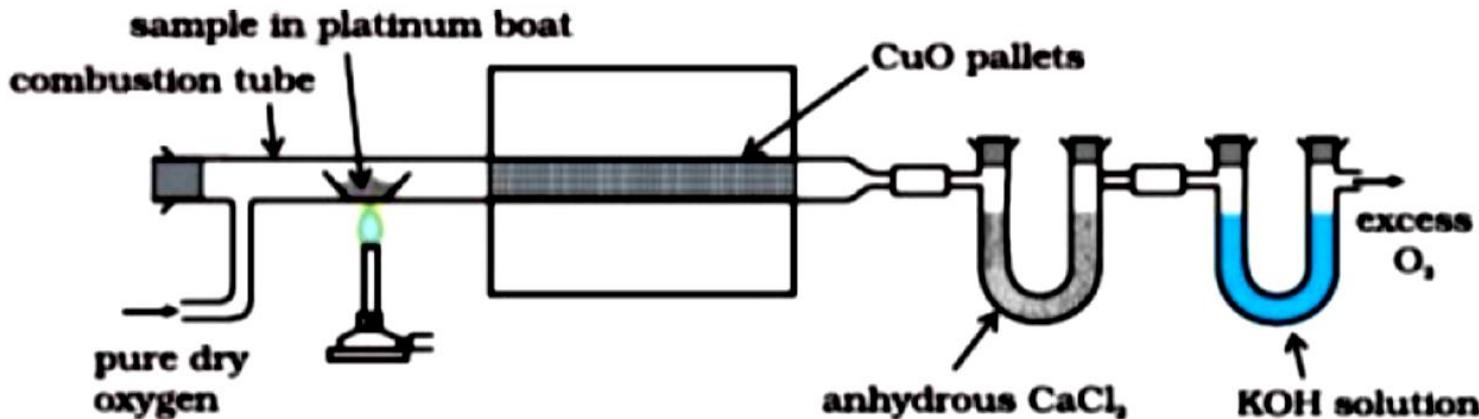
c) % Ash =  $\frac{W_3 \times 100}{W} = \frac{0.460 \times 100}{2.5} = 18.4\%$

d) % Fixed Carbon =  $100 - [\% \text{ moisture} + \% \text{ VM} + \% \text{ Ash}]$   
=  $100 - [5.4 + 48 + 18.4] = 28.2\%$

# Ultimate Analysis

## 1) Carbon and 2) hydrogen:

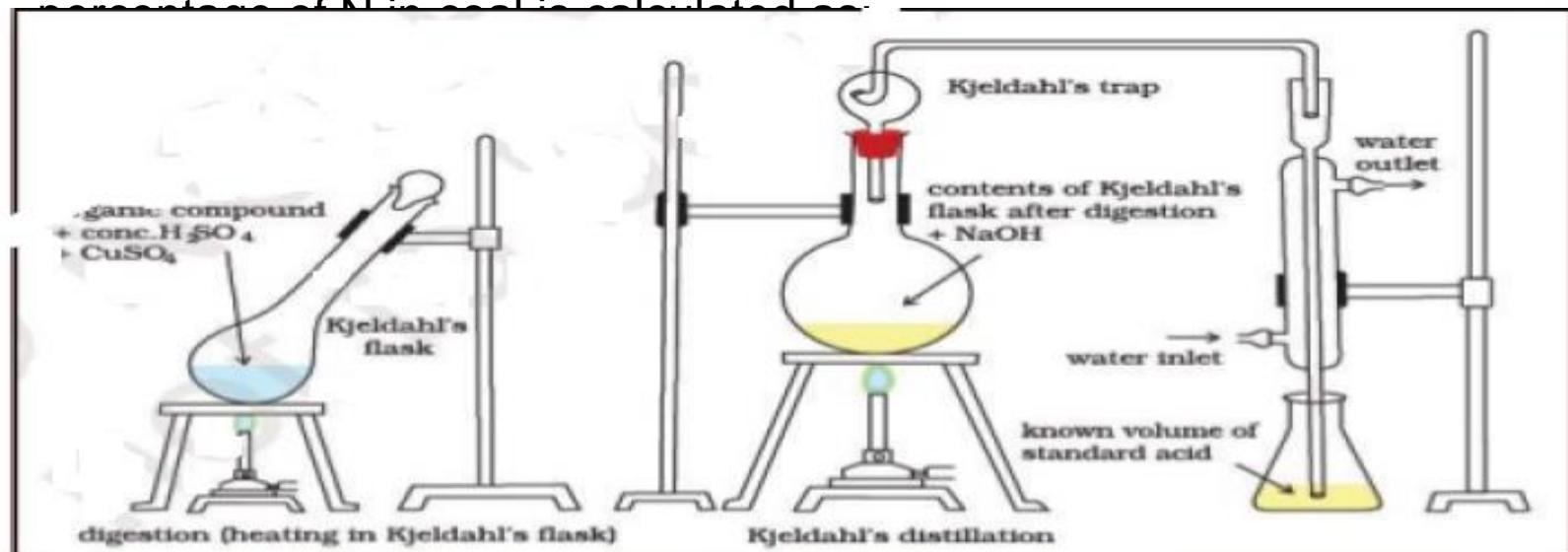
- About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO<sub>2</sub> and H<sub>2</sub>O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl<sub>2</sub> tubes of known weights.
- The increase in weights of these are then determined.
- C + O<sub>2</sub> ---->CO<sub>2</sub>
- 2H<sub>2</sub> + O<sub>2</sub>-----> 2H<sub>2</sub>O
- KOH + CO<sub>2</sub>-----> K<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O
- CaCl<sub>2</sub> + 7 H<sub>2</sub>O-----> CaCl<sub>2</sub>.7 H<sub>2</sub>O



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

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

**3) Nitrogen by Kjeldahl's Method:** About 1 g of accurately weighed powdered 'coal is heated with concentrated H<sub>2</sub>SO<sub>4</sub> along-with K<sub>2</sub>SO<sub>4</sub>(catalyst) in a long-necked flask(called Kjeldahl's flask). After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard KOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated.



$$\text{Percentage of N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

Sulphur is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphatThe washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of S} = \frac{\text{Weight of BaS0}_4 \text{ residue obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

Ash determination is carried out as in proximate analysis.

(5) Oxygen: It is obtained by difference. Percentage of O = 100 - Percentage of (C + H + S + N + ash)

### **Significance of ultimate analysis:**

- (1) Carbon and hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible constituent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal
- (2) Nitrogen has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.
- (3) Sulphur, although contributes to the heating value of coal, yet on combustion produces acids ( $\text{SO}_2$  and  $\text{SO}_3$ ), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% and derived from ores like iron pyrites, gypsum, etc., mines along-with the coal. Presence of sulphur is highly undesirable in coal to be, used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur (formed as combustion products) pollute the atmosphere and leads to corrosion.
- (4) Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1. 7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

Numerical 1: 0.2g of Coal Sample is accurately weighed and is burnt in a combustion apparatus. The gaseous products of combustion are absorbed in potash bulb and calcium chloride tubes of known weights. The increase in weight of potash bulb and  $\text{CaCl}_2$  tube are 0.66g and 0.08g respectively. Calculate the % C and % H in coal sample.

Numerical 2: 3g of coal was heated in Kjeldahls flask and  $\text{NH}_3$  gas evolved was absorbed in 40mL of 0.5N HCl. After absorption the excess acid required 18.5mL of 0.5N KOH for exact neutralization. 2.3g of coal sample in quantitative analysis gave 0.35g  $\text{BaSO}_4$ . Calculate % of N and S in coal sample.

Soln: Volume of  $\text{NH}_3$  consumed by 0.5N HCl is in terms of 0.5N KOH

40ml of 0.5N HCl = 40mL of 0.5N KOH---assumed---V1 \_\_\_\_\_ blank

Unreacted acid = 18.5ml of 0.5N KOH----V2 \_\_\_\_\_ back titration

Vol of acid reacted with absorbed  $\text{NH}_3$  in term of 0.5N KOH =  $40 - 18.5\text{ml} = 21.5\text{mL}$

% N = volume of acid consumed(V1-V2) x N KOH x 1.4

weight of coal sample

% S = Wt of  $\text{BaSO}_4$  formed x 32x 100  
wt of coal sample x 233

Numerical 3: 2.5 g of coal was heated in Kjeldahls flask and  $\text{NH}_3$  gas evolved was absorbed in 40mL of 0.5 N HCl. After absorption the excess acid required 8.5mL of 0.25N KOH for exact neutralization.

Soln:

Blank titration = 40mL of 0.5N HCl = 40mL of 0.5N KOH

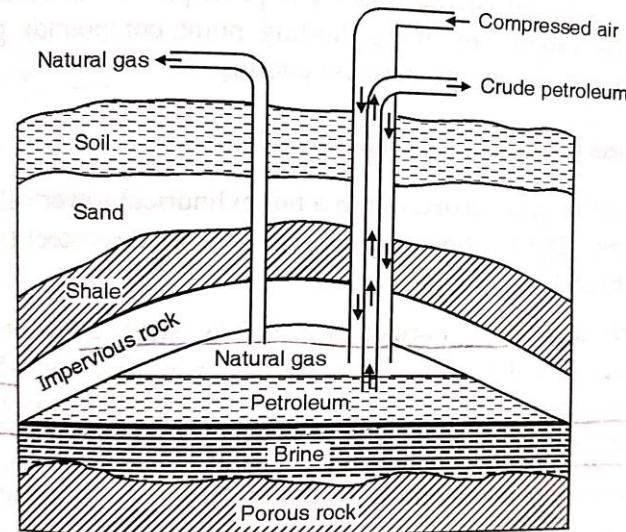
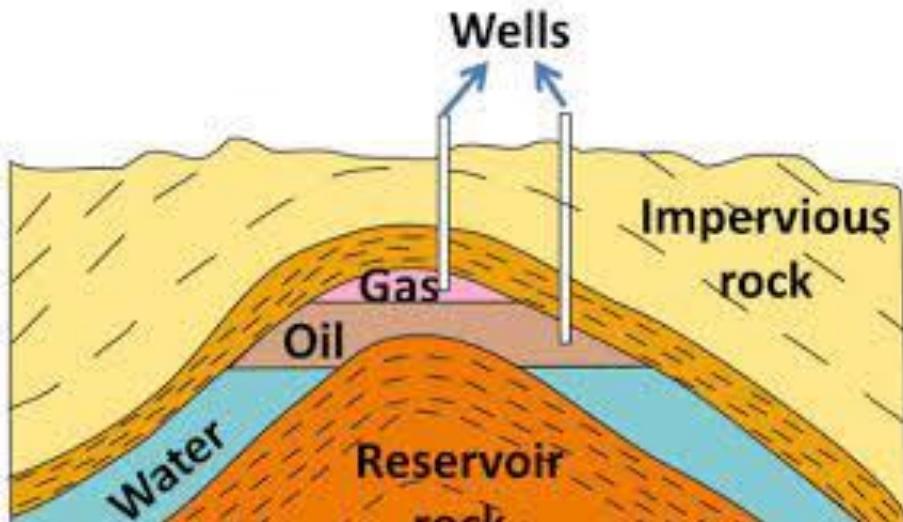
Back titration = 8.5mL of 0.25N KOH = 4.25 ml of 0.5N KOH---- $n_1v_1=n_2v_2$

**Liquid Fuels** These are naturally found under the sea surface. Liquid fuels find extensive use in domestic and industrial fields. Petroleum or crude oil is a dark greenish brown or black coloured viscous oil found deep in earth's crust. The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, O and S. The average composition of crude oil is C = 80 - 87 %, H = 11-15%, S = 0.1 - 3.5%, (N + O) = 0.1- 2.5%. Classification of petroleum Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.

- i) Paraffinic-base type crude oil: It contains saturated hydrocarbons from  $\text{CH}_4$  to  $\text{C}_{35}\text{H}_{72}$  and little amount of naphthalenes and aromatics.
- ii) Asphaltic-base type crude oil: It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.
- iii) Mixed-base type crude oil: It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.

# Mining of petroleum

- Petroleum gets formed and collected under the earth at around few hundreds to few thousand feet below the surface of the earth.
- It is accompanied by layer of natural gas under the earth. It is brought to surface by penetrating the earth's surface by way of drilling holes and inserting pipes.
- The layer of natural gas surrounding to the stock of petroleum helps to get petroleum piped out with pressure (hydrostatic pressure exerted by natural gas.).



3.7.1 : Mining of petroleum and natural gas under a dome shaped rock

# Refining of Petroleum

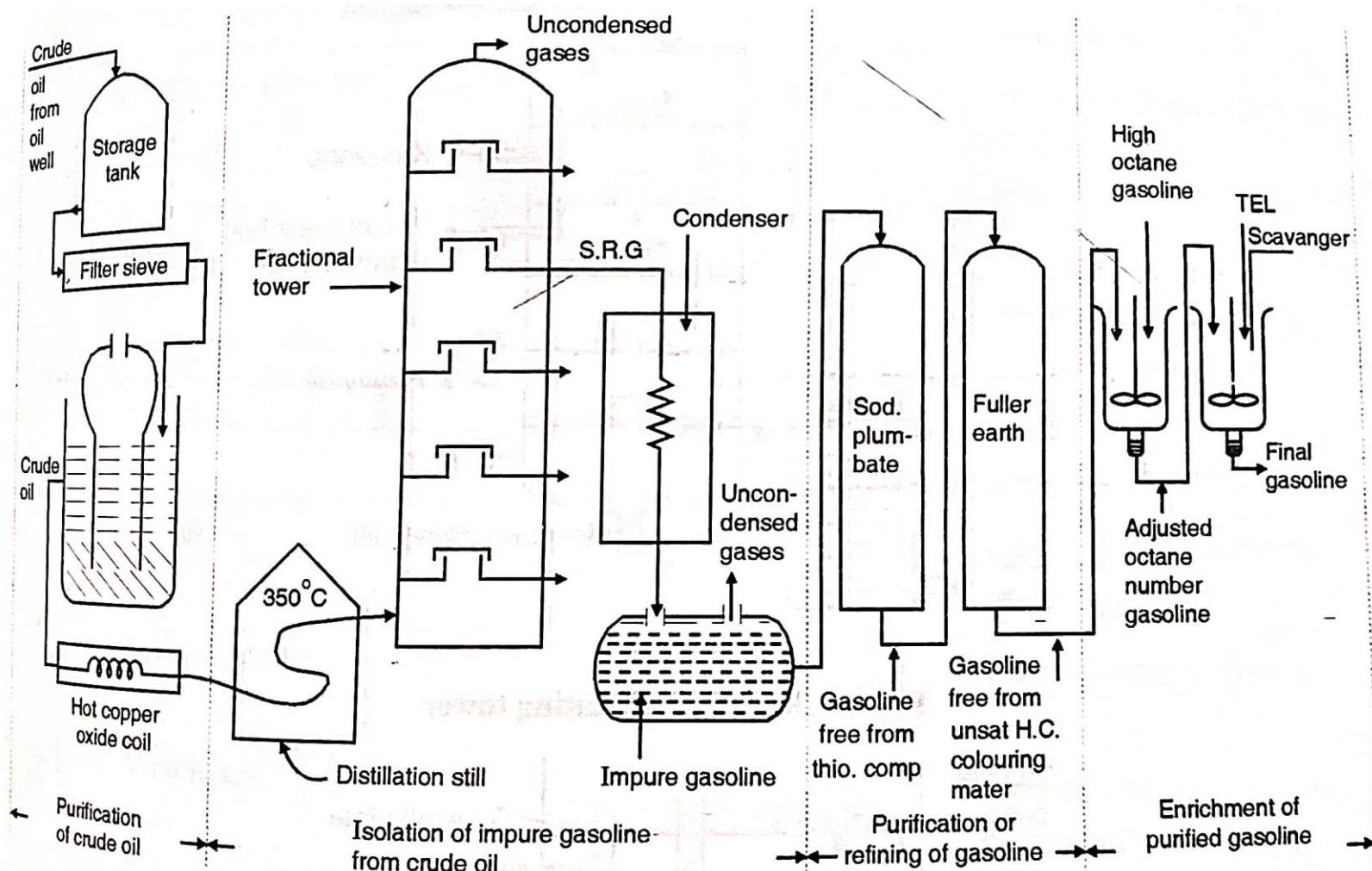
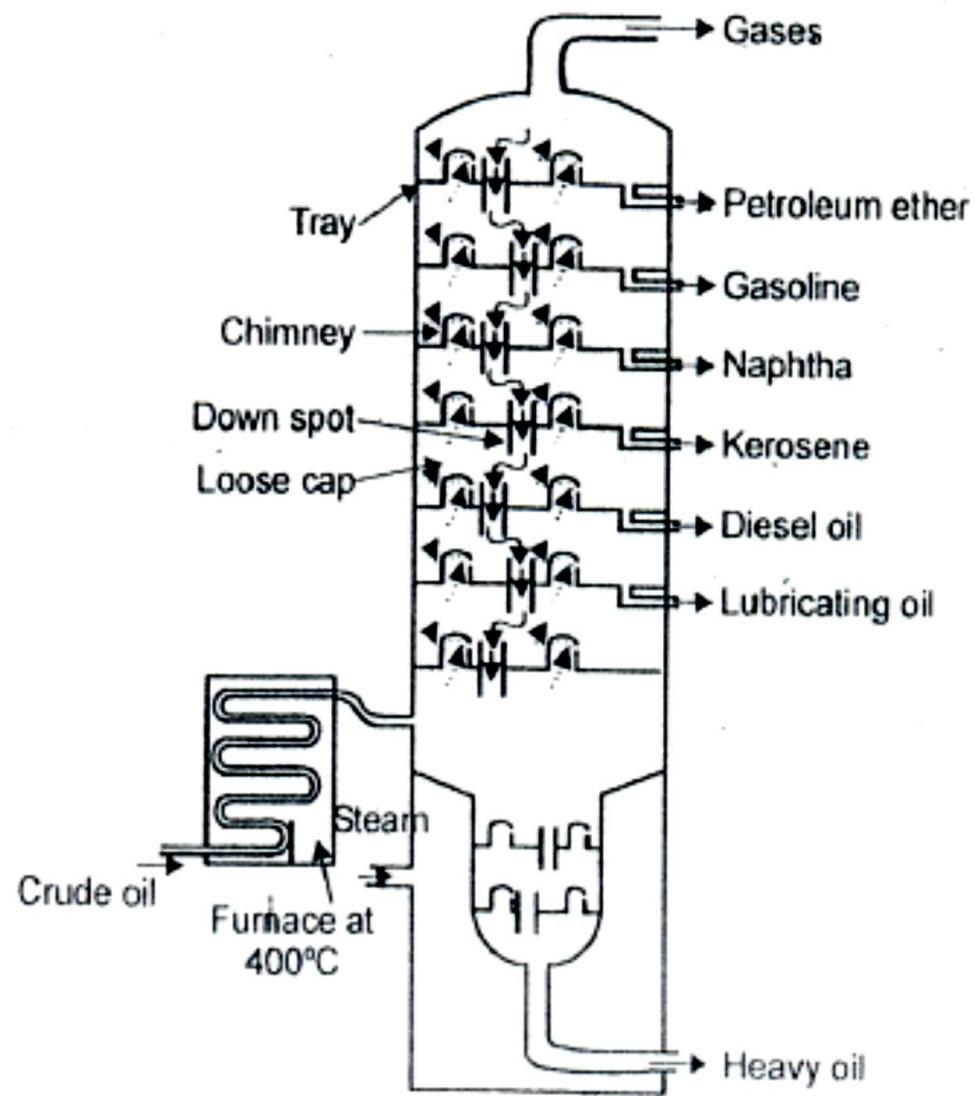


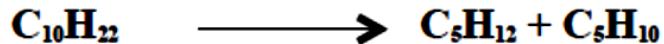
Fig. 3.7.2 : Petroleum Refining - Isolation of impure gasoline from crude oil through purification and enrichment.



Sr. No.	Fraction Name	Carbon Content	Boiling Range (°C)	Application
1	Uncondensed Natural Gas	C1-C4	< 30	Used as domestic fuel, IC engine
2	Petroleum Ether	C3-C7	30-70	Aviation Fuel and solvents
3	Gasoline or Petrol	C5-C8	40-120	Fuel in IC engine
4	Naphtha or Solvent Spirit	C9-C10	120-180	Solvent, dry cleaning
5	Kerosene	C10-C16	180-250	Illuminant, jet engine
6	Diesel	C12-C18	250-320	Fuel in Internal Combustion engine
7	Heavy Oil i) Lubricating oil ii) Petroleum jelly iii) Grease iv) Wax	C17-C30	300-400	Cracking i) Lubricant ii) Shoe polish, candle, iii) Lubricant iv) Candle, water proofing
8	Residue i) Asphalt ii) Coke	C30 and above	> 400	i) Road making ii) Fuel in molding arc light rods

## Cracking

The decomposition of bigger (high molecular weight) hydrocarbon molecules into simpler (low molecular weight), low boiling hydrocarbons is called cracking.



The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straight-run gasoline which is not good, hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process. The cracked gasoline gives better engine performance i.e., they are suitable for spark ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons,

There are two methods of cracking in use

1. Thermal cracking
2. Catalytic cracking

### **---Thermal cracking:**

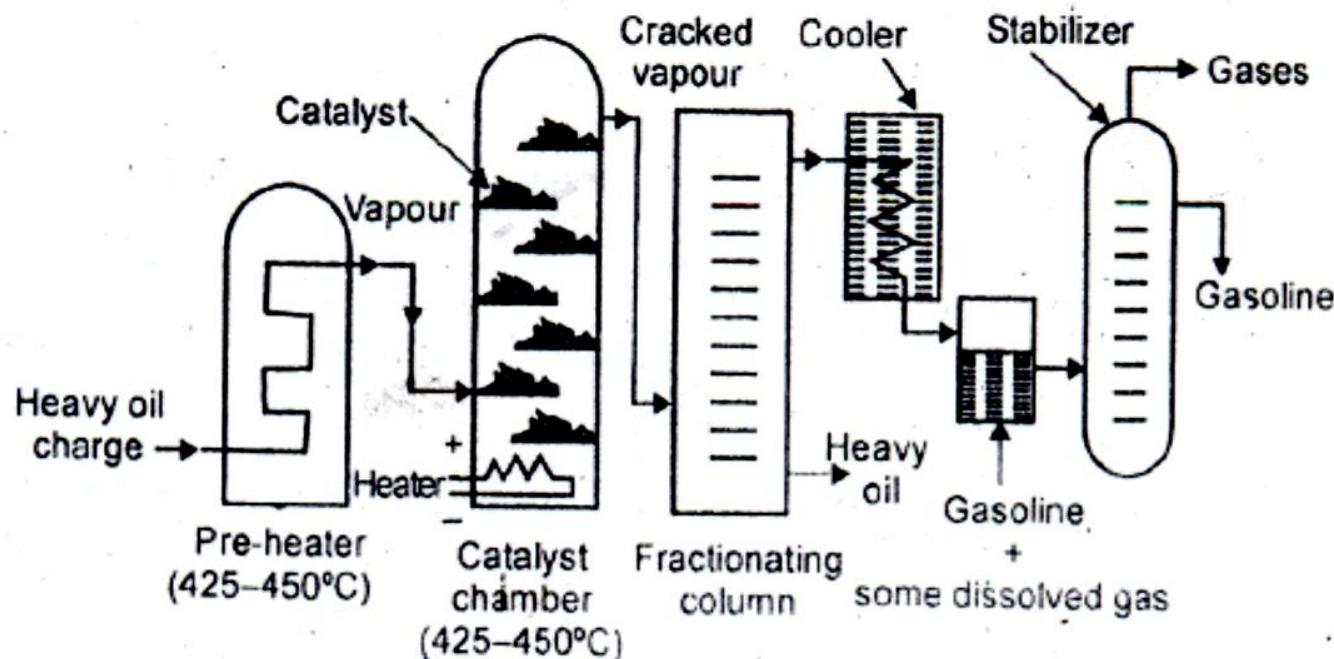
In this process, the heavy oil is subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins and hydrogen. The cracked products are then separated by fractional distillation. This process is carried out in liquid phase at a temperature of 475 – 530 °C and under pressure of 100 kg/cm<sup>2</sup> is called Liquid-phase thermal cracking. When it is carried out at temperature of 600-650 °C (heavy oil is vapourised) and under a low pressure of 10-20 kg/cm<sup>2</sup>, such process is called Vapour-phase thermal cracking.

### **---Catalytic cracking**

In this process, cracking is carried out in presence of a catalyst at lower temperature (400 °C to 500 °C) and pressures (1 to 5 kg/cm<sup>2</sup>). The catalyst like aluminium silicate or alumina [Al<sub>2</sub>O<sub>3</sub>] used in cracking gives higher yield and better quality of gasoline. There are two types of catalytic cracking in use

### i) Fixed-bed catalytic cracking

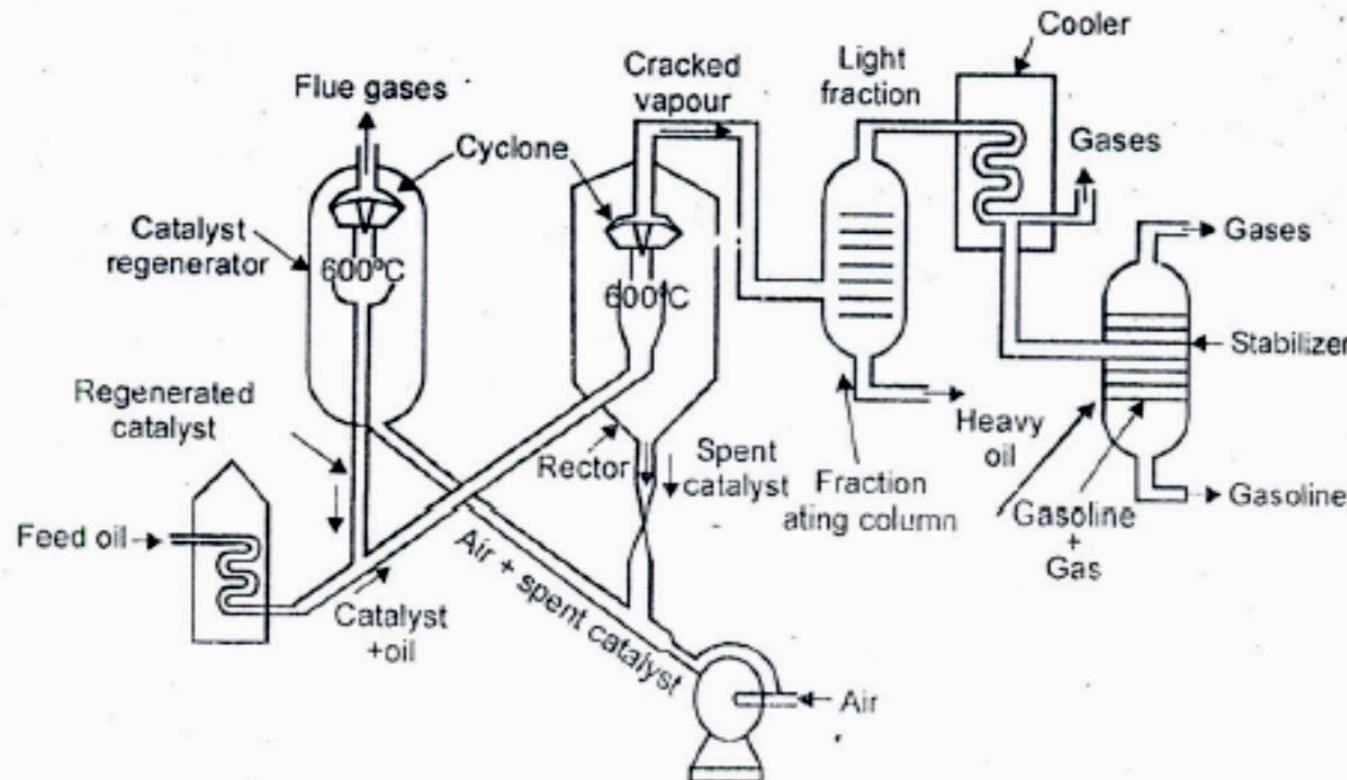
The heavy oil is passed through the heater, where the oil is vapourised and heated to (400 °C to 500 °C) and then forced through a catalytic chamber containing the catalyst beds of silica alumina gel ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) or bauxite mixed with clay and zirconium oxide maintained at 400 to 500 °C and 1.5 kg/cm<sup>2</sup> pressure. During their passage through the tower, cracking takes place about 30–40% of the charge is converted into gasoline and about 2–4% carbon is formed which gets deposited on the catalytic bed.



The vapours produced are then passed through a fractionating column, where heavy oil fractions get condensed. The vapours are then admitted into a cooler, where some of the gaseous products 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. When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber.

## ii) Fluid (Moving)-bed catalytic cracking

In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530 °C and pressure of about 3 to 5 kg/cm<sup>2</sup>. The top of the reactor, there is a centrifugal (cyclone) separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself. The carbon deposited on the catalyst powder is burnt off in the regenerator and the temperature rises to about 590 °C or more. The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline. The product contains a higher proportion of aromatics and iso-paraffins.



## **Advantages of catalytic Cracking:**

1. The yield of petrol is higher
2. The quality of petrol i.e. octane number is higher
3. Lower pressure is needed for catalytic cracking
4. The product of cracking can be easily controlled hence better knocking characteristic
5. Isomerization of branched chain product occurs hence improving the quality of fuel.
6. Catalyst is selective in cracking and therefore they permit cracking of only high boiling hydrocarbon.
7. Decomposition of aromatics removes only side chains but no ring is broken hence improving octane number.
8. Very little amount of undesirable sulphur.

# Knocking in Petrol engine



Knocking is defined as sharp metallic noise produced in internal combustion engine due to premature ignition of fuel; and result in loss of energy and wear and tear of engine.

The fuel air mixture is heated to temperature equal to ignition temperature as a result of compression. The spark plug than ignites the mixture and combustion takes place uniformly.

It is possible that portion of air mixture undergoes self-ignition due to overheating of air fuel mixture. The resulting shock wave dissipates its energy by throwing the piston which in turn hit the cylinder walls. This result in sharp noise similar to rattling of hammer is called Knocking.

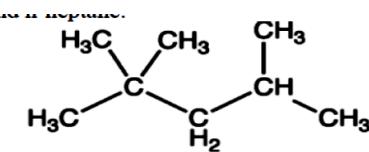
Factors on which knocking depend:

- i) Engine Design
- ii) Chemical composition of fuel
- iii) Running Condition

Since knocking in petrol engine is due to premature ignition of fuel mixture, it can be controlled

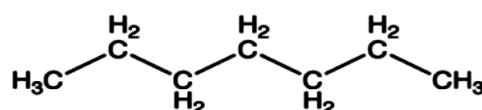
# Octane Number

- A petrol engine produces cracking noise and vibration together called as knocking, if petrol vapours entered in engine along with air burns instantly (small explosion) with the firing of spark.
- The tendency of knock depends not only upon the quality of petrol but also on the engine design and conditions of engine run, compression ratio.
- The knocking tendency of a petrol can be measured by using standard engine run under set conditions. The knocking character of a petrol is expressed as octane number.
- The knocking reduces efficiency and increases maintenance of engine.
- It is found that iso-octane liquid has very good combustion characters and it produces a very little knock.
- On contrary, n-heptane liquid detonates and produces high knocking in the engine. Therefore the octane number of iso-octane is taken as 100 and that of n-heptane is taken as zero.



**2,2,4-trimethyl Pentane (Iso Octane)**

**Octane Rating = 100**



**n- Heptane**

**Octane Rating = 0**

## Definition of Octane Number:

Octane number of a petrol engine is defined as the percentage of iso-octane in the mixture of iso-octane and n-heptane which has similar knocking to the petrol sample.

If a sample of petrol gives as much knocking as the mixture of 65% iso-octane and 35% n-heptane then the octane number of petrol is 65.

The relationship between octane number of a hydrocarbon and its structure can be given as below.

Aromatics>cycloalkanes>alkenes>branched alkenes>straight chain alkanes

## Standard requirements of petrol

1. Octane number of petrol should be at least 85 for motorcycles and cars.
2. Octane number of petrol should be well above 100 for aero plane and helicopter.

The straight run petrol obtained from refineries has octane number below 60, while the petrol after catalytic reforming has octane number above 85.

## Increasing octane number of petrol.

1. By addition of antiknocking agents like tetraethyllead.
2. By addition of alkylate fraction of petrol i.e. branched chain alkane of higher molecular weight.
3. By adjusting compression ratio suitably.
4. By addition of benzene or toluene to petrol.

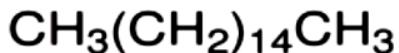
## Diesel Engine and Cetane Number

In the diesel engine, air is first drawn into cylinder and compressed to a pressure of about 500 Psi. This compression is accompanied by rise in temperature to about 500 degree. Towards the end of compression stroke, diesel is injected in the form of finely divided spray in to hot air. The fuel droplet absorb heat from air and it is ignited by spark plug and then it combust uniformly. The combustion of fuel in diesel engine is not instantaneous; the interval between the start of fuel injection and ignition is called ignition delay. It depends on the a) Engine Design b) injector design c) chemical composition of fuel

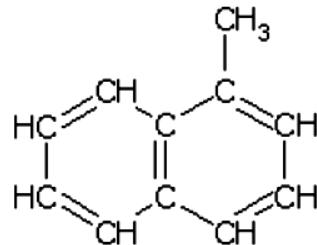
If ignition delay is long, it will lead to fuel accumulation in engine even before ignition. When ignited an explosion result as combined effect of temperature and pressure. This is responsible for knocking in diesel engine.

n-alkanes > Cycloalkanes > alkenes >branched alkanes >aromatics

Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl naphthalene, which has the same ignition lag as the fuel under test".



Cetane



-methyl naphthalene  
(cetane number 0)

Cetane Rating = 100

The cetane number of diesel oil can be increased by adding additives called dopes.

Important dopes: Ethyl nitrate, Iso-amyl nitrate.

# Antiknocking Agents

Antiknocking agents are the compounds which help to increase the octane number of the fuel by decreasing the knocking.

By the addition of these agents the gasoline/petrol can be improved in its quality.

Tetraethyl lead is normally used as anti-knocking agent.

The process of addition / mixing of any such anti-knocking agents to improve the quality of gasoline is known as doping.

TEL is prepared by reacting ethyl chloride with lead sodium alloy at a temp of 70°C.



The reaction mixture is cooled upto 40°C and is further purified.

Other anti knocking agents used are tetramethyl lead, iron carbonyl;etc.

About 0.5ml of TEL per litre is added for motor petrol and about 1mL of TEL per litre is added for aviation fuel.

Properties:

-colourless liquid with sweet odour, having specific gravity 1.62, It boils at 200°C with decomposition. It is highly poisonous.

## Mode of action of TEL

TEL get converted into cloud of fine oxide of metal i.e. either lead oxide or whichever metal present. These fine particles react with hydrocarbon in petrol forming corresponding compounds like hydrocarbon peroxides molecules. This reaction reduces/slow down the chain oxidation reaction and thus delays detonation.

## Disadvantages of TEL

1. It is extremely harmful for the engine because when leaded petrol burns PbO is formed which gets deposited on inner wall of engine cylinder.
2. Also piston of engine gets jammed.

## TEL Scavengers

To avoid this disadvantages of TEL, a small amount of ethylene dibromide is added. Ethylene dibromide reacts with Pb or PbO<sub>2</sub> at 200°C to form PbBr<sub>2</sub>.

Thus PbBr<sub>2</sub> being volatile gets removed from engine along with exhaust gases. Thus accumulation of lead in engine is avoided, but it pollutes air.

# Unleaded Petrol(ULP)

## Disadvantages of using TEL

- i) When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life.
- ii) To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases. But this creates atmospheric pollution.
- iii) aromatic phosphates can be used instead of TEL
- iv) Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

## Unleaded Petrol:

The petrol whose knocking property is reduced without addition of TEL is called unleaded petrol. The anti-knocking properties of petrol can be improved by adding MTBE (methyl tertiary butyl ether). MTBE has oxygen atom in the form of ether and supplies oxygen for the combustion and thus reducing the formation peroxy free radicals.

# Calculation of Quantity of air required for combustion of fuel.



1mole 1mole 1mole



2mole 1mole 2mole

2) STP conditions 22.4L of gas = mol wt g/mole of gas

3) Air contains 21% oxygen by volume and 23% oxygen by mass.

4) Molar mass of air = 28.94g/Mole = 28.94Kg/KMole

5) Oxygen required for combustion

= theoretical O<sub>2</sub> required – O<sub>2</sub> present in fuel

O<sub>2</sub> Quantity =  $32/12 C + 8(H-O/8) + S$

Where C, H, O, S are the masses of elements.

6) Quantity of Air = Oxygen Quantity x 100.....Kg

23

7) Volume of Air = Vol of Oxygen x 100.....m<sup>3</sup>

21

8) Volume of Air = Quantity of Air (Kg) x 22.4..... m<sup>3</sup>

Mol. mass of air (28.94 Kg)

= Quantity of Air (g) x 22.4..... L

Mol. mass of air (28.94 g)

Numerical1: Analysis of coal sample gave C =80%, H =6%, S =2.5%, Ash = 3.5%. Calculate the quantity of air and volume of air required for complete combustion of 1kg of coal.

Sol:

Given: C=80% = 0.8Kg,

$$H = 6\% = 0.06Kg$$

$$S = 2.5\% = 0.025 \text{ Kg}$$

$$0 = 8\% = 0.08 \text{Kg}$$

$$\begin{aligned}
 \text{Quantity of O}_2 &= 32/12 C + 8 (\text{H-O}/8) + S \\
 &= (32 \times 0.8)/12 + 8 [0.06 - (0.08/8)] + 0.025 \\
 &= 2.558 \text{Kg}
 \end{aligned}$$

Quantity of Air =Oxygen Quantity x 100.....Kg

23

$$= 2.558 \times 100 / 23 = 11.12 \text{ Kg}$$

Volume of Air = Quantity of Air (Kg) x 22.4..... m<sup>3</sup>

Mol. mass of air (28.94 Kg)

$$= 11.12 \times 22.4 / 28.94 = 8.6 \text{ m}^3$$

**Numerical2:** Analysis of coal sample gave C =85%, H =10%, O =5%. Calculate the quantity of air and volume of air required for complete combustion of 5kg of coal.

Soln:

Given: C=85% = 0.85Kg,

$$H = 10\% = 0.1\text{Kg}$$

$$O = 5\% = 0.05\text{Kg}$$

$$\text{Quantity of O}_2 = 32/12 C + 8(H-O/8) + S$$

$$= (32 \times 0.85)/12 + 8 [0.1 - (0.05/8)] + 0$$

$$= 3.017\text{Kg} \text{----for 1kg of coal}$$

$$\text{Quantity of Air} = \frac{\text{Oxygen Quantity} \times 100}{23} \text{.....Kg}$$

$$23$$

$$= 3.017 \times 100/23 = 13.11\text{Kg} \text{----for 1kg of coal}$$

$$\text{Volume of Air} = \frac{\text{Quantity of Air (Kg)} \times 22.4}{\text{Mol. mass of air (28.94 Kg)}} \text{ m}^3$$

$$\text{Mol. mass of air (28.94 Kg)}$$

$$= 13.11 \times 22.4/28.94 = 10.147 \text{ m}^3 \text{ -----For 1Kg of coal}$$

For 5Kg of coal

$$\text{Wt. of air} = 13.11 \times 5 = 65.55\text{Kg}$$

$$\text{Vol of air} = 10.147 \times 5 = 50.74 \text{ m}^3$$

**Numerical3:** Analysis of coal sample gave C =78%, H =8%, Ash = 2.5%%, S = 2%. Calculate the quantity of air and volume of air required for complete combustion of 5kg of coal.

**Numerical3: Analysis of coal sample gave C =78%, H =8%, Ash = 2.5%%, S = 2%. Calculate the quantity of air and volume of air required for complete combustion of 5kg of coal.**

Given:

Numerical4: Calculate volume of air containing 25% oxygen by volume at 27°C and 760mm pressure which will be required for complete combustion of 3Kg fuel containing C =75%, H =23%, Ash =2%.

Soln:

Given: C=75% = 0.75Kg,

H = 23% = 0.23Kg

Ash = 2%

$$\begin{aligned}\text{Quantity of O}_2 &= 32/12 \text{ C} + 8 (\text{H-O}/8) + \text{S} \\ &= (32 \times 0.75)/12 + 8 [0.23 - (0.0/8)] + 0 \\ &= 3.84 \text{ Kg} \text{---for 1kg of coal} \\ &= 3.84 \times 3 = 11.528 \text{ Kg for 3Kg of fuel.}\end{aligned}$$

Vol of O<sub>2</sub> at STP, 0°C = 273K and 760mm Hg pressure

32Kg of O<sub>2</sub> = 22.4m<sup>3</sup> of O<sub>2</sub>-----NA Molecules

$$\begin{aligned}11.528 \text{ Kg of O}_2 &= ? \text{ m}^3 \text{ of O}_2 = 22.4 \times 11.528/32 \\ &= 8.069 \text{ m}^3 \text{ of O}_2\end{aligned}$$

At 27°C = 300K and 760mm of Hg pressure

$$P_1V_1/T_1 = P_2V_2/T_2$$

Hence,

$$760 \times 8.069 / 273 = 760 \times V_2 / 300$$

$$V_2 = 8.867 \text{ m}^3 \text{ of O}_2$$

$$\text{Vol of Air} = \frac{\text{vol of O}_2 \times 100}{25} = \frac{8.867 \times 100}{25} = 35.468 \text{ m}^3 \text{ of air}$$

Wt. of air or Quantity of Air.

$$\text{Volume of Air} = \frac{\text{Quantity of Air (Kg)} \times 22.4}{\text{Mol. mass of air (28.94 Kg)}} \text{ m}^3$$

$$\text{Mol. mass of air (28.94 Kg)}$$

$$\text{Wt. of Air} = \frac{\text{Vol of Air} \times \text{Mol mass of Air (28.94)}}{22.4} = 45.823 \text{ Kg}$$

$$22.4$$