

UNIT-I:

Natural Sources and their Chemistry

Water Technology

Introduction

Water exists in three states: solid, liquid and gaseous. The important sources of water are (i) rain water, (ii) ground water and (iii) sea water. Rain water carries all the washed out minerals, salts and organic matter from the earth's surface and it reaches to water bodies such as ponds, lakes and rivers. Also, these impurities seep into underground and are stored as ground water. Sea water is highly alkaline due to the presence of dissolved salts.

The natural water contains numerous organisms and dissolved gases (ex: oxygen), which is essential for aquatic organisms. The pure water is one which is free from organisms. Water is required mainly for drinking and cooking, also for industry, agriculture and many other activities. Pollution of water implies that it contains a lot of inorganic and organic substances introduced by human activities, which change its quality, not suitable for any purposes and also harmful for living organisms. Any alteration in physical, chemical or biological properties of water, as well as the addition of any foreign substance makes it unfit for health and which decreases the utility of water, is known as water pollution. The major impurities present in the water bodies are described below

Impurities:

- 1) Water takes up the impurities when it comes in contact with soil or ground Water becomes impure when it comes in contact with sewage or industrial waste.
- 2) Organic impurities in water are generally introduced by decomposition of plants and animals.

Nature of impurities in water:

- 1) ***Dissolved gases:*** The water mainly contains carbon dioxide and oxygen. If water contains ammonia, hydrogen sulphides and oxides of sulphur gives bad smell and taste to water.
- 2) ***Suspended impurities:*** These are insoluble impurities, which can be removed by filtration or settling. There are two types Clay, silica, oxides of Iron are inorganic impurities. Wood and disintegrated part of dead animals are organic impurities.
- 3) ***Microscopic matter:*** These consists mainly bacteria and other microorganisms (algae and fungi). Generally responsible for water borne diseases
- 4) ***Dissolved mineral salts:*** These are the soluble impurities in water includes carbonates, bicarbonates chlorides and sulphides of calcium and magnesium. Oxides of iron lead etc.
- 5) ***Organic matter:*** It includes vegetable and animal matters i.e., decay plants and animals.
- 6) ***colloidal impurities:*** They consisting of proteins, amino acids, ferric hydroxides, clay and lumatic acid etc.,

Potable water

Water of sufficient quality to serve as drinking water or water that is safe for human consumption is called potable water.

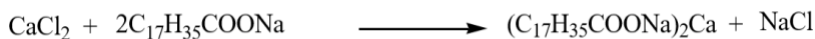
The following are characteristics of potable water

- It should be sparkling clear, soft, pleasant in taste, perfectly cool and odourless
- Its turbidity level should not exceed 10 ppm
- Its alkalinity should not be high ($\text{pH} = 8.0$)
- The total dissolved solids should not exceed 500 ppm
- It should be free from heavy metals such as lead, arsenic, cadmium, chromium and manganese salts
- It should be free from dissolved gases such as Hydrogen sulphide.
- It should be free from disease producing micro-organisms.

Water analysis

Hard water

Water which does not produce sufficient lather with soap solution readily but forms a white or grey precipitate. The soap (potassium or sodium salts of fatty acids like stearate) gets precipitated in the form of insoluble salts of calcium and magnesium which is termed as scum.

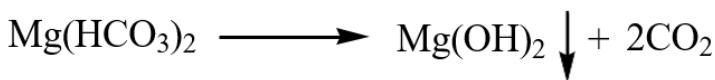


There are two types of hardness of water

Temporary hardness:

It is due to the presence of bicarbonates of calcium and magnesium. It can be removed by boiling. On boiling, bicarbonates of calcium and magnesium get precipitated as insoluble carbonates and hydroxides.

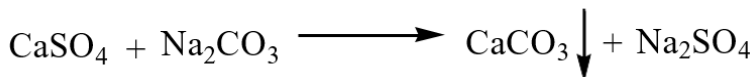
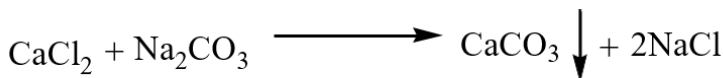
It is also called **carbonate or alkaline hardness**.



Permanent hardness.

It is due to the presence of chlorides and sulphates of calcium and magnesium. It can be removed by using chemicals.

It is also called **non-carbonate or non-alkaline hardness.**



Unit of Hardness

Ppm:

Number of parts of hardness causing substance present in 10^6 parts of water. Generally, it is mg/dm^{-3} .

Degree French

Number of parts of hardness causing substance present in 10^5 parts of water.

Degree Clarke

Number of grains of hardness causing substance present in 1 Gallon of water.

Calcium carbonate equivalence

Any sample of water contains various types of impurity in various amounts. The degree of hardness due to all these substances are unified in the forms of CaCO_3

Reasons for representing in calcium carbonate equivalence

- CaCO_3 is water insoluble
- CaCO_3 doesn't impart hardness
- Its molecular weight is 100 which make calculation easy.

Due to this reason hardness is expressed in calcium carbonate equivalence

$$\text{Equivalents of CaCO}_3 = \frac{\text{Mass of hardness causing substance} \times \text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of hardness causing substance}}$$

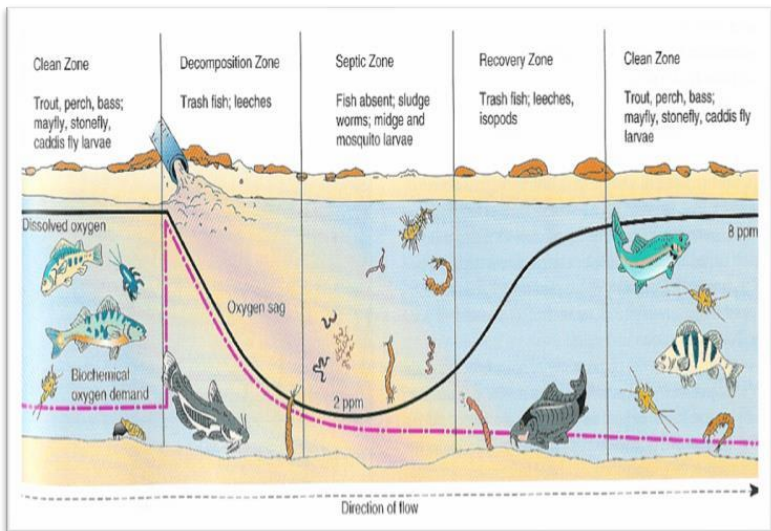
Chemical equivalence of CaCO_3 , CaCl_2 , MgCl_2 , MgSO_4 and MgCO_3 are 50, 68, 55.5, 47.5, 60 and 42.

Equivalents are as follows

$$\begin{aligned} 100\text{g of CaCO}_3 &\equiv 111\text{g of CaCl}_2 \\ &\equiv 136\text{g of CaSO}_4 \\ &\equiv 95\text{g of MgCl}_2 \\ &\equiv 120\text{g of MgSO}_4 \\ &\equiv 162\text{g of Ca(HCO}_3)_2 \\ &\equiv 146\text{g of Mg(HCO}_3)_2 \end{aligned}$$

Dissolved oxygen

Oxygen is poorly soluble in water. The solubility of water depends on the concentration of the salts and temperature. Dissolved oxygen is consumed by aquatic animals for their respiration. Aerobic bacteria consume the DO for the oxidation of biodegradable matter.



Dissolved oxygen in environment

Determination of dissolved oxygen (DO) by Winkler's method

DO in water is determined by Winkler's method. This method is based on the indirect iodometric titration. Manganese sulphate reacts with alkaline azide solution to give Manganese hydroxide. Manganese hydroxide reacts with DO to give basic manganese hydroxide and precipitates. Precipitation is dissolved by addition of conc. H_2SO_4 and nascent oxygen is liberated. Nascent oxygen oxidizes Potassium iodide to iodine. The liberated iodine is titrated against standard $\text{Na}_2\text{S}_2\text{O}_3$ using starch indicator.



Procedure:

150 cm³ of waste water is taken in a BOD bottle. To this add 2ml of MnSO₄ and 2 cm³ of alkali-azide-iodide to the reagent bottle. Obtained Basic Manganese hydroxide precipitation is dissolved using 2 cm³ of con H₂SO₄. Take a 50 cm³ of the above reaction mixture into 250 cm³ conical flask. Add 4-5 drop of starch indicator and titrate the liberated iodine against standard Sodium thiosulphate, till the colour changes from blue to colour less.

Calculation

$$(N_1V_1)_{\text{sample}} = (N_2V_2)_{\text{Sodium thiosulphate}}$$

$$N_1 = \frac{N_2V_2}{V_1 \text{ sample}}$$

$$\begin{aligned} \text{Amount of oxygen available in the sample} &= N \times \text{Gram equivalent of oxygen} \\ &= N_{\text{sample}} \times 8 \text{ g} \\ &= N_{\text{sample}} \times 8000 \text{ mg} \\ &= D_1 \text{ mg} \end{aligned}$$

Note:

- The Azide destroys the oxides of nitrogen due to this reason alkali is mixed with azide
- The oxygen carrier in Winkler's method is basic Manganic oxide Mn(OH)₂
- Starch is an adsorption indicator which is made of Amylose and Amylopectin.

Biological Oxygen Demand(BOD)

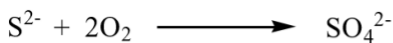
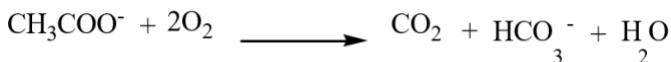
Definition: “ The amount of oxygen required in milligrams for the biological oxidation by the microorganism to bring about oxidation of biological compounds present in 1 dm³ waste water over a period of 5 days at 20 °C.”

The biodegradable impurities present in the waste water are oxidized by aerobic bacteria, using dissolved oxygen. Biodegradable matter such as carbohydrates, proteins, oils and fats utilized by aerobic bacteria's as source of energy.

Characteristics of BOD

- It is expressed in parts per million (ppm) or mg/dm³.
- Larger the concentration of decomposable organic matter, greater is the BOD and consequently more is the nuisance value.
- Strictly aerobic conditions are required.
- Determination is slow and time consuming.

Some of the possible reaction during BOD estimation



Winkler's method BOD measurement:

In this method BOD is determined by measuring the dissolved oxygen contents before and after 5 days incubation by indirect iodometric method.

Principle:

A known volume of sewage sample is diluted with known volume of dilution water (containing microorganisms). A mixed group of organism should be present. This solution is divided in to two equal parts in BOD bottle. The DO of sample (D_1) at day-1 and the DO of the sample after incubation after **5** days (D_2) were determined and then BOD is calculated.

Procedure:

Preparation of dilution water: 1 dm³ of distilled water thoroughly aerated by bubbling compressed air about a day. 1cm³ of phosphate buffer, 1cm³ of MgSO₄, 1 cm³ of CaCl₂, 1cm³ of FeCl₃ are added and mixed well and 2 cm³ of sludge is added.

Note: 25 cm³ of waste water is diluted to 1000 ml, and divided in two BOD bottles (500 ml each)

Blank titration:

DO (D_1) content of the one bottle determined immediately. Add 2 cm³ of MnSO₄ and 2 cm³ of alkaline KI to the reagent bottle containing a known volume of water. Obtained Basic manganese hydroxide Precipitation is dissolved by the addition of 2 cm³ con H₂SO₄ leading to give dark yellow color. Take a 50 cm³ of the above reaction mixture into 250 cm³ conical flask. Add 4-5 drop of starch indicator and titrate the liberated iodine against standard Sodium-thiosulphate, till the colour changes from blue to colour less.

Sample titration:

The second bottle is incubated for 5 days at 20°C, after 5 days unconsumed DO is determined as above procedure and it is found to be D_2 .

Observation and calculation

D₁ is the DO of the sample in mg/dm³ at the start of the experiment

D₂ is the DO of the sample in mg/dm³ after 5 days.

DO in Dilution water (D₁)

$$(N_1 V_1)_{\text{sample}} = (N_2 V_2)_{\text{Sodium thiosulphate}}$$

$$N_1 = \frac{N_2 V_2}{V_1 \text{ sample}}$$

Amount of oxygen available in the sample
= N X Gram equivalent of oxygen
= N **sample** X 8 g
= N **sample** X 8000 mg
= D₁ mg

DO in incubator sample (D₂)

$$(N_1 V_1)_{\text{sample incubator}} = (N_2 V_2)_{\text{Sodium thiosulphate}}$$

$$N_1 = \frac{N_2 V_2}{V_1 \text{ sample from incubator}}$$

Amount of oxygen available in the sample incubator
= N X Gram equivalent of oxygen
= N **sample incubator** X 8 g
= N **sample incubator** X 8000 mg
= D₂ mg

$$\text{BOD} = D_1 - D_2 \times \frac{\text{Volume of water after dilution}}{\text{Volume of water before dilution}}$$

Importance of BOD:

BOD is most important in sewage treatment, as it indicates the amount of decomposable organic matter in the sewage or extent of pollution or amount of dissolved oxygen. On the basis, environments design the treatment.

Larger the concentration of decomposable organic matter, greater is the BOD and consequently more is the nuisance value. Strictly aerobic conditions are required. Determination of BOD is little slow and time consuming.

Problems:

20 ml of sewage sample was diluted to 600 ml and equal volumes were filled in two BOD bottle. Do in one bottle was determined immediately and 200 ml of the solution required 4.2 ml of N/40 $\text{Na}_2\text{S}_2\text{O}_3$ solution. The second sample was incubated for 5 days and in DO determined; 200ml solution required 2.2 ml of N/40 $\text{Na}_2\text{S}_2\text{O}_3$ solution. Calculate BOD of the solution.

Volume of sample before dilution =20 ml Volume

Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for sample after 5 days = 2.2ml(V_3)

Normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution = $\text{N}/40 = 1/40 = 0.025 \text{ N}$

Volume of water sample taken =200ml.(V_2)

D₁ Determination

$$(N_1 V_1)_{\text{sample}} = (N_2 V_2)_{\text{Sodium thiosulphate}}$$

$$= \frac{0.025 \times 4.2}{200}$$

$$= 5.25 \times 10^{-4}$$

Amount of oxygen available in the sample (D_1) = $N \times$ Gram equivalent of oxygen

$$= 5.25 \times 10^{-4} \times 8 \text{ g}$$

$$= 4.2 \text{ mg}$$

D₂ Determination

$$(N_1 V_1)_{\text{sample incubator}} = (N_2 V_2)_{\text{Sodium thiosulphate}}$$

$$= \frac{0.025 \times 2.2}{200}$$

$$= 2.75 \times 10^{-4}$$

Amount of oxygen available in the incubator sample (D_2) = $N \times$ Gram equivalent of oxygen

$$= 2.75 \times 10^{-4} \times 8 \text{ g}$$

$$= 2.2 \text{ mg}$$

$$\text{BOD} = D_1 - D_2 \times \frac{\text{Volume of water after dilution}}{\text{Volume of water before dilution}}$$

$$= (4.2 - 2.2) \times \frac{600}{20}$$

$$= 600 \text{ mg/dm}^3$$

Chemical oxygen demand:

Definition: “It is the amount of oxygen in milligrams required to complete oxidation of organic and inorganic compounds present in one 1 dm^3 of waste water by using strong oxidizing agent such as $\text{K}_2\text{Cr}_2\text{O}_7$.”

Principle

A known volume of waste water sample is refluxed with excess of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in Sulphuric acid medium in the presence of Ag_2SO_4 and HgSO_4 . $\text{K}_2\text{Cr}_2\text{O}_7$ acts as oxidizing agent in acidic media which oxidizes all the oxidizable impurities present in waste water. The amount of unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ is determined by titration with known strength FAS (Ferrous ammonium sulfate). The amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed for the oxidation corresponds to COD of waste water.

In this titration Ferroin is used as indicator. This indicator is redox indicator which contains Fe^{+2} ions. This indicator is red in colour. Oxidizing agents oxidize the iron in the indicator to +3 oxidation state which is in pale blue colour.

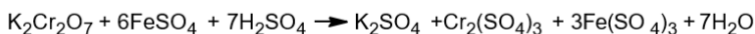
Procedure

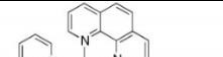
- Pipette out 25 ml of waste water into a 250 ml conical flask. To this 1g of mercuric sulphate and 1 g silver sulphate are added followed by the addition of 25ml of potassium dichromate solution of known strength.
- The above mixture is refluxed for two hours and cools the mixture. Titrated the mixture against standard FAS solution,

till the colour changes from green to brown using Ferrion as an indicator.

- Once again blank titration is carried out same procedure without waste water

Reaction involved



Indicator structure	Reaction of Indicator
 <p>1,10-Phenanthroline Iron (II) complex</p>	$[\text{Fe} (\text{C}_{12}\text{H}_8\text{N}_2)_3]^{+3} + \text{e}^- \rightleftharpoons [\text{Fe} (\text{C}_{12}\text{H}_8\text{N}_2)_3]^{+2}$ <p>Pale blue Deep Red</p>

Observation and calculation

Volume of FAS used for Blank titration is $V_1 \text{ cm}^3$

Volume of FAS used for back titration is $V_2 \text{ cm}^3$

Amount of $K_2Cr_2O_7$ reacted with impurities of FAS= $(V_1-V_2) \text{ cm}^3$

1000 cm³ of 1N FAS = Gram equivalent of oxygen

$$(V_1 - V_2) \text{ cm}^3 \text{ of 'X' N FAS} = \frac{(V_1 - V_2) \times X \times 8 \times 1000}{1000}$$

= A mg of oxygen

25 cm³ of waste water = A mg of oxygen

1000 cm³ of waste water contains _____mg of oxygen
= 'Z' mg of oxygen

COD of the waste water sample= 'Z' mg/dm³

Importance:

- 1) The COD test is widely used for measuring the pollution level of domestic and industrial wastes.
- 2) The major advantages of COD test are that the determination is completed in three hours as compared to the 5 days required for BOD determination.

Note

- Ag_2SO_4 acts as catalyst in the oxidation of long chain fatty acids and pyridine like impurities.
- The role of HgSO_4 is to avoid the Chloride ion hindrance.

Problem 1:

A 25 cm^3 of sewage sample for COD is reacted with 25 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution and the unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ requires 9.0 cm^3 of N/4 FAS solution. Under similar conditions, in blank titration 15.0 ml of FAS is used up. Calculate the COD of the sample.

Volume of FAS used for Blank titration is 15 cm^3

Volume of FAS used for back titration is 9.0 cm^3

Amount of $\text{K}_2\text{Cr}_2\text{O}_7$ reacted with impurities of FAS = $15 - 9 = 6 \text{ cm}^3$

1000 cm^3 of 1N FAS = Gram equivalent of oxygen = 8 g of oxygen

$$6 \text{ cm}^3 \text{ of } 0.25\text{N FAS} = \frac{6 \times 8 \times 0.25}{1000}$$

$$= 0.012 \text{ g of Oxygen}$$

25 cm^3 of waste water = 12 mg of Oxygen

1000 cm^3 of waste water = ?

COD of the sample = **$480 \text{ mg} / \text{dm}^{-3}$**

Sewage treatment:

Sewage is the liquid waste coming out from domestic and industrial source, etc. The domestic sewage contains heavy load of BOD, pathogens bacteria, colour, odour and bad smell etc. Sewage water is discharged into water bodies, leads to deficiency of dissolved oxygen and leads to the death of the oxygen. Pathogen bacteria are causing water borne diseases.

The sewage treatment is done to remove contaminants from waste water and suitable for discharge into environment or for reuse.

Primary treatment (Mechanical treatment)

This treatment is used to remove suspended solids, odour, colour, grease and oil.

It involves following stages

i) Screening: It is the process of removal of larger floating materials like, wood pieces, glass pieces and leaves, etc. from the raw water.

Here, raw water is allowed to pass through screens having small openings which retain the floating and suspended coarse particles.

ii) Sedimentation: It is the process of removing suspended impurities like clay and other colloidal matter.

It is carried out in sedimentation tank where raw water is allowed pass through from the bottom of the tank and slowly rises upwards. The suspended particles settled/pulled down due to gravity. This process removes only 75% of the suspended matter.

Note: In case, fine suspended particles are not settled down due to gravity are removed by adding coagulating agents such as Potash Alum, Ferrous sulphate.

iii) Removal of oil or grease: It is carried in skimming tank, where compressed air is blown through the raw water. Oil and grease from froth and float on the surface and is skimmed off.

Secondary treatment (Biological Treatment)

This treatment is used to remove biologically oxidizable matter, dissolved salts using bacteria.

It involves two important methods viz., trickling filter and activated sludge process.

Sludge

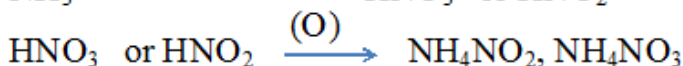
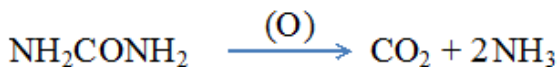
The matter which settles down at the bottom after the treatment is called sludge and the liquid is called effluent.

Activated sludge process:

This treatment involves removal of dissolved colloidal and organic matter that escapes from primary treatment process. It can be achieved by treating with microbes. It involves an aerobic oxidation of organic matter.

Waste water after primary treatment is mixed with required quantity of activated sludge (containing microorganisms and aerobic bacteria) in an aeration tank as shown in fig.

The mixture is then aerated by blowing air and agitated for several hours. Because of the aerobic conditions, the organic matter present in the sewage undergoes biological degradation and converted into compounds like nitrates, sulphates, carbon dioxide and also synthesis of new bacterial cells.



The purified water plus sludge is sent to a tank where sludge settles down. A part of the sludge is used for purification of fresh batch of sewage while the rest is pumped to sludge disposal tank. Purified water is pumped out and collected separately.

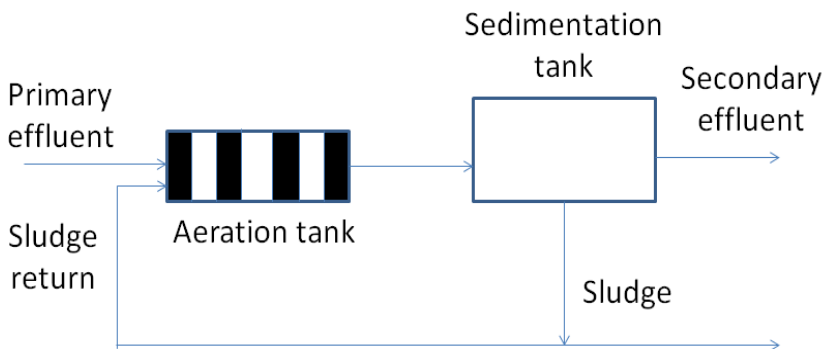
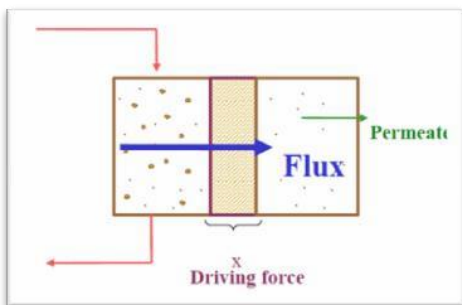


Fig: Activated sludge tank

Membrane Technology

Membrane also known as selective barrier between two phases that have thin barrier that permits selective mass transport and the phase that acts as a barrier to prevent mass movement, but allows restricted and / or regulated passage of one or more species.



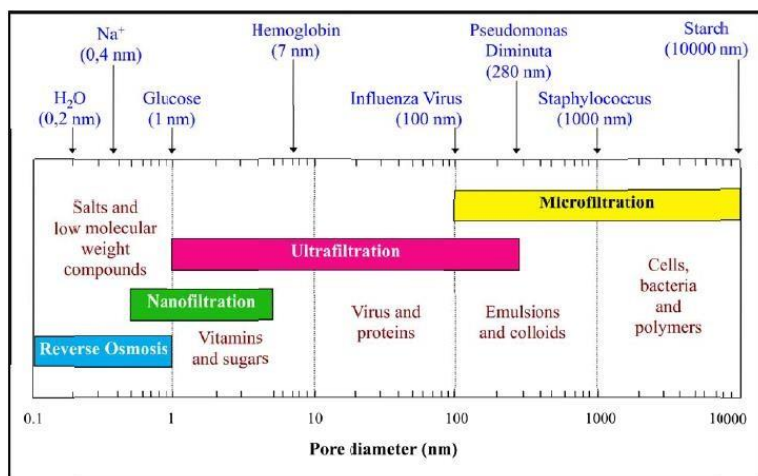
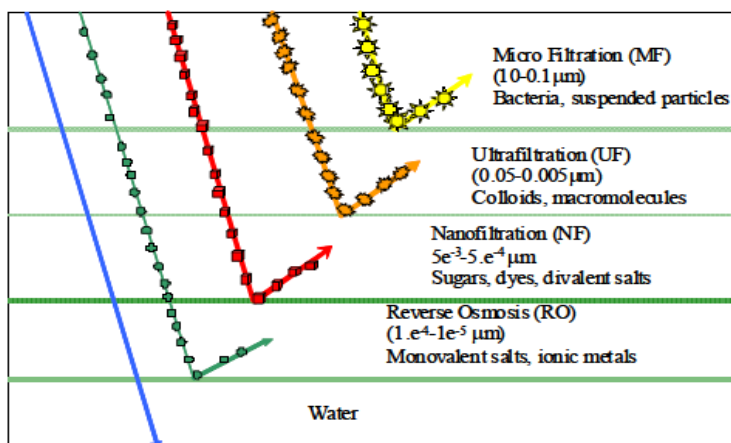
The basic membrane separation process

The membrane technology deals with the use of polymer membranes for the water purification. The basic principle involved in the membrane technology is osmosis.

Advantages of membrane technology

- **Energy savings**-The energy consumption is very low as there is no phase change.
- **Low temperature operation**-Almost all processes proceed at room temperature, thus they can deal with compounds that are not resistant at high temperatures.
- **Recovery**-Both the concentrate and permeate could be recovered to use.
- **Water reuse**-When applied to recover water, they avoid the transport of large water volumes and permit the reduction of the Chemical Oxygen Demand (COD) loading in sewage plants.
- **Compact operation**-This permits to save space. Easy scale-up. Because usually they are designed in modules, which can be easily connected.
- **Automatic operation**-The most of the membrane plants are managed by expert systems.
- **Tailored systems**-In many cases, the membranes and systems can be specifically designed according the problem.

The membrane operations more widely used are those based in applying a pressure difference between both sides of the membrane. The membrane separation process broadly classified in to micro filtration, ultra filtration, nano filtration, and reverse osmosis based on the pore size of the membrane as well as external pressure applied.



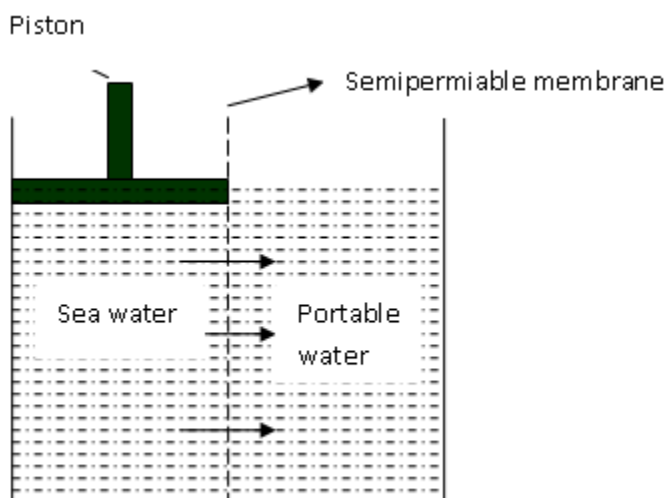
Types of membrane separation process

Reverse osmosis:

Many company of drinking water in our country used the concept of Reverse Osmosis (RO). Reverse Osmosis (RO) is a process for desalting water that uses membranes that are permeable to water but essentially impermeable to salt. Pressurized water containing dissolved salts contacts the feed side of the membrane; water depleted of salt is withdrawn as a low-pressure permeates. The ability of membranes to separate small solutes from water has been known for a very long time. In 1931 the process was patented as a method of desalting water and the term reverse osmosis was coined. This Reverse Osmosis has the smallest pores 0.0001-0.001 microns and has the highest-pressure requirement 10-100 bar.

The movement of solution molecule through semi permeable membrane from higher concentration to lower concentration or the process which reverse to the natural spontaneous osmosis is called reverse osmosis.

RO system tube contains a semi permeable membrane made up of Polymethylacrylate and polyamide. Brackish water and fresh water is separated by semi permeable membrane. When the brackish water (1000ppm) supplied with high pressure, water flow from brackish water to fresh water, Fresh water is collect from fresh water outlet and brackish water (2000ppm) is discharged in to the environment. The flow of pure water propositional to the applied pressure. The mechanism of reverse osmosis is represented below.



Representation of process of Reverse Osmosis

Advantages of reverse osmosis:

- 1) Removes nearly all contaminant ions and most dissolved non-ions,
- 2) Relatively insensitive to flow and total dissolved solids (TDS level and suitable for small systems with a high degree of seasonal fluctuation in water demand,
- 3) RO operates immediately, without any minimum break-in period,
- 4) Low effluent concentration possible,
- 5) Bacteria and particles are also removed, and
- 6) Operational simplicity and automation allow for less operator attention and make RO suitable for small system applications.

Disadvantages:

- 1) High capital and operating costs,
- 2) Managing the wastewater (brine solution) is a potential problem,
- 3) High level of pre-treatment is required in some cases,
- 4) Membranes are prone to fouling and
- 5) Discharged Brackish is harder than the previous one
- 6) Produces the most wastewater at between 25-50 percent of the feed.
- 7) Colloidal silica is not removed by this process.

Poly-sulfone and polyurethane based membranes in membrane technology

There are many polymers are used in membrane technology for the purification of water. Amongst all Polysulfone and polyurethane membranes are commercially important because of their unique structure which is essential for the salt rejection. Also, their structure can be modified according to the requirement.

In fabrication of the membranes for water purification following important parameters are considered.

- Membrane materials. Organic polymers, inorganic materials (oxides, ceramics, metals), mixed matrix or composite materials.
- Membrane cross-section. Isotropic (symmetric), integrally anisotropic (asymmetric), bi- or multilayer, thin-layer or mixed matrix composite.
- Preparation method. Phase separation (phase inversion) of polymers,
- Sol-gel process, interface reaction, stretching, extrusion, track- etching, micro-fabrication.
- Membrane shape. Flat-sheet, hollow fiber, hollow capsule.

There are different methods of preparation of membranes are available in the literature they are as follows

- Precipitation in a non-solvent (typically water) non solvent induced, NIPS
- Solvent evaporation induced, EIPS;

Precipitation by absorption of non-solvent (water) from the

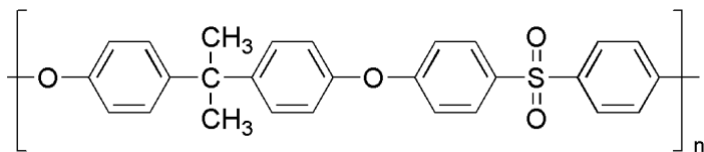
- Vapor phase vapour induced, VIPS;
- Precipitation by cooling-thermally induced, TIPS.

Generally, the membrane prepared using NIPS methods are used in high pressure RO purification techniques.

Polysulfone

Polysulfone is a polymer which contains both hydrophilic and hydrophobic functionalities. Where, sulfone group behaves as hydrophilic and two methyl side group along with aromatic rings acts as hydro phobic functionalities. If Polysulfone is used as membrane for water purification then these methyl groups actsas brushes and avoids the deposition of salts and hence fouling of membrane.

Structure of Polysulfone as follows.



Chemical Fuels

Fuel: A fuel is the substance which on combustion produces a large amount of heat.



As most of the fuels contain carbon or carbon and hydrogen, the combustion involves the oxidation of carbon to carbon dioxide and hydrogen to water. Sulphur, if present, is oxidized to sulphur dioxide while the mineral matter forms the ash.

Fuels like coal, crude oil, natural gas known as fossil fuels found under earth crust.

Chemical fuels: The fossil fuels, wood, vegetable oils etc. which produce heat on burning are known as chemical fuels.

Classification of chemical fuels:

Chemical fuels are classified as primary and secondary fuels.

Fuels, which occur in nature, are called **primary fuels**. Fuels, which are derived from primary fuels, are called **secondary fuels**.

Chemical fuels are further classified as solids, liquids and gases. A complete classification of fuels with examples is shown in the following Table.

Physical state	Primary fuels	Secondary fuels
Solid	Wood, coal	Charcoal, coke
Liquid	Petroleum	Petrol, diesel, kerosene
Gas	Natural Gas	LPG

Importance of hydrocarbons as fuels:

Fossil fuels contain mainly hydrocarbons. These hydrocarbons are important sources of energy in daily life. Hydrocarbons are used as energy sources in cooking, lighting, automobiles, production of electricity in thermal power plants etc. These hydrocarbon fuels meet 80% of the world's energy demand. Thus hydrocarbons are important sources of energy**Characteristics of a Good/ideal fuel:**

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

1. It should possess high calorific value.
2. It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.
3. It should not produce poisonous products during combustion. In other words, it should not cause pollution o combustion.
4. It should have moderate rate of combustion.
5. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
6. It should not leave behind much ash on combustion.
7. It should be easily available in plenty.
8. It should have low moisture content.
9. It should be cheap.
10. It should be easy to handle and transport.

Calorific value

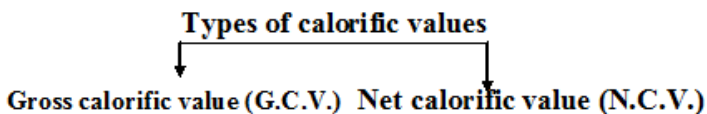
It is an important parameter of fuels is calorific value. It gives useful information about its heating efficiency. The performance of a fuel is expressed in terms of its calorific value. Calorific fuel is defined as the amount of heat released when unit quantity (mass or volume) of a fuel is burnt completely in air oxygen

S. I. unit of calorific value:

For solids, calorific value is expressed in J kg^{-1} (Joules per kg). For gaseous fuels it is expressed in J m^{-3} (Joules / m^3).

Definition of net calorific value:

It is defined as the amount of heat released when unit quantity of a fuel is completely burnt in air or oxygen and the products of combustion are let off into the atmosphere.



Gross Calorific Value (G.C.V.)

It is defined as “the amount of heat obtained on complete combustion of unit mass of a solid or liquid fuel or unit volume of a gaseous fuel (STP) and on cooling the products of combustion are cooled to room temperature (298K)”.

The gross calorific value is also called as **higher calorific value**.

Usually, fuel contains some hydrogen. The hydrogen atoms are bonded to carbon atoms in the fuel. When the fuel is burnt, hydrogen forms water vapors. The water vapors if cooled, we get certain

amount of heat, as the water has high latent heat of 2450 joules/gm or 587 cal/gm.

Thus during the study of calorific value of a fuel, we get some heat directly by combustion of fuel and in addition we get certain amount of heat by cooling the products of combustion cool to room temperature.

The G.C.V. is of only theoretical importance because in actual practice, we do not have any provision of cooling the products of combustion during combustion of a fuel in an engine, furnace or any other fuel burning device and the product gases leaves with some heat.

Net Calorific Value (N.C.V.)

It is defined as the amount of heat liberated when a unit quantity (unit volume in the case of gaseous fuel) of fuel is completely burnt in air or oxygen and the products of the combustion are allowed to escape.

N.C.V. is also called as **lower calorific value**.

A fuel containing hydrogen produces water, on combustion. Out of the total heat produced in combustion of the fuel, the water takes away a considerable portion of the heat for evaporation and actually less heat is available for heating.

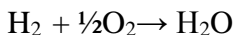
There is no any furnace, engine or device designed to collect the heat being taken away by the water vapors. Therefore practically we get lower calorific value than the theoretically expected.

$$\text{Gross Calorific Value} = \text{Net calorific value} + \text{Heat associated with steam}$$

$$= \text{Net calorific value} + \text{GCV} - 0.09 \times \text{H} \times 587$$

Calculation of Heat associated with steam

Let the percentage of hydrogen
in the fuel be 'H'



Since 2kg of hydrogen produces 18 kg of steam,

H kg of Hydrogen will produce $\frac{18}{2} \times H$ kg of steam, i.e.,

100kg of fuel which contains H kg of Hydrogen will produce
9H kg of steam.

1 kg fuel produces $= \frac{9H}{100} = 0.09H$ kg of steam

Latent heat of steam $= 587 \times 4.187 \text{ J/Kg}$

Heat liberated by condensation of 0.09x kg of steam

$= 0.09H \times 587 \times 4.187 \text{ KJ NCV} = \text{GCV} - \text{Heat associated with steam}$

$$\text{NCV} = [\text{GCV} - 0.09H \times 587 \times 4.187] \text{ KJ/Kg}$$

Note: **The unit of latent heat of water and unit of G.C.V.,
N.C.V. should be same.**

Knocking of IC engine:

Knocking in petrol engines:

In petrol engines, the mixture of petrol and air is drawn in to the cylinder. The fuel- air mixture is compressed by the piston and is ignited by an electric spark. As the flame front travels in the combustion chamber, rapidly expanding combustion products compress the remaining unburnt fuel and raise its temperature. If the flame front travels rapidly at an optimum speed, the combustion of unburnt fuel takes place smoothly. On the other hand, if the

flame front travels too slowly, the entire last portion of fuel mixture may get heated up beyond its ignition temperature and undergo instantaneous explosive combustion. This results in emission of a characteristic rattling sound called “knocking”.

Knocking is the rattling noise or metallic sound produced in an internal combustion engine due to uneven combustion (detonation) of fuel and air mixture.

The reasons for Knocking are

(1) Very high compression ratio causes preignition.

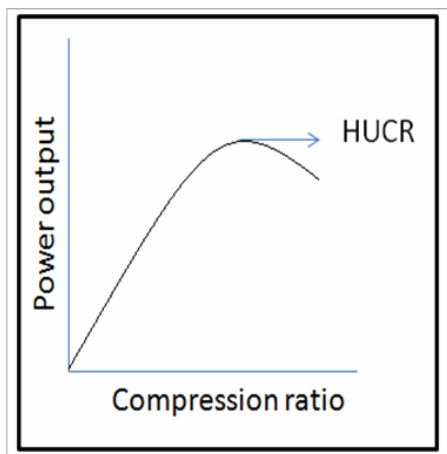
Compression ratio is the ratio of the volume of the fuel and air mixture (V_1) at the end of suction stroke to the volume of the mixture (V_2) at the end of compression stroke.

$$\text{Compression ratio (CR)} = V_1/V_2$$

The value (CR) will always be greater one. Power output of IC engine increases continuously with increase in compression ratio.

The compression ratio corresponding to maximum power output is known as highest useful compression ratio (HUCR).

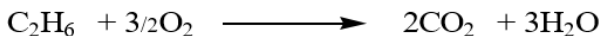
Very high compression ratio means that the fuel and air are compressed to a maximum extent, leads to increase in the temperature of the cylinder. Hot spots are formed inside. When the fuel and air mixture are compressed hot spots ignites the fuel even before spark plug produces spark. This phenomenon is called preignition which leads to knocking.



(2) Peroxide formation leads to self Ignition

A. **Under normal conditions** there is a slow oxidation of the fuel.

Normal combustion takes place due to the chain reaction. The overall reaction may be represented as



B. **Under knocking conditions**, the rate of combustion is very high. It involves following steps.

1. Oxygen combines with hydrocarbon molecule forming peroxides.



Ethane

Ethane peroxide

2. The peroxides decompose readily to give a number of gaseous products. For example,



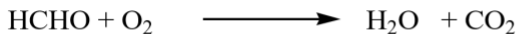
Ethane peroxide

Acetaldehyde



Acetaldehyde

Formaldehyde



Formaldehyde

Fast reaction leads to rapid increase of pressure. This results in knocking.

(3) Chemical structure of the fuel:

Knocking tendency decreases with the increase in compactness of the molecule and increases with the increase in the length of hydrocarbon chain.

Ex., i) 2, 2-dimethyl pentane knocks lesser than 2-methyl hexane

ii) n-butane knocks lesser than n-hexane.

The tendency to knock has been found to decrease in the order

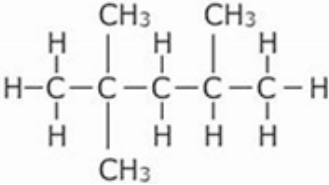
n-alkane > mono substituted alkanes > cycloalkane > alkenes > Polysubstituted alkanes > aromatic compounds.

Octane Number:

Graham Edger proposed an arbitrary scale for expressing the knocking characteristics of gasoline in combustion engine as octane number in 1972 on the basis of antiknock properties.

It has been found that n-heptane, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$, knocks very badly and hence, its antiknock value has been arbitrarily given **zero**. On the other hand, isooctane (2, 2, 4 –trimethylpentane) gives very little knocking, so its antiknock value is given as **100**.

Thus, Octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under test in knocking characteristics.

Reference fuels	Chemical structure	Octane
Isooctane (2,2,4 –trimethylpentane)		100
n-heptane	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	0

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

Anti-knocking Agents

The octane rating of gasoline samples can be increased by the addition of certain organometallic compounds called anti-knocking agents and the process is called “doping”.

- 1) An extensively used anti-knocking agent is tetraethyl lead $\text{Pb}(\text{C}_2\text{H}_5)_4$ 0.5ml/litre. (but it causes air pollution by Pb.)
- 2) Addition of alkylate fraction to petrol i.e. branched chain alkane of higher mol. wt.
- 3) Addition of benzene, toluene, xylene (BTX) to petrol.
- 4) Addition of methyl t-butyl ether (MTBE) or ethyl t-butyl ether.
- 5) Adjusting suitable compression ratio

Quality of petrol can be improved by adding:

1. Antioxidant to improve oxidation resistance.

2. Octane no. improvers like MTBE.
3. Freezing point depressant like ethanol, glycol to minimize ice formation in fuel line in cold regions.
4. Detergents like fatty amines to clean fuel line and carburetor.

Knocking in diesel engines

It works on the principle of compression ignition. Air is drawn into the cylinder and compressed to a pressure of about $3.5 \times 10^{-3} \text{ kg m}^{-2}$. During compression cylinder gets heated around 350°C . Then diesel is introduced in the form of spray which is spontaneously get ignited and burns producing pressure on the piston. It takes some time for the fuel to get ignited. The time interval between the fuel injection and ignition is called **ignition delay**. It will be milliseconds.

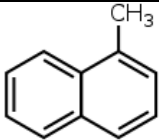
The **shorter ignition delay** leads to burning of the fuel at the rate which it is injected. Whereas **longer ignition** delay results in accumulation of the fuel in the engine and this causes an explosive combustion when ignited. As a result the **diesel engine knocks**.

Cetane Number of Diesel

Cetane number is a measurement of the combustion quality of diesel fuel during compression ignition. It is a significant expression of the quality of a diesel fuel. Cetane number is a measure of a fuel's ignition delay, the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels.

The suitability of a diesel fuel is determined by its cetane value which is the percentage of n-hexadecane in a mixture of n-

hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel sample.

Reference fuels	Chemical structure	Cetane number
α -methyl naphthelene		100
Cetane(hexadecane)	$\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-CH}_3$	0

Relative order of cetane no. values

n -alkanes > cycloalkanes > alkenes > branched alkanes > Aromatics

How to increase cetane no.

Alkyl nitrates (principally 2-ethylhexyl nitrate) and di-*tert*-butyl peroxide are used as additives to raise the cetane no.

- Antioxidant to improve oxidation resistance during storage.
- Lubricity additives for lubrication of fuel injection system.
- Detergents to clean fuel line and carburetor.

Power Alcohol

When ethyl alcohol is used as fuel in internal combustion engine, it is called as power alcohol. It contains 25% of alcohol and 75% petrol.

Advantages of Power Alcohol:

- (i) Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about 65. Therefore addition of ethyl alcohol to petrol increases its octane number.
- (ii) Alcohol has property of absorbing any traces of water if present in petrol.
- (iii) If a specially designed engine with higher compression ratio is used, then the disadvantage of lower C.V. of ethyl alcohol can be overcome.
- (iv) Ethyl alcohol contains 'O' atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are reduced largely.
- (v) Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign currency considerably.
- (vi) Power alcohol is cheaper than petrol.

Disadvantages of Power Alcohol:

(i) Ethyl alcohol has C.V. 7000 cal/gm much lower than C.V. of petrol 11500 cal/gm. Use of power alcohol reduces power output upto 35%.

(ii) Ethyl alcohol has high surface tension and its atomisation, especially at lower temperatures, is difficult causing starting trouble.

(iii) Ethyl alcohol may undergo oxidation to form acetic acid, which corrodes engine parts.

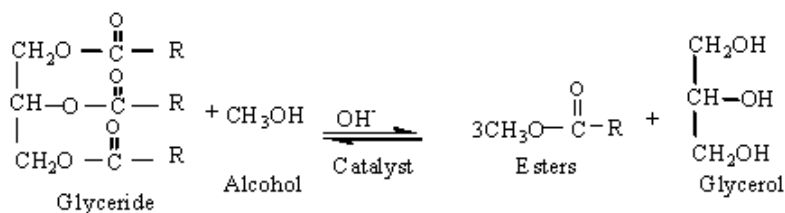
(iv) Ethyl alcohol obtained by fermentation process directly cannot be mixed with petrol but it has to be dehydrated first.

(v) As ethyl alcohol contains 'O' atoms, the amount of air required for complete combustion of power alcohol is lesser and therefore carburettor and engine needs to be adjusted or modified, when only ethyl alcohol is used as fuel.

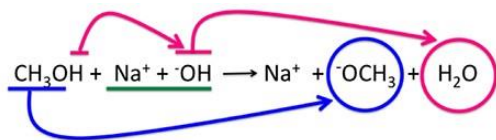
Biodiesel

Chemically biodiesel is the mixture of methyl esters of long chain carboxylic acids. It is eco-friendly fuel obtained from renewable sources like vegetable oils and animal fats. Common vegetable (edible and Non-edible) oils used are Soyabean oil, palm oil, peanut oil, cotton seed oil, corn oil, pongamial oil, Jatropha oil etc. Vegetable oils are the triglycerides, which have high viscosity, flash point and low heating value. Hence they cannot be used as such in diesel engine. Triglycerides are need to be converted into biodiesel by a process is called **Transesterification**.

During the transesterification, the triglyceride is treated with methanol or ethanol in the presence of a base like KOH/NaOH, forms methyl or ethyl esters of fatty acids (biodiesel) **Conditions:** Temperature: 55-60 C, Catalyst-KOH/NaOH, Reaction time-1-8 hrs.



Separation:



As above two products are immiscible phases, we can easily drain off the glycerine/glycerol by washing with water and biodiesel can be collected.

Extra information:

Compounds present in biodiesel are like,

Methyl palmitate $\text{H}_3\text{C} - (\text{CH}_2)_{14} - \text{COOCH}_3$

Methyl stearate $\text{H}_3\text{C} - (\text{CH}_2)_{16} - \text{COOCH}_3$

Methyl oleate $\text{H}_3\text{C} - (\text{CH}_2)_7 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOCH}_3$

Methyl linoleate $\text{H}_3\text{C} - (\text{CH}_2)_5 - (\text{CH} = \text{CH})_2 - (\text{CH}_2)_7 - \text{COOCH}_3$

Advantages of Biodiesel:

- (i) Biodiesel is cheaper, as it is manufactured from cheap, non-edible or waste oil or animal fats.
- (ii) It has high cetane numbers 46 to 54 and high C.V of about 40 kJ/gm.
- (iii) It is regenerative and environment friendly.
- (iv) It does not give out particulate and CO pollutants, as Oxygen atoms in biodiesel help for complete combustion.
- (v) It has certain extent of lubricity, due to higher oiliness of the esters.

- (vi) Its use provides good market to vegetable oils and reduces our dependence on diesel on foreign countries, saving currency.
- (vii) It is clean to use biodiesel in diesel engines.

Limitations of Biodiesel:

- (i) Cloud and pour points of biodiesel are higher than diesel and can cause problem in fuel flow line. So it cannot be used in cold regions.
- (ii) Biodiesel may have dissolving action rubber hoses, gaskets.
- (iii) There is shortage of vegetable oils and the starting material if costly, the biodiesel will be costly.
- (iv) Biodiesel strongly adheres on metals and can become gummy.

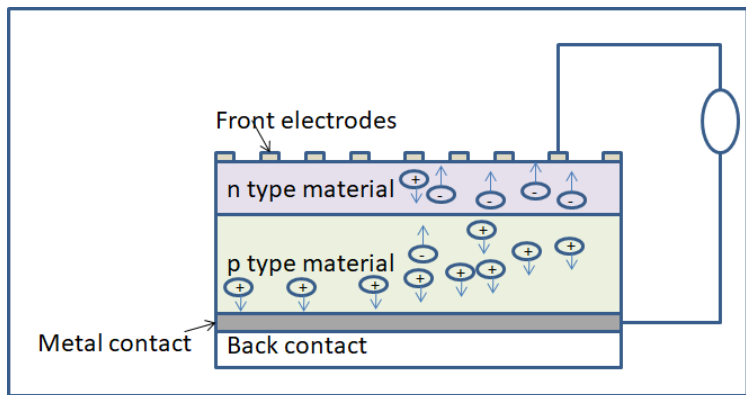
Solar Energy

Introduction

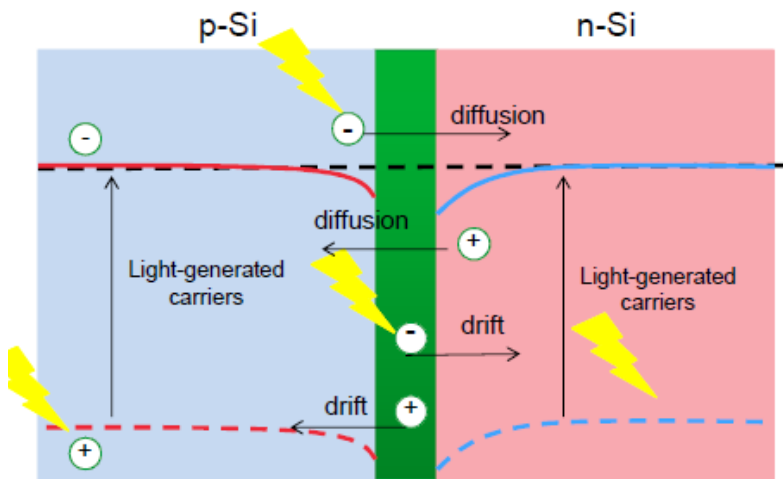
Solar energy is a renewable energy and it inexhaustible. The earth is receiving approximately 1.8×10^{11} MW of energy which is thousands times larger than the requirement of energy for present consumption. Thus solar energy is the only energy that fulfils all our present and future energy needs if we utilize properly. Solar energy can be directly converted in to heat energy or electricity. The device which coverts sunlight directly in to electricity through photovoltaic effect is called as solar cell. The solar cells are broadly classified as i) Inorganic solar cells, ii) Organic/polymer solar cells iii) Dye sensitized solar cells (DSSC). Amongst them inorganic solar cells are currently in global market. The amorphous silicon solar cells are classified under inorganic solar cells.

Construction of amorphous silicon solar cells

A typical silicon solar cell consists of n-type material (Phosphorus doped silicon) and a p-type (Boron doped silicon) material made of silicon. In the fabrication of device these n-type and p-type materials are joined to form a p-n junction. On top of n type connecting front electrodes are placed. The metal back contact is attached to p-type layer. An antireflective coating is filled in between the front electrodes to avoid the reflection of sunlight. Finally p-type and n-type layers are joined externally to the circuit. The complete solar cells are sealed to avoid the environmental contact.



Typical representation of solar cells



Diffusion of electron hole pair in silicon solar cells

Working:

When sunlight is incident on solar cells photon strikes on p-n junction. Then electron hole pair will be created at the junction by the absorption of photon. This electron hole pair diffuses towards respective layer based on affinity. The electrons diffuse towards n-type later and holes are diffused towards p-type layer. These layers are connected externally through a circuit, hence current will be generated.

Advantages of Solar Cells

- Solar cell is renewable energy which can be continuously drawn from the sun.
- It is economic friendly energy because once it installed there will be minimum maintenance charges for small usage.
- Solar energy is environment friendly and green energy because it doesn't produce any greenhouse gasses and no pollutants.
- It doesn't involve any combustion reaction or radioactive residue hence no pollution

Disadvantages of Solar Cells

- Space utilization: Solar cells required large area for installation
- It requires high investment cost for a big power plant
- During the rainy season power production is less hence grid maintenance will be difficult.
- Solar energy is produced only in the day time hence storage will be a big challenge

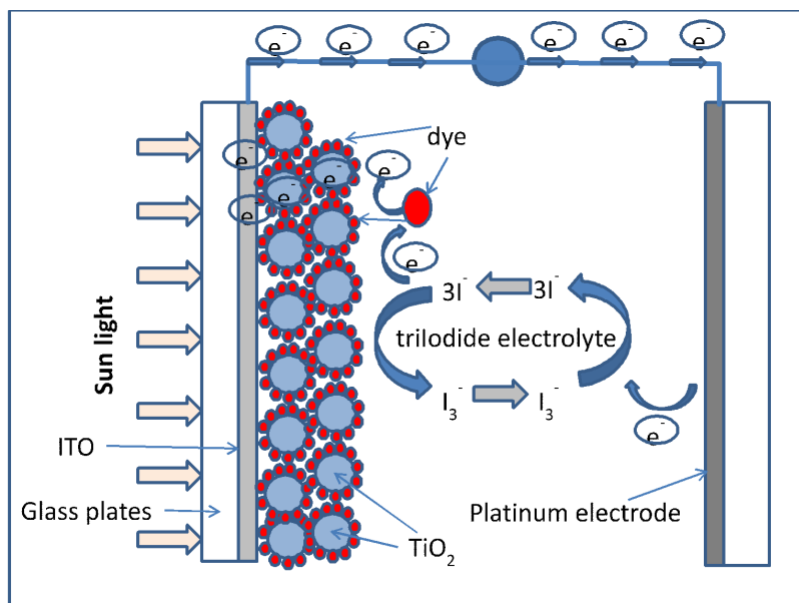
Dye sensitized solar cells

Photovoltaic effect is a process in which conversion of sunlight directly into electrical energy. The process of light dependent voltage between two electrodes in an electrode system was first discovered by Henry Becquerel in the year of 1839. In 1954 first silicon solar cell was discovered the initial efficiency was found to be 6%. The discovery of DSSC was started in 60^s by German scientists Gerischer and Tributsch. Later Michel Grätzel a Swiss scientist introduced porous electrode consists of Nano TiO_2 for construction of DSSC, which helped to increase the efficiency of solar cells up to 7%. This

discovery of DSSC is a pioneer in the field of photovoltaics, thereafter vast research is going on in the field.

Device fabrication

It consists of two electrodes cathode and anode generally cathode is made of graphite or platinum. Anode is made of transparent conducting oxide such as Indium tin oxide. Anode is coated with a layer of nano porous materials (TiO_2 or ZnO). Further these nano porous materials are coated with light absorbing organic/inorganic dye molecules. Here the nano porous materials acts as photo-sensitizer also it provides road way for electrons. A triiodide electrolyte system is employed in between the electrodes, which helps in electron transfer process.



Dye sensitised solar cells mechanism of working.

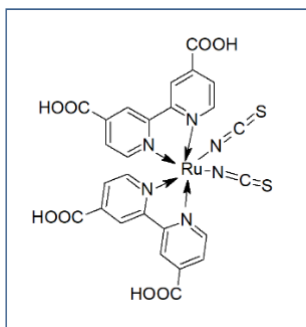
Mechanism of working

When light photon strikes the solar cell it passes through ITO layer and it reaches the dye molecule. Once the photon hits the dye molecule, dye undergoes excitation with the liberation of electron, which travels through the network TiO_2 nanoparticles and finally it reaches to cathode. The cell is completely filled with Triiodide electrolyte. The electron from the cathode directly reduces the triiodide molecule to three iodide molecules. Further this iodide molecule reaches the dye molecule oxidizes to form triiodide again with the liberation of electrons, which can be easily absorbed by dye molecules. And similar cycle continues whenever sunlight falls on the solar cells.

Note:

In DSSC TiO_2 nano particles are used as conducting media for electrons, because they have an unique property of welding together and to form a good network for the electron to travel through

Selection of dye molecule is an important criteria, because dye with different color can absorb different wavelength of light hence they produce different amount of energy.



N_3 ruthenium dye used in DSSC