

D. INDUSTRIAL CHEMISTRY

CHAPTER-10

WATER TREATMENT

●Introduction:

Water is Nature's most wonderful, Abundant and useful compound. For the Existence of the human Beings, animals and plants water is rated to be of the greatest importance without food, human can survive for a number of days, but water is such an essential that without It one can't survive. Water is not only essential for the lives of animals and plants but also occupies a unique position in industries, probably, its most important age as an engineering material is the steam generation.

●Types of water:

Surface Water: Surface water is water in river, lake , Pond etc. Surface water is naturally replenished by rainfall and naturally lost through discharge by evaporation and evapotranspiration.

Ground Water: It refers to the water presents under the beneath of the earth surface.

RainWater: The purest form of water.

Sea Water:

●Impurities in water:

Dissolved Impurities:

(a) Dissolved gases: O_2 , CO_2 , H_2S etc.

(b) Inorganic salts:

(i) Cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , Al^{3+} etc.

(ii) Anions: CO_3^{2-} , Cl^- , SO_4^{2-} , NO_3^- etc.

(c) Organic matter: Pesticides, detergents

Suspended Impurities:

(a) Inorganic: Clay and sand.

(b) Organic: Domestic waste: general biological rubbish and decay products, soap, detergents, Industrial discharges from e.g. food processing and intensive agriculture, papermaking, organic chemical industry. Includes fats, oils and solvents, Residues of pesticides, herbicides etc

Microscopic Matters: Bacteria, algae, fungi, virus, protozoa etc.

●Hardness:

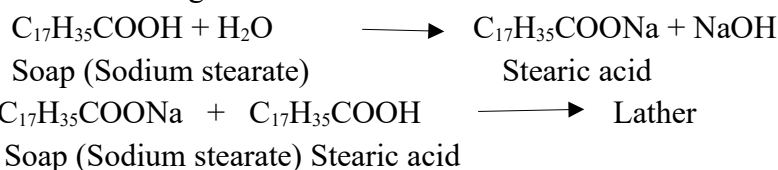
"Hardness in water is that characteristics, which prevents the lathering of soap". In other way we may define it as "soap consuming capacity of water".

Cause of Hardness:

Hardness is due to presence of certain salts of Ca^{2+} , Mg^{2+} and other heavy metal ions like Al^{3+} , Fe^{3+} and Mn^{2+} in water.

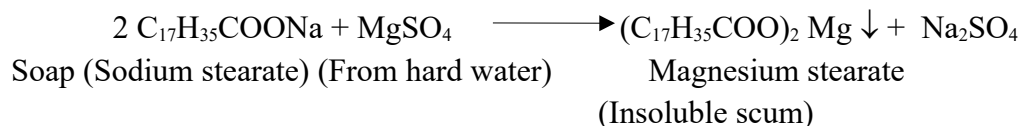
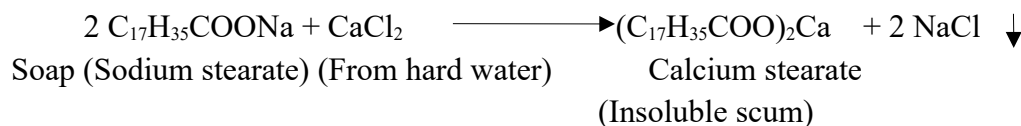
Mechanism of cause of hardness: It can be explained by the reaction of soap in soft and hard water.

Reaction of soap in soft water : When soft water is treated with soap, lather is produced according to the following reaction:



Reaction of soap in hard water:

A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic and stearic acid), does not produce lather, but on the other hand forms insoluble white scum or precipitate which do not possess any detergent action. This is due to the formation of insoluble soap of calcium and magnesium. Typical reaction of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below.



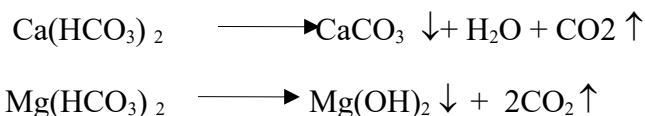
Actually hardness is due to presence of chlorides, sulphates, bicarbonates, carbonates of Ca^{2+} , Mg^{2+} and other heavy metal ions like Fe^{2+} , Al^{3+} and Mn^{2+} . The presence of CO_2 also breaks up Na or K soaps into free fatty acids and does not allow lather to be formed.

Types of Hardness: Hardness is of two types

1. Temporary Hardness:

(a) Temporary hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonates of iron and other metals also. Thus, the main salts responsible for temporary hardness are $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.

(b) Temporary hardness can be removed by mere boiling of water. On boiling, bicarbonates decomposed and yield in soluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.



(c) Temporary hardness is also known as **carbonate hardness or alkaline hardness**.

Alkaline hardness is due to the presence of bicarbonates, carbonates and hydroxides of the hardness producing metal ions. This is determined by titration with HCl using methyl orange as indicator.

2. Permanent Hardness:

(a) It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Hence, the salts responsible for permanent hardness are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ etc.

(b) Unlike temporary hardness, permanent hardness is not destroyed on boiling.

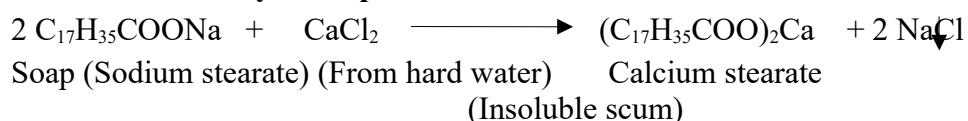
(c) It is also known as **non-carbonate or non-alkaline hardness**.

(d) The difference between total hardness and alkaline hardness gives the nonalkaline hardness.

Disadvantages of Hard Water:

Hardness causing impurities present in the hard water exert following effects:

Effect on efficiency of soap: It is decreased due to the formation of scum.

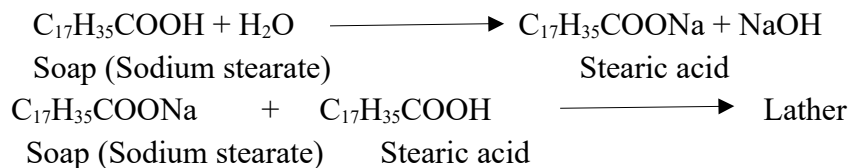


Effect on economy: It is decreased due to decrease in the efficiency of soap in hard water as the consumption of soap is increased.

Effect on health: It adversely affects digestive system and increased possibilities of forming calcium oxalate crystals in the urinary track on drinking.

Effect on domestic uses:

Washing: Hard water, when used for washing purposes, it does not lather freely with soap, on the other hand, it produces sticky precipitate (*i.e.* scum) of calcium and magnesium soaps. The formation of such insoluble sticky precipitates continues till all calcium and magnesium salts present in water are precipitated. After that, the soap (*i.e.*, sodium stearate) gives lather with water.



This causes wastage of lot of soap being used. The sticky precipitate adheres on the fabric giving spots and streaks. Iron salts may cause staining of cloth.

Bathing: Sticky scum produced by hard water with soap depresses the cleansing quality of soap and a lot of it is wasted.

Cooking: Due to presence of dissolved hardness producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an unpleasant taste and muddy looking extract. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

Effect on industries: Due to presence of dissolved salts, it exerts adverse effects on various industries like

(i) Textile industries: Wastage of soap, Scum adhere to the fabric and exact shades of colour cannot

be produced on such fabrics during dyeing. Salts may cause coloured spots on fabrics, thereby spoiling their beauty.

(ii) Sugar industries: Difficulties in crystallization of sugar. Produced sugar may be deliquescent.

(iii) Dyeing industry: Dissolved salts may react with costly dyes, which gives result of impure shade. Spot on fabric being dyed.

(iv) Paper industry: Dissolved salt may react with the chemicals used to give shining to paper. Iron salts may affect colour of paper being produced.

(v) Laundry industry: Wastage of soap. Iron salts may effect coloration of cloths.

(vi) Concrete industry: Effect adversely the hydration of cement and final strength of the hardened concrete.

(vii) Pharmaceutical industries: It may produce certain undesirable products in the pharmaceutical products like drugs, injections, ointments etc.

(viii) **Effect on steam generation in boilers:** For steam generation, boilers are almost invariable employed. If the hard water fed directly to the boilers, there arise many troubles such as:

- (i) Scale and sludge formation, (ii) corrosion (iii) priming and foaming, and carry over,
- (iv) caustic embrittlement.

(ix) **Effect on laboratories:** Hardness causing ions interference in various reactions therefore it is not a suitable solvent

Degree of Hardness: Although hardness of water is never present in the form of the calcium carbonate, because it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent amount of CaCO_3 . The reason for choosing CaCO_3 as the standard for reporting

hardness water is the ease in calculation as its molecular weight is exactly 100. Moreover, it is the most insoluble salt that can be precipitate in water treatment.

Equivalents of $\text{CaCO}_3 = [\text{Amount of hardness producing substance}] \times [\text{Chemical equivalent of } \text{CaCO}_3 (= 50)] \times 2 / [\text{Chemical equivalent of hardness producing substance}] \times 2$

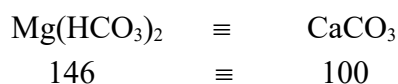
$= [\text{Amount of hardness producing substance}] \times 100 / [\text{Chemical equivalent of hardness producing substance} \times 2]$

$= [\text{Amount of hardness producing substance}] \times (\text{Multiplication factor})$ in mg /lit. or ppm.

Multiplication factor: Weight of MgSO_4 , $\text{Mg}(\text{HCO}_3)_2$, MgCl_2 and CaCl_2 actually present, may be converted in terms of weight of CaCO_3 by multiplying 100/120, 100/146, 100/95 and 100/111 respectively.

Factors used for such conversion are called multiplication factor.

It can be shown as follows:



Where, we are comparing hardness due to $\text{Mg}(\text{HCO}_3)_2$ in terms of CaCO_3 equivalents.

X quantity of $\text{Mg}(\text{HCO}_3)_2 = X \times 100/146$ amount of CaCO_3 thus the factor 100/146 is multiplication factor (M.F.) for $\text{Mg}(\text{HCO}_3)_2$.

Multiplication factor = $100 / [\text{Chemical equivalent of hardness producing substance} \times 2]$

M.F. for various compounds are shown in Table 1

Table 1.: Multiplication factors for various compounds

Compounds/Salt/Ions	Molar mass	Multiplication factor(for conversion into CaCO_3 equivalent)
$\text{Ca}(\text{HCO}_3)_2$	162	100/162
$\text{Mg}(\text{HCO}_3)_2$	146	100/146
CaCO_3	100	100/100
MgCO_3	84	100/84
CaSO_4	136	100/136
CaCl_2	111	100/111
MgSO_4	120	100/120
MgCl_2	95	100/95
$\text{Mg}(\text{NO}_3)_2$	148	100/148
CO_2	44	100/44
Ca^{2+}	40	100/40
Mg^{2+}	24	100/24
H^+	1	100/2
NaAlO_2	82	100/64
$\text{Al}_2(\text{SO}_4)_3$	342	$3 \times 100/342 = 100/114$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	100/278
HCl	36.5	$100/2 \times 36.5 = 100/73$
H_2SO_4	98	100/98

Units of Hardness:

Part per million: parts of CaCO_3 eq. hardness in 10^6 parts of water. “It is the number of parts by weight of CaCO_3 equivalent hardness present per million parts of water”

Milligram/litre: Mg of CaCO₃ eq. hardness in 1 lit. of water. “It is the number of mg of CaCO₃ equivalent hardness present per lit of water “1 mg/lit = 1 ppm”.

Degree French(°Fr): Parts of CaCO₃ eq. hardness in 105 parts of water. “It is the parts of CaCO₃ equivalent hardness present per 105 parts of water.”

Degree clark(°Cl): Parts of CaCO₃ eq. hardness in 70,000 parts of water. “It is the number of Grains (1/7000 lb)*of CaCO₃ equivalent hardness present per gallon (10 lb) of water or parts of CaCO₃ equivalent hardness present per 70,000 parts of water”.

Milliequivalent/litre(1 meq/lit): Meqs of CaCO₃ eq. hardness in 106 parts of water. “It is the number of milliequivalents of CaCO₃ equivalent hardness present per lit of water” 1 meq/lit. = 50 ppm.

Relation between Units of Hardness:

1ppm=1mg/lit=0.1°Fr=0.07°Cl=0.02 meq/lit

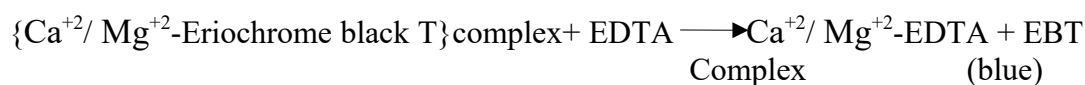
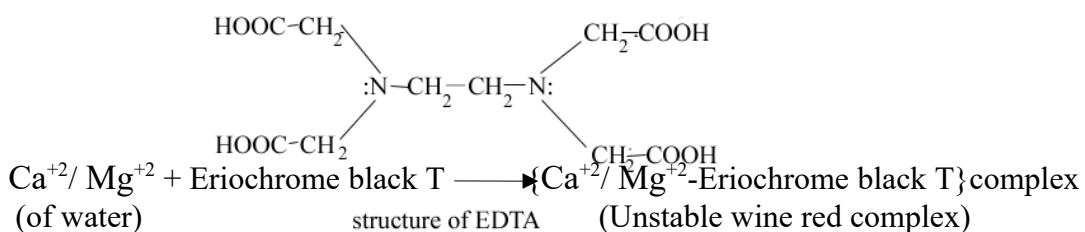
Or 50ppm=50mg/lit=5°Fr=0.35°Cl=1 meq/lit

Determination of Hardness by EDTA method:

CHEMICALS

1. Buffer solution
2. Eriochrome black T indicator
3. Standard EDTA Solution
4. Standard Calcium Solution
5. Unknown hard water sample

THEORY : When Eriochrome Black T dye is added to the hard water at pH around 10 it gives wine red coloured unstable complex with Ca⁺² and Mg⁺² ions of the sample water. Now when this wine red-coloured complex is titrated against EDTA solution (of known strength) the colour of the complex changes wine red to original blue colour showing the endpoint.



The indicator used is a complex organic compound (sodium – 1 – (1-hydroxy 2-aphthylazo)-6-nitro-2-naphthol-4-sutphonate), commonly known as Eriochrome black T(EBT). It has two ionisable phenolic hydrogen atoms.

Advantages of EDTA method

This method is definitely preferable to the other methods, because of :

- i) Greater accuracy,
- ii) convenience and
- iii) more rapid procedure.

PREPARATION OF REAGENTS

1. Buffer solution: Dissolve 16.9 g NH₄Cl in 143 ml NH₄OH. Add 1.25 g magnesium salt of EDTA to obtain sharp change in colour of indicator and dilute to 250 ml. If magnesium salt of

EDTA is not available, dissolve 1.179 g disodium salt of EDTA (AR grade) and 780 mg $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or 644 mg $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 50 ml distilled water. Add this to above solution of NH_4Cl in NH_4OH and dilute to 250 ml.

2. Eriochrome black T (EBT) indicator: Mix 0.5 gm dye with 100 gm NaCl to prepare dry powder.

3. NaOH (2N): Dissolve 80 gm NaOH and dilute to 1000 ml.

4. Standard EDTA Solution 0.01M: Dissolve 3.723 gm EDTA disodium salt and dilute to 1000 ml. Standardized against standard calcium solution, 1ml = 1mg CaCO_3 .

5. Standard Calcium Solution: Weigh accurately 1gm CaCO_3 and transfer to 250 ml conical flask. Then add 1:1 HCl till CaCO_3 dissolve completely. Add 200 ml dist. water and boil for 20 to 30 min. then cool and add methyl red indicator. Add NH_4OH 3N drop wise till intermediate orange colour develops. Dilute to 1000 ml to obtain **1ml = 1mg CaCO_3** .

Procedure

1. Standardization of EDTA

a. Pipette out 10 ml of standard hard water into a conical flask.

b. Add 5 ml of buffer solution and few drops of Eriochrome Black-T. The indicator, which is originally blue color would acquire a wine-red color.

c. Titrate with EDTA solution taken in the burette, till the wine red color changes to blue which is the end point. Let the burette reading of EDTA be V_1 ml.

2. Determination of Total hardness

Repeat the above titration method for sample hard water instead of standard hard water. Let the burette reading of EDTA be V_2 ml.

3. Determination of Permanent hardness

Take 100 ml of sample hard water in 250 ml beaker. Boil it to remove temporary hardness to about half of this volume and cool to room temperature. Filter through filter paper to remove insoluble CaCO_3 and MgCO_3 . Make up the volume to the original 100 ml by adding distilled water. Now pipette out 20 ml of this solution into a clean conical flask. Then repeat the process of titration steps as mentioned above. Let the burette reading of EDTA be V_3 ml.

Calculations:

1. Standardization of EDTA

$$1 \text{ ml of SHW} = 1 \text{ mg of } \text{CaCO}_3$$

$$V_1 \text{ ml of EDTA} = 50 \text{ ml of SHW}$$

$$1 \text{ ml of EDTA} = \frac{50}{V_1} \text{ ml of SHW} = \frac{50}{V_1} \text{ mg of } \text{CaCO}_3$$

2. Total hardness

$$50 \text{ ml of unknown hard water} = V_2 \text{ ml of EDTA}$$

$$= V_2 \times \frac{50}{V_1} \text{ mg of } \text{CaCO}_3$$

$$50 \text{ ml of unknown hard water} = 1000 \times \frac{V_2}{V_1} \text{ mg of } \text{CaCO}_3 = 1000 \times \frac{V_2}{V_1} \text{ ppm}$$

$$\text{Total hardness} = 1000 \times \frac{V_2}{V_1} \text{ ppm}$$

3. Permanent hardness

$$50 \text{ ml of boiled water} = V_3 \text{ ml of EDTA}$$

$$= V_3 \times \frac{50}{V_1} \text{ mg of } \text{CaCO}_3$$

$$50\text{ml of boiled water} = 1000 \frac{V_3}{V_1} \text{mg of CaCO}_3 = 1000 \times \frac{V_3}{V_1} \text{ppm}$$

$$\text{Permanent hardness} = 1000 \times \frac{V_3}{V_1} \text{ppm}$$

4. **Temporary hardness = Total hardness - Permanent hardness**

$$\begin{aligned} &= (1000 \times \frac{V_2}{V_1} \text{ppm}) - (1000 \times \frac{V_3}{V_1} \text{ppm}) \\ &= 1000 \times \frac{V_2 - V_3}{V_1} \text{ppm} \end{aligned}$$

●**SOFTENING OF WATER:**

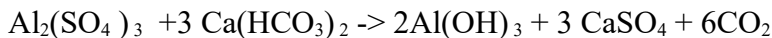
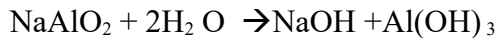
Removal of hardness producing ions from water is known as softening of water. It can be carried out by the following methods

(1) LIME-SODA PROCESS:

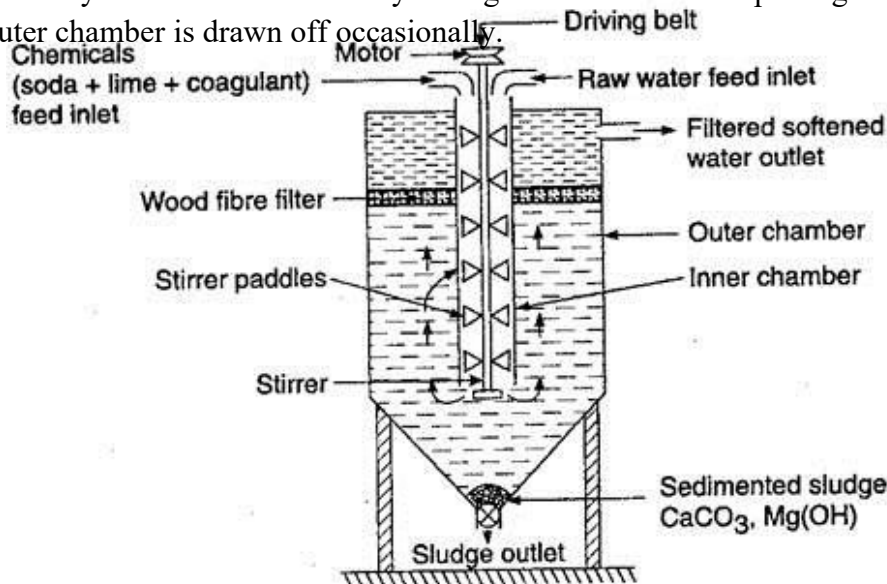
In this Method, the soluble calcium and Magnesium salts in water are chemically converted into insoluble Compounds by adding calculated amounts of lime Ca(OH)_2 and soda Na_2CO_3 calcium carbonate CaCO_3 and magnesium hydroxide Mg(OH)_2 . So Precipitated, are filtered off.

(A) COLD LIME-SODA PROCESS:

In this Method, Calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (Like Alum, aluminum sulphate, sodium aluminate, Etc.) Which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminate as coagulant, also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.



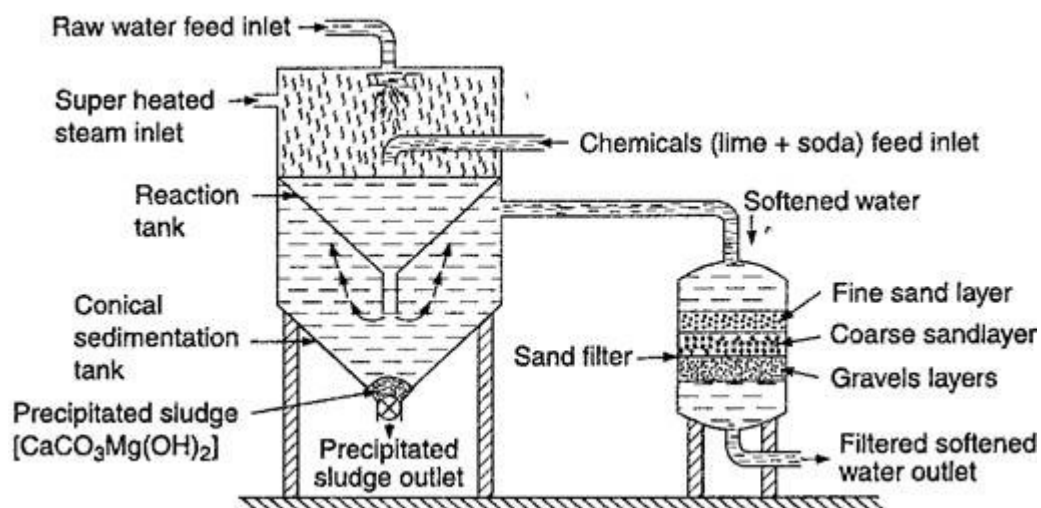
Method: Raw water and calculated quantities of chemicals (Lime+soda+coagulant) are fed from the top into the inner vertical circular chambers, fitted with a vertical rotating shaft carrying a number of paddles , As the raw water and chemicals flow down there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened ware comes into the outer chamber of the lime the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally a flow out continuously through the outlet at the top sludge settling at the bottom of the outer chamber is drawn off occasionally.



(B) HOT LIME-SODA PROCESS:

Involves in treating water with softening chemicals at a temperature of 80° to 150° C. Since hot process is operated at a temperature close to the boiling point of the solution, so (a) the reaction proceeds faster; (b) the softening capacity of hot process is increased to may fold; (c) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed;(d) much of the gases (Such as CO₂ and air) Driven out of the water;(e) Viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters, and (f) Hot Lime-Soda Produces water of comparatively lower residual hardness of 15 to 30ppm.

Hot lime-soda plant consists essentially of three parts (a) a 'reaction tank' in which raw water, chemicals and steam are thoroughly mixed; (b) a 'conical sedimentation vessel' in which sludge settles down, and (c) a 'Sand filter' which ensures complete removal of sludge from the softened water.



Advantages of L.S.Process:

- (i) It is a very economical
- (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed
- (iii) The process increased the pH value of the treated water, thereby corrosion of the distribution pipes is reduced
- (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced
- (v) To certain extent, iron and manganese are also removed from the water.
- (vi) Due to alkaline nature of treated- water, amount of pathogenic bacteria's in water is considerably reduced

Disadvantages of L.S.Process:

- (i) For efficient and economical softening, careful operation and skilled supervision is required
- (ii) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (iii) This can remove hardness only up to 15ppm, which is not good for boilers

Difference between hot lime soda and cold lime soda process

Hot lime-soda process	Cold lime soda process
High temperature(80°C)	Room temperature (25-30°C)
Low residual hardness 15-30ppm	High residual hardness 60ppm

No coagulant is required	Coagulant is required
It is a rapid process	It is a slow process.
Filtration is easy viscosity of water is low	Filtration is not easy
Dissolved gases are removed	Dissolved gases are not removed

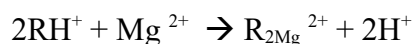
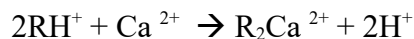
(2) ION EXCHANGE PROCESS:

Ion exchange resins are insoluble, cross linked long chain organic polymers with micro porous structure, and the functional groups attached to the chains are responsible for the Ion –exchanging properties resins containing acidic functional groups (-COOH, -SO₃H etc,) are capable of exchanging their H⁺ ions with other cat ions, which comes in their contact where as those containing basic functional groups(-NH₂=NH,hydrochloride) are capable of exchanging their anions with other anions, which comes in their contact Ion exchange resins may be classified as

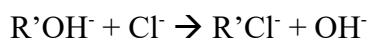
I. Cation exchange resin(RH⁺) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cat ions in water

II. Anions exchange resins(ROH) are styrene-divinyl benzene or amine-formaldehyde, copolymers, which contains amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix these after treatment with dilute .NaOH solutions become capable to exchange their OH⁻ anions with anions

PROCESS: The Hard water is passed first through cat ion exchange column, which removes all the cat ions like Ca²⁺ etc, from it and equivalent amount of H⁺ ions released from this column to water, thus



After Cat ion exchange column, the hard water is passed through anion exchange column which removes all the anions like SO₄²⁻, Cl⁻ etc present in the water and equivalent amount of OH⁻ ions are released from this column to water thus:



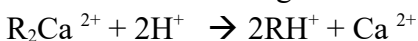
H⁺ and OH⁻ ions get combined to produce water molecule



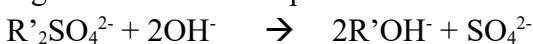
The water coming out from the exchanger is deionized or demineralised water

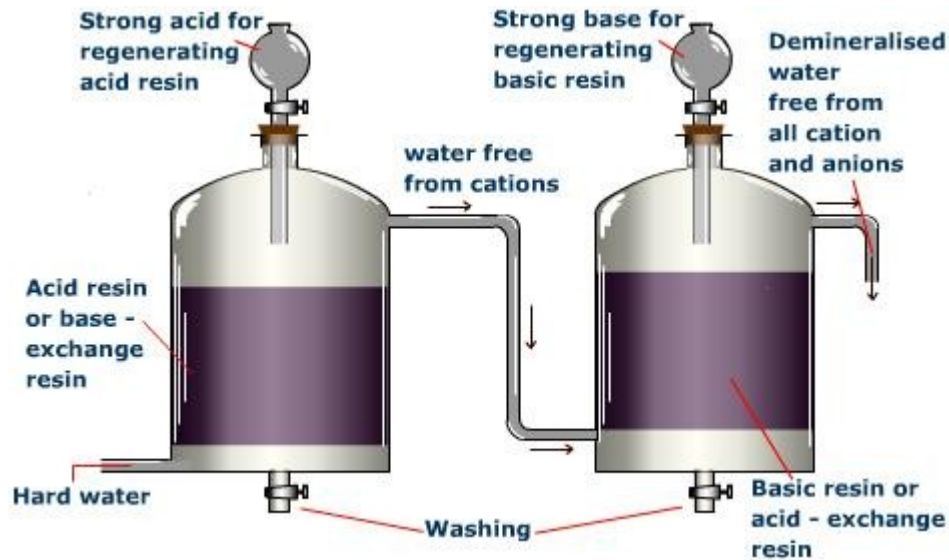
REGENERATION: When capacities of cation and anion exchangers to exchange H⁺ and OH⁻ ions respectively are lost, they are then said to be exhausted

The exhausted cat ion exchange column is regenerated by passing a solution of Diluted HCL Or Dilute H₂SO₄. The regeneration can be represented as



The exhausted anions exchange column is regenerated by passing a solution of diluted NaOH. The regeneration can be represented as





Advantages:

- Process used to soften highly acidic or alkaline water
- It produces water of very low hardness
- One of the most appropriate technologies to removes dissolved inorganic ions effectively
- Possibility to regenerate resin

Disadvantages:

- The equipment is costly
- If water contains turbidity out-out of the process is reduced
- Does not remove effectively bacteria
- High operation costs over long-term
- The process of regenerating the ion exchange beds dumps salt water into the environment (regeneration)

CHAPTER-11

LUBRICANTS

INTRODUCTION

Whenever a machine works, its moving, sliding or rolling parts rub against each other with the result of that a friction is developed. This friction causes a lot of wear and tear of the concerned surfaces. Further due to friction, large amount of energy is dissipated in the form of heat and thus causes loss in the efficiency of a machine. Moreover, the heat produced due to friction causes damage to the moving parts.

The above ill effects can be minimized by applying a thin layer of certain substances known as lubricant in between the moving parts.

The process of applying the lubricant in between the two moving or sliding surfaces is called as lubrication.

Lubricant:

Lubricant may be defined as the substance which reduces the friction between the two moving surfaces or parts of a machine.

Characteristics of a lubricant

It should have enough viscosity and oiliness.

It should have flash and fire points higher than the operating temperature of the machine.

It should be chemically inert.

It should not come out of the surface under pressure.

It should not evaporate easily.

It should stick on the surface.

It should leave low carbon residue.

It should not form emulsion with water.

It should have cloud and pour points lower than the operating temperature of the machine.

The volatility of the lubricating oil should be low.

It should possess a higher resistance towards oxidation and corrosion.

Classification of lubricants

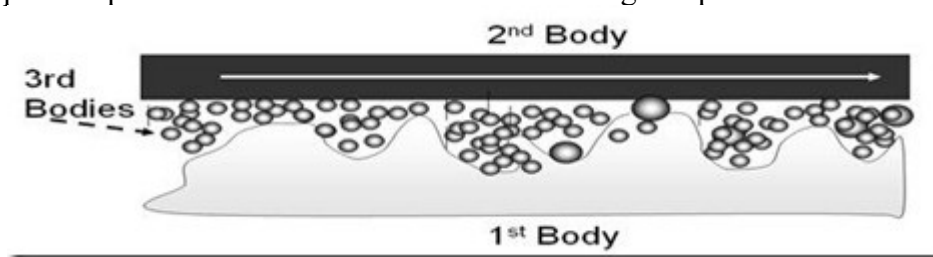
Lubricants may be broadly classified as follows.

1. Solid lubricants 2. Semi-solid lubricants 3. Liquid lubricants

1. Solid lubricants *Definition* : Solid lubricants are deposited in the valleys to create a smoother surface.

Description: They are designed to protect against metal contact by coming between two peaks at the moment of contact. This results in the deformation of the peak, rather than formation of welded joints.

Even between highly loaded stationary surfaces the lamellar structure is able to prevent contact. Large lubricant particles perform better on relative rough surfaces and at low speed, while finer particles perform better on smooth surface and higher speeds



(1st and 2nd are sliding surfaces and 3rd is solid lubricant filling the valley)

Example: Layered Compounds like graphite, boron nitride, molybdenum disulphide, talc, teflon, mica, calcium fluoride, cerium fluoride, tungsten disulfide etc

The most widely used solid lubricants are graphite and molybdenum sulphide. Solid lubricants are used in the areas like for heavy machinery working as a crude job at very high loads, when the operating temperature or load is very high, where a liquid or semi-solid lubricant film cannot be maintained.

a. Graphite

Graphite is an allotrope of carbon. Graphite has a layered structure of carbon atoms. The carbon atoms are joined together by strong covalent bonds. The adjacent layers are held together by the weak Vanderwall's force. Thus, they form a network of hexagons. Graphite is soapy to touch, non-inflammable and not oxidized in air below 375°C. It is used as a lubricant in the form of powder or as suspension in oil or water. It fills the cavities and prevents the friction. It is used for lubricating the joints or railways tracks.

Graphite can be used as a dry powder or as a colloidal dispersion. A dispersion of graphite in water is called aqua dag and that in oil is called oil dag.

Uses

It is used as a lubricant in IC engines, air compressors, lathes, food-stuff industry, railway track joints, general machine job works, etc.

2. Semi-solid lubricant Example: Grease and Vaseline

Grease: It is a mixture of mineral oil and soap. It is used for heavy load and low speed machines. It is mainly used in bearing and gears. Grease is a semi-solid lubricant obtained by thickening of lubricating oil by the addition of a metallic soap. The thickener is usually sodium, calcium, and lithium or aluminium soap.

Greases are manufactured by saponification of fats with alkali followed by adding hot lubricant oil under severe agitation. Their properties depend on both the base used for saponification and the fatty acid present in the oil.

3. Liquid lubricants:

Vegetable oils: They are commonly used liquid lubricants.

Examples: Castor oil, coconut oil, etc.

They are classified as drying and semi-drying oils. They are easily oxidized by atmosphere.

Animal oils

They are oils of animal origin. They are mainly animal fats. Examples: Tallow oil, whale oil, lards oil, coconut oil and olive oil etc. They are very costly. Hence, they find little use as lubricants. They are also easily oxidized by atmosphere.

Mineral oil

Hydrocarbons with higher molecular mass obtained by the fractional distillation of petroleum are used as lubricants. They are obtained from the paraffin residue.

Examples: Paraffin oil, lubricating oil, etc.

Blended oils

They are mixture of vegetable oils and petroleum products. They show improved properties. Different oils are suitably mixed depending on the requirement. They are synthetic lubricants.

Lubrication: The process of prevention of metal to metal contact by means of an intervening layer of fluid or fluid like material is termed as Lubrication.

Purpose of Lubrication:

- It acts as a thermal barrier and reduces friction and wear
- It prevents the surface of metal from deposition of welded joints
- Avoids seizure of moving surfaces
- Acts as coolant
- Acts as a seal and prevents entry of dust, moisture, & dirt between moving parts
- Some lubricants acts as corrosion inhibitors thus reduce operational cost

CHAPTER-12

FUELS

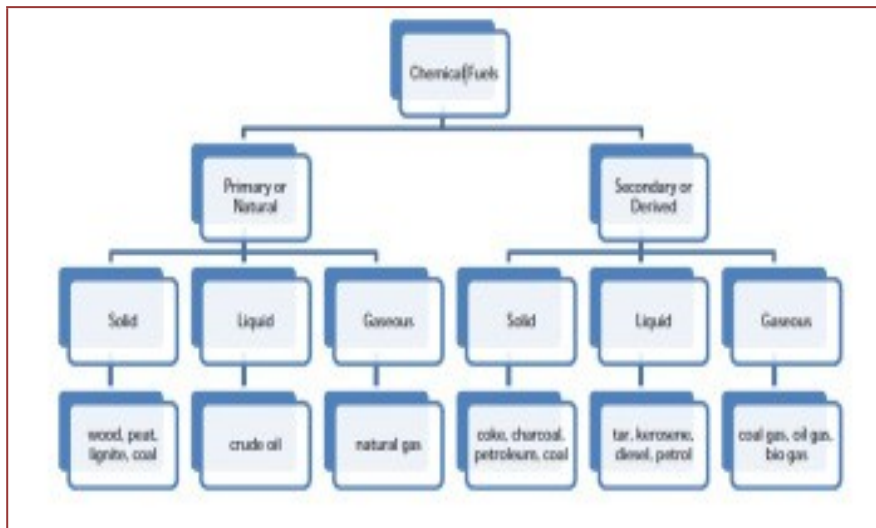
INTRODUCTION:

In this present age of rapid industrial development, the power requirement is increasing day-by-day. Heat energy is the main source of power. Burning of carbon, an exothermic reaction produces heat energy. Hence, the carbon compounds have been used as the main source of heat energy.

- **Fuel:**

A fuel is a substance, which on proper burning gives large amount of heat energy on combustion. It is used for domestic and industrial purposes. They contain carbon as a main constituent.

- **Classification of fuels:**



Fuels are classified into 1. Natural or primary fuels and 2. Artificial or secondary fuels. Each type is further sub-divided into solid, liquid and gaseous fuels.

Sl.No.	State of fuel	Natural	Artificial
1	Solid	Wood, peat, lignite, coal	Wood charcoal, coke
2	Liquid	Crude petroleum	Kerosene, petrol, diesel, alcohol
3	Gaseous	Natural gas	Water gas, producer gas, biogas, coal gas, LPG

Relative advantages of solid, liquid and gaseous fuels

Sl. No.	Property	Solid fuel	Liquid fuel	Gaseous fuel
1	Calorific value	Low	Greater than solid fuel and less than gaseous fuel	Very high
2	Smoke production	High	Low	Nil
3	Ash formation	Ash produced	Very low	Nil
4	Storage	Large space needed	Less space needed	Minimum space needed
5	Transportation	More labour involved	Much less labour involved	Transported easily through pipelines

6	Ignition	Difficult	Easy	Very easy
7	Flame control	Difficult	Easy	Very easy

Characteristics of an ideal/good fuel

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 or 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 of a fuel

Calorific value of a fuel is the total quantity of heat liberated when a unit mass or volume of the fuel is completely burnt.

Unit of heat

Heat energy is measured in terms of calorie or kilocalorie.

Calorie is the quantity of heat required to raise the temperature of 1 gram of water through 1° Centigrade (1 kcal = 1000 calories)

The calorific value of a fuel is expressed in two different ways

1. Gross calorific value(GCV) or Higher calorific value(HCV)

Gross calorific value of a fuel is defined as the total quantity of heat liberated when a unit mass of the fuel is completely burnt and the combustion products are cooled to room temperature

$$\text{Gross calorific value} = \text{Heat of reaction} + \text{Latent heat of steam produced} + \text{Sensible heat obtained by cooling the combustion products to room temp.}$$

2. Net calorific value(NCV) or Lower calorific value(LCV)

The net calorific value of a fuel is the actual amount of heat available when unit mass of the fuel is completely burnt and combustion products are permitted to escape.

$$\text{Net Calorific Value} = \text{Gross calorific value} - \text{Latent heat of water vapour formed.}$$

Dulong's formula:

Dulong suggested a formula for the calculation of the calorific value of the solid or liquid fuels from their chemical composition which is as given below.

$\text{GCV or HCV} = 1/100[(8080 \times \%C) + 34500\{\%H - (\%O/8)\} + (2240 \times \%S)]$ kcal/kg or cal/gm
 where C, H, O and S are carbon, hydrogen, oxygen and sulphur in percentages respectively in the fuel. In the above formula the oxygen is assumed to be in combination with hydrogen and only extra surplus hydrogen supplies the necessary heat.

• Solid fuels

Wood

It is a low-grade fuel. Freshly cut wood contains 25-50% moisture. Moisture may be reduced to 25% on air-drying. The composition of moisture free wood is C = 55%; H₂ = 6%; O₂ = 43% and ash = 1%. The calorific value of dried wood is 3500 to 4500 kcal/kg. It burns with a long and non-smoky flame. It is used as a domestic fuel.

Coal

Coal is a natural fuel formed by the slow carbonization of vegetable matter buried under the earth some thousands of years ago. It is classified into four kinds based on the carbon content and the calorific value as Peat, Lignite, Bituminous coal and Anthracite

1. Peat

It is the first stage of formation of coal from wood. It is brown, fibrous jelly-like mass. It contains 80-90% moisture. The composition of peat is C = 57%; H₂ = 6%; O₂ = 35% and ash = 2.5%. The calorific value of peat is 5400 kcal/kg. It is a low-grade fuel due to high water content.

Uses

It is used as fertilizer.

It is used as packing material.

2. Lignite

Lignite is immature form of coal. It contains 20-60% moisture. Air-dried lignite contains C = 60-70% and O₂ = 20%. It burns with a long smoky flame. The calorific value of lignite is 6500-7100 kcal/kg.

Uses

It is used as a domestic fuel.

It is used as a boiler fuel for steam production.

It is used in the manufacture of producer gas.

3. Bituminous coal

It is a high quality fuel. Its moisture content is 4%. Its composition is C = 83%; O₂ = 10%; H₂ = 5% and N₂ = 2%. Its calorific value is 8500 kcal/kg.

Uses

It is used in metallurgy.

It is used in steam production.

It is used for making coal gas.

It is also used for domestic heating.

4. Anthracite coal

It is the superior form of coal. It contains C = 92-98%; O₂ = 3%; H₂ = 3% and N₂ = 0.7%. It burns without smoke. Its calorific value is 8700 kcal/kg.

Uses:

It is used for steam production and house hold purposes.

It is used for direct burning in boilers and in metallurgy.

It is used in thermal power plant.

It is used in coal tar distillation.

It is used in glass furnaces.

•Liquid fuels

a. Petroleum

Petroleum (Crude oil) is a naturally available liquid fuel. It is a dark greenish-brown viscous oil found deep in earth's crust. It is composed of various hydrocarbons with small amount of other organic compounds as impurities.

Refining of petroleum

The process of purification and separation of various fractions present in petroleum by fractional distillation is called refining of petroleum. Refining is carried out in oil refineries.

Fractional distillation

It is the process of separation of various components of a liquid mixture based on the difference in their boiling points by repeated evaporation and condensation.

Refining of petroleum – Process

The crude oil is treated with copper oxide to remove sulphur impurities. Then it is repeatedly washed with sulphuric acid to remove basic impurities. It is then washed with sodium hydroxide to remove acidic impurities. Then it is subjected to fractional distillation and various fractions are collected. The various fractions obtained and their uses are given in the table below.

Products of fractional distillation of petroleum and their uses:

Sl. No.	Fractions	Temperature	Uses
1	Gases	Below 30°C	Used as industrial and domestic fuel
2	Petroleum ether	30°C to 80°C	Used as a solvent
3	Gasoline or petrol	40°C to 180°C	Used as a solvent, fuel and in dry cleaning
4	Kerosene oil	180°C to 250°C	Used as illuminant and fuel
5	Diesel oil or gas oil	250°C to 320°C	Used as fuel for diesel engine
6	Heavy oil or lubricating oil	320°C to 400°C	Used for lubrication, cosmetics, in medicines
7	Residue or asphalt or pitch	Above 400°C	Used for road making, water proofing of roofs

DIESEL OIL

It is relatively a high boiling point fraction of petroleum obtained between 250°C to 320°C.

It is a mixture of hydrocarbons in terms of carbon atoms C15-C18

Its calorific value is about 11,000 kcal/kg. It is used as fuel for compression ignition engine.

Its antiknock value can be improved by doping with isoamyl nitrate.

•Gaseous fuels

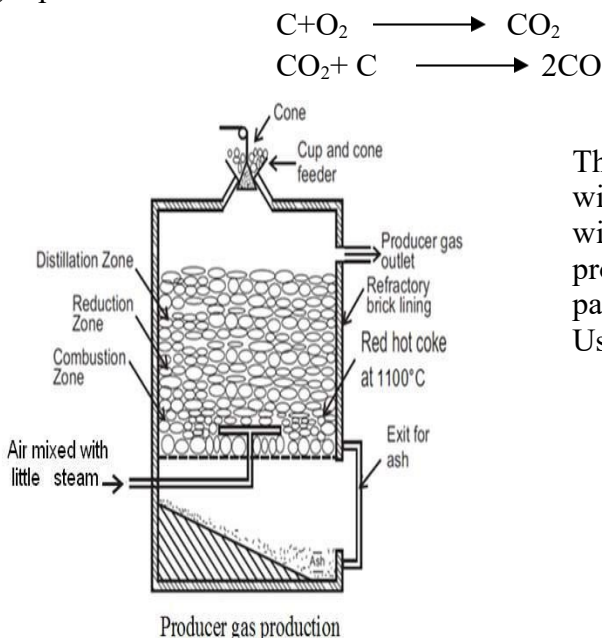
Examples: Producer gas, water gas, CNG and LPG

Producer gas

Producer gas is a mixture of carbon monoxide and nitrogen. It also contains traces of hydrogen and carbon dioxide. The average composition of producer gas is CO = 22-30%; H₂ = 8-12%; N₂ = 52-55% and CO₂ = 3%. Its calorific value is about 1300 kcal/m³.

Preparation

Producer gas is prepared by passing air over a red hot coke at about 1100°C in a reactor called gas producer.



The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it is provided with cup and cone arrangement and an exit for producer gas. At the bottom, it has an inlet for passing air. There is an exit for the ash at the base.

Uses

It is used as a fuel in the extraction of metal.

It is used in the manufacture of glass.

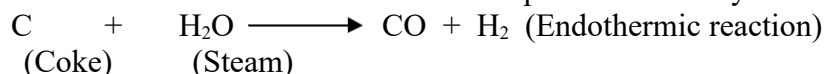
It is used as a reducing agent in metallurgy.

Water gas

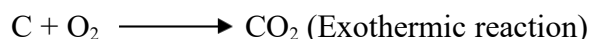
Water gas is a mixture of carbon monoxide and hydrogen. It also contains traces of carbon dioxide and nitrogen. The average composition of water gas is CO = 41%; H₂ = 51%; N₂ = 4% and CO₂ = 4%. Its calorific value is 2800 kcal/m³.

Preparation

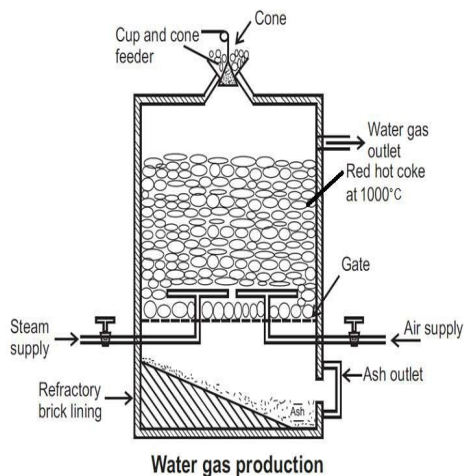
Water gas is prepared by passing steam and little air alternatively over a red hot coke at about 1000°C in a reactor. It is an endothermic reaction. So the temperature of the system decreases.



But, the reaction between carbon and air is exothermic and raises the temperature to about 1000°C



Thus, the steam and air are sent in alternatively to maintain the temperature at about 1000°C.



The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it has cup and cone feeder and an exit for water gas. At the base, inlet pipes for steam and air are provided. At the bottom, outlet for ash is also available.

Uses

- It is used as a source of hydrogen gas.
- It is used as an illuminating gas.
- It is used as a fuel in ceramic industries.

CNG (Compressed natural gas)

CNG is a good alternative fossil fuel. It mainly contains methane.

CNG is made by compressing natural gas which is found in oil deposits landfills and waste water treatment plants to less than 1% of its volume, it occupies at standard atmospheric pressure.

It is stored and distributed in hard containers at a pressure of 2900-3600 psi.

Advantages

It is cheaper than petrol or diesel.

It emits fewer pollutants like CO₂, CO, etc. In New Delhi, it is used as a fuel for entire city bus fleet, taxis and three wheelers.

It is safer than other fuels. In the event of a spill, it disperses quickly in air because, it lighter than air.

LPG (Liquefied petroleum gas)

It is a mixture of propane and butane.

It is stored in steel cylinder under high pressure.

When the cylinder is opened, it comes out in the form of gas.

Commercially, it is supplied under various trade names.

Its calorific value is 27,800 kcal/m³.

Uses

It is mainly used as a domestic fuel.

It is used as a fuel in diesel engines.

It is used as a motor fuel.

QUESTIONS

PART – A

Define fuel.

Define fossil fuel.

Define calorific value of a fuel.

How are fuels classified?

Give two examples for solid fuels.

Give two examples for liquid fuels.

Give two examples for gaseous fuels.

What are the varieties of coal?

What is petroleum?

What is meant by cracking?

What is producer gas?

Give the composition of producer gas.

What is water gas?

Give the composition of water gas.

What are the components present in CNG?

Mention the uses of CNG.

What are the components present in LPG?

Mention the uses of LPG.

PART – B

What is refining of petroleum?

Write a note on liquid hydrogen as fuel.

Give the composition and uses of producer gas.

Give the composition and uses of water gas.

Give the composition and uses of CNG.

Give the composition and uses of LPG.

PART – C

Write a note on solid fuels.

Explain the fractional distillation of petroleum.

Describe the manufacture of producer gas. List its uses.

Describe the manufacture of water gas. List its uses.

Write a note on CNG.

Write a note on LPG.

Compare the relative advantages of solid, liquid and gaseous fuels.

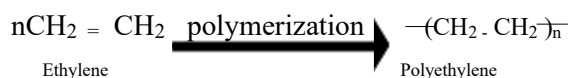
CHAPTER-13

POLYMER

INTRODUCTION

Polymers can be defined as the large molecules (macro molecular) formed by the linkage of small molecules called monomers. (In Greek language poly means many & mer means units)

E.g.:- poly ethylene



Thus the repeated unit of polymer is called monomer. The number of repeating units in a polymer chain is called degree of polymerization. For e.g.:- if 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerization is 100.

Polymers form very important components in our daily life. The polymers are highly useful in domestic industrial & medical fields. The following are the reasons for the extensive use of polymers.

- 1) Most of the polymers are non-toxic & safe to use
- 2) They have low densities (light in weight) so transportation polymers will be easy.
- 3) They possess good mechanical strength.
- 4) These are resistant to corrosion & won't absorb moisture when exposed to the atmosphere.
- 5) These can function as good thermal & electrical insulators.
- 6) These can be moulded and fabricated easily.
- 7) They possess esthetic colors

But the limitations for the use of polymers are

1. Some polymers are combustible.
2. The properties of polymers are time dependent
3. Some of them cannot withstand high temperature.

It is also interesting to note that many carbohydrates, Proteins & enzymes, DNA & RNA are natural polymers.

Polymerization

Polymerization is the process of converting small, low molecular weight organic molecules into long, high molecular weight organic molecules either by addition reaction or by condensation reaction. The small molecules are called monomers and the products are called polymers.

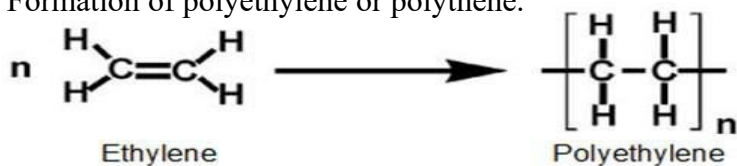
There are two types of polymerization.

1. Addition polymerization
2. Condensation polymerization

1. Addition polymerization

In this type of polymerization, polymers are formed by simple addition reaction between small molecules containing double or triple bonds.

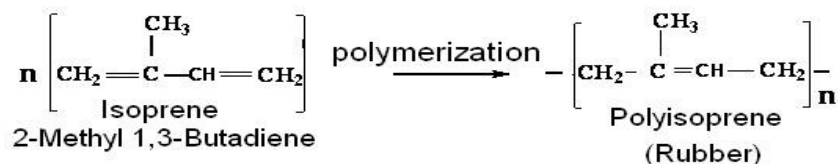
Example: Formation of polyethylene or polythene.



7	Scrap recovery	Scrap can be reused	Scrap cannot be reused
8	Example	Polythene, PVC, nylon	Bakelite

RUBBER

Rubber is a natural elastic polymer of isoprene (C_5H_8). It is obtained from the milk of rubber called 'Latex'.



Defects of natural rubber

The natural rubber obtained from latex cannot be used in industries because it has the following defects.

It becomes soft and sticky during summer.

It becomes hard and brittle during winter.

It swells up in oils.

It flows plastically due to prolonged stress.

Chemicals easily affect natural rubber.

Vulcanization

Vulcanization is process of heating the natural rubber with sulphur at 140°C in CO_2 atmosphere. By vulcanization, the hardness of rubber is improved. Example: sulphur.

Vulcanization of rubber

Vulcanization is compounding of rubber with sulphur. Vulcanization is process of heating the natural rubber with sulphur at 140°C in CO_2 atmosphere.

The double bonds present in rubber chain opened and cross linked through sulphur atoms. Hence the vulcanized rubber becomes very hard.

The hardness of rubber increases as the percentage of sulphur increases. 2 to 4% sulphur addition gives soft elastic rubber. When sulphur content is more than 30%, hard rubber called 'Ebonite' is obtained.

Properties of vulcanized rubber

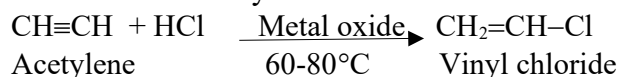
Vulcanized rubber has very little electrical and thermal conductivity. Hence, it is mainly used for electrical insulation purposes.

It has high elasticity and tensile strength.

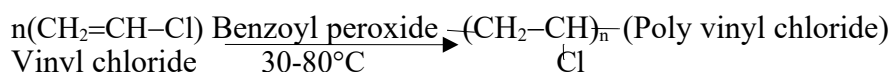
Corrosive chemicals and oils do not affect it.

It is also not affected by atmosphere.

Polyvinyl chloride (PVC):- The monomer used for the manufacture of PVC is vinyl chloride. Vinyl chloride is prepared by treating acetylene with HCl at $60-80^\circ\text{C}$ and in presence of a metal oxide catalyst



Poly vinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or H_2O_2 .



Uses: It is used for making safety helmets, refrigerator components, tyres, cycle & motor cycle mud guards
It is used for making rain coats, table-cloths, handbags curtains & electrical insulators, radio, T.V components. All PVC – shoes for beach wear.

Uses of Bakelite:-

It is used for making electric insulator parts like switches, plugs, switch boards, etc.

For making moulded articles like telephone parts cabinet of radio and television.

As an anion exchanger in water purification by ion exchange method in boilers

As an adhesive (binder) for grinding wheels etc., in paints and varnishes and For making bearings used in propeller shafts, paper industry and rolling mills

Advantages of vulcanized rubber over natural rubber:-

The tensile strength increase

Vulcanized rubber has excellent resilience

It is resistance to organic solvents like CCl₄, Benzene petrol etc.

It has only slight thickness

It has low elasticity

QUESTIONS

PART – A

What is polymerization?

What are the types of polymerization?

How polythene is formed?

How Bakelite is formed?

PART – B

Explain addition polymerization with an example

Explain condensation polymerization with an example.

What are thermoplastics? Give an example.

What are thermosetting plastics? Give an example.

PART – C

List the differences between thermoplastics and thermosetting plastics.

Pesticides are chemical substances that are meant to control pests, including weeds. The term pesticide includes all of the following: herbicide, insecticides (which may include rodenticide, bactericide, fungicide). The most common of these are herbicides which account for approximately 80% of all pesticide use. Most pesticides are intended to serve as plant protection products (also known as crop protection products), which in general, protect plants from weeds, fungi, or insects.

A pesticide is a chemical or biological agent (such as a virus, bacterium, or fungus) that deters, incapacitates, kills, or otherwise discourages pests. Target pests can include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes (roundworms), and microbes that destroy property, cause nuisance, or spread disease, or are disease vectors. Along with these benefits, pesticides also have drawbacks, such as potential toxicity to humans and other species.

Examples: DDT, gamma-xylene, Aldrin

Insecticides are chemical substances used to control and kill the insects like ants, housefly, etc.

Examples: Endrin, DDT, gamma-xylene, Aldrin

Herbicides or weedkillers, are substances used to control unwanted plants.

Selective herbicides control specific weed species, while leaving the desired crop relatively unharmed, while non-selective herbicides (sometimes called total weedkillers in commercial products) can be used to clear waste ground, industrial and construction sites, railways and railway embankments as they kill all plant material with which they come into contact.

Examples: Glyphosate, 2,4-D and dicamba, EPTC, trifluralin, etc.

Fungicides are biocidal chemical compounds or biological organisms used to kill parasitic fungi or their spores.

A fungistat inhibits their growth. Fungi can cause serious damage in agriculture, resulting in critical losses of yield, quality, and profit. Fungicides are used both in agriculture and to fight fungal infections in animals. Chemicals used to control oomycetes, which are not fungi, are also referred to as fungicides, as oomycetes use the same mechanisms as fungi to infect plants.

Examples: copper sulphate solution, phenol, bleaching powder, etc.

Biofertilizer is a substance which contains living microorganisms which, when applied to seeds, plant surfaces, or soil, colonize the rhizosphere or the interior of the plant and promotes growth by increasing the supply or availability of primary nutrients to the host plant.

Biofertilizers add nutrients through the natural processes of nitrogen fixation, solubilizing phosphorus, and stimulating plant growth through the synthesis of growth-promoting substances. Biofertilizers can be expected to reduce the use of synthetic fertilizers and pesticides.

The microorganisms in biofertilizers restore the soil's natural nutrient cycle and build soil organic matter. Through the use of biofertilizers, healthy plants can be grown, while enhancing the sustainability and the health of the soil. Since they play several roles, a preferred scientific term for such beneficial bacteria is "plant-growth promoting rhizobacteria" (PGPR). Therefore, they are extremely advantageous in enriching soil fertility and fulfilling plant nutrient requirements by supplying the organic nutrients through microorganism and their byproducts. Hence, biofertilizers do not contain any chemicals which are harmful to the living soil. Biofertilizers provide "eco-friendly" organic agro-input.

Biofertilizers such as *Rhizobium*, *Azotobacter*, *Azospirillum* and blue green algae (BGA) have been in use a long time. *Rhizobium* inoculant is used for leguminous crops. *Azotobacter* can be used with crops like wheat, maize, mustard, cotton, potato and other vegetable crops. *Azospirillum* inoculations are recommended mainly for sorghum, millets, maize, sugarcane and wheat. Blue green algae belonging to a

general cyanobacteria genus, *Nostoc* or *Anabaena* or *Tolypothrix* or *Aulosira*, fix atmospheric nitrogen and are used as inoculations for paddy crop grown both under upland and low-land conditions. *Anabaena* in association with water fern *Azolla* contributes nitrogen up to 60 kg/ha/season and also enriches soils with organic matter.