SATHYABAMA
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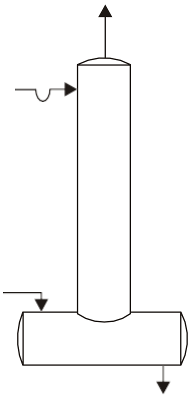
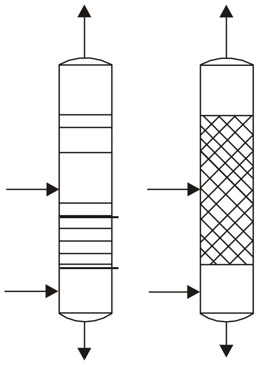
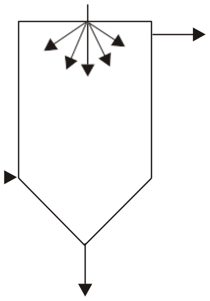
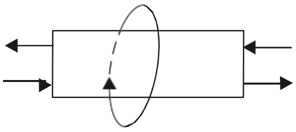
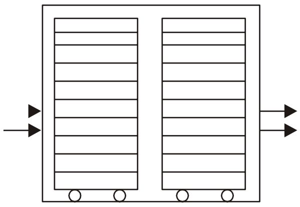
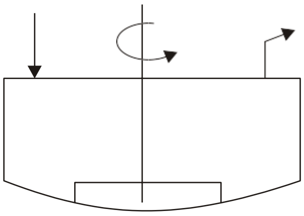
SCHOOL OF BIO AND CHEMICAL ENGINEERING

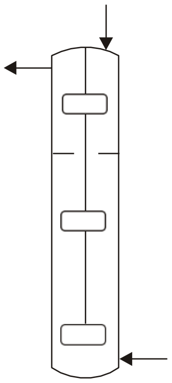
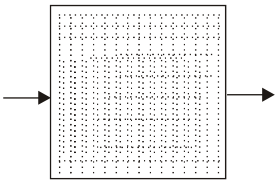
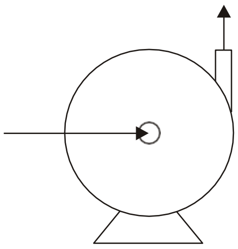
DEPARTMENT OF CHEMICAL ENGINEERING

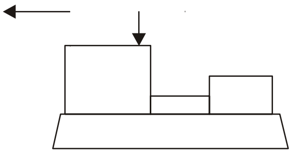
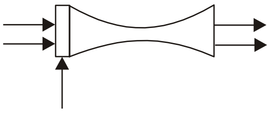
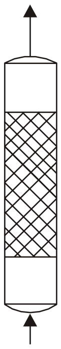
UNIT – 1 INTRODUCTION - CHLORO ALKALI INDUSTRIES-SCHA 1305

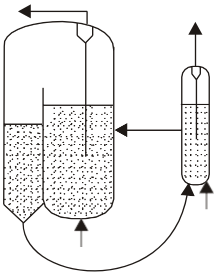
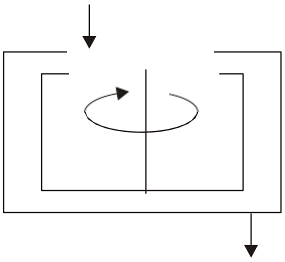
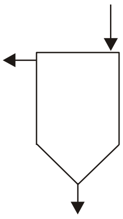
Process Equipment Symbols

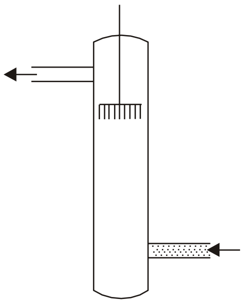
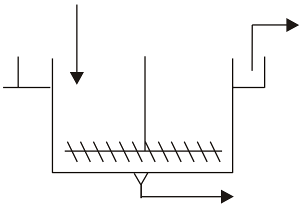
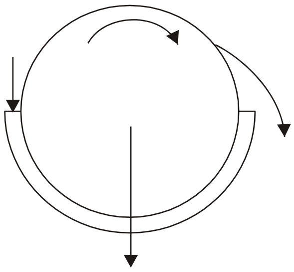
UnitOperation	*SchematicRepresentation*	*Comments*
1. Distillation **(a) Batch**		**Utilized for intermittent operation and handling small volumes** **of feed and product**
(b) ContinuosFractionator		**Suitable for high volume continuous separation of complex mixtures** **eg. petroleum fraction**
2. Drying ofSolids **(a) SprayDrier**		**Employed for large capacity operation on liquid feed to give powered, spherical,free flowing product ;used in prodution of pigments, detergents,synthetic resins and misc inorganic salts**

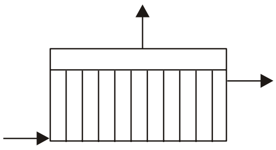
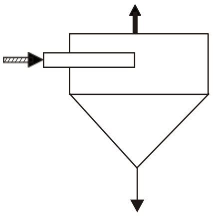
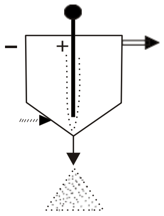
UnitOperation	*SchematicRepresentation*	*Comments*
(b) RotaryDrier		**Suitable for drying free flowing granular solids which do not dust or stick ; high temp models are kilns for calcining cement, lime, etc.**
(c) Tunnel Driver		**Best suited to drying pastes or powders in trays ; also used** **to dry pottery, lumber, leather, etc., In sheet shaped forms**
3. Evaporation **(a) OpenPan**		**Used for small batches ; often of viscous mat's ;** **such designs are easy to clean**

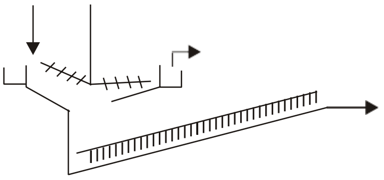
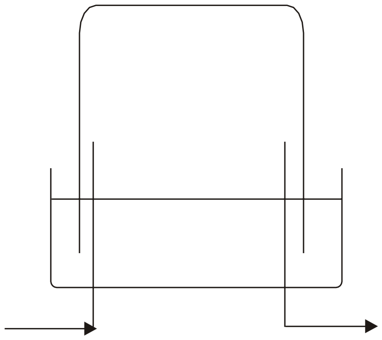
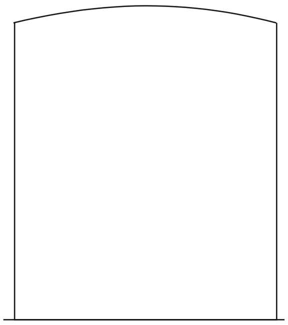
UnitOperation	*SchematicRepresentation*	*Comments*
4. Extraction **(a) Liquid -liquid**		**Used to contact solvent and feed to give raffinate and extract ; widely adapted to removal of** **napthenes from lube oil fractions Using solvents such as furfural**
(b) Solid-Liquid (Leaching)		**Involves removal of a solute from a Solidbymeansofaliquidsolvent Often used in ore treatment to Recover metal values**
5. FluidHandling **(a)Centrifugal pump**		**Mostwidelyusedforliquidsofall types;simpleinconstructionand maintenance**

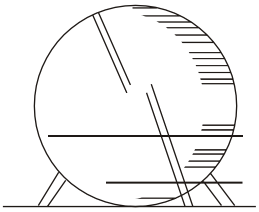
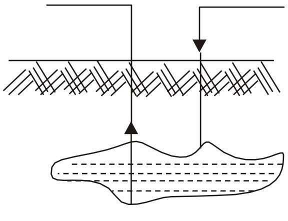
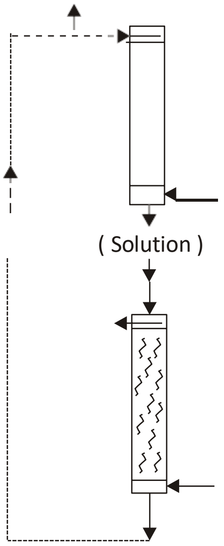
UnitOperation	*SchematicRepresentation*	*Comments*
(b) Reciprocating Pump Or Compressor		**Generally used for higher pressure delivery ; may be used for metering or proportioning**
(c) Jet Ejector		**Used for lower pressure operation or production of vacuum ; steam often used as motive fluid**
6. Fluid - Solid Contacting (**a) Fixed Bed**		**Most widely used type of catalytic rector ; used with precious metal catalysts to minimize attrition losses ; catalyst usually in form of pellets**

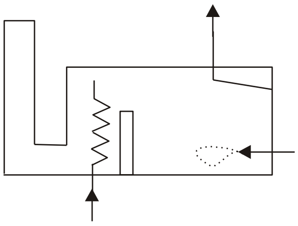
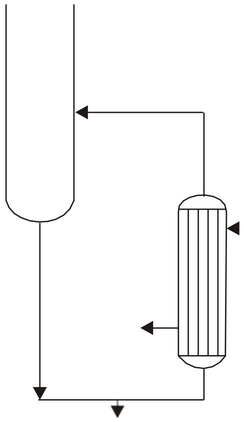
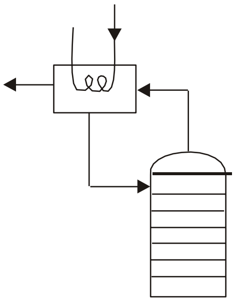
UnitOperation	*SchematicRepresentation*	*Comments*
6 . Fluid Bed		**Used to contact finely divided solids with reactant gases** ***e.g.*, Cracking catalyst with oil vapor and then with air ; also used in roasting of sulfide ores to give oxides and SO_2**
7. Fluid - SolidSeparation		
(a) Centrifugation		**Used to separate very finely divided solids from liquid or liquids from liquid emulsions**
(b) Setting Tank		**Simple device used to remove large particles from gas stream by simple setting in low velocity zone**

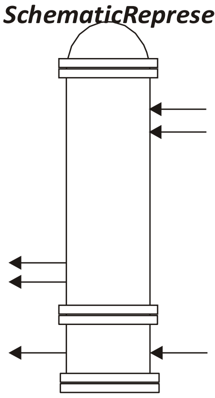
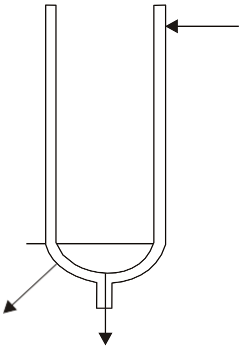
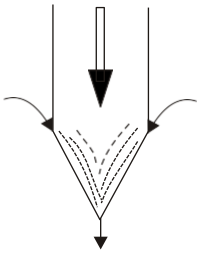
UnitOperation	*SchematicRepresentation*	*Comments*
(c) Wet Scrubber		**Effective means of removing suspended particles from gas stream by contact with liquid shower**
(d) Crystallizer		**Hot, nearly-saturated solutions are stirred and cooled to effect nucleation and crystal growth ; widely used with inorganic salts.**
(e) Filter (Rotary)		**Vacuum applied to interior of drum pulls filtrate out of cake; used to separate minerals from slurries, pulp fibers from water, etc.**

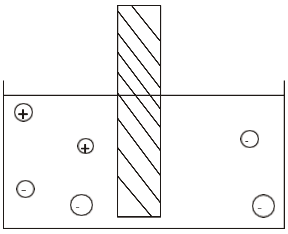
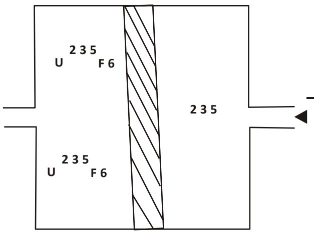
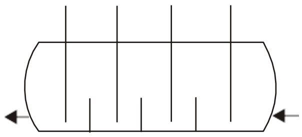
UnitOperation	***SchematicRepresentation***	***Comments***
(f) Filter Press		**Simplest type of pressure filter; widely used ; plates and fabric filter media may be made of a variety of corrosion resistant materials**
(g) Cyclone Separator		**Used to separate solid particles or liquid droplets from gases to permit product recovery or to cut down product loss and air pollution**
(h) Electrostatic Precipitator		**Used to remove fine dusts or mistssuspendedingases;featureshighcollection efficiency at widevariety of operatingconditions.**

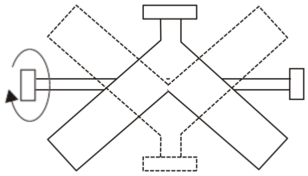
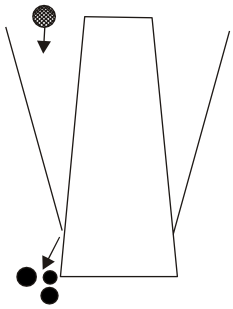
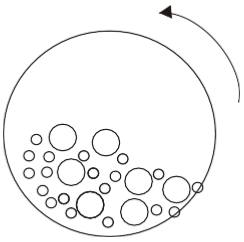
UnitOperation	*SchematicRepresentation*	*Comments*
(j)Thickener **-Classifier**		**Used to separate slurry into sludges and clear liquids ; used widely in mineral industries and in sewage effluent clarification**
8 . FluidStorage **(a) Gas Holders**		**Used for low pressure storage of gases at constant pressure using** **liquid seal (usually water)**
(b) Tanks		**Widely used for storage of liquids of all types , usually at atmospheric pressure ; may have floating roof**

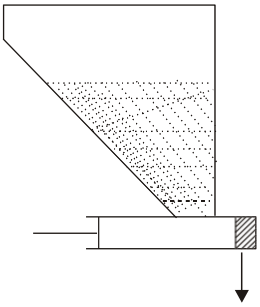
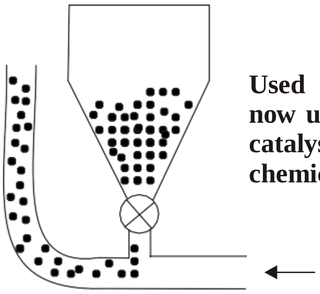
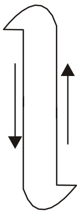
UnitOperation	*SchematicRepresentation*	*Comments*
(c) Pressurized Spheres		**Used for pressurized storage of liquified gases or high vapor pressure liquids to permit safe storage with no vaporlosses**
(d) Underground Caverns		**Used for large volume storage of liquids or of liquified gases**
9 . Gas-LiquidContacting		
(a) Absorption		**Used for taking up a soluble gas in a solvent liquid and producing a solution plus a lean exit gas ;*e.g.,*Used in H_2S removal from hydro-carbons**
(b) Stripping		**Used for removing a soluble gas from solution by counter-current contact with an inert gas ; used to recover solute gas and regenerate solvent for subsequent absorption step**

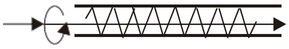
UnitOperation	*SchematicRepresentation*	*Comments*
10. Heat Exchange		
(a) Fired Heater		**Used to heat petroleum fraction to distillation or cracking temperatures in direct fired tubes.**
(b) Reboiler		**Uses natural circulation to circulate fractionating tower bottom in heat exchange with steam *,e.g.,* to provide necessary heat forfractionation**
(c) Condenser		**Usually water-cooled tubular construction to provide reflux and overhead product from fractionating column**

UnitOperation	*SchematicRepresentation*	*Comments*
(d) Shell And Tube Exchanger		**Common type of device for process heat exchange**
(e) Jacketed Kettle		**Common construction for reaction kettles ; water or brine may be used for cooling ; hot water, oil or Dowtherm for heating**
(f) Direct Mixing (Quenching)		**Features intimate contact of coolant fluid (*e.g.*, water) with process gases to give quick quench, *e.g.*,in hydrocarbon pyrolysis to acetylene**

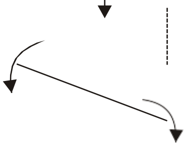
UnitOperation	***SchematicRepresentation***	***Comments***
11. Membrane Separation **(a)Dialysis**		**Used to separate malt's in sol's having widely different mole.** **E*.g.,* Caustic from sugar or cellulose**
(b) Gaseous Diffusion		**Uses micro porous (e.g., Ni) barriers in multistage operation to separate light (e.g., $U_{235}F_6$) from heavy (e.g., $U_{235}F_6$)components**
12. Mixing **(a) Agitation**		**May be used for liquid - liquid or solid - solid mixing in single or multiple compartments ; widely used in processindustries**

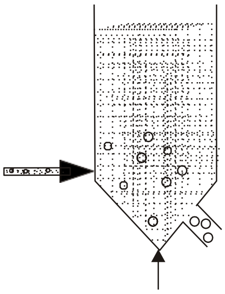
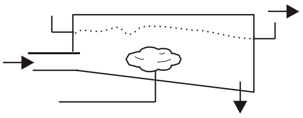
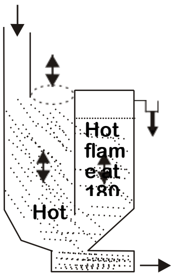
Unit Operation	*Schematic Representation*	*Comments*
(b) Solids Blending		**The device shown divides and recombines a granular mass over and over again to effect uniformity**
13. Size Reduction and Enlargement **(a) Crushing**		**Used typically in 4:1 size reduction of hard materials from -5 to -20 mesh or -1 to -4 mesh**
(b) Grinding		**Wet or dry grinding may be carried out in presence of balls, pebbles of rods; feed may be -4 to -100 mesh and reduction ratio 10 - 15 to 1**

UnitOperation	*SchematicRepresentation*	*Comments*
(c) Pelletizing		**Used to make tablets from powders of Medicinals, cata- Catalysts, etc**
14. Solids Handling		
(a) Pneumatic Conveying		**Used originally for grain; now used widely for cement, catalysts, coke and powdered chemicals**
(b) Bucket Elevators		**Used for elevating materials; can be used for moving powdered or granular mat’ls to and from storage or between reaction vessels as in moving bed catalytic processes**

UnitOperation	*SchematicRepresentation*	*Comments*
(c)Screwconveyor		**Versatile ; can be used to mix and heat or cool ; can be operated underpressure ; useful for powders or sticky material.**
(d) Belt Conveyor		**Can be used to handle large volumes over long distances economically ; used near horizontal ; belting may be fabric or rubber**

15. Solid / Solid Separation

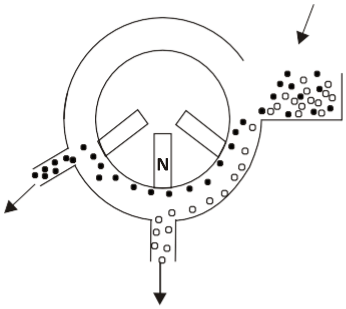
(a) Screening		**Wire , plastic or fabric screens are used to separate solids of varying sizes**

UnitOperation	*SchematicRepresentation*	*Comments*
(b) Elutriation		**May be used to remove fines from a solid by passage of a gas to fluidize and transport the fines**
(c)FrothFloatation		**Finely ground (- 50 mesh) ores are suspend in water in presence of floating reagents (e.g.., RCOONa) and blow with air ; desired product collects in froth.**
(d) Jigging		**One of the oldest processes used for separation of minerals from lighter gangues as a well as for separating coal from heavier contaminants**

UnitOperation	SchematicRepresentation	Comments

(e) Magnetic Separation

Used to remove tramp iron from feed to subsequent grinding and pulverizing steps; also used to concentrate magnetic iron ores



MANUFCATURE OF SODA ASH

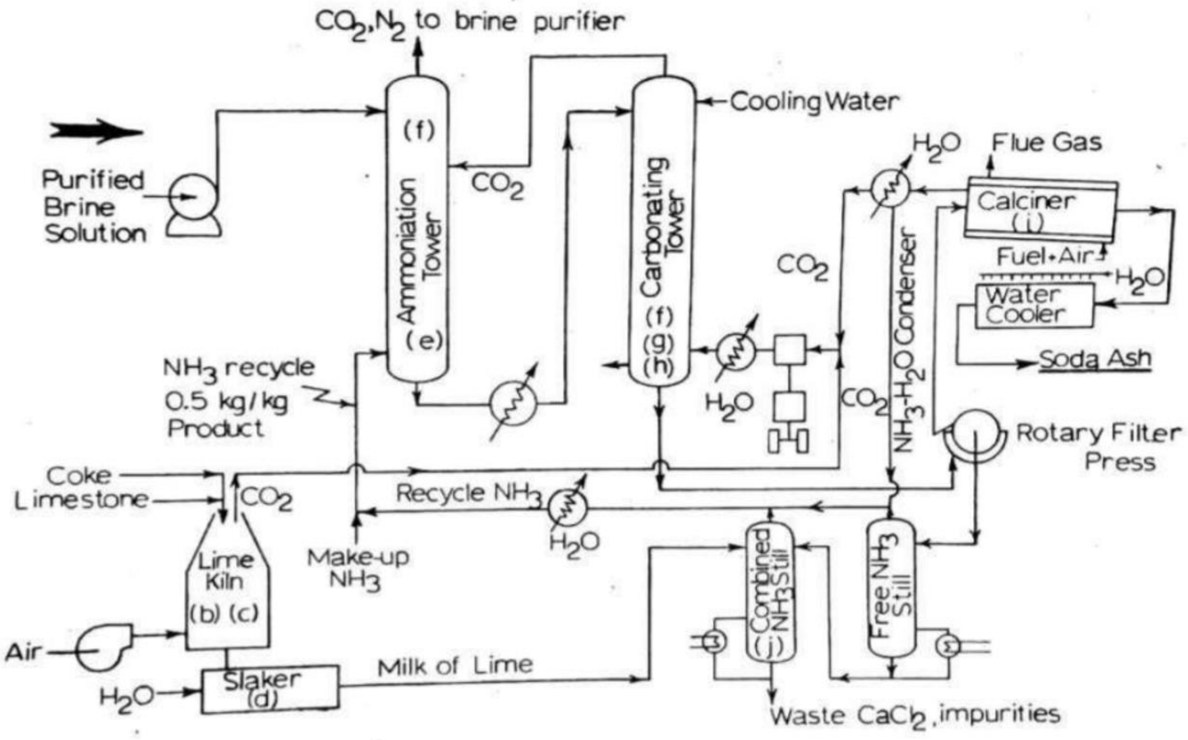
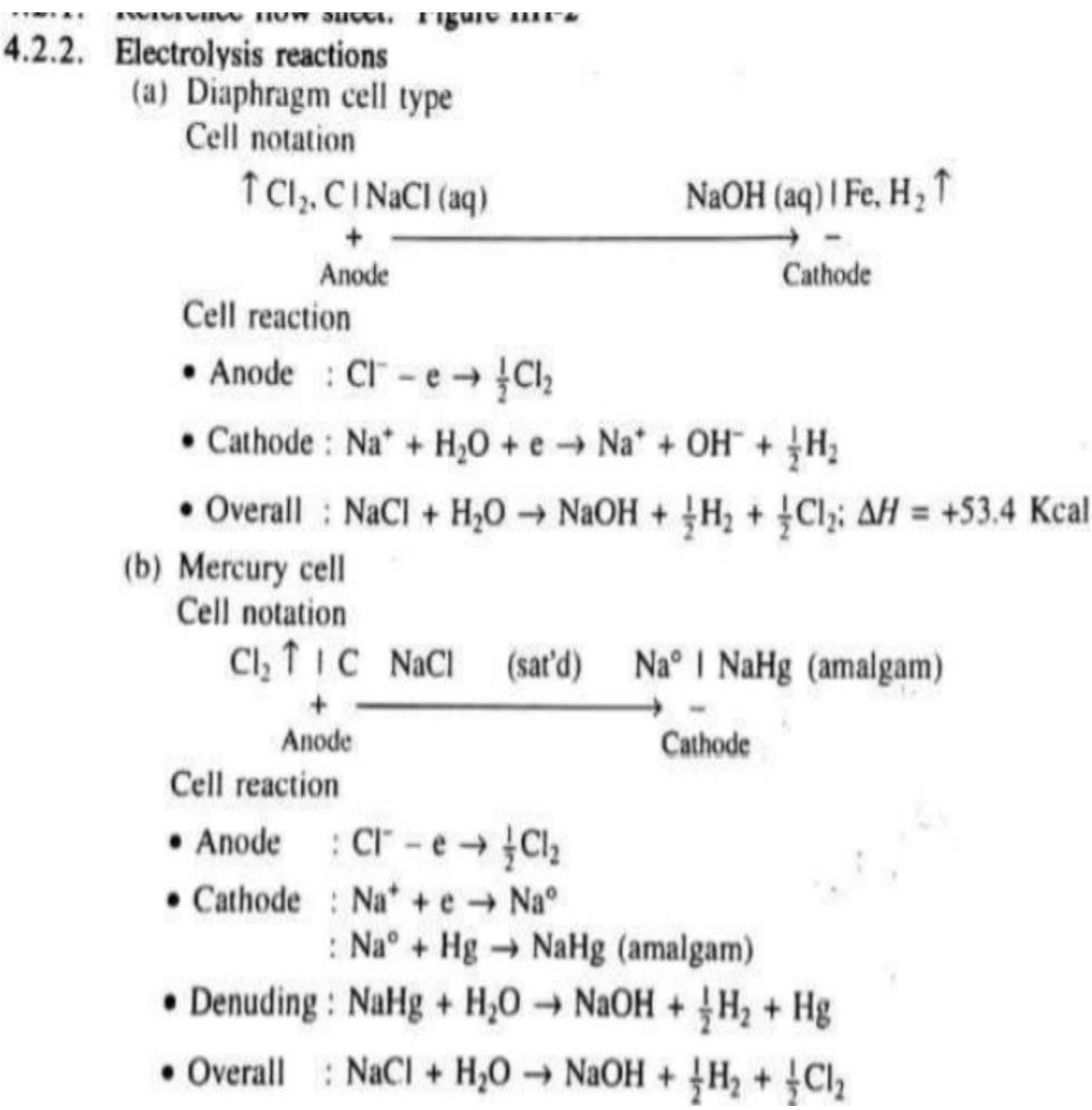


Figure 1.1 Manufacture of soda ash by Solvay process

CHLORINE -CAUSTIC SODA



4.2.2. Electrolysis reactions

(a) Diaphragm cell type

Cell notation

$$\uparrow \mathrm{Cl_2, C \mid NaCl\,(aq)} \qquad \mathrm{NaOH\,(aq) \mid Fe, H_2} \uparrow$$

$$\underset{\text{Anode}}{+} \longrightarrow \underset{\text{Cathode}}{-}$$

Cell reaction

- Anode : $Cl^- - e \rightarrow \frac{1}{2}Cl_2$
- Cathode : $Na^+ + H_2O + e \rightarrow Na^+ + OH^- + \frac{1}{2}H_2$
- Overall : $NaCl + H_2O \rightarrow NaOH + \frac{1}{2}H_2 + \frac{1}{2}Cl_2$; $\Delta H = +53.4$ Kcal

(b) Mercury cell

Cell notation

$$\mathrm{Cl_2} \uparrow \mid \mathrm{C} \quad \mathrm{NaCl} \quad \text{(sat'd)} \quad \mathrm{Na^\circ} \mid \mathrm{NaHg}\ \text{(amalgam)}$$

$$\underset{\text{Anode}}{+} \longrightarrow \underset{\text{Cathode}}{-}$$

Cell reaction

- Anode : $Cl^- - e \rightarrow \frac{1}{2}Cl_2$
- Cathode : $Na^+ + e \rightarrow Na^\circ$
  : $Na^\circ + Hg \rightarrow NaHg$ (amalgam)
- Denuding : $NaHg + H_2O \rightarrow NaOH + \frac{1}{2}H_2 + Hg$
- Overall : $NaCl + H_2O \rightarrow NaOH + \frac{1}{2}H_2 + \frac{1}{2}Cl_2$

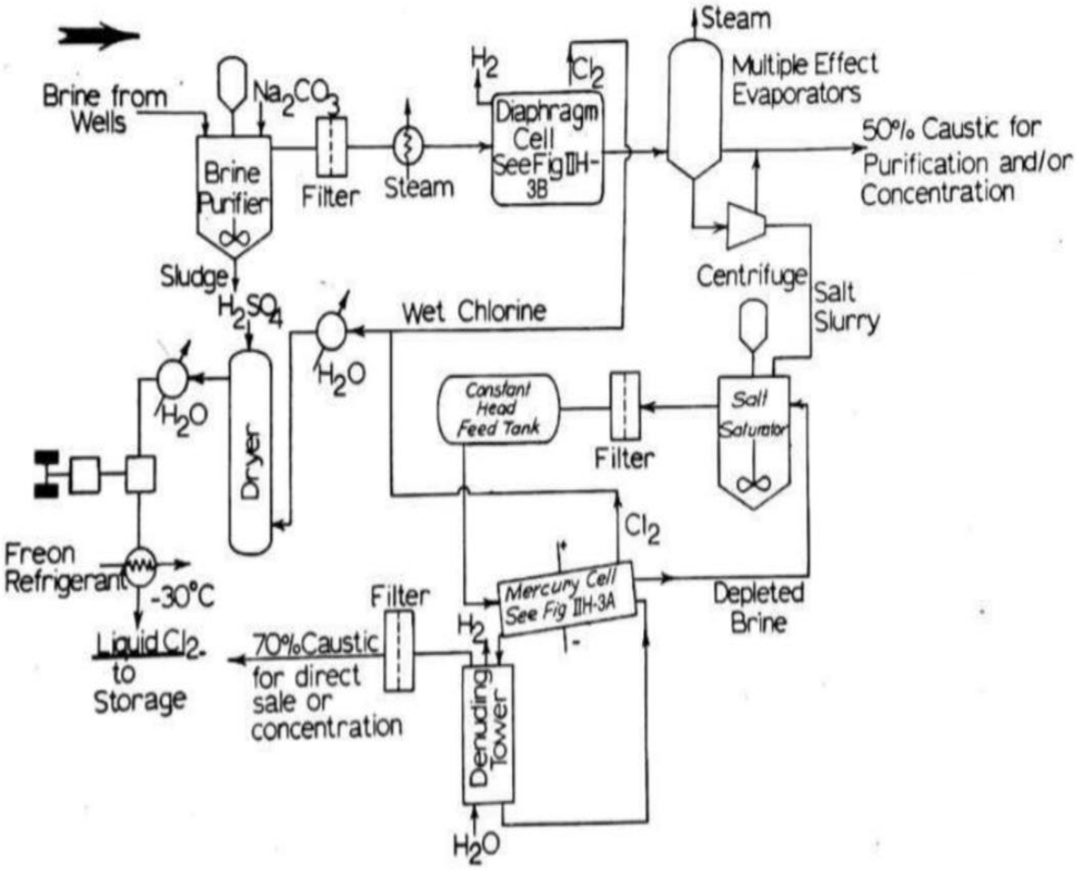


Figure 1.2 Electrolytic process for chlorine-caustic soda Production

REFERENCES

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SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 2 SULPHUR, SULPHURIC ACID AND SILICATE INDUSTRIES
SCHA1305

SULFURIC ACID

INTRODUCTION

Sulfuric acid (H_2SO_4) is a highly corrosive strong mineral acid. It is a colorless to slightly yellow viscous liquid which is soluble in water at all concentrations. It is one of the most important heavy industrial chemicals due to it has a number of large-scale uses particularly in the phosphate fertilizer industry. About 60 % of the sulfuric acid produced is utilized in fertilizer manufacture.

Sulfuric acid was called "oil of vitriol" by Medieval. The study of vitriol began in ancient times. Sumerians had a list of types of vitriol that classified according to substance's colour.

Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter (potassium nitrate, KNO_3), in the presence of steam in the 17thcentury. Decomposition of saltpeter followed by oxidation produces SO_3, which combines with water to produce sulfuric acid. Joshua Ward used the method for the first large- scale production of sulfuric acid in 1736.

John Roebuck, produce less expensive and stronger sulfuric acid in lead-lined chambers in 1746. The strength of sulfuric acid by this method is 65%. After several refinements, this method, called the "lead chamber process" or "chamber process", remained the standard for sulfuric acid production for almost two centuries.

The process was modified by Joseph Louis Gay-Lussac and John Glover which improved concentration to 78%. However, the manufacture of some dyes and other chemical processes require a more concentrated product. Throughout the 18th century, this could only be made by dry distilling minerals in a technique similar to the original alchemicalprocesses.

Pyrite (iron disulfide, FeS_2) was heated in air to yield iron(II) sulfate, $FeSO_4$, which was oxidized by further heating in air to form iron(III) sulfate, $Fe_2(SO_4)_3$, which, when heated to 480^0C, decomposed to iron(III) oxide and sulfur trioxide, which could be passed through water to yield sulfuric acid in any concentration. But the production expenses are veryhigh.

More economical process i.e. the contact process was patented by Peregrine Phillips in 1831. Today, nearly all of the world's sulfuric acid is produced using thismethod.

MANUFACTURE

The Industrial manufacture of sulfuric acid is done mainly by two processes

1. The Lead Chamberprocess

2. The Contactprocess

1. The lead chamberprocess

The Lead Chamber process for the manufacture of sulfuric acid dates back about 200 years. Although less efficient than the contact process, it is still of considerable commercial importance.

Raw Materials

Basis: 1000kg Sulfuric acid
(98% yield) Sulfur =400kg

Air =399kg

Manufacture

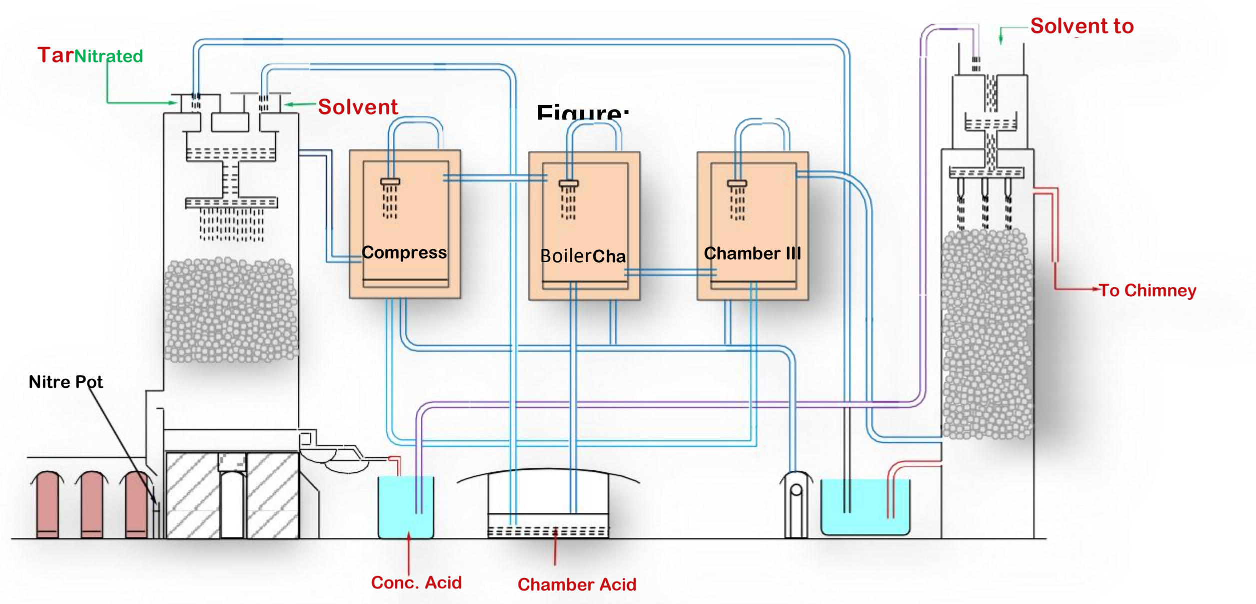

Figure: Manufacturing of Sulfuric acid by Chamber process

Sulfur dioxide is obtained by burning sulfur or by roasting pyrites. There are two function of burner

1. To oxidize sulfur to maximumextent
2. To produce and constant supply of gas containing maximum concentration ofSO2

The burner of the furnace should expose large surface of melted sulfur and should be provided secondary air in order to burn sublimed burner. This is necessary due to low heat of combustion and high vapour pressure of sulfur. At about 400^{0}C, pyrite (FeS2) decompose in to FeS and sulfur vapour, the later oxidized to SO2 in presence of excess air. The residual

FeS also oxidizes to Fe_2O_3 and SO_2. Iron oxide (Fe_2O_3) slightly catalyzed oxidation of SO_2 to SO_3. Burner gas should contain sufficient oxygen for carry out further oxidation of SO_2 to SO_3.

The burner gases which contain SO_2, N_2, O_2 and dust or fine particle of pyrites are passed through dust chamber followed by Cottrell electrical precipitator or centrifugal separator in order to remove dust or fine particle of ore. Dust chambers are provided with horizontal shelves or baffles followed by filtration through crushed coke or similar material.

Now, burner gases are passed through niter oven made of cast iron in which equimolecular proportion of $NaNO_3$ and H_2SO_4 is heated. Resulting nitric acid reacts with SO_2 to give mixture of nitric oxide (NO) and nitrogen dioxide (NO_2) which are carried with burner gases.In modern plant oxides of nitrogen are produced by passing mixture of ammonia and air through heated platinum gauze acting as catalyst (same as manufacture of HNO_3 by ammonia oxidation process)

After passing burner gases to dust chamber and niter oven, they pass through 5 meter square and 10 -15meter high Glower tower which is packed with flint stone, quartz, tile or acid resisting bricks. The packing in the tower is loosely stacked at the bottom to facilitate mixing of hot gases. The hot burner gases passes up this tower is at 450 - 650^{0}C and dilute H_2SO_4 from the lead chamber and nitrosyl sulfuric acid from Gay-Lussac tower are made to trickle down the Glower tower by means of sprayers. Here, burner gases are cooled down to 70-80^{0}C, dilute chamber acid is concentrated up to 78% and nitrosyl sulfuric acid (nitrous vitriol) is denitrated by action of water.

The tower acid is drawn off from the bottom of the tower and collected in the container called acid egg. The acid from base of Glower tower is cooled to 40^{0}C by air coolers.

The mixture of SO_2, Oxides of nitrogen and air is then passed to series of rectangular vessels made of lead (lead chamber) having 15-45 meter length, 6-7 meter width and 7 meter length. The number of chambers depends upon the size of plant, but usually they are 3 to 6 in number. The chambers are arranged in two parallel rows. Steam from low pressure boiler or pure filtered water is sprayed from top of the chamber. Mixture of gases is converted into H_2SO_4 having 65-70%v strength is collected at the bottom of the chamber. Dilute sulfuric acid obtained in any of the chamber is called chamber acid. A part of chamber acid is pumped to Glower tower, and the rest is sent forconcentration.

The unabsorbed remaining gases contain oxides of nitrogen and SO_2 from lead chamber are then passed through Gay-Lussac tower at the top of which Glower acid is sprayed to recover oxides of nitrogen.

The oxides of nitrogen recovered in the form of nitroso sulfuric acid are pumped to Glower tower to again regenerate oxides of nitrogen.

When pyrite is used as raw material, the chamber acid may contain arsenious oxide (from pyrite), lead sulfate from lead chamber are removed by treatment of H2S and dilution of acid respectively. Dilute acid may be further concentrated into Glower tower.

.CEMENT MANUFACTURE

MANUFACTURE

It involves the following steps

1. Mixing of rawmaterial
2. Burning
3. Grinding
4. Storage andpackaging

1. Mixing of raw material

Mixing can be done by any one of the following two processes

(a) Dryprocess
(b) Wetprocess

a) DryProcess

Lime stone or chalk and clay are crushed into gyratory crusher to get 2-5 cm size pieces.

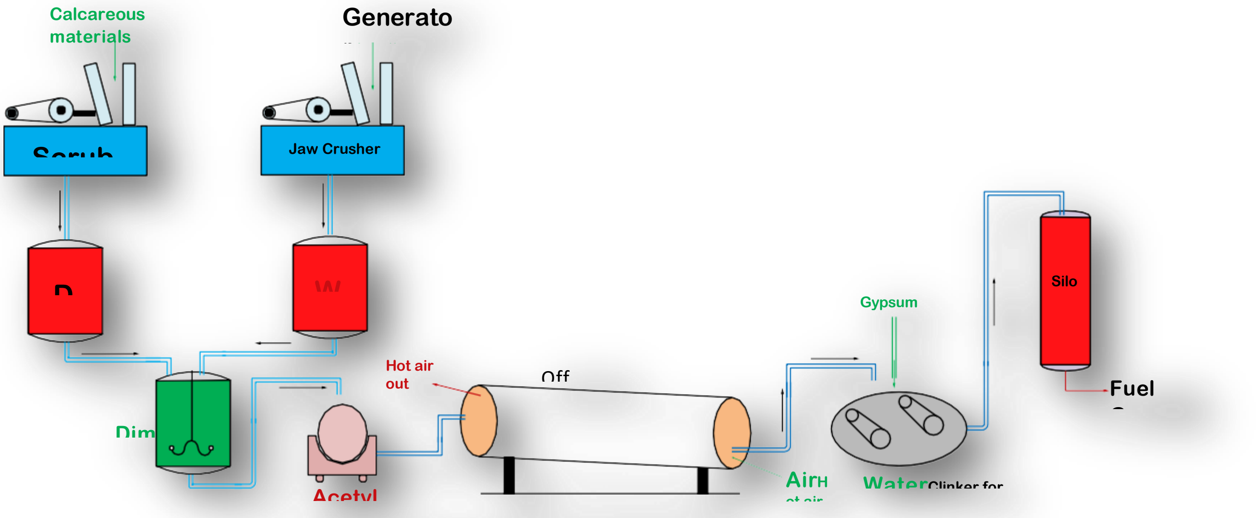

Figure: Manufacturing of Cement by Dry

Crushed material is ground to get fine particle into ball mill or tube mill. Each material after screening stored in a separate hopper. The powder is mixed in require proportions to get dry raw mix which is stored in silos (storage tank) and kept ready to be fed into the rotary kiln. Raw materials are mixed in required proportions so that average composition of the final product is maintained properly.

b) Wetprocess

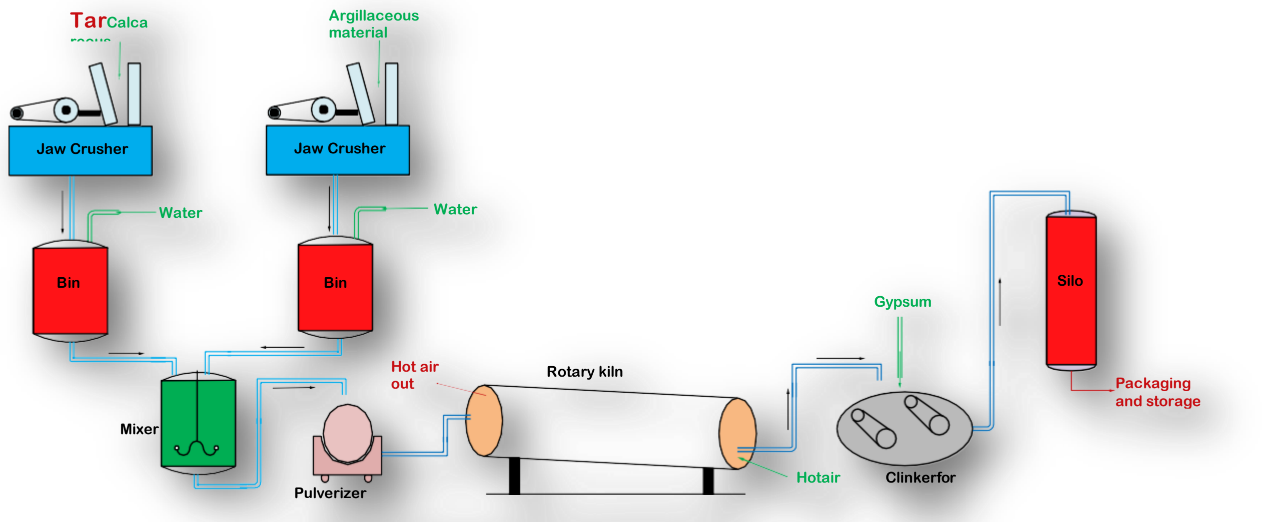

Figure: Manufacturing of Cement by Wet Process

Raw materials are crushed, powdered and stored in silos. The clay is washed with water in wash mills to remove adhering organic matter. The washed clay is stored separately. Powdered lime stone and wet clay are allowed to flow in channel and transfer to grinding mills where they are intimately mixed and paste is formed known as slurry. Grinding may be done either in ball mill or tube mill or both. Then slurry is led to correcting basin where chemical composition may be adjusted. The slurry contains 38-40% water stored in storage tank and kept ready for feeding to a rotarykiln.

Comparison of dry process and wet process

Criteria	**Dry process**	**Wet process**
Hardness of raw material	Quite hard	Any type of raw material
Fuel consumption	Low	High
Time of process	Lesser	Higher
Quality	Inferior quality	Superior quality
Cost of production	High	Low
Overall cost	Costly	Cheaper
Physical state	Raw mix (solid)	Slurry (liquid)

The remaining two operations burning and grinding are same for both the process.

2. Burning

Burning is carried out in rotary kiln which rotating at 1-2 rpm at its longitudinal axis. Rotary kiln is steel tubes having diameter in between 2.5-3.0meter and length varies from 90-

120meter. The inner side of kiln is lined with refractory bricks. The kiln is rested on roller bearing and supported columns of masonry or concrete in slightly inclined position at gradient of 1 in 25 to 1 in 30. The raw mix or corrected slurry is injected into the kiln from its upper end. Burning fuel like powdered coal or oil or hot gases are forced through the lower end of the kiln so long hot flame is produced.

Due to inclined position and slow rotation of the kiln, the material charged from upper end is moving towards lower end (hottest zone) at a speed of 15meter/hour. As gradually descends the temperature is rises. In the upper part, water or moisture in the material is evaporated at 400^{0}C temperature, so it is known as drying zone.

In the central part (calcination zone), temperature is around 1000^{0}C, where decomposition of lime stone takes place. After escapes of CO_2, the remaining material in the forms small lumps called nodules.

$$CaCO_3 \longrightarrow CaO + CO_2$$

The lower part (clinkering zone) have temperature in between 1500-1700^{0}C where lime and clay are reacts to yielding calcium aluminates and calcium silicates. This aluminates and silicates of calcium fuse to gather to form small and hard stones are known as clinkers. The size of the clinker is varies from 5-10mm.

$2CaO+SiO_2 \longrightarrow Ca_2SiO_4$ (dicalcium silicate (C_2S)) $3CaO+SiO_2$
$\longrightarrow Ca_3SiO_5$ (tricalcium silicate(C_3S))

$3CaO+Al_2O_3 \longrightarrow Ca_3Al_2O_6$ (dicalcium aluminate(C_2A))

$4CaO + Al_2O_3+Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10}$
(tetracalciumaluminoferrite(C_4AF))

As clinkers are coming from burning zone, they are very hot. The clinkers are cooled down by air admitting counter current direction at the base of rotary kiln. Resulting hot air is used for burning powdered coal or oil and cooled clinkers are collected in small trolleys or in small rotary kiln.

3. Grinding

Cooled clinkers are ground to fine powder in ball mill or tube mill. 2-3% powdered gypsum is added as retarding agent during final grinding. So that, resulting cement does not settle quickly, when comes in contact with water. After initial set, cement - water paste becomes stiff, but gypsum retards the dissolution of tri-calcium aluminates by forming tricalcium sulfoaluminate which is insoluble and prevents too early further reactions of setting and hardening.

$$3CaO.Al_2O_3+xCaSO_4.7H_2O \longrightarrow 3CaO.Al_2O_3.xCaSO_4.7H_2O$$

4. Storage andpackaging

The ground cement is stored in silos, from which it is marketed either in container load or 50kg bags.

Pretreatments to raw material

- **Wetprocess**

Cement manufacture by wet process used either chalk or lime stone as one of the raw material. Following treatment should be given to them before its use. The remaining procedure after the treatment is same forboth.

Chock should be finely broken up and dispersed in water in a wash mill. The clay is also broken up and mixed with water in wash mill. The two mixtures are now pumped so as to mix in predetermined proportions and pass through a series of screens. The resulting cement slurry flows into storage tanks.

Limestone should be blasted, then crushed, usually in two progressively smaller crushers (initial and secondary crushers), and then fed into a ball mill with the clay dispersed in water. The resultant slurry is pumped into storagetanks.

Impurity profile of raw materials

The amount of different components in Portland cement as oxides is tabulated in table: 1which shows that CaO and SiO2 by far constitute the major part of the finalproduct.About one-third of the raw meal mass can be attributed to Loss on Ignition (LOI), which is almost exclusively due to the calcination of the CaCO3 used as a precursor for forming CaO. This corresponds to the fact that the raw meal contains about 75 wt% of CaCO3.

The mass loss in the calcination process corresponds to a raw meal to cement clinker ratio of about 1.5, if the raw meal is dry when fed into the kiln system. The raw meal composition stated in table: 1 is usually obtained by blending limestone and clay (clay being rich in Si, Fe and Al oxides). If needed, correctives like sand and iron ore can be added to the raw meal in order to achieve the correct composition.

In order to ensure the proper quality of the final product, the amount of certain minor components is limited. Column 4 in table: 1 shows some general upper limits for certain elements, but the exact amount that can be allowed depends on a wide range of factors such as what the cement will be used for, the amount of other impurities, production facilities and so on, which is why the acceptable amount must be determined from case to case. The limits stated in table: 1 cannot be exceeded significantly, and in many cases it is actually desirable to be well beow these limits.

Components	**Content in clinker**	**Content in raw meal**	**Impurity limits**
	Wt. %	Wt. %	Wt. %
CaO	63.8-70.1	~43	
SiO2	19.7-24.3	~14	
Al2O3	3.8-6.8	~4	

Fe_2O_3	1.3-1.6	~5	
MgO	0.0-4.5		5
SO_3	0.2-2.1		4.5
K_2O	0.3-1.8		0.8 as $(NaO_2)e^{*}$
Na_2O	0.0-0.3		0.8 as $(NaO_2)e^{*}$
Mn_2O_3	0.0-0.7		0.5
TiO_2	0.2-0.5		
P_2O_5	0.0-0.3		0.2
CO_2	0.0-0.8		
H_2O	0.0-1.1		
Cl_2			0.1
LOI	0.1-1.6	~34	3

*$(NaO_2)e$, the effective amount of alkali, is calculated as 0.658(%K_2O) + %Na_2O.

Table :1 Composition of Portland cement clinker and raw meal and impurities limit

If the raw materials used in this process contain sulfide, can lead to emissions of SO_2 from the preheater tower. SO_2 emissions are most often caused by the oxidation of pyritic sulfide, which occurs between 300 and 600^{0}C. Of the formed SO_2, around 50% is often said to be emitted from the preheater. However, large variations in this number have been observed, with the circulation of CaO from the calciner given as the main reason for thisphenomenon.

Also, the chlorine level in raw material should be below 0.1% , if it will exceed then free chlorine will accumulate in rotarykiln.

K_2O and Na_2O, known as the alkalis have been found to react with the reactive silica found in some aggregates, the products of the reaction causing increase in volume leading to disintegration of the concrete. The increase in the alkalis percentage has been observed to affect the setting time and the rate of the gain of strength of cement.

SO_3 form low percentage of cement weight. SO_3 comes from the gypsum added (2-6% by weight) during grinding of the clinker, and from the impurities in the raw materials, also from the fuel used through firing process.

MgO, present in the cement by 1-4%, which comes from the magnesia compounds present in the raw materials. MgO by 5%, to control the expansion resulted from the hydration of this compound in the hardened concrete. When the magnesia is in amorphous form, it has no harmful effect on the concrete.

Other minor compounds such as TiO_2, Mn_2O_3, P_2O_5 represent < 1%, and they have little importance.

Engineering aspects Cyclone preheater

The raw materials are preheated or calcined in preheater or series of cyclones before entering to the rotary kiln. A preheater, also called as suspension preheater is a heat exchanger in which the moving crushed powder is dispersed in a stream of hot gas coming from the rotary kiln. Common arrangement of series of cyclones is shown infigure.

The heat transfer of hot kiln gases to raw meal is takes place in co-current. The raw materials are heated upto 800^0C within a less than a minutes. About 40% of the calcite is decarbonated during the heat transfer.

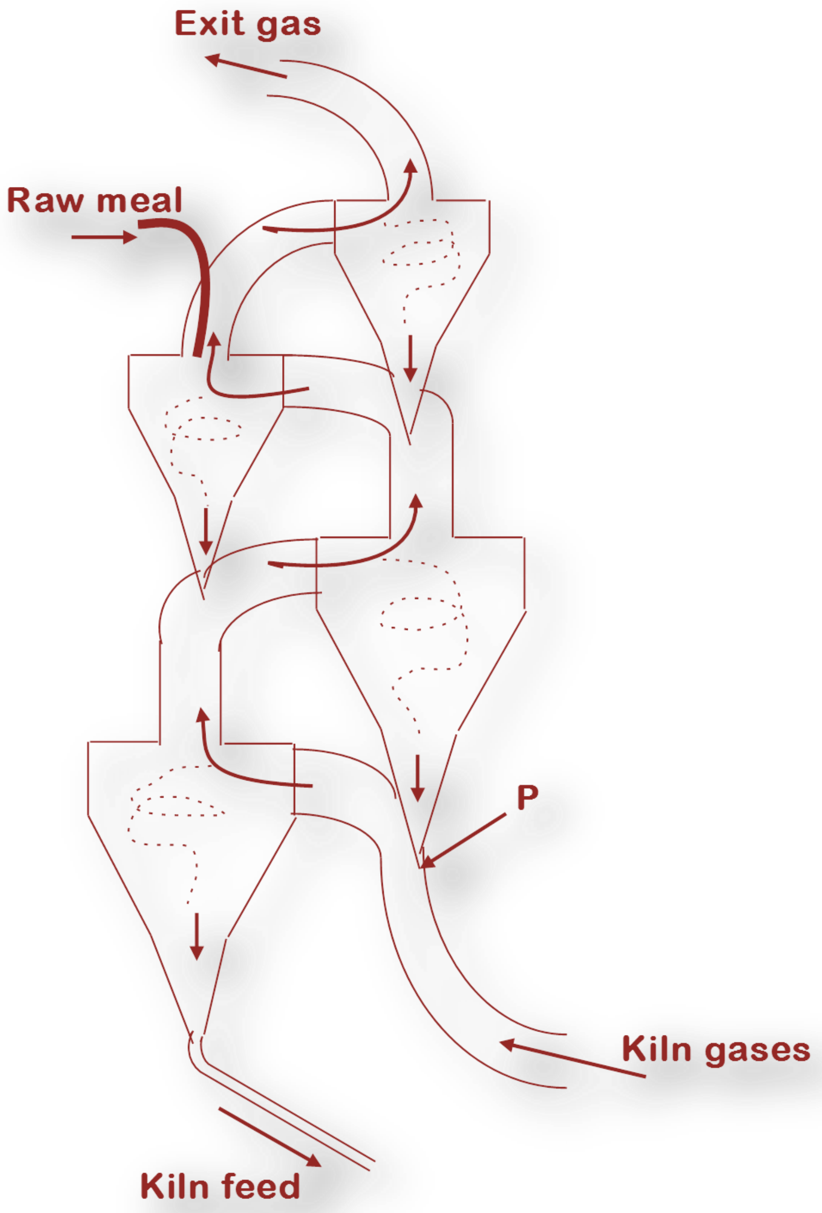

Figure: Cyclone preheaters

The quality and quantity of fuel used in the kiln can be reduced by introducing a proportion of the fuel into preheater. 50 – 65 % of the total amount of fuel is introduced into preheater or precalciner which is often carried out by hot air ducted fromcooler.

The fuel in the precaliner is burnt at relatively low temperature, there so heat transfer to the raw meal is very efficient. The material has residence time in the hottest zone of a few seconds and its exit temperature is about 900^0C, 90 – 95% of calcite is decomposed. Ash from the fuel burn in the precalciner is effectively incorporated into mix.

Advantages of precalination

- Decrease the size ofkiln
- Decrease in capitalcost
- Increase in rate of material passes to thekiln.
- Decrease in rate of heat provided which ultimately lengthens the life of refractorylining
- Less NOx is formed, since much of the fuel is burnt at a low temperature, and with some designs NOx formed in the kiln may be reduced tonitrogen.

Rotary Kiln

Rotary kiln is a tube, sloping at 3 – 4 % from the horizontal and rotating at 1 – 4 revolution/minute into which material enters at the upper end and then slides, rolls and flows counter to the hot gas produced by a flame at the lower or front end.

The kiln is lined with refractory bricks. The type and size of the bricks may vary depending up on the length of rotary kiln and the maximum temperature employed. Further, arranging the bricks in a ring requires perfect closing of the ring which is difficult, time consuming and expensive. Two types of the joints, the radial and axial joints are used for bricks. The redial joints are between the brick in each ring and axial joints are between the successive rings. The bricks are coated with thin layer of clinker for extending the life as well asinsulation.

The rotary kiln used which precalciner is 50 – 100 meter long having length to diameter (L/D) ratio between 10 to 15. The kiln having very small L/D ratio ensures rapid clinker formation and quick reaction run without recrystallization phenomena. Due to this higher hydraulic activity of cement is achieved.

Conveyors

The following types of conveyors are used during the cement manufacturing process.

- Beltconveyor
- Bucketconveyor
- Screwconveyor
- Roll

er conveyor

- **Belt conveyor**

Belt conveyor is used for transportation of raw material form storage to the initial crushing devises mostly jaw crusher. Belt conveyor consists of two or more pulleys, with a continuous loop of material or the conveyor belt which rotates about them. Either one or both of the pulleys are powered, moving the belt and the material on the belt forward. The powered pulley is called the drive pulley while the unpowered pulley is called the idler.

- **Bucket conveyor**

Bucket conveyor are used for transportation of crushed material and clay to mixing zone in cement industries. A bucket conveyor, also called a grain leg, is a mechanism for carrying the bulk materials vertically. It consists of buckets to contain the material, a belt to carry the buckets and transmit the pull, means to drive the belt and accessories for loading the buckets or picking up the material, for receiving the discharged material, for maintaining the belt tension and for enclosing and protecting theelevator.

- **Screwconveyor**

A screw conveyor or auger conveyor is a mechanism that uses a rotating helical screw blade, called a "flighting", usually within a tube, to move liquid or granular materials. Screw conveyors are often used horizontally or at a slight incline as an efficient way to move semi-solid materials. Screw conveyor are used for transportation of material for storage to homogeneous siloes.

- **Rollerconveyor**

Roller conveyors are line restricted device and consist of rollers mounted between two side members. Bearings are usually incorporated in the idlers to cut down the mechanical losses. An unpowered gravity roller conveyor is set at an appropriate incline and goods move down it by gravity. In power unit normally an electric motor drive the rollers via chains or belt, providing controlled movement of goods. They are generally used for transportation of packed material.

PROPERTIES

- Cement-modification improves the properties of certain silt clay soils that are unsuitable for use in subgrade construction. The objectives may be to decrease the soil‘s cohesiveness (plasticity), to decrease the volume change characteristics of expansive clay, to increase the bearing strength of a weak soil, or to transform a wet, soft subgrade into a surface that will support constructionequipment.
- **Tricalcium Silicate (C3S):** Hardens rapidly and is largely responsible for initial set and early strength. In general, the early strength of Portland cement concrete is higher with increased percentages ofC3S.
- **Dicalcium Silicate (C2S):** Hardens slowly and contributes largely to strength increases at ages beyond 7days.

- **Tricalcium Aluminate (C3A):** Liberates a large amount of heat during the first few days of hardening and together with C3S and C2S may somewhat increase the early strength of the hardening cement. It affects settingtime.
- **TetracalciumAluminoferrite (C4AF):** Contributes very slightly to strength gain. However, acts as a flux during manufacturing. Contributes to the colour effects that makes cementgray.

CEMENT CLASSIFICATION

7. Puzzolanacement

Puzzolana is a volcanic powder. It is found in Italy near Vesuvius. It resembles surkhi which is prepared by burning bricks made from ordinary soils. It can also be processed from shales and certain types of clays. Puzzolana material should be used in between10 to30%.

Advantage

- Evolves less heat duringsetting
- Possesses higher tensilestrength
- Imparts higher degree of watertightness
- Attains comprehensive strength withage
- Can resist action ofsulfates
- Imparts plasticity and workability to mortar and concrete prepared fromit.
- Offers great resistance toexpansion
- It ischeap

Disadvantages

- Compressive strength in early days isless
- Possesses less resistance to erosion and weatheringaction

This cement is used to prepare mass concrete of lean mix and for marine structures. It is also used in sewage works and for laying concrete under water.

8. Hydrophobiccement

It contains hydrophobic admixtures such as acidol, naphthelene soap, oxidized petroleum etc., which decrease the wetting ability of cement grains and form a thin film around cement grains. When water is added to hydrophobic cement, the absorption films are torn off the surface and they do not in any way, prevent the normal hardening of cement. However, in initial stage, the gain in strength is less as hydrophobic films on cement grains prevent the interaction with water. However, its strength after 28 days is equal to that of ordinary Portland cement.

When hydrophobic cement is used, the line fine pores in concrete are uniformly distributed and thus the frost resistance and the water resistance of such concrete are considerably increased.

9. Expandingcement

It is produced by adding an expanding medium like sulfoaluminate and establishing agent to ordinary cement. Hence this cement expands whereas other cements shrink.

It is used for the construction of water retaining structures and for repairing the damaged concrete surfaces.

10. Low heatcement

Considerable heat is produced during the setting action of cement. It contains lower percentage of tricalcium aluminate (C3A) and higher percentage of dicalcium silicate (C2S) which reduce the amount of heat produced.

This type of cement possesses less compressive strength. Initial setting time is about one hour and usual setting time is about 10 hours. It is mainly used for mass concrete work.

11. Quick settingcement

It is produced by adding a small percentage of aluminium sulfates and by finely grinding the cement. Percentage of gypsum or retarder for setting action is also greatly reduced. Addition of aluminium sulfate and fineness of grinding accelerate the setting of cement. The setting action of cement starts within five minutes addition of water and it becomes hard like stone in less than 30 minutes. Mixing and placing of concrete should be completed within very short period. This cement is used lay concrete under static water or running water.

12. Sulfate resistingcement

In this cement percentage of tricalcium aluminate is kept below 5 to 6% which increase in resisting power againstsulphates.

CEMENT

CHEMICAL COMPOSITION

According to IS: 269-1975, composition of ordinary Portland cement should satisfy the following conditions

- Ratio of percentage of lime to that of silica, alumina and iron oxide shall be in between 0.66 - 1.02 which is calculated by the formula asfollow

- Ratio of percentage of alumina to that of iron oxide shall not be less than0.66
- Weight of insoluble residue shall not exceed2%
- Weight of magnesia shall be less than6%

- Total sulfur content shall not be more than2.75%
- Total loss on ignition shall not exceed4%.

PHYSICAL REQUIREMENT

Setting time

Initial : Not less than 30 minutes Final
: Not more than 600minutes

Compressive strength

Compressive strength of 1:3 cement mortar cube of cement and sand.

3 days : Not less than1.6 kg/mm^2 7 days : Not less an .2 kg/mm^2

Soundness

It expresses the expansivity of the cement set in 24 hours between 25^{0}C and 100^{0}C.

Un-aeratedcement : Maximum
10mm Aeratedcement : Maximum5mm

Fineness

It should not less than 215m^2/kg

SETTING AND HARDENING OF CEMENT

The setting and hardening of cement is due to hydration and hydrolysis of its constituents. The hydration products of cement are cementious but not cement. The heats of hydration of cement constituents decides the formulation of cement for different applications as well as useful in preventing the water in cement paste from freezing in winter and in accelerating the setting and hardening processes. If heat liberated is not dissipated rapidly particularly in large constructions like dam serious stress cracking may occur. Further, the knowledge of reaction speed is important, because it determines the time of setting and hardening.

On hydration, the cement constituents generally give rise to hydrated calcium silicate (CSH) obtained as poorly crystallized gels (3CaO.3SiO23H2O) commonly known as tobermorite gels having structural resemblance to the mineral tobermorite found in Tobermory, Scotland.

When cement is gauged with water, the C3A, C3S and C3SF phases reacts very rapidly and gauging water becomes saturated with Ca(OH)2 formed in hydration reactions. The C2S phase hydrated rather slowly. The initial settling is attributed to the reaction of C3A, C3S andC3AF.

When the cement powder comes into contact with the water in the paste, two phenomena takes place

- Setting: After 25hours
- Hardening: After one year, but proceeds to completion only afterdecades

The reactions take place when cement first comes into contact with water, are as follows

$C3A+6H2O \longrightarrow C3A.6H2O$ ------------------------ (1)

$C3AF+nH2O \longrightarrow CF.(n-6)H2O+C3A.6H2O$ ------ (2)

$C3S+H2O \longrightarrow C2S+C.H2O$ ------------------------ (3)

The fluxes are therefore the first components to be hydrated, with evolution of large amount of heat. The alite react after few hours of contact with water.

During the second stage setting process stops and the hardening process starts. Hardening involves both the reaction in which tetracalcium aluminate hydrate.

is formed and the hydration of the original belite after dicalcium silicate formed in reaction (3) has been hydrated

$C3A.6H2O + C.H2O + 6H2O \longrightarrow C4A.13H2O$ ---- (4)

$C2S+nH2O \longrightarrow C2S.nH2O$ ---- (5)

Reaction (5) takes place between setting and hardening, while the same reaction is much slower in case of belite present in the clinker, and components manufactured from the cement attain their definitive compactness and mechanical strength after one year.

Overall, the water in the cement paste, which initially served to soak it and to make it fluid, is consumed by the cement at certain rate, depending on its structural characteristics, which bring hydrolysis of cement constituents, act as water of crystallization via hydration reaction and in promotion of colloidal phenomena

Reaction (4) tends to occur on its own at the expense of the free lime in the surroundings as the lime which is formed in reaction (3) is insufficient, at least at the start, to furnish large amounts of calcium hydroxide demanded by high rate of reaction (1) which leads to the promoter (C3A.6H2O) of reaction (4) itself.

However, when there is shortage of free lime, decalcification of dicalcium silicate occurs into compounds which are poorer in lime (C3S2 and CS type) which by hydration more rapidly than C2S to form. To avoid these serious irregularities in the hardening and setting of the cement, it is necessary to preclude the environment from becoming a large consumer of C.H2O by improving it from the C3A.6H2O which is formed by reaction(1)

$C_3A.6H_2O + 3CaSO_4.2H_2O + 19H_2O C_3A.3CaSO_4.31H_2O$------------- (6)

Gypsum is capable of combining with tricalcium aluminate hydrate as in reaction (6). The calcium sulfoaluminate which is formed concurrently with $C_4A.13H_2O$ from reaction (4) indirectly stabilize the C_2A, and moreover can be leadvia reaction (5) to mass getting the highest possible mechanical properties. For, these reasons, gypsum is considered as an essential additive with the aim of regularizing the setting and hardening ofcement.

Further, the setting properties of cement depend on the proportions of alumina and ferric oxide in it, greater proportion of these bringing about acceleration of setting process. The setting time to the cement is controlled by grinding about 2-5% of gypsum with the cement clinker. The setting time is not directly influence by gypsum; a small increase beyond limit, it may produces large increase in setting time, also large amount of it leads to cracking of set cement due

to expansion. Plaster of Paris and anhydrite also retard the setting of cement but they are more vigorous in theiraction.

Among the substances that affect the setting time of Portland cement containing gypsum as retarder, some retard the process (sugar) and some accelerate the process (CO_2, Alkali carbonates &chlorides and alkaline-earth metals except Ca, NaOH, KOH etc.), some retard the set at low concentrations and accelerate the process at high concentrations ($CaCl_2$, NH_4Cl, $FeCl_3$ etc.)

USES

- In the production of concrete, it plays a crucial role in setting and hardening theconcrete.
- On being mixed with other aggregates, Portland cement begins to serve a dual purpose. First, it provides for the concrete products to be workable when wet and second, it provides them to be durable whendry.
- It is also brought into usage in mortars, plasters, screeds and grouts as a material which can be squeezed into gaps to consolidate thestructures.
- Civil (piers, docks, retaining walls, silos, warehousing, poles, pylons,fencing)
- Building (floors, beams, columns, roofing, piles, bricks, mortar, panels,plaster)
- Transport (roads, pathways, crossings, bridges, sleepers, viaducts, tunnels, stabilization, runways,parking)
- Agriculture (buildings, processing, housing, feedlots,irrigation)
- Water (pipes, culverts, kerbing, drains, canals, weirs, dams, tanks,pools)
- Used by the retaining walls and the precast concrete block walls as a major component to build a strong foundation ofconcrete.
- By mixing it with water, Portland cement literally turns into a plastic stone and thereby it can be used for purposes and in places where stone was to be used and that too by keeping within the financiallimits.
- Concrete casing, made by utilizing Portland cement, they can be effectively protect the surface from air, water orcorrosion.

- Due to its ability to prevent corrosion, it is also put to use in ships, tanks and bunkers.
- It may be moulded to obtain a hard and fire-proof material which may be employed in designing buildings, shop floors, reservoirs and otherfoundations.
- Any structure that is meant to support huge amounts of weight will bring Portland cement into use. These structures range from ground floors of multi- storey buildings to bridge floors and from bridge spans todams.
- A blaze or an overwhelming fire may leave a structure completely burnt but with the use of Portland cement, this can beprevented.
- GLASS INDUSTRIES

INTRODUCTION

When silica or quartz is heated up to 1650^0C it melts to a colourless liquid which on cooling gives glass. This fused mass is highly sensitive to temperature change therefore it requires special heat treatment so that ordinary glass can be manufacture which is much stable to temperature change. The glass of various commercial qualities is prepared by heating sand or quartz along with metal oxide orcarbonates.

TYPES OF GLASSES

1. Soda-lime or softglasses

The raw materials are silica (sand), calcium carbonate and soda ash. Their approximate composition is Na2O.CaO.6SiO2. About 90% of all glasses produced belong to soda lime glass. The low cost, low melting point soda-lime glass has resistant to de-vitrification and to water. However, they have poor resistance to common reagents like acids.

Uses: They are used as window glass, electric bulbs, plate glass, bottles, jars, building blocks and cheaper tablewares, where high temperature resistance and chemical stability are required.

2. Potash-lime or hardglasses

Silica (sand), calcium carbonate and potassium carbonate are the basic raw material for potash lime glass. Their approximate composition is K2O.CaO.6SiO2. They possess high melting point, fuse with difficulty and have good resistance to acids, alkalis and other solvents compare to ordinary glasses.

Uses: These glasses are costlier than soda-lime glasses and are used for chemical apparatus, combustion tubes, etc., which are to be used for heating operations.

3. Lead glass or Flintglass

Instead of calcium oxide, lead oxide is fused with silica. As much as 80% of lead oxide is incorporated for dense optical glasses. In addition, K2O is used instead of sodium oxide. So, its approximate composition isK2O.PbO.6SiO2. Lead glass is more expensive than ordinary lime-soda glass, but it is much easier to shape and to work with. Lead glass has a lower softening temperature and higher refractive index than soda glass. It has excellent electrical properties. It is bright, lustrous and possesses high specific gravity (3 to 3.3).

Uses: Lead glasses are used for high quantity table wares, optical lenses, neon sign tubing, cathode ray tubes, electrical insulators and in the art objects because of their high luster. High lead content glasses are used for extra dense optical glasses, for windows and shields to protect personnel from X-rays and gamma rays in medical and atomic energy fieldsrespectively.

4. Borosilicate glass or Pyrex glass or Jenaglass

It is the most common of the hard glasses of commerce which contain virtually only silica and borax with a small amount of alumina and still less alkaline oxides. Borosilicate glass has the followingcomposition.

Component	SiO_2	B_2O_3	Al_2O_3	K_2O	Na_2O
Percentage	80.5	13	3	3	0.5

Boron and aluminium oxides substitutes Na_2O and CaO used the lime-soda glasses which results in a glass of low thermal coefficient of expansion, and high chemical resistance. Borosilicate glasses have a very much higher softening point and excellent resistivity to shock.

Uses: They are used in pipelines for corrosive liquids, gauge glasses, superior laboratory apparatus, kitchenwares, chemical plants, television tubes, electrical insulators etc.

5. 96% Silicaglass

It is produced and shaped as typical borosilicate glass, having dimensions bigger than desired. The heat treatment to the article, separate the glass into two layers, one consisting mainly of silica and the other of the alkali oxides and borates. Then article is dipped in hot acid which dissolves away the alkali oxides and boron oxide layer, leaving behind a fine porous structure consisting of about 96% silica, 3% B_2O_3 and traces of other materials. This glass is then washed carefully and annealed to 1200^0C. The shrinkage of about 14% takes place and hard firm shape is produced which is almost gaslight. The translucent 96% glass, if it is so desired heated to a higher temperature and made almost transparent orclear.

It is expensive than other types of glasses. The expansion coefficient is very low which accounts for its high resistance to thermal shot. The softening temperature is about 1500^0C. They possess high chemical resistance to most corrosive agents. They are corroded by only HF, hot H_3PO_4 and concentrated alkalinesolutions.

Uses: They are used where high temperature resistance is required and articles can be safely used at temperature up to 800^0C. They are used for the constructed chemical plants, laboratory crucibles, induction furnace linings, electrical insulators.

6. 99.5% silica glass orVitreosil

It is produced by heating SiO2 to its melting point (1,750^{0}C). Because of absence of fluxing agents, it is extremely difficult to get rid of the bubbles. Shaping of the glass is difficult due to high viscosity at its working temperature. The final product is translucent. It has high softening temperature about 1650^{0}C, compare to 96% silica glass. Its thermal expansion is very low. Due to their opaque nature, they tend to be mistaken for pipe when dirty and are, therefore, often broken accidentally.

If vitreosil glass is heated for long periods above its melting point, it finally becomes transparent and is then known as ―clear silica glass‖. It has considerable transmission properties e.g. 1mm of this material allows no less than 93% of light to pass corresponding figure for good optical glass is only 6%.

Uses: uses are similar to 96% silica glass. It is exposed for the construction of pipelines for hot concentrated acid. Clear silica glass is used mainly for plant ware, chemical laboratory wares, electrical insulating materials, and in electrical heat furnaces.

7. Alumino-silicateglass

They possess exceptionally high softening temperature and having the typical constituent as follow

Component	SiO2	Al2O3	B2O3	MgO	CaO	Na2O & K2O
Percentage	55	23	7	9	5	1

Uses: it is used for high pressure mercury discharge tubes chemical combustion tube, certain domestic equipment etc.

8. Safetyglass

Thin layer of vinyl plastic is introduced between two or three flat sheets of glass and the whole is subjected to slight pressure. It is then heated till the glass layers and plastic layers merge into one another to give a sandwich. On cooling the glass becomes quite tough. When such a glass breaks it does not fly into pieces as the inner plastic layer tends to hold back the broken pieces of theglass.

Uses: It is mostly used in automobile and aero plane industries as wind shield.

9. Optical or Crookesglasses

They contain phosphorus and lead silicate, together with a little cerium oxide, is capable of absorbing harmful UV light. Very careful manufacturing process of

heating the molten mass for prolonged time secured the homogeneity of the glass. In general optical glasses have low melting points and are relatively soft. Their chemical resistant and durability are appreciably lower than those of ordinary glasses.

Uses: Used for manufacture of lenses.

10. Polycrystalline glass orPyroceram

It is the most recent development of producing glass by adding one or more nucleating agents to a special or convectional glass batch. Then it is shaped into desired form and subjected to controlled heat treatment.

The nucleating agents induced the formation of a large number of sub- microscopic crystalline which act as centers for further crystal growth. Crystalline glass is not ductile, but it has much greater impact strength than ordinary glass. It exhibits high strength and considerable hardness and can be formed and shaped into articles by any methods of manufacturing.

11. Toughenedglass

It is made by dipping articles still hot in an oil bath, so that certain chilling takes place. There so, outer layers of the articles shrink and acquire a state of compression; while the inner layers are in a state of tension. Such a glass is more elastic and capable of withstanding mechanical and thermal shocks. When such a glass breaks, it does not fly but is reduced to fine powder.

Uses: It is used for window shields of fast moving vehicles like cars, trucks, aeroplane; window shields of furnaces, automatic opening doors and large show cases.

12. Insulatingglass

It is a transparent unit prepared by using two or more plates of glass separated by 6-13 mm thick gap, field up with dehydrated air and then thematically sealing around the edges. This provides a high insulation against heat. Thus, if such a glass is used for separating apartments, it does not transmit heat and consequently the apartments will remain cool during summer and warm during winter.

Uses: It is used as thermal insulating materials

13. Wiredglass

It is formed by embedding a wire mesh at the center of the glass sheet during casting due to this when glass breaks it do not fall into splinters. Additionally, it is more fire resistant than ordinaryglass.

Uses: It is used mainly for making fire-resisting doors, windows, skylights, roofs

14. Laminatedglass

It is made by pressing or bonding together two or more sheets /plates of glass with one or more alternating layer of bonding material like plastic resin, asphalt or synthetic rubber.

The essential qualities of the laminated glass are

- It is shatter-proof, i.e. its pieces do not fly off when suddenlybroken.
- It is shock-proof, i.e. it can with stand sudden changes of temperature and pressure withoutbreaking.

A bullet-resistant laminated glass is manufactured by pressing together several layers of glass with vinyl resins in alternate layers. Ordinary, thickness of such glass varies from 12.7 mm - 76.5 mm. Even thicker types are made for specificuses.

Uses: As safety glass in aircrafts, automobiles, helicopters, submarines. Bullet resistant lamination glass finds application in making automobile wind screens, looking windows etc.

15. Glasswool

It is a fibrous wool-like material composed of intermingled fine threads or filaments of glass which is completely free from alkali. Glass filaments are obtained by forcing molten mass of glass through small orifice of average diameter of 0.005 - 0.007mm continuously which is sent to rapidly revolving drum resulting in wool like form. It has low electrical conductivity and eight times higher tensile strength than steel. It does not absorb moisture and it is completely heatproof.

Uses: It is employed for heat insulation purpose, e.g., insulation of metal pipe lines, motors, vacuum cleaners, walls and roofs of houses. Being resistant to chemicals, glass wool is used for filtration of corrosive liquids like acids and acidic solution. It is used for electrical and sound insulation. It is also employed in air filter as dust filtering material. It is also used for manufacturing fiber-glass, by blending with plastic resins.

16. PhotosensitiveGlass

It is UV sensitive high alumina soda lime glass. The positive in UV region on glass is developed by thermal treatment only at 540-550°C. The desired photo activity in UV region can be obtained by admixture of high alumina soda lime glass with small amounts of Cu_2O $NaCN.SnO_2$ and abeitic acid in appropriate amounts. A blue colour is promoted by NaCN absence of tin oxide. In presence of tin oxide an impression in red is observed. By manipulation the ingredients in glass, brown and yellow images can also be possible. A potash alumina glass mixed with $LiSiO_3$, cerium andsilver,saltsinappropriateproportionshavealsobeenusedasphotosensitive glass.

17. Photochromicglass

Large number of microscopic particles of silver halides trapped in the three dimensional silicate networks in fixed concentration. On exposure light, temporary colour centers consisting of silver particles only are produced and these add quickly producing total darkness. The intensity of darkness depends upon the concentration of silver. Because reversible darkening is controlled by the radiations in the UV region quite abundant in day light, the photo blackening does not occurs markedly in the lamp light night.

18. Fiber glass

Fiber glass is nothing but molten glass process mechanically to a flexible thread of filament. A hot platinum nozzle filled with molten glass forces out the fluid in the form of a thin continuous thread which when caught by a rapidly moving disc gets converted into fiber through elongation and twist given by the disc fabrics made of glass are bad conductors of heat and electricity and are noninflammable. Hence articles made of fiber glass are fireproof.

Uses: Such type of glass is used in textiles and reinforcing and can be spun into yarn, gathered into a mat, and made into insulation and a great variety of other products may be with it.

MANUFACTURE OF GLASS

RAW MATERIAL

The raw material in manufacture of glass may be selected from the following.

Sand, soda ash, calcium oxide, fled spar, borax, magnesia, zinc, alumina, lead oxide, manganese oxide, selenium metal, broken glass, fluxes, colouring agent, reducing agent, oxidizing agentetc.

Oxide should satisfy following conditions

- Every oxygen atom must be attached with 2-4 cations e.g. SiO_2, B_2O_3, GeO_2, P_2O_5 and As_2O_5
- The oxygen polyhedral must share the corner position and not theedge.
- At least three corners of each tetrahedron must beshare.

The oxides used for glass manufacture are classified into following groups

a) Networkformer
b) Networkmodifier
c) Intermediate glassformers
d) Oxidizingagent
e) Refiningagent
f) Cullet
g) Colouringagent

a) Network former

These are oxides of elements which are surrounded by four oxygen atoms in the tetrahedral chain forming glass.

b) Networkmodifier

These are large diameter elements having higher co-ordination number. On simple melting they do not give glass but in presence of other network forming oxides they can give glassy products easily. The important network modifiers are oxides of alkali metal, alkaline earth metals, lead, zincetc.

Intermediate glass formers

They do not give glass on melting but in presence of some network formers using their co-ordination number they start giving glass. E.g., Oxides of aluminum, silica

c) Oxidizingagent

Material like sodium nitrate or certain peroxides are used to reduce the colour of impurities like iron oxides and manganese oxide

d) Refiningagent

To reduce or to eliminate quantity of air bubbles from molten glass refining agents like arsenic oxide or small amount of feldspar is added to glass.

e) Cullet

Waste or broken glass species are called cullet. In normal glass production 33% of charge is broken glasses. Recycling of cullet increases the rate of production.

f) Colouringagent

Metal oxide is added as colourant during manufacture of colour glasses e. g. oxides of chromium and iron give green glass while copper and cobalt give blue glass.

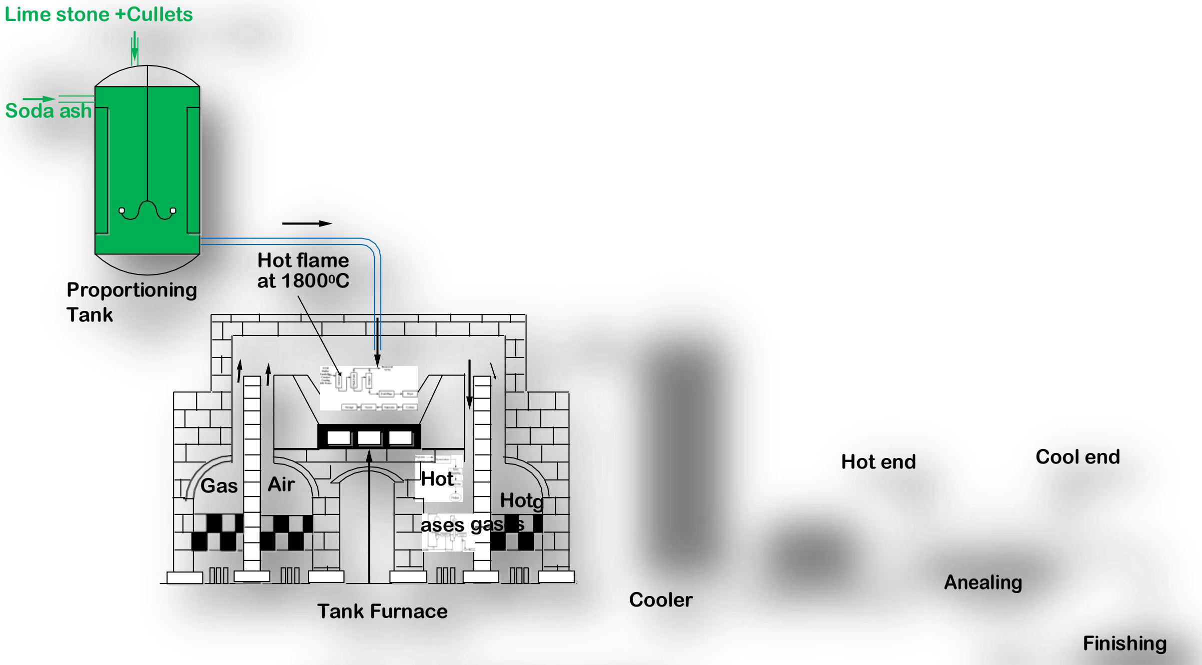

Figure :Manufacture of Glass

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SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 3 INDUSTRIAL GASES AND PAINTS- SCHA1305

CARBON DIOXIDE

INTRODUCTION

Carbon dioxide (CO_2) is composed of two oxygen atoms covalently bonded to a single carbon atom. It is a trace gas with a concentration of 0.039% by volume in atmosphericair.

In the seventeenth century, Jan Baptist Van Helmont observed that during burning of charcoal in the closed vessel, the mass of the resulting ash was much less than that of the original charcoal. His explanation was that the rest of the charcoal had been transmuted into an invisible substance termed as "gas" or "wild spirit"

Carbon dioxide‘s properties were studied by Joseph Black in 1750. He found that limestone could be heated or treated with acids to yield a gas (fixed air). He observed that gas was denser than air and supported neither flame nor animal life. Black also found that when bubbled through an aqueous solution of lime, it would precipitate calcium carbonate. Based on this phenomena he illustrate that CO_2 is produced by animal respiration and microbial fermentation. Joseph Priestley, in 1772 invented the soda water preparation by dripping sulfuric acid on chalk in order to produce carbon dioxide, and forcing the gas to dissolve by agitating a bowl of water in contact with the gas. Humphry Davy and Michael Faraday first liquefied CO_2 at elevated pressure in 1823. While in 1834 Charles Thilorier solidifies CO_2, in pressurized container of liquid carbondioxide.

In higher animals, the carbon dioxide travels in the blood from the body's tissues to the lungs where it is breathed out. CO_2 is an end product in organisms that obtain energy from breaking down sugars, fats and amino acids with oxygen as part of their metabolism, in a process known as cellular respiration. This includes all plants, animals, many fungi and some bacteria. During photosynthesis, plants, algae, and Cyanobacteria absorb carbon dioxide, light, and water to produce carbohydrate energy for themselves and oxygen as a waste product. However, in darkness, photosynthesis cannot occur, and during the resultant respiration small amounts of carbon dioxide are produced.

Carbon dioxide is also produced by combustion of coal or hydrocarbons, the fermentation of liquids and the breathing of humans and animals. In addition, it is emitted from volcanoes, hot springs, geysers and other places where the earth‘scrust is thin; and is freed from carbonate rocks by dissolution. CO_2 is also found in lakes at depth under the sea, and commingled with oil and gas deposits.

SOURCES OF CO2

- By burning of carbonaceousmaterials

$C+O_2 \longrightarrow CO_2$ (10 to18% Pure) $\Delta H = -23.16$kcals

- In the production of H_2 by steam water gas 16% pure CO_2 isobtained.
- In manufacture of alcohol (ethanol) by the fermentation process. 99.9 % pure CO_2 isobtained.
- In calcinations of $CaCO_3$ 40% CO_2 isobtained

1000°C

$CaCO_3 \longrightarrow CaO + CO_2(40\%)$

MANUFACTURE

Raw materials

Coke
or coal
Air

Reaction

$C+O_2 \longrightarrow CO_2$ (10 to18% Pure) $\Delta H = - 23.16$kcals

Manufacture

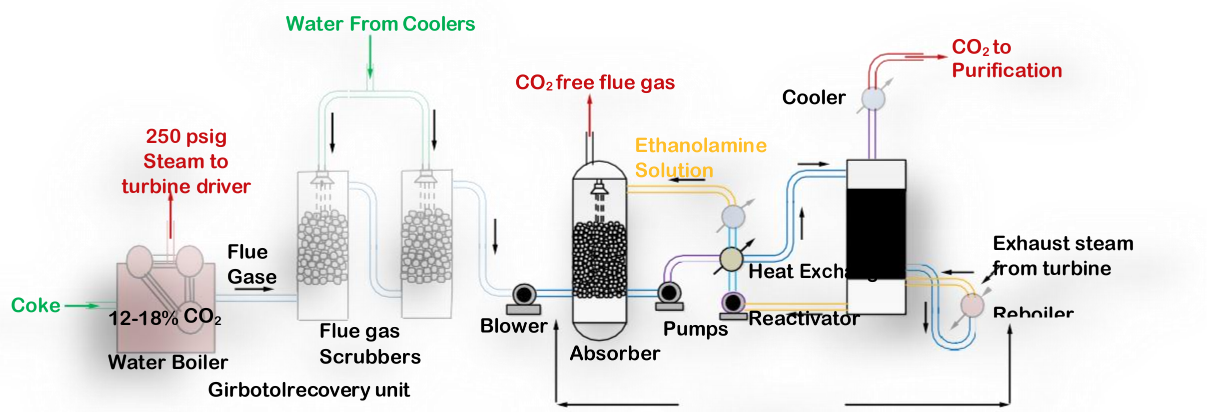


Figure: Manufacture of Carbon dioxide from Coke

Coke, coal, fuel or gas is burned under a standard water-tube boiler for the production of 200-250psig steam. The flue gases containing 10-18% CO_2 are taken from the boiler at 345^{0}C and passed through two packed towers where they are cooled and cleaned by water. After passing through the scrubbing towers, the cooled flue gases pass through a booster blower and into the base of the absorption tower in which CO_2 is absorbed selectively by a solution of ethanolamines passing countercurrent to the gas stream. CO2 free flue gases are exhausted to atmosphere from top of the tower. The CO2 bearing solution passes out of the bottom of the absorption tower are sprayed from the top of a reactivation tower. Where CO2 is stripped from the amine solution by heat and the reactivated solution returns through the heat exchanger equipment to the absorption tower. CO2 and steam pass out through the top of the reactivation tower into a gas cooler in which the steam condenses and returns to the tower as reflux. CO2 gas is stripped out at the pressure of about 300 psig. If liquid or solid CO2 is desired, it may be further purified for odour removal beforecompression.

Energy economics

All the pumps and blowers and turbine are driven by high pressure steam from the boiler. The low-pressure exhaust steam is used in the reboiler of the recovery system and the condensate returns to the boiler. Although there is some excess power capacity provided in the high-pressure steam for driving other equipment, such as compressors in CO2 liquefaction plant, all the steam produced by the boiler is condensed in the recovery system. This provides a well-balanced plant in which few external utilities are required and combustion conditions may be controlled to maintain efficientoperation.

METHODS OF RECOVERY

The processes most commonly used for recovery of carbon dioxide are

1. Ethanolamineprocess
2. Sodium carbonateprocess
3. Potassium carbonateprocess

All the processes are in commercial use and choice of suitable process will depend on the individual conditions. In all the process CO2 is recovered by absorption-desorption. First CO2-bearing gases are passed countercurrent to a solution that removes the CO2 by absorption and retains it until desorbed by heat in a separate piece of equipment. Due to relatively low water solubility of CO2, water alone is not used as a absorption medium. Alkali carbonate and ethanolamine solutions are used due to the higher solubility of CO2 with the absorbingmedium.

1. Girbotol amineprocess

It was developed by the Girdler Corporation of Louisville, Kentucky. The various operation used in the process are discussed earlier during the manufacture of CO2 from coke. The process uses aqueous solutions of an mono-, di- or tri- ethanolamine as absorptionmedium.

$$2OHC2H4NH2 + H2O+CO2 \rightleftharpoons (OHC2H4NH3)2CO3$$

The operation are depends on the reversible nature of the above reaction. Forward reaction proceeds at low temperatures (65^{0}C) and absorbs CO2 from the gas in the absorber. The amine solution, rich in CO2, passes out of the bottom of the tower and through heat exchanger, where it is preheated by hot, lean solution returning from the re-activator. Then solution passes countercurrent to a stream of CO2 and steam, which strips CO2 out of the solution. As the solution reaches to bottom of the tower, where heat is supplied by a steam heated or direct fired re-boiler, it has been reactivated. This hot solution (140^0C) passes out of the tower, through the heat exchanger and cooler, and returns to the absorber tower. In the case of flue gases containing oxygen, small side stream of solution is passed through re-distillation unit, where the oxidation products are removed and the distilled amine is returned to the process.

Advantages

- Complete removal of carbondioxide
- Regeneration up to 100% with moderate steam consumption ispossible
- Higher absorption of CO2 in thesolution
- Lower operatingcost

2. Sodium carbonateprocess

$$Na2CO3 + H2O + CO2 \rightleftharpoons 2NaHCO3$$

Recovery of pure carbon dioxide from gases containing other diluents, such as nitrogen and carbon monoxide, is based on the reversibility of the above reaction. This reaction proceeds to the right at low temperatures and takes place in the absorber where the CO2 bearing gases are passed countercurrent to sodium carbonate solution. CO2 absorption rate depends up on temperature, pressure, partial pressure of CO2 in the gas, and solution strength. Reverse reaction will proceed when heat is applied and is carried out in lye boiler. A heat exchanger serves to preheat the strong lye as it approaches the boiler and cool the weak lye returning to the absorber. Additional weak lye cooling is accomplished in lye cooler to permit the reaction to proceed further to the right in the absorber. CO2 gas and water vapour released from the solution in the boiler pass through steam condenser where the water condenses out and returns to the system. The cool CO2 proceeds to the gas holder andcompressors.

Engineering aspects

Absorber

Absorber is constructed by a carbon-steel filled with coke, raschig rings, or steel turnings. The weak solution is spread from top of the bed and contacts the gas intimately on the way down. In another variation tower filled with sodium carbonate solution and allow the gas to bubble up through the liquid.

Later provides better gas and liquid contact but high power is required to force the gas through the tower.

Lye boiler

The lye boiler may be a direct fired boiler or a steam heated boiler. The separation efficiency may be increased by adding a tower section with bubble-cap trays. For better efficiency and conversion, series of absorbers are used and designed to re-circulate the lye over it and only 20-25% of solution flowing over this tower passes through the lyeboiler.

3. Potassium carbonateprocess

As potassium bicarbonate has more solubility than its corresponding sodium salt, it provides better absorption of CO_2 than other process. Operation and equipment layout of process are similar to sodium carbonate process.

Variations of the potassium carbonate process have come into commercial use in recent years.

Hot potassium carbonate process

Absorbent solution flows directly from the lye boiler to the absorber without cooling. This process used for removing CO_2 from NH_3 synthesis gas mixtures, and from natural gas. These gas streams are treated at 250 psig, or higher pressure which increases the partial pressure of CO_2 so that the hot K_2CO_3 solution (20-30%) will absorb substantial amount of CO_2 at 110^0C. The solution sends to the CO_2 stripping tower operating at or near atmospheric pressure. Part of the absorbed CO_2 flashes out of the solution as it enters the stripping tower, and the balance is stripped from the solution by steam. The overall energy requirements for CO_2 recovery by the hot carbonate process are lower than for other processes when the gases being scrubbed have high carbon dioxide partialpressures.

Use of additives

This variation has been developed by Vetrocoke in Italy. Use of various additives like amino acids, arsenic trioxide, and selenium and tellurium oxides in hot potassium carbonate absorbent solution which increase CO_2 absorption rate, and decrease the steam required for stripping CO_2 from the solution. The Vetrocoke processes have also employed air stripping for removing CO_2 from additive

containing hot potassium carbonate solutions in cases in which CO_2 is not recovered as a pure gas.

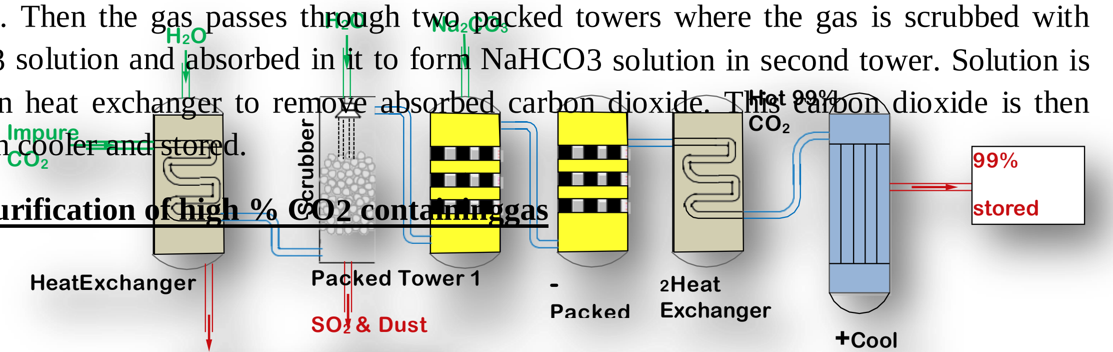
PURIFICATION

Carbon dioxide obtained in the impure state can be purified by different ways. There are two main categories for purification of carbon dioxide.

1. Purification of low % CO2 containinggas.
2. Purification of high % CO2 containinggas.

1. Purification of low % CO2 containinggas

18% hot CO2 gas passes through exchanger to lower the temperature. Then it is passes through rubber in which the water is percolated from the top to remove SO2 and dust particles. Then the gas passes through two packed towers where the gas is scrubbed with Na2CO3 solution and absorbed in it to form NaHCO3 solution in second tower. Solution is heated in heat exchanger to remove absorbed carbon dioxide. This carbon dioxide is then cooled in cooler and stored.



2. Purification of high % CO2 containinggas

Elect

Figure: Manufacturing of Hydrogen by

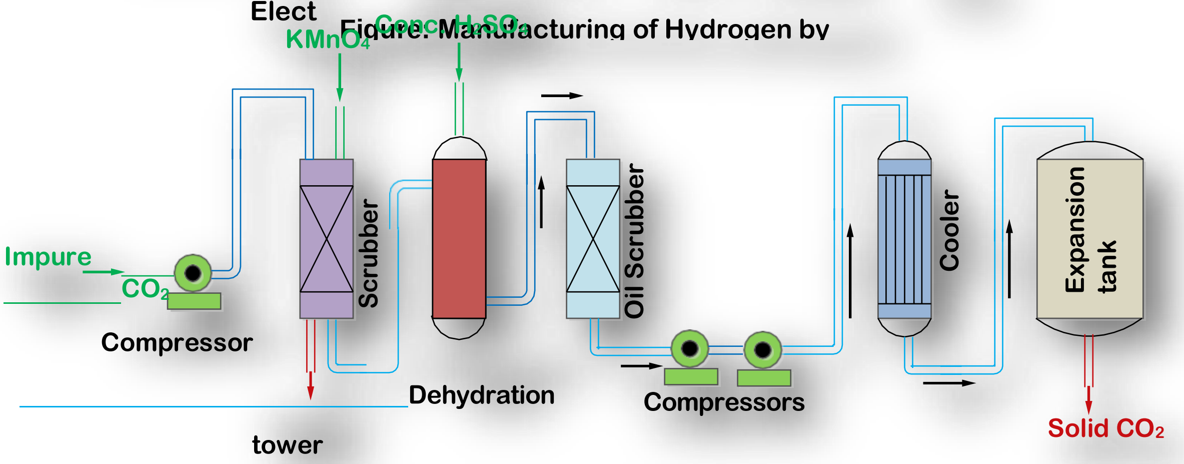


Figure: Purification of high % CO_2 containing gases

Gases are first compressed to 80psi pressure and passes through a scrubber to remove organic matters with KMnO4. The gas is then dehydrated using silica gel or activated alumina or conc. H2SO4 by passing through dehydration tower. Then the gas passes through an oil scrubber to remove bad odour of gas. Now the gas is, compressed in two stages, 80 psi to 300 psi and 300 psi to 900 psi for getting compressed gas or liquid respectively. For liquid CO2 the temperature is brought down much below 31.1°C. After compression by cooling of CO2, the liquid is stored at -10° C temperature. If the liquid CO2 is passes through an expansion tank and pressure is released then the solid CO2 is formed at -40° Ctemperature.

PROPERTIES

- Molecular formula : CO2
- Molecular weight :44.01gm/mole
- Appearance : Colourlessgas
- Odour : Odourlessgas
- Boiling point : -57^{0}C
- Melting point : -78^{0}C
- Density : 1. 977kg/m^{3} @ 1atm and 0^{0}C
- Solubility : Soluble in water

USES

- As solid CO2 in refrigerationprocess
- Liquid CO2 is needed incarbonated.
- Used in creating inertatmosphere.
- As fireextinguisher
- Gaseous CO2 used as a neutralizingagent
- Gaseous CO2 is the basic raw material for production of Na2CO3,NaHCO3

OXYGEN AND NITROGEN

INTRODUCTION

Oxygen

Oxygen (O2) composed of two atoms of the element at (O) bind to form dioxygen, a very pale blue, odorless, tasteless diatomic gas. Diatomic oxygen gas constitutes 20.8% of the volume of air. It is necessary to sustain global life.

Oxygen is the highly reactive nonmetallic element that readily forms compounds or oxides with almost all other elements. Oxygen is a strong oxidizing agent and has the second-highest electronegativity after fluorine than of all the elements. By mass, after hydrogen and helium, oxygen is the third-most abundant element in the universe. Free oxygen is too chemically reactive to appear on Earth without the photosynthetic action of living organisms, which use the energy of sunlight to produce elemental oxygen from water. Elemental O2 only began to accumulate in the atmosphere after the evolutionary appearance of these organisms, roughly 2.5 billion years ago.

As larger constituent by mass of water, oxygen comprises most of the mass of living organisms. Elemental oxygen is produced by cyanobacteria, algae and plants, and is used in cellular respiration for all complex life. Oxygen is toxic to anaerobic organisms, which were the dominant form of early life on Earth until O2 began to accumulate in theatmosphere.

Oxygen was independently discovered by Carl Wilhelm Scheele and Joseph Priestley in 1773 and 1774 respectively, but work was first published by Priestley. Antoine Lavoisier named as oxygen in 1777, whose experiments with oxygen helped to discredit the then-popular phlogiston theory of combustion and corrosion.

Oxygen is produced industrially by fractional distillation of liquefied air, use of zeolites with pressure-cycling to concentrate oxygen from air, electrolysis of water and other means.

Nitrogen

Nitrogen (N2) is a colorless, odorless, tasteless, and mostly inert diatomic gas at standard conditions, constituting 78.09% by volume of Earth's atmosphere. Nitrogen occurs in all living organisms, primarily in amino acids, proteins and in the nucleic acids (DNA and RNA). The human body contains about 3% by weight of nitrogen, the fourth most abundant element after oxygen, carbon, andhydrogen.

Nitrogen was discovered by Daniel Rutherford in 1772, who called it noxious air or fixed air. He also explains that nitrogen does not support combustion. At the same time by Carl Wilhelm Scheele, Henry Cavendish, and Joseph Priestley, referred it as burnt air or phlogisticated air. Antoine Lavoisier referred nitrogen as inert gas and as "mephitic air" or azote, in which animals died and flames were extinguished. English word nitrogen entered the language in1794.

The extremely strong bond in elemental nitrogen causing difficulty for both organisms and industry in breaking the bond to convert the nitrogen into useful compounds, but large amounts of useful energy released when the compounds burn, explode, or decay back into nitrogen gas.

Analysis of Air

Air mainly consist of two gases oxygen and nitrogen, which are practically considered to constitute 1/5 and 4/5 of air by volume respectively. The list of various gases present in air by weight percent is as under

Name of the gas	**% by weight in air**
Oxygen	20.99
Nitrogen	78.01
Carbon dioxide	0.03 - 0.07
Argon	0.94
Hydrogen	0.01

Neon	0.0015
Helium and Krypton	0.01 - 0.02

Except CO2 the concentration of all the gases listed above are present in air are constant. However water vapoursand traces of ozone and iodine are present in air in variable amounts. Also, composition of air also depends on altitude and distance to sea, in neighbourhood of industry, built up urban areas, nearby volcanic phenomena. Other gases such as CO, H2S and NO2 are also present in air.The critical temperature and critical pressure of some gases are as follows.

Sr. No.	**Gases**	**Critical temperature (^{0}C)**	**Critical pressure (atm.)**
1.	Ethylene	+9.5	50.65
2.	Methane	-82.85	45.6
3.	Nitrogen	-147.13	33.49
4.	Hydrogen	-239.9	12.8
5.	Oxygen	-118.75	49.7
6.	Acetylene	+35.5	61.55
7.	Ammonia	+132.5	112.3
8.	Carbon monoxide	-138.7	34.6
9.	Carbon dioxide	+31.3	72.9

Liquefaction of air by Joule - Thomson effect

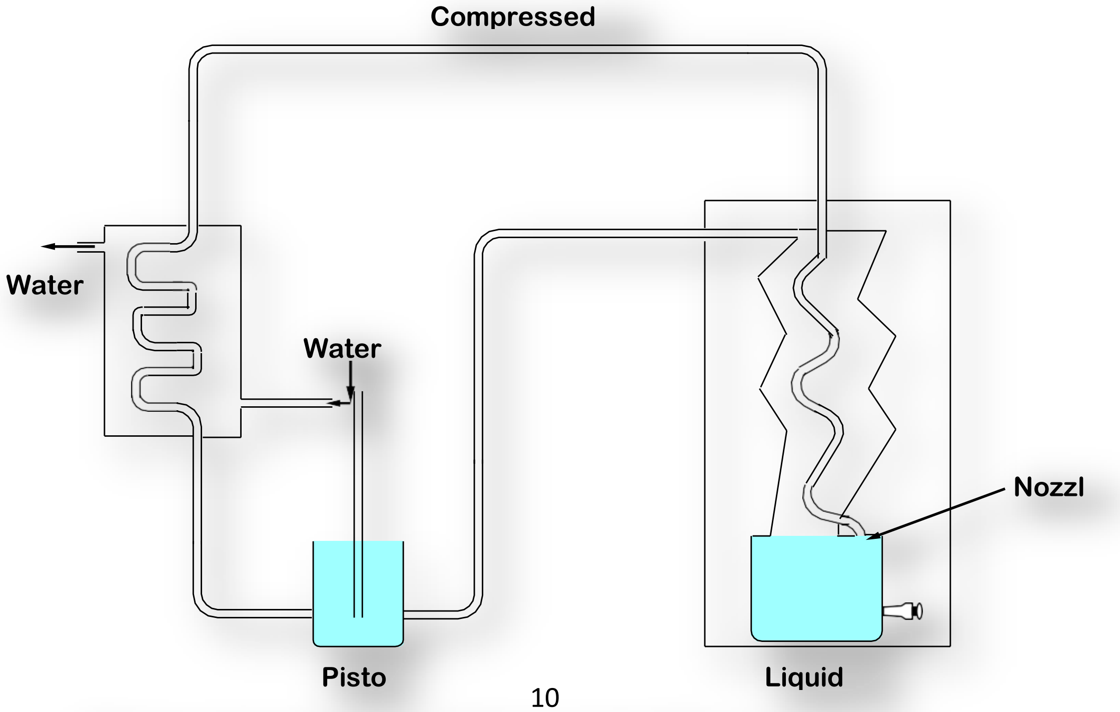


Figure: Liquefaction of Air by Joule Thomson

CO2 free air is compressed to 200atm and is cooled by water. The condensed water is removed by passing through activated alumina. Then air is passed through inner coil of heat exchangers. The valve with nozzle is provided at the end of the inner coil. Then gas is allowed to suddenly expand by opening the valve, which result in decrease of temperature of air. After expanding the cold air goes out through the outer coil, is then recompressed to 200atm pressure, cooled by water andthenagainallowedtotransversetheinnercoil.Thetemperatureofthe

incoming air further falls due to the presence of cold air in the outer coil. Now as the cooled air suddenly expands through the nozzle, the air suffers cooling, the temperature becomes lower than in the first operation. The colder air now passes through the outer coil producing an atmosphere of lower temperature. Hence when the cooled compressed air passes repeatedly through the inner coil and subsequently undergoes Joule-Thomson effect, the temperature of the air further drops. In this way progressive cooling takes place until the temperature of air falls below the critical temperature of oxygen and nitrogen. When this happens air undergoes liquefaction in the inner coil, so on opening the valve liquid air falls in the container. A part of liquid air evaporates, through the outer coil, maintaining the low temperature below the critical temperature.

MANUFACTURE

Oxygen in pure condition is obtained as a byproduct in the manufacture of H2 by electrolytic process is described in Module: 2, Lecture: 4. Oxygen and nitrogen are usually separated by rectification of liquidair.

Linde's process (O2 and N2)

The first rectification of N2 and O2 using Joule Thomson effect was carried out by Linde in 1906. After six year Claude rectified them by combined effect of external work and internal work in cooling the air to liquefaction point.

Raw materials

Basis: 1000kg Oxygen (95%)

Air	=3600Nm^3
Steam	=1750kg
Coolingwater	=5000kg
Electricity	=450-480KWH

Manufacture

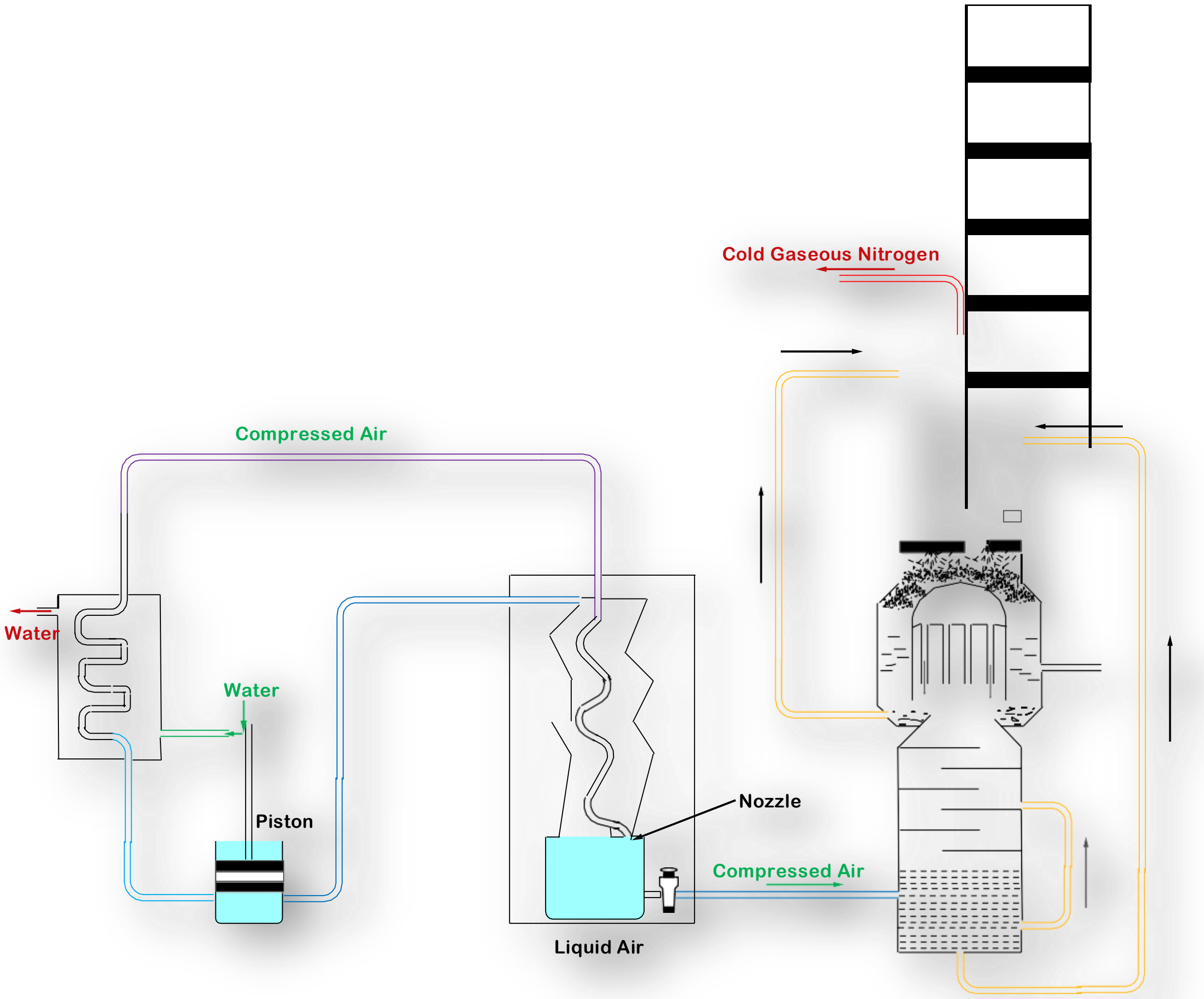


Figure:Manufacturing of Nitrogen & Oxygen by Linde's

The distillation tower is specially designed bubble cap tray double columns arranged one above another. The two distillation columns are having intermediate distillation dome for effective separation of liquid enriched with O2. The column feed is liquefied air at 200atm pressure introduced at the bottom of the column. Since the boiling point of O2 (-183^{O}C) and N2 (-195^{O}C) are very low, column does not require any external heating. Distillation take place only due to release of vacuum. Thus a number of recycling from lower column to upper column and lower column to dome is required. The construction of dome includes number of internal pipes so that distillate of the lower column collides to the roof and is returned back to the column as reflux. The compressed air which arrives from the first section of the plant which acts as the heating fluid in the heater at the base of the enrichment column. The same air, always contained within a tube, passes out from the Iower column of the tower only to reenter it higher up after the pressure to which it is subjected is reduced by means of a valve, resulting in the lowering of its temperature. Nitrogen with a small oxygen impurity collects at the top of the enrichment column, and after expansion to atmospheric pressure; this nitrogen is sent to back as the reflux in the rectification column situated above. The liquid which collects in the heater at the base of the enrichment column is fed, after expansion to atmospheric pressure onto a suitable plate of the rectificationcolumn.

Only after number of recycling, liquid with 82% concentration of O_2 is taken in outer part of dome. This liquid goes to further rectification in upper column where it is refluxed with N_2 rich liquid coming from lower column. The final separation in the upper column takes place which has less number of trays. Gaseous N_2 is the top product of the column and the bottom product is liquid O_2.

Claude process

In Claude process, progressive cooling of compressed air is done by external work and Joule - Thomson effect. 70% of air is cooled by external work and 30% by Joule - Thomson effect.

Two variants of Claude process Molecular sieve variant

Cooling of air is brought about primarily by expansion with the performance of work. Therefore, there is no need to equip the plant with cycles that use refrigerants or make use of very high pressures which are employed when free expansion is used, in order to producecooling.

Evaporation to diffusion

Cooling of the air can be adopted such as causing liquids which can evaporate to diffuse air. It is then safe to reabsorb them when necessary.

Operation of a rectification column

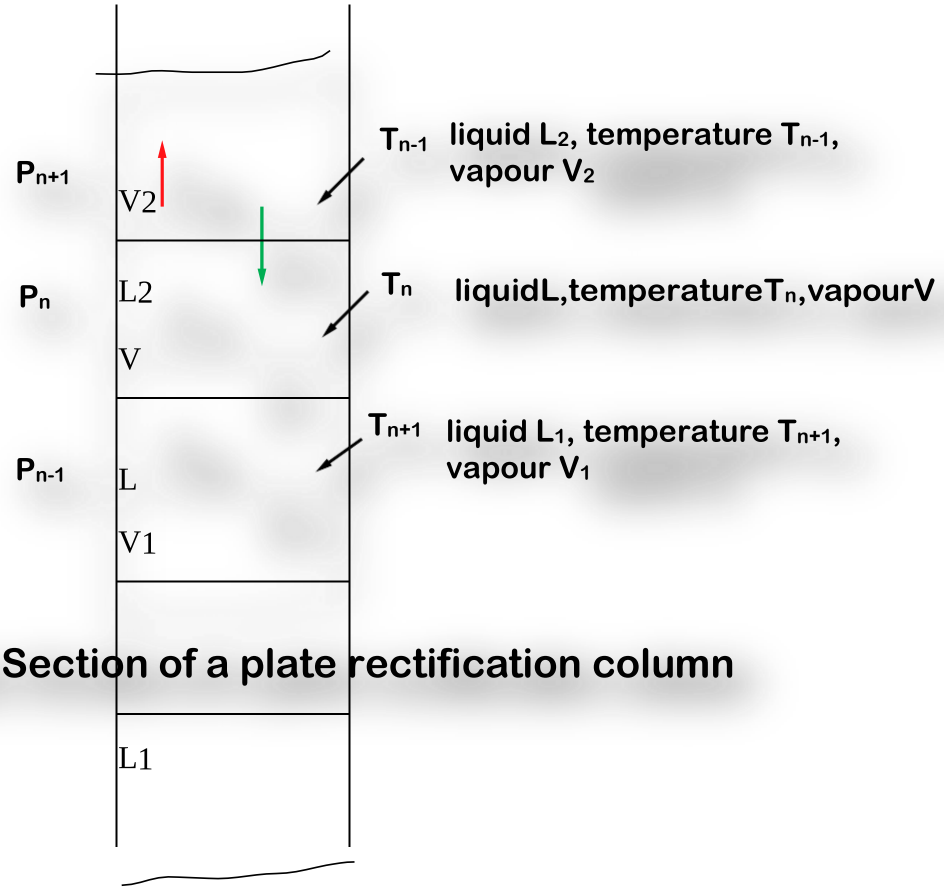


Figure: Section of a plate rectification column

Rectification is carried out in a 'plate column', which is tall cylindrical structure inside which repeated condensations and evaporations take place on plates, which lead to a continuous change in the composition of the binary system throughout the length of the column. This is continued until one of its pure components exists at top of the column and the other at the bottom of the column.

For better understanding of rectification of binary mixture a small section of column is shown in figure which is formed by three plates: an intermediate plate Pn. and two collateral plates Pn-1 and Pn+1 which are arranged below and above the plate Pn respectively.

- V1, V,andV2 be the vapours which, as they pass toward the top of the column, leave the plates Pn-1, Pn, and Pn+1respectively
- L1, L, and L2 be the liquids which, as they pass down the column, descend from the plates Pn-1, Pn, and Pn+1respectively
- Tn+1, Tn and Tn-1 be the temperatures of the plates Pn-1, Pn, and Pn+1respectively

The rectification of liquid mixture is exclusively on the basis of heat exchange of the different fraction present in liquid form as well as vapour form. As shown in the diagram plate Pn is considered as the reference plate having temperature Tn and liquid composition L, vapour composition V. As pressure is released the more volatile component i. e. N2 is evaporated out partly and goes to the upper plate Pn+1. The composition of liquid L2 is having less concentration of N2 at temperature Tn-1. Similarly liquid below the reference plate is Pn-1 has higher concentration of O2 and vapour V1 having higher composition of O2 at temperatureTn+1.

Thus the separation of more volatile component N2 in vapour form and low volatile component O2 in the liquid form is achieved.

Finally:

- The liquids which fall down from the plates toward the heater in the base of the column (L2, L, L1) become progressively richer in the less volatile component(oxygen)
- The vapours which rise toward the top of the column (V1, V, V2) gradually become enriched in the more volatile component(nitrogen)

Subsequently, in a column fitted with a suitable number of plates, O2 is obtained in pure state at the base of the column and the N2 is obtained in a practically pure state at the top of the column.

For, perfect operation of a rectification column always requires that:

- The liquid should always be introduced onto a plate which supports a liquid of the same composition as that of the feedstock liquid Part of the distillate from the top of the column is recycled in the form of a 'reflux' with the aim of repeated washing on all of the plates which refine the vapours moving towards the top of the column

Condensation medium

The separation of liquid air into nitrogen and oxygen is not as simple as the fractionation of any other binary mixture. Because the separation is carried out at very low temperature around -200^{0}C. It is difficult to find a suitable medium for the refluxing of a liquid air distillate at this temperature. The only possible media for the condensation of the reflux would be liquid helium or liquid hydrogen, the use of which is clearly unacceptable on both economic and operational grounds.

Engineering aspects

Two-section fractionating tower

Designing a fractionating tower consisting of two columns which are arranged one above the other is the economically acceptable solution. The upper column is about twice the height of the lower column, and both of them are fitted with plates spaced at intervals. The average numerical ratio of the repartitioning between the two columns is42-25.

The upper column has all the requisites of a rectification column, while the lower column functions as a simple enrichment column. As a bottom reboiler, the lower column has a boiler with a curved base. There is no condenser at the top of the rectification column, and it is closed by means of a gently curved cover with an outlet aperture.

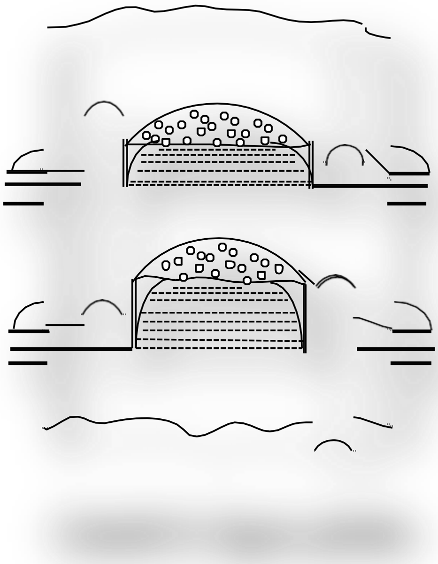
Fundamentally, one is concerned with two columns, one being situated above the other, working at different pressures

- Lower column operating at6atm
- Upper column operates only slightly above atmosphericpressure

The heat exchanger provided between the two columns acts as a condenser with respect to the lower column and a boiler with respect to the upper column precisely as a result of the two different pressures which appertain in the two compartments.

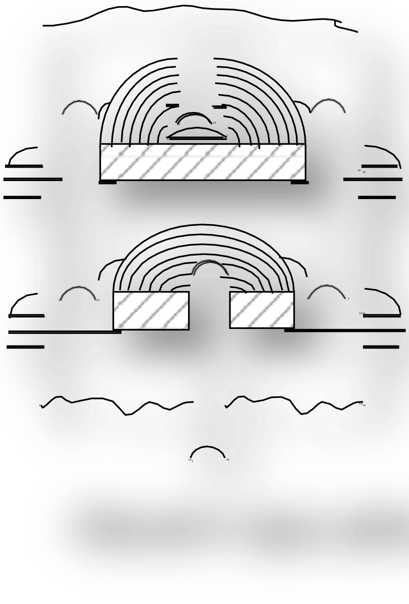
More precisely: the upper column is supplied with a feedstock of a composition which is proportionate with that of the liquid situated on the plate where the feedstock is let in, and receives a suitable reflux at the top, while the lower column is fed almost normally but is not refluxed, and , instead of leading to practically pure components, it produces a liquid which is enriched in the oxygen at the bottom and in the nitrogen at the top of thecolumn.The shape of the plates differs according to the type of plant in which they operate.

Linde method



Every plate is made up from two metal plates which are separated from one another by a certain spacing and perforated with very small apertures in the lower plate and quite large holes in the upper plate.

Claude method



The column plants using claude‘s method is strips of thin steel plate wound into a spiral with separation of the order of tenth of a millimeter between thespirals.

On account of the capillarity due to the small apertures in the lower half of the Linde plates and the small cavities between the spirals of the Claude plates,the down-flows of the liquids are retarded, thereby favouring perfect contact between the descending liquids and the rising vapours. Material of constriction should be chosen in such a way that can resist very low temperature.

PROPERTIES

Oxygen

- Molecularformula :O2
- Molecularweight :32gm/mole
- Appearance : Colourlessgas
- Odour :Odourless
- Boilingpoint :-182.95^{0}C
- Meltingpoint :-218.79^{0}C
- Density : 1.429gm/L(0^{0}C,101.325kPa)
- Solubility : Sparingly soluble inwater

Nitrogen

- Molecularformula :N2
- Molecularweight :28gm/mole
- Appearance : Colourlessgas
- Odour : Odourlessgas
- Boilingpoint :-195.79^{0}C
- Meltingpoint :-210^{0}C
- Density : 1.251gm/L(0^{0}C,101.325kPa)
- Solubility : Slightly soluble inwater

USES

Oxygen

- It is used to produce oxyacetylene flame to cutting and welding themetals
- Used in L. D. process for steelproduction
- Used for artificial respiration in case ofpatients
- Used for mountain climbers and high attitude aero planesflights

Nitrogen

- Used in manufacture of synthetic ammonia, nitricacid
- Used in manufacture organic nitrates like propellants andexplosives,
- Synthetically produced nitrates are key ingredients of industrialfertilizers
- Used in producing nitrogenoxide.
- Applied to create inertatmosphere.

HYDROGEN

INTRODUCTION

Hydrogen (H2) is colourless, odourless, tasteless, non-toxic, nonmetallic, highly combustible diatomic gas. Atomic hydrogen is found rare on Earth because it readily forms covalent compounds with most elements, water and organic compounds. Hydrogen plays an important role in acid basechemistry.

The most common isotope of hydrogen is protium (^{1}H) with a single proton and no neutrons. As the only neutral atom with an analytic solution to the Schrödinger equation, the study of the energetics and bonding of the hydrogen atom played a key role in the development of quantummechanics.

Robert Boyle produced hydrogen by reaction between iron filings and dilute acid in 1671. Henry Cavendish identified hydrogen gas as a discrete substance in 1766. He named the gas from a metal-acid reaction as "flammable air". The name hydrogen was given by Antoine Lavoisier in 1783, when he and Laplace reproduced Cavendish's finding that water is produced when hydrogen is burned. Antoine- Laurent de Lavoisier produced hydrogen by reacting flux of steam with metallic iron through an incandescent iron tube heated in a fire.

Anaerobic oxidation of iron by the protons of water at high temperature can be schematically represented by the set of following reactions

$$Fe + H_2O \longrightarrow FeO + H_2$$

$$2\,Fe + 3H_2O \longrightarrow Fe_2O_3 + 3H_2$$

$$3\,Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

Hydrogen was first liquefied by James Dewar in 1898 by using regenerative cooling in the vacuum flask. He produced solid hydrogen the next year. Deuterium was discovered in December 1931 by Harold Urey, and tritium was prepared in 1934 by Ernest Rutherford, Mark Oliphant, and Paul Harteck. Heavy water, which consists of deuterium in the place of regular hydrogen, was discovered by Urey's group in 1932. François Isaac de Rivaz built the first internal combustion engine powered by a mixture of hydrogen and oxygen in 1806.

MANUFACTURE

The various method used for production of hydrogen gas are as follows.

1. Electrolyticprocess
2. Lane process or iron steamprocess
3. Steam hydrocarbonprocess
4. Liquefaction of coal gas and coke ovengas
5. Bosch process or water gas-steamprocess

1. ElectrolyticProcess

Pure hydrogen along with oxygen is manufactured by electrolytic process. It is also obtained as a by-product in the production of caustic soda by electrolysis of aqueous solution of sodium chloride as discussed in Module: 3, Lecture: 9. Heavy water may be prepared on a large scale by burning deuterium separated from hydrogen obtained byelectrolysis.

Reactions

In acidulated water

$H2SO4 \rightleftharpoons 2H^{+} + SO4^{-2}$

At cathode

$2H^{+}+2H2O \longrightarrow 2[H3O]^{+}$

$[H3O]^{+}+e^{-} \longrightarrow H^{+} \quad +$

$H2O\ H^{+}+H^{+} \longrightarrow H2$

At anode

$SO4^{-2} \longrightarrow SO4 + 2e^{-}$

$SO4+H2O \longrightarrow H2SO4 + O^{-2}$

$O^{-2}+O^{-2} \longrightarrow O2$

In KOH solution

$KOH \rightleftharpoons K^{+} + OH^{-}$

At cathode

$K^{+}+e^{-} \longrightarrow K$

$K+H2O \longrightarrow KOH \ +$

$H^{+}\ H^{+}H^{+} \longrightarrow H2$

At anode

$2OH^{-} \longrightarrow H2O \quad +$

$O^{-2}\ O^{-2}+O^{-2} \longrightarrow O2$

In Ba(OH)2 solution

$Ba(OH)2 \rightleftharpoons Ba^{+2} + 2OH^{-}$

At cathode

$Ba^{+2}+2e^{-} \longrightarrow Ba$

$Ba+H2O \longrightarrow Ba(OH)2 + H2$

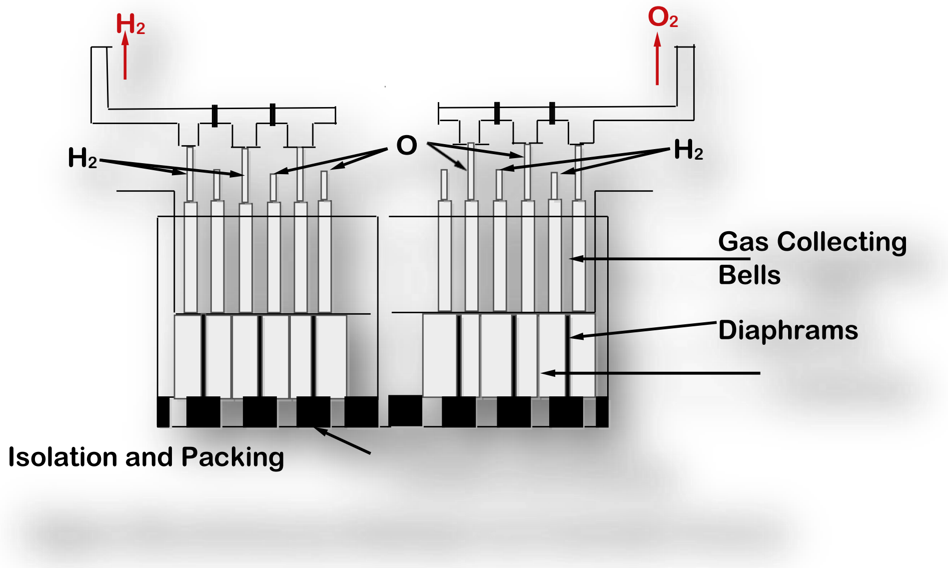
At anode

$2OH^{-} \longrightarrow 2OH + 2e^{-}$

$2OH^{-} \longrightarrow O^{-2} \quad +$

$H2O\ O^{-2}+O^{-2} \longrightarrow O2$

Manufacture



Construction

Both unipolar and bipolar cells are used for electrolysis. In case of unipolar cells, iron elsheets and nickel coated iron sheets are used as cathodes and anodes respectively. Both anodes and cathodes are placed close to one another to prevent the loss of voltage. Asbestos diaphragm is placed between anode and cathodecompartment.

In case of bipolar cells the same sheet act as both anode and cathode as the electrodes are connected in series. The cell is partitioned by vertical iron sheet; the anode side of the sheet is electroplated with nickel. Vertical asbestos sheet as diaphragm is placed between the anode side and cathode side of former sheet. The same sheet acts as anode of one cell and cathode of the cell behind it. The anode and cathode compartments are connected to two separate horizontal pipes by means of standpipes, to lead away oxygen and hydrogen respectively. 250 cells are connected in series, and current of 10000amp is passed to operate the cells. The purity of $H2$ and $O2$ are 99.95% and 99.6%respectively.

Working

Pure hydrogen can be manufacture by electrolysis of brine or water. Since water is non-conductor of electricity and can be made conductor by addition of small quantities of pure $H2SO4$ or KOH or $Ba(OH)2$. 2:1 volume of $H2(g)$ and $O2(g)$ are simultaneously liberated at cathode and anode respectively

Produced hydrogen contains small quantity of oxygen, which can be removed by passing the gas over the catalyst gently heated palladium asbestos. The gas obtained by electrolysis is very pure and used for hydrogenation ofoils.

Engineering aspect

The energy consumption is high due to resistance cause by the bubbling. This is somewhat mitigated by conducting electrolysis under pressure. The decomposition voltage is 1.23 volts, so that the evolution of 2gms of hydrogen 53.6amp.hour is necessary. Hence to generate 1000litre of H_2 at 18^0C and 1atm pressure 2.8KWH are required because of overvoltage of the electrode and ohmic resistance of the electrolyte and diaphragm

2. Lane process or steam hydrogen process

Rawmaterial

Iron Steam

Reaction

$Fe_3O_4 + CO + H_2 \rightleftharpoons Fe + 2FeO + CO_2 + H_2O$

$Fe + 2FeO + 2H_2O \rightleftharpoons Fe_3O_4 + 2H_2$

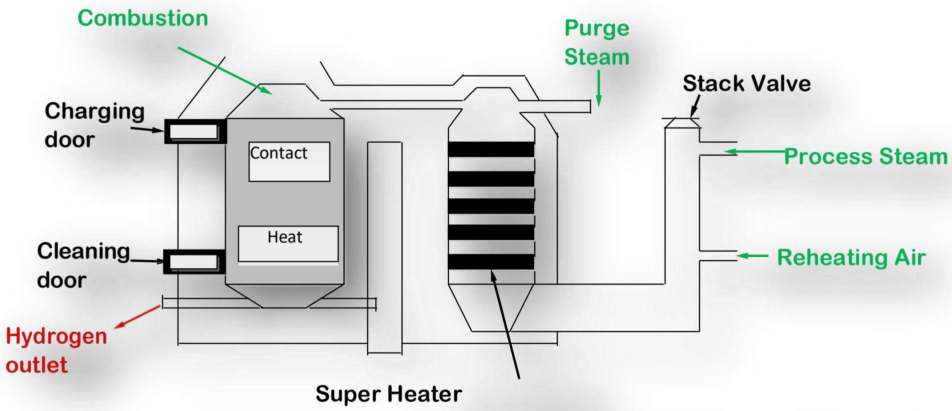


Figure: Manufacturing of Hydrogen by Lane Process

Manufacture

Iron oxide and water gases are charged to fire bricks lined generator which is heated externally by burning of producer gas or other gaseous fuel. The first action is endothermic and the second action is exothermic. The temperature is maintained in both actions at 650^0C, first by heating the iron oxide and second by passing superheated steam through the iron forming iron oxide by the heat of the reaction and that of the steam. The reducing gas is passed through the heated iron oxide from the bottom of the generator. The spent gas coming out of the generator is burnt, and the hot products of combustion are sent through the super heater which is a chamber filled with checker work. The time cycle is 20 minutes, then excess of steam is passed through the super heater from the bottom and then passes through the mass of iron from above, the hydrogen goes out through the pipe at the bottom of the generator. The time cycle of passing steam is 10 minutes. The hot hydrogen from the generator is cooled by passing through a cooler. The excess of steam condenses and dissolves the H2S, which is practically completely removed. The gas is then scrubbed with weak NaOH solution to remove CO2 and then mixed with steam is passed over heated iron oxide catalyst to convert CO to CO2. The gas is then scrubbed with weak NaOH solution for the second time; pure hydrogen gas is thus produced.

Kinetics

The production of hydrogen depends upon the exothermic reaction between red hot iron and steam. The continuity of production with the help of same mass of iron is maintained by reducing with water gas, the iron oxide produced by the iron-steam reaction, and repeating the cycle of oxidation and reduction. In actual practice the iron oxide is not completely reduced, and the water gas is not completelyoxidized.

Engineering aspects

The iron mass must have a large exposed surface, and should be resistant to disintegration. Such mass of iron was produced by calcining FeCO3 (spathic iron ore) and then reducing the iron oxide to spongy iron having a large surface.

ACETYLENE

INTRODUCTION

Acetylene ($C2H2$) is colorless gas used as a fuel and a chemical building block. As an alkyne, acetylene is unsaturated because its two carbon atoms are bonded together in a triple bond having CCH bond angles of 180^0. It is unstable in pure form and thus is usually handled as a solution. Pure acetylene is odorless, but commercial grades usually have a marked odor due toimpurities.

In 1836 acetylene identified as a "new carburet of hydrogen" by Edmund Davy. The name "acetylene" was given by Marcellin Berthelot in 1860. He prepared acetylene by passing vapours of organic compounds (methanol, ethanol, etc.) through a red-hot tube and collecting the effluent. He also found acetylene was formed by sparking electricity through mixed cyanogen and hydrogen gases. Berthelot later obtained acetylene directly by passing hydrogen between the poles of a carbonarc.

MANUFACTURE

Acetylene manufacture by following processes

1. From calciumcarbide
2. From paraffin hydrocarbons by pyrolysis (Wulffprocess)
3. From natural gas by partial oxidation (Sachasseprocess)

Nowadays acetylene is mainly manufactured by the partial oxidation of natural gas (methane) or side product in ethylene stream from cracking of hydrocarbons. Acetylene, ethylene mixture is explosive and poison Zigler Natta catalyst. There so acetylene is selectively hydrogenated into ethylene, usually using Pd-Ag catalysts.

Acetylene was the main source of organic chemicals in the chemical industry until 1950. It was first prepared by the hydrolysis of calcium carbide, a reaction discovered by Friedrich Wöhler in 1862.

$$CaC2+2H2O \longrightarrow Ca(OH)2 + C2H2$$

Calcium carbide production requires extremely high temperatures, ~2000^0C, necessitating the use of an electric arc furnace.

Also hydrocarbon cracking is carried out in an electric arc furnace. In which electric arc provides energy at very high flux density so that reaction time can be kept at a minimum. There so the design of the electro-thermal furnace is one of the important factors.

In one design (Huels process) gaseous feedstock enters the furnace tangentially through a turbulence chamber, then passes with a rotary motion through pipe in which the arc is passed between a bell shaped cathode and anode pipe. The rotary motion of the gas causes the arc to rotate and thus reducing fouling. The arc is operated at 8000kw D.C. at 7000volts and 1150amp cathodes are said to last 800hours while anodes only150hours.

In other design, fresh hydrocarbon and recycle gas are fed to the arc. The effluent reaction gases are quenched and purified. 35%w purified acetylene along with 17%w ethylene and 10%w carbon black, H_2 and other products in minor amount is obtained in one pass through furnace.

The difference is that the arc is rotated by means of an external magnetic coil, and quenching is carried by propane and water in 1st and 2nd step respectively. Some propane cracking improves the yield of acetylene. The propane quench cools the arc gases to 1095^0C in 0.0001 to 0.0004 sec while the water quench cools the mixture to 300^0C in 0.001 to 0.003 sec. Power consumption is 12.36kwhr/kg of pure acetylene. 21-22%v acetylene is obtained in the productgases.

1. From calcium carbide Raw materials

Basis: 1000 cu ft. acetylene
Calciumcarbide(85%) = 100kg Water =815kg

Sources of raw material

Calcium carbide is manufactured from lime and coke in 60:40 ratio in electric furnace at $2000\text{-}2100^0$C temperature.

Reaction

$$CaC_2+2H_2O \longrightarrow Ca(OH)_2+C_2H_2 \quad \Delta H = -32.5\text{kcals}$$

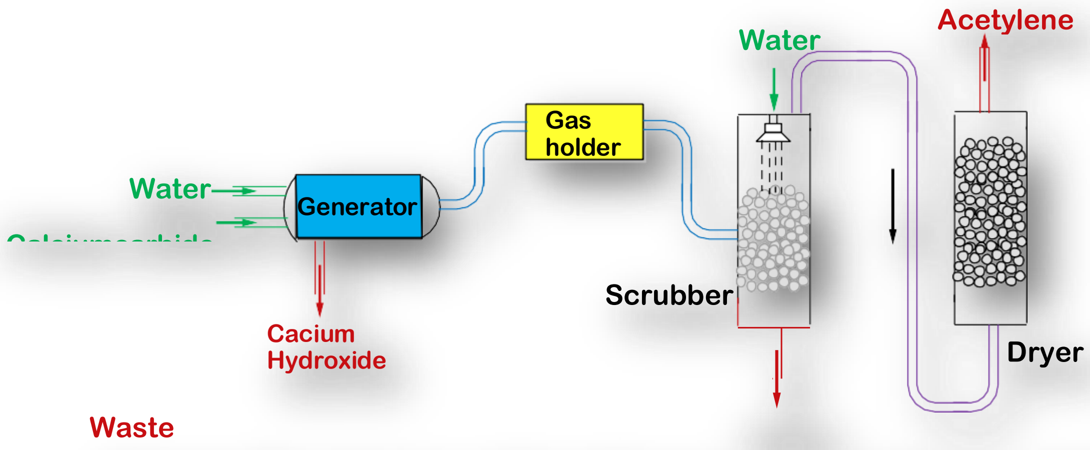


Figure: Manufacture of Acetylene by using Calcium

Manufacture

There are two methods for the manufacture of acetylene from calcium carbide

- Wetprocess
- Dryprocess

In the wet process, calcium carbide is added to large quantity of water releasing acetylene gas and calcium hydrate as residue. Later is discharged in the form of lime slurry containing approximately 90% water.

In the dry process, in order to eliminate the waste of calcium hydrate equal amount of water is added to CaC2 (1:1 ratio) in a generator. The heat of reaction (166 Btu/ft^3 of acetylene) is used to vaporize the excess water over the chemical equivalent, leaving a substantially dry calcium hydrate which is suitable for reuse as a lime source. The temperature must be carefully controlled below 150^{0}C at 15psi pressure throughout the process because the acetylene polymerizes to form benzene at 600^{0}C and decomposes at 780^{0}C. Further with air-acetylene mixture explodes at480^{0}C.

The crude acetylene gas containing traces of H2S, NH3 and phosphine (PH3) form generator is either scrubbed with water and caustic soda solution or sent to purifier where the impurities are absorbed by the use of iron oxide or active chlorine compounds. The dry gas is fed to cylinders or sent to manufacturing units.

2. From paraffin hydrocarbons by pyrolysis

(Wulff process) Rawmaterials

Basis: 1000kg acetylene (100%)

Natural gas	= 262000Sef
Steam (600psig)	= 26308kg
Electricity	=140kWH
Cooling water	=25000gal
Process water	=200gal
Solvent (make up)	=2.95kg

Reaction

$C_4H_{10} \longrightarrow C_2H_2 + C_2H_4 + CO + H_2$

$C_2H_4 \longrightarrow C_2H_2 + H_2$

$2CH_4 \longrightarrow C_2H_2 + 3H_2 \quad \Delta H = +96.7\text{kcals}$

Manufacture

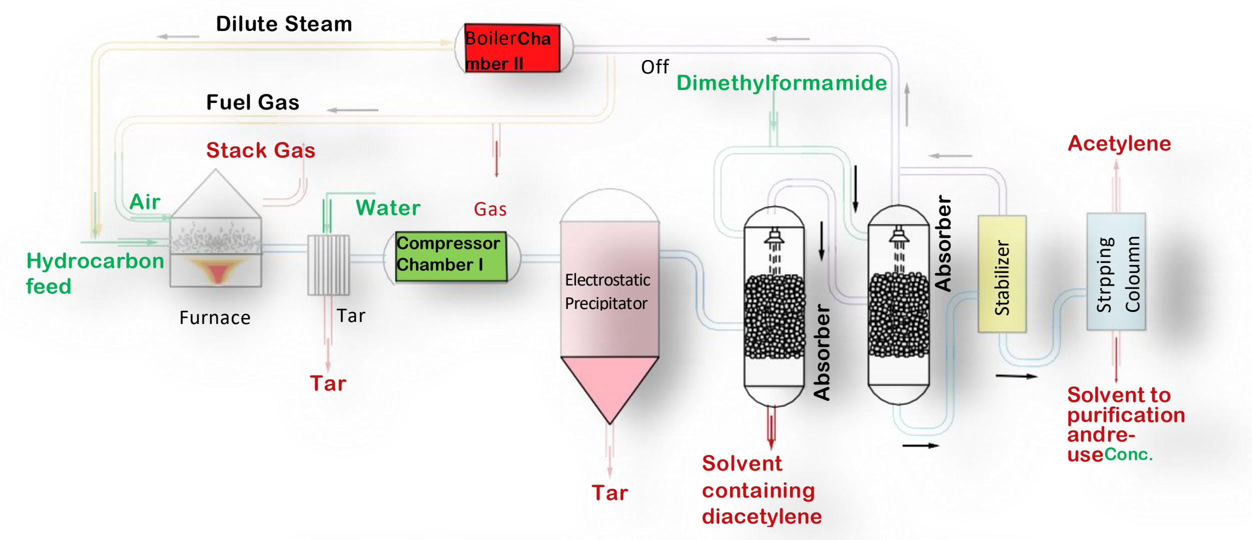


Figure: Manufacture of Acetylene by Wulff

In the Wulff process acetylene may be produced by thermal decomposition of hydrocarbons such as methane, ethane, propane, butane, ethylene etc.

Pyrolysis is carried out in the Wulff regenerative furnace which is a rectangular steel box filled with refractory bricks checker work. Before the hydrocarbon feed is sent to the chamber, it is diluted with steam (up to 1:8 ratios). The feed is carried through the chamber at sub-atmospheric pressure by virtue of a large vacuum pump. Which reduced the residence time as little as 0.03 sec; cracked gas leaves the chamber at about 370°C. The maximum temperature in the furnace just after the heating cycle approaches 1315°C. The furnace is operated in four minutes cycle in which the checker work is first heated for one minute and then feed gas pyrolyzed for one minute. The same sequence of operation is then done in reverse direction through the furnace. To facilitate reversal of the gas flow, fuel gas burners and hydrocarbon feed pipes are located on each side of the combustion chamber. To allow continuous flow of cracked gases to the purification train, two furnaces are usually operated on staggered cycles. Cooled cracked gases from the chamber are then further quenched in a tar trap, where steam and various tars are removed. The gas is compressed to atmospheric pressure, passed through a knock-out forum and electrostatic precipitator, and sent to the recovery system.

Usually diacetylene and acetylene are separated by absorption in DMF (dimethyl formamide). By proper adjustment of solvent ratio and temperature, diacetylene may be removed in the first scrubbing column. In the acetylene absorber small quantities of ethylene, CO2 and higher acetylenes are also absorbed. Most of the acetylene-free off-gases used for various heat exchanging operation like used as fuel for the steam boilers, for combustion chamber heatingetc.

Acetylene rich solution is sent to stabilizer, where less soluble components are removed by stripping. Acetylene is then removed from the solvent in a second stripping column. The solvent is readied for reuse by stripping out high boilers by blowing with off gas from the acetylene absorber-followed by rectification.

Usually, off-gas from the acetylene recovery system is used as fuel for heating the combustion chamber. The volume of off-gas is much more than is required for fuel, so it may be either recycled to the furnace or used as a raw material for some other operation.

Yield of acetylene (98.5 to 99.3 % purity) varies with the hydrocarbon feed stock used. Average yields for the once-through process are 22.5 kg per 100kg

methane, 38.6 kg per 100kg ethane, and 35.5kg per 100kg propane. The off-gas is principally ethylene, carbon monoxide, hydrogen and methane.

Kinetics and thermodynamics

The principal conditions which must be considered are as follows

Energy requirement to convert hydrocarbons to acetylene is very high and which can be supplied by very high temperature. For paraffinic feedstock, the heat of formation for a gram atom carbon in acetylene decreases with the increasing length of the chain and it increases in the case of olefinic hydrocarbons. The heat of formation is of the order of magnitude required for the dissociation ofsteam.

$$2CH_4 + 174{,}000\,Btu \longrightarrow C_2H_2 + 3H_2$$

The formation of acetylene begins at a relatively high temperature; in the case of methane occurs around 815^{0}C. The temperature required decreases with the increase in the number of carbon atoms of the hydrocarbonfeed.

The decomposition of hydrocarbons to carbon and hydrogen begins at relatively low temperatures. E.g. decomposition of methane occurs at 450^{0}C. Hence, the decomposition into the elements proceeds in competition with the formation of acetylene. However, the rate of acetylene formation is greater than that of the decomposition reaction. There so care should be taken that the hydrocarbon feed must reach at relatively high temperatures (above 675^{0}C) in the shortest possible time and then the attained equilibrium must be immediately quenched to about 285^{0}C in order to preserve the acetylene formed. The time interval for the reaction should be of the order ofmilliseconds.

3. From natural gas by partial oxidation (Sachasse process)

Rawmaterials

Basis: 1000kg acetylene (99.5%) plus 340000 Cu ft. off gas (345 Btu/Cu ft.)

Natural gas = 190000 Sef
Oxygen (95%) = 5400kg
Solvent = 2.3kg
Power = 15000kWH
Steam = 4535.9kg
Water (cooling) = 22710liter

Reaction

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$2CH_4 \longrightarrow C_2H_2 + 3H_2 \quad \Delta H = +\,79.8\,kcals$$

Manufacture

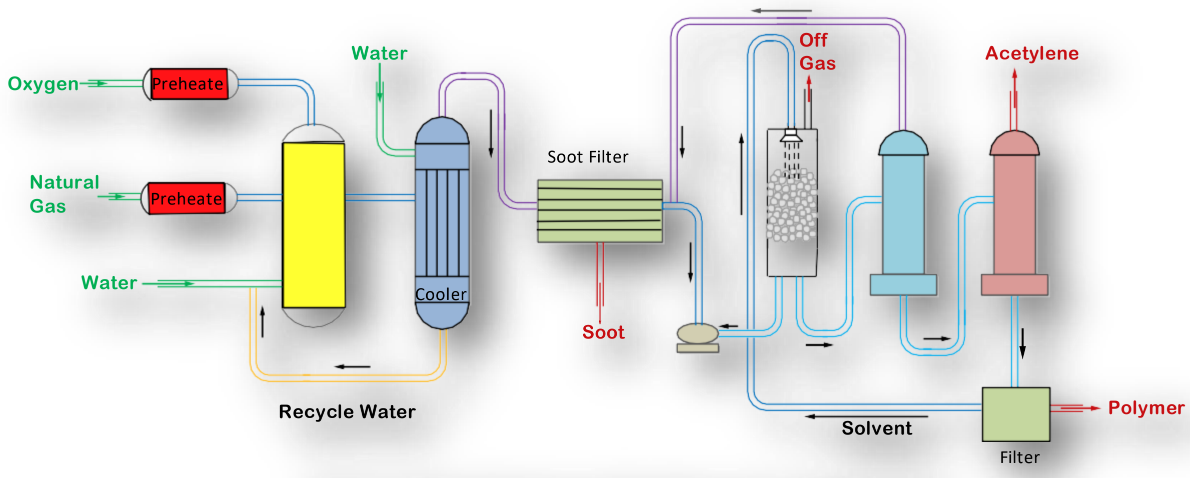


Figure:ManufacturingofAcetylenefromNaturalGas

Acetylene may be produced from a variety of hydrocarbon feed stocks (natural gas, LPG, naphtha, fuel oil, even crude oil) by high-temperature cracking. Heat for the cracking operation is developed by partial oxidation of the feed stock with oxygen. The heat evolved cracks the excess hydrocarbon to acetylene. After rapid quenching with water, the acetylene is separated from the gas stream by absorption-desorption in a suitable solvent. The process is known as Sachasse process using natural gas as rawmaterial.

Natural gas (1mole) and low purity oxygen (0.65moles 95%O2) are preheated separately to 510^{0}C and fed to a specially designed burner.

The converter is vertical cylindrical unit built in three sections

- Mixingchamber
- Flameroom
- Quenchchamber

After rapid and through mixing of oxygen and methane in the mixing chamber, the gases are fed to the flame room through the portal in a burner block designed to prevent back travel or blow-off. The heat of combustion heats the gases to 1550^{0}C to allow cracking of the excess methane to acetylene. The residence time is 0.001 to 0.01 seconds. The decomposition of acetylene is prevented by rapid quenching of the resulting gases with water to 38^{0}C. Thecooledeffluent gases on the dry basis contain 8% acetylene, 54% H2, 26% CO, 5% CH4, 4% CO2 and 3% N2 and higher acetylenes. These gases are run to a filter where using carbon black, acetylene of 99.5% or higher purity is produced (23.5kg/1000kg of acetylene is separated and purified in a manner as described for the Wulff process).

PROPERTIES

- Molecularformula :C2H2
- Molecularweight :26.04gm/mole
- Appearance : Colourlessgas
- Odour : Odourlessgas
- Boilingpoint : -84^{0}C (sublimationpoint)
- Meltingpoint : -80.8^{0}C@1.27atm
- Density :1.097kg/m^3
- Solubility : Soluble in acetone andDMF
- It is transported under high pressure in acetone soaked on porous material packed in steelcylinders
- It is lighter thanair
- It is somewhat poisonous innature
- It burns with luminous flame and forms explosive mixture withair

USES

- In the chemical manufacture of acrylonitrile, vinyl chloride, vinyl acetate, acrylatesetc.
- In manufacture of acetaldehyde, trichloroethylene, acetic acid, polyvinyl alcohol, perchloroethyleneetc.
- In manufacture of propagryl alcohol, butyrolactone, vinyl pyrrolidineetc.
- In metallurgy industries for welding andcutting

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SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 4 NATURAL PRODUCTS- SCHA1305

4.1EDIBLE AND ESSENTIALOILS

Oils are organic molecule of carbon, hydrogen, oxygen and sometimes nitrogen and sulfur. It is composed of long chain fatty acids and esters (glyceride ester) as well as derivative ofglycerine, long chain fatty alcohol, sulfate and sulfonates. Oils like caster oil, linseed oil are non edible and oils like ground nut oil, coconut oil are edible . Oil is used in producing vanaspati ghee, soaps and detergents, cosmetics, medicines, polymers, paints and varnishes and in many other applications.

4.1.1 VEGETABLE OILEXTRACTION

Raw material: Seeds of oilseed plant

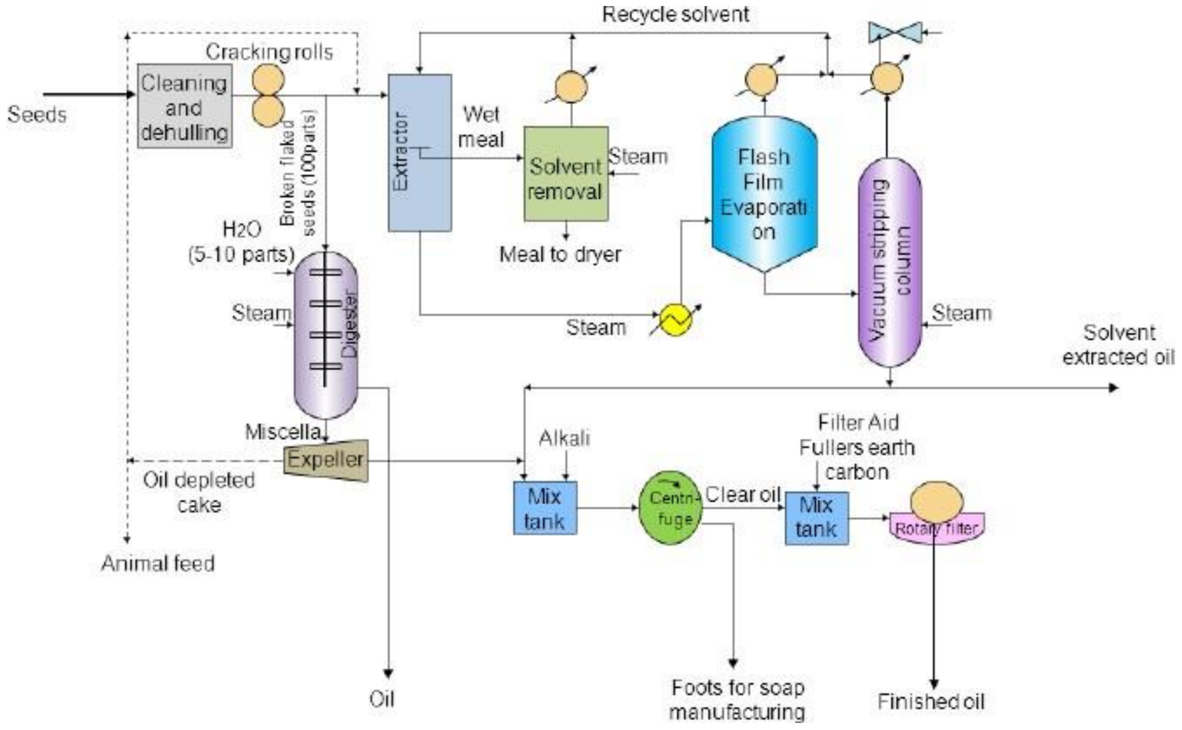


Figure 4.1 Flow sheet for vegetable oil extraction

Functional role of various processes
Cleaner and dehulling:

4.1.1.1 Mechanical cleaning is done to remove stones and other undesirablematerial.

4.1.1.2 Dehulling remove hulls, dry outer covering ofseed.

Cracking rolls:

4.1.1.3 Crushing rolls crush the oil seeds and gets flacked seeds.

Digester:

4.1.1.4 100 parts of flaked seeds are thoroughly mixed with 5-10 parts of water by rotating blades.

4.1.1.5 Softening by means of heat and moisture is donehere.

4.1.1.6 Steam is added for heatingpurpose.

4.1.1.7 Acid is formed by hydrolysis ofester.

4.1.1.8 The seeds get swollenup.

Expeller:

4.1.1.9 The swollen seeds are crushed under greatpressure.

4.1.1.10 Cells of seeds get ruptured and oil isreleased.

4.1.1.11The tapering shape ensures more application of pressure on theseeds

4.1.1.12The oil depleted cake is either sent for solvent extraction or used as animalfeed.

4.1.1.13Oil is sent forpurification.

Mix tank:

4.1.1.14The extracted oil is treated with alkali like NaOH or Na2CO3 to remove fattyacids.

4.1.1.15 It also removes heavy metals, which can start oxidation ofoil.

Centrifuge:

4.1.1.16Acids are separated in centrifugeseparator.

4.1.1.17These separated acids are used as foots for soapmanufacturing.

Rotary filter:

4.1.1.18 The clear oil is treated with some bleaching agent like"Fullers Earth

Carbon” in filter aid before rotaryfilter.

4.1.1.19Rotary drum filter is used for removal of seed particles which may bepresent.

4.1.1.20This finished oil isproduced.

4.1.1.21From this process around 1-2% oil content remains in the meal.

Extractor:

4.1.1.22The flaked seeds or oil extracted seeds from crushing rolls are fed on a movingbed.

4.1.1.23 Oil depleted cake is also added in extractor.

4.1.1.24The solvent extracts oil from theseeds.

4.1.1.25 The wet meal (the left seed part) is collected in the middle and is sent for solvent removal.

Solvent removal:

4.1.1.26Steam is used to extract solvent carried by the oilseeds.

4.1.1.27The rotating blades ensure better exposure tosteam.

4.1.1.28The solvent free meal is sent to dryer and then used as animalfeed.

4.1.1.29Solvent is collected from top and is recycled after cooling it in heatexchanger.

Flash film evaporator:

4.1.1.30The solvent is preheated bysteam.

4.1.1.31Oil is concentrated here by evaporating the more volatile component(hexane).

4.1.1.32The hexane is recycled back to extractor after heatrecovery.

4.1.1.33The use of flash evaporator reduces the cost of vacuum strippingcolumn.

Vacuum stripping column:

4.1.1.34The oil from flash evaporator is fedhere.

4.1.1.35The stripping is done by steam i.e. steam carries away thehexane.

4.1.1.36 And it is under vacuum for the reason that the boiling point of hexane and oil are close to eachother.

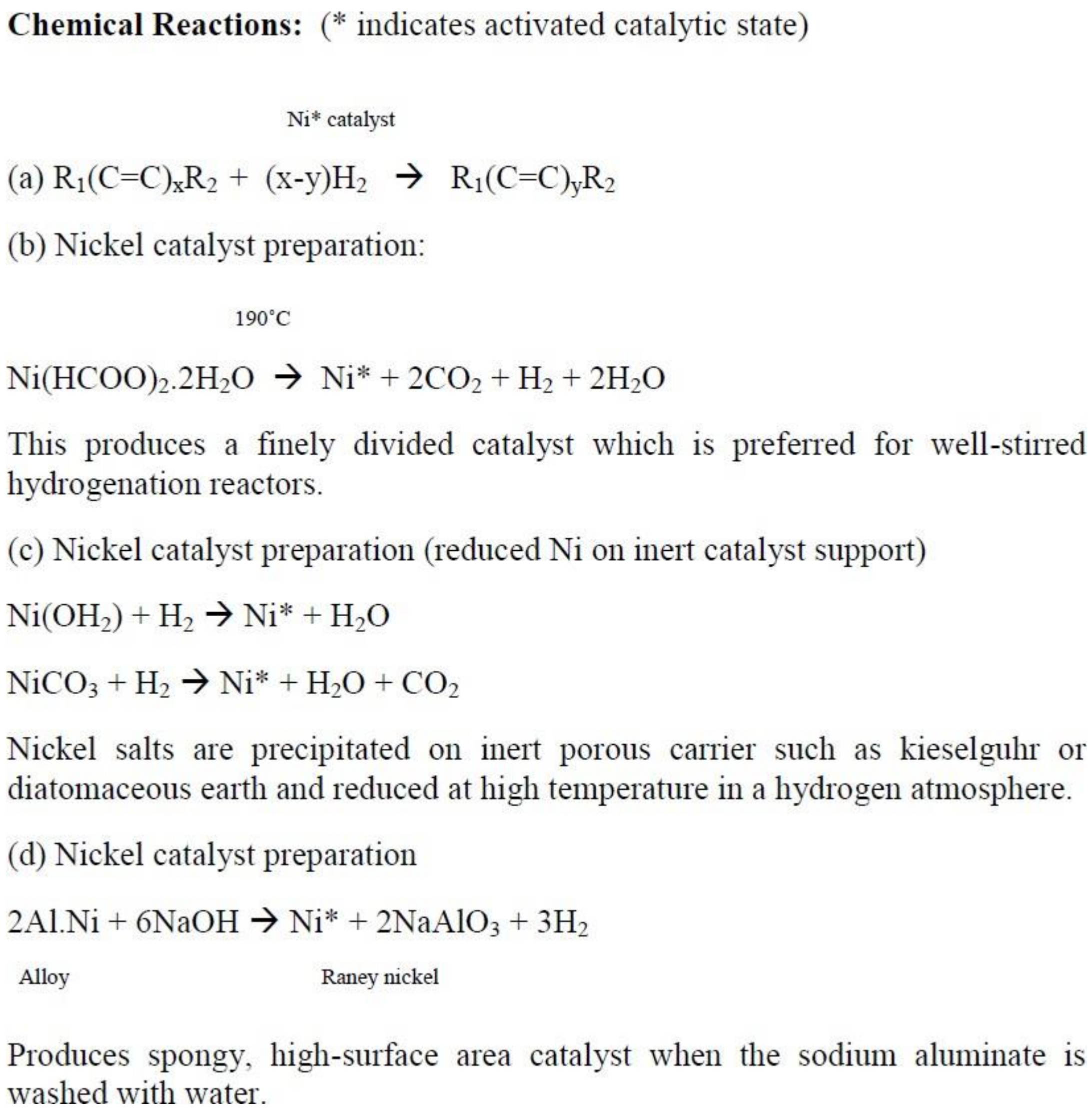
4.1.1.37Jet ejector is used here to generatevacuum.

4.1.1.38The hexane is recycledagain.

4.1.1.39Oil produced here is either directly used or sent forpurification.

4.1.2 HYDROGENATION OFOIL

Hydrogenation process is used to remove double bonds and to make fats and oil saturated. Hydrogenation also raises its melting point and improves its resistance to rancid oxidation. The most common end product of hydrogenation is Vanaspati ghee. Other products include vegetable ghee, hardened industrial oils and partially hydrogenated liquid oil.



Chemical Reactions: (* indicates activated catalytic state)

(a) $R_1(C=C)_xR_2 + (x-y)H_2 \xrightarrow{\text{Ni* catalyst}} R_1(C=C)_yR_2$

(b) Nickel catalyst preparation:

$Ni(HCOO)_2.2H_2O \xrightarrow{190^{\circ}C} Ni^* + 2CO_2 + H_2 + 2H_2O$

This produces a finely divided catalyst which is preferred for well-stirred hydrogenation reactors.

(c) Nickel catalyst preparation (reduced Ni on inert catalyst support)

$Ni(OH_2) + H_2 \rightarrow Ni^* + H_2O$

$NiCO_3 + H_2 \rightarrow Ni^* + H_2O + CO_2$

Nickel salts are precipitated on inert porous carrier such as kieselguhr or diatomaceous earth and reduced at high temperature in a hydrogen atmosphere.

(d) Nickel catalyst preparation

$\underset{\text{Alloy}}{2Al.Ni} + 6NaOH \rightarrow \underset{\text{Raney nickel}}{Ni^*} + 2NaAlO_3 + 3H_2$

Produces spongy, high-surface area catalyst when the sodium aluminate is washed with water.

Raw material: Oils which is to be saturated and pure hydrogen.

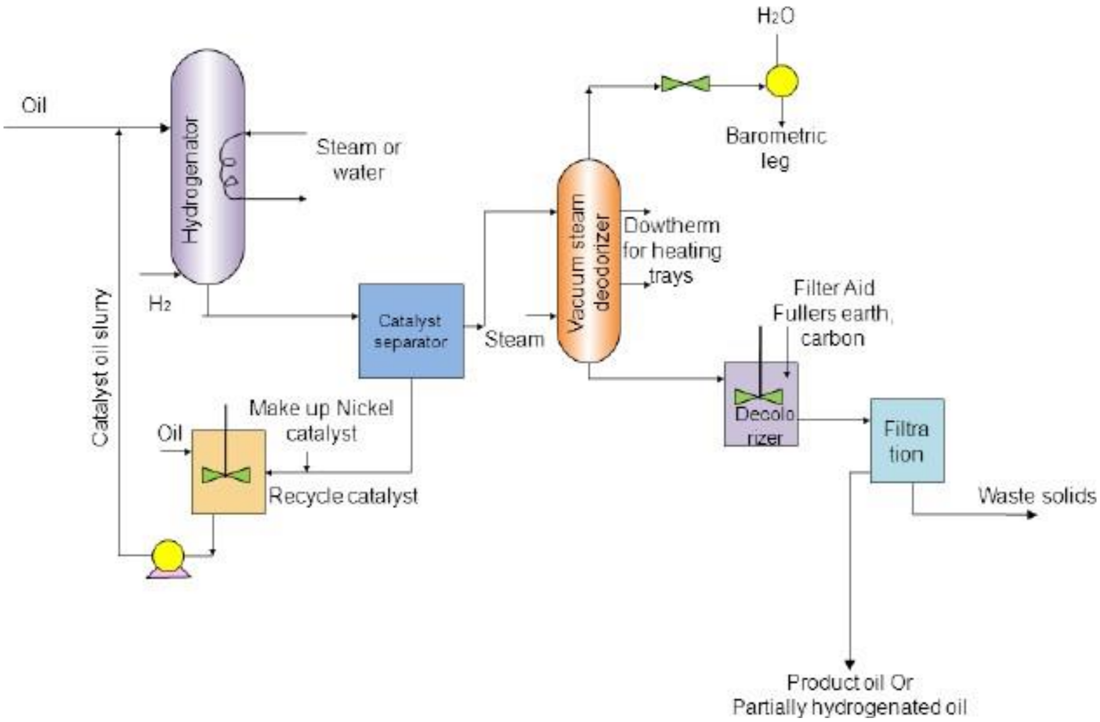


Figure 4.2 flow sheet for hydrogenation of oil

Functional role of main units

Hydrogenator:

4.1.2.1 Oil is fed to thehydrogenator.

4.1.2.2 Hydrogen, and steam is introduced init.

4.1.2.3 The catalyst oil slurry of concentration 5 to 15 kg per ton of oil is alsoput.

4.1.2.4 The reaction is slightly exothermic so steam is sometimes turnedoff.

Deodorizer:

4.1.2.5 The hydrogenated oil is now fed to vacuum steamdeodorizer.

4.1.2.6 It operates in continuousbasis.

Finishing

4.1.2.7 Oil colour is removed by treating with fuller’s earth orcarbon.

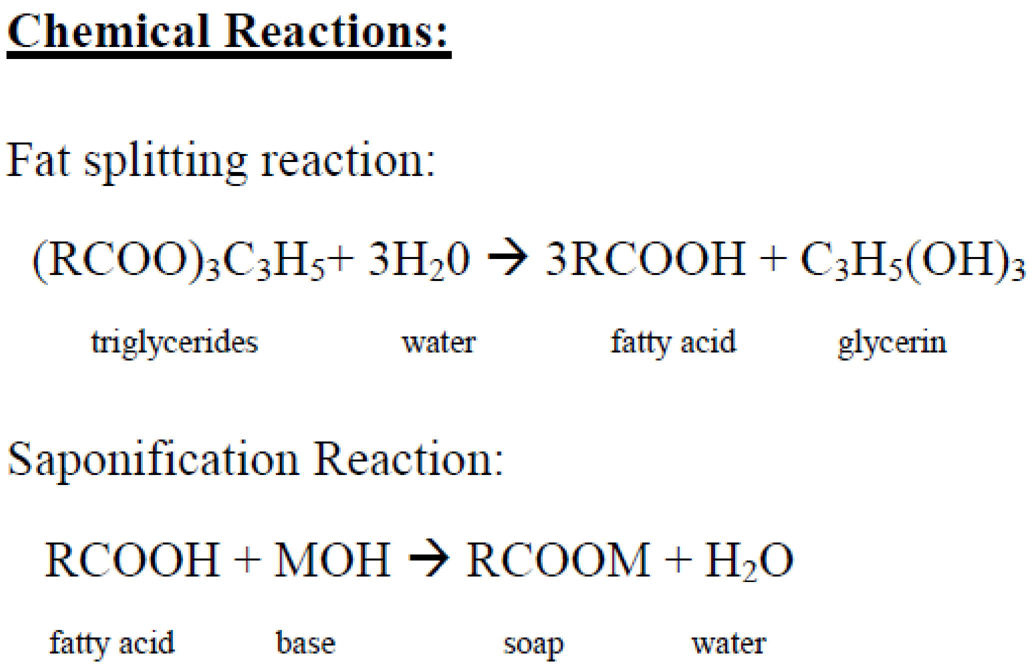
4.1.2.8 It is then filtered, mixed with somevitamins.

4.1.2.9 Now the finished oil is sent for packaging andstorage.

4.2 SOAPS AND DETERGENTS

4.2.1 Introduction

Soaps are sodium or potassium salts of fatty acid. Common fatty acids used are oleic acid, stearic acid, palmitic acid, lauric acid and myristic acid . Soaps are used for human comfort, cleanliness and for industrial use. Soap is a surface active agent or surfactant. The soap molecules contain both hydrophilic part and hydrophobic part. The hydrophilic part of soap is carboxylate head group and hydrophobic part is aliphatic chain. The dirt or grease is cleaned by key mechanism. Most marketed bar soaps contains TiO2 as an opacifier or as a whitener. A variety of dyes are also used to produce coloursoaps.



Chemical Reactions:

Fat splitting reaction:

$$(RCOO)_3C_3H_5 + 3H_20 \rightarrow 3RCOOH + C_3H_5(OH)_3$$

triglycerides	water	fatty acid	glycerin

Saponification Reaction:

$$RCOOH + MOH \rightarrow RCOOM + H_2O$$

fatty acid	base	soap	water

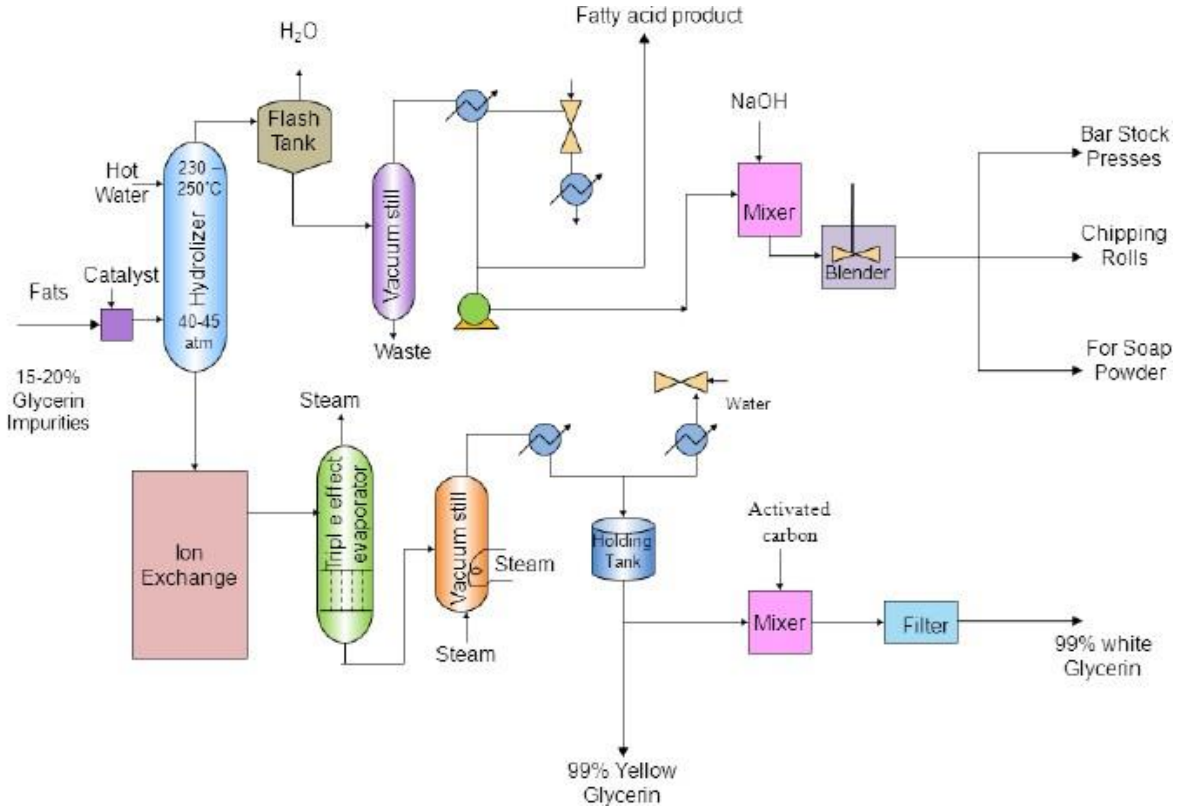


Figure 4.3 Flow sheet of manufacture of soaps, fatty acids and glycerin

Functional role of various processes

Hydrolyser

4.2.1.1 The fat and catalyst are mixed together and enter thehydrolyser.

4.2.1.2 Hot water is addedhere.

4.2.1.3 Intimate mixing is required for the water oil immisciblephase.

4.2.1.4 Water has 10 – 15% solubility in oil andfats.

4.2.1.5 Temperature is maintained at 230˚C - 250˚C and pressure at 40 – 45 atm for reaction between water and organiccompound.

4.2.1.6 The fatty acids stream is produced as top product while glycerin stream is produced as bottom product**.**

Fatty acid stream block
Flash tank:

4.2.1.7 Fatty acids from the hydrolyser enters the steam flash tank to remove water & concentrate the fattyacids.

Vacuum still:

4.2.1.8 The concentrated fatty acids enter a high vacuumstill.

4.2.1.9 Jet ejecter is used to generate vacuum in thestill.

4.2.1.10Wastes are separated from thebottom.

4.2.1.11 Fatty acid is also taken out as a marketableproduct.

Mixer:

4.2.1.12Fatty acid produced from vacuum still is now pumped tomixer.

4.2.1.13 Base such as NaOH or KOH is mixed in appropriate proportions and mixedthoroughly.

4.2.1.14After mixing a viscous mass isproduced.

Blender:

4.2.1.15 The viscous mass from the mixer is sent to theblender.

4.2.1.16 Ingredients like scents, anti fungal&anti bacterial chemicals etc. is mixed in theblender.

4.2.1.17 The blender removes the solid mass which is then sentto:

4.2.1.18 Chipping rolls: to manufacture soapstrips.

4.2.1.19 Spray dryer: To get soap powder (used in manufacture of liquidsoaps).

4.2.1.20 Bar Press Stock: To press and cut the viscous mass into bars ofsoap**.**

Glycerin stream block
Ion Exchange:

4.2.1.2115 – 20% glycerin along with impurities from the hydrolyser goes for ionexchange.

4.2.1.22Here salt and colour is removed fromglycerin.

Triple effect evaporator:

4.2.1.23The product stream from ion exchanger is sent to triple effectevaporator.

4.2.1.24The glycerin solution is concentrated inevaporator.

Vacuum still:

4.2.1.25 The glycerin obtained from vacuum still is called yellow glycerin. It is used for industrial use.

4.2.1.26 The steam produced from evaporator is used in vacuum still to further concentrate the glycerin.

Mixer:

4.2.1.27For removing color, yellow glycerin is treated with activated carbon inmixer.

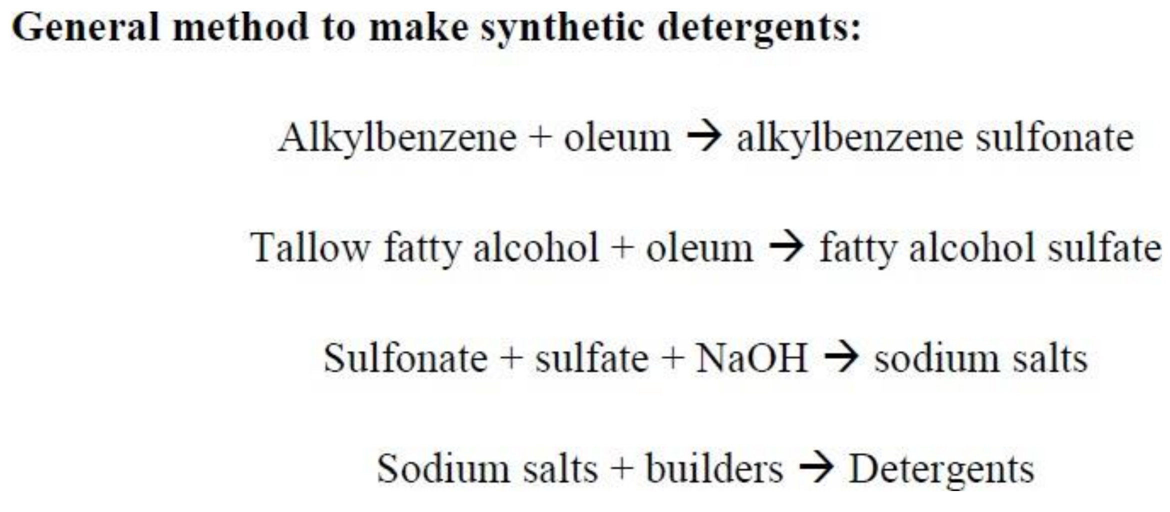
Filter:

4.2.1.28Activated carbon is separated from thesolution.

4.2.1.2999% white glycerin is produced. The yield is 30 – 35kg per ton of soapproduced.

4.2.2 DETERGENTS

Detergents have better surface tension lowering action than soaps. Due to excessive foaming, it is unable to reduce organic content of sewage effluent. Biodegradation of detergent is an important environmental factor. Detergents react with hard water ions. Detergents are of four types - anionic, cationic, non- ionic and amphoteric. Most common type is anionic which is generally made up of sodium salts of an organic sulfate orsulfonate.



General method to make synthetic detergents:

Alkylbenzene + oleum → alkylbenzene sulfonate

Tallow fatty alcohol + oleum → fatty alcohol sulfate

Sulfonate + sulfate + NaOH → sodium salts

Sodium salts + builders → Detergents

4.3 PULP, PAPER AND SUGAR

4.3.1 INTRODUCTION

Chemical industry is one of the oldest industries and playing an important role in the social, cultural and economic growth of a nation and in providing basic needs of humankind - food, shelter and clothing have become an indispensable part of our life. The chemical industry is a key contributor to the world economy and produces more than 8000 products, which is a vital part of agricultural and industrial development in India and has key linkages with several other downstream industries such as automotive, consumer durables, engineering and food processing. Organic chemicals are one of the important sectors of the Indian chemical industry, which provide a vital development role by providing petroleum products, chemical feedstock, basic chemicals, intermediates, and important products like polymer, synthetic fibre, synthetic rubber, paints, varnish, pesticides and explosives, dyes, specialty chemicals. Major feed stocks for chemical industries are coal, petroleum, biomass, oils and fats, sulphur, salt, lime stone, rock phosphateetc.

A process engineer at operation in chemical plant shall have a deeper understanding of the technology on which the process plant is built to produce the profit making chemicals. A chemical engineer with sound knowledge in process technology has the following distinct advantages:

- Ability to clearly distinguish the functional role and importance of various processes and operations in the processplant
- Technical knowledge with respect to the selection of important parameters such as Temperature, Pressure and underlying physical principles of aprocess.
- Ability to distinguish various process streams and their conditions of operation (Temperature, pressure andphases)
- Basic knowledge for process troubleshooting and necessary safety precautions associated to aprocess/operation.

To master chemical process technology five crucial steps are involved namely:

a) Raw-Materials and reactions: A chosen process route to manufacture desired chemicals with appropriate purities will eventually lead to preparing a list of raw-materials and utilities. Thereby, prominent reactions can be also known.

b) Conceptual process flow-sheet: A conceptual process flow-sheet where a chemical engineer has an abstract representation of the actual process flow-sheet will enable quicker learning. A conceptual process flow-sheet typically constitute the followingattributes:

- Raw-material purification (Solid-fluid operations such as cyclone separators, bag filtersetc.)
- Raw-material processing (Heat exchange operations such as furnace heating, coolingetc.)
- Raw-material to product transformation (Reaction operations using CSTR, PFR, PBR and Batch reactors)
- Product purification (In separation processes such as flash, distillation, absorption and extraction)
- Product processing (heat exchangers, phase changeunits)
- Recycle of un-reacted raw-materials as recycle streams to the reactionoperations.

c) Process intensification in the form of heat-integration, stream utilization and waste reduction and multiple recycle streams: These options are in fact optional and they enrich the energy enhancement and waste reduction efficiency ofa

process plant. Originally, chemical plants developed without such process intensification policies have been subjected to rigorous research and case study investigations to identify opportunities for cost reduction and better energy/waste management.

d) Additional critical issues related to various unitoperations/processes

- Safety issues: What safety issues are most relevant and need frequentmonitoring

e) Alternate technologies: For a desired function of a process unit, can thereby alternate technologies that could reduce the cost and even then provide the same functional role and desired flow rates and compositions of the emanatingstreams.

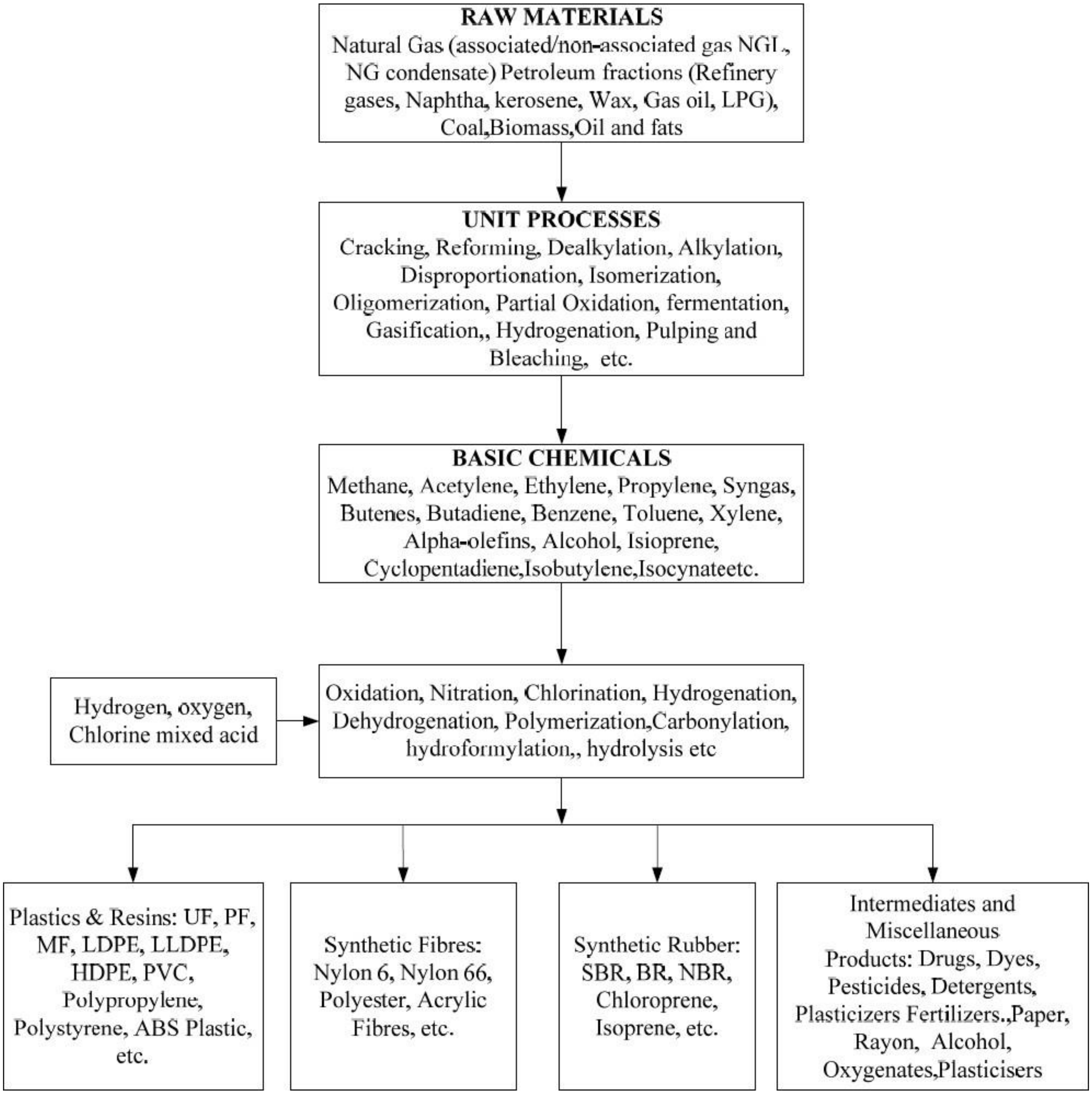


Figure4.4 Structure of Organic ChemicalIndustry

4.2 Process Technology in the Manufacture of Pulp andPaper

- **Acquisition of Raw Material:** Hard wood, soft wood, bagasse, wheat and Ricestraw, sabai grassetc.
- **Raw Material Preparation :**Debarking, Chipping, Cutting,Screening

- Pulping

1.Chemical: Sulphate (Kraft), Soda Pulping, SulphatePulping

2.Semi Chemical:NSSC

3.Mechanical Pulping: Stone Ground Wood (SGW)

Thermo Mechanical Pulp(TMP)

Refiner Mechanical Pulp(RMP)

Cold Soda Refiner Mechanical Pulp (CRMP) Sulfite: Acid Sulfite higher % of free SO2 (Ca, Mg, Na, Ammoniabase)

Bisulfite: (little or no free SO2 (Ca, Mg, Na, Ammoniabase)

- **Washing and Screening:** 3-4 stage washing, screening andcenricleaning
- **Bleaching**: CEHH, CEH, CEHD for chemical pulp Hydrogen peroxide, Sodium peroxide, Hydrosulfite for mechanical
- **Stock preparation:** Beating and refining for imparting suitable properties by making paper, addition of sizing chemicals, colour and additives
- **Paper Making:** Conversion of pulp from stock preparation into a sheet of paper using Fourdrinier Machine or Mould machine
- **Chemical Recovery:** Concentration of spent liquor, burning, causticising and classification ofliquors
- Powergeneration
- **Waste paper processing:** sorting, ,screening, hydro pulping, screening and centricleaning
- Chlorine generation and Bleach liquorPreparation

4.3 PREPARATION OF WOOD PULP BY SULFATE (KRAFT)PROCESS

What is pulp?

4.3.1 Pulp is a commercial fibrous material obtained from bamboo, wood, bagasse (waste material) etc. by mechanical and chemicalmeans.

4.3.2 Pulping means disintegration of bulky fibrous material to smallfibres.

4.3.3 There are mainly three modes of production ofpulp:

(a) Mechanical

(b) Chemical

(c) Semichemical

Sulfate (Kraft) Pulping Process

4.3.4 Most popularly usedprocess.

4.3.5 This is an alkalineprocess.

4.3.6 Na_2SO_4 is added to the cooking liquor. So its common name is sulfateprocess.

4.3.7 The presence of sodium sulfide makes bleaching of pulp easier and the paper produced has betterstrength.

Chemical reactions involved

(i) Digestion (hydrolysis and solubilization oflignin)

$$R\text{-}R' + NaOH \rightarrow R''COONa + ROH$$

$$R\text{-}R' + Na_2S \rightarrow \text{Mercaptans}$$

(ii) Chemical recovery from blackliquor

(a) Smelting

$$2NaR + \text{air} \rightarrow Na_2CO_3 + CO_2 \text{ (lignin)}$$

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

(fromR) (whiteliquor)

(b) Causticizing

$$Na_2CO_3\text{ (aq)} + Ca(OH)_2\text{(s)} \rightarrow 2NaOH\text{ (aq)} + CaCO_3\text{(s)}$$

(greenliquor) (whiteliquor)

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Functional role of various processes

Chipper bin:-

- Chips are fed in thisdevice.
- Cut logs are conveyed to the chipper where rotary disks with heavy knives reducethe wood to size 2-5cm flatchips.
- Size reduction is done to maximize penetration of processchemicals.

Digester tower: -

- Continuous digester tower is 25 – 30 mtall.
- Chips are preheated with volatilizing turpentine and non-condensablegases.
- For controlling digestion temperature, cooking liquor is withdrawn as side streamsand circulated through heatexchanger.
- Digestion is done to free lignin and other non-cellulosiccontent.

- Cooking time is about one and a half hours at170°C.
- To avoid mechanical weakening of fibres, digested chips are cooled with recycledblack liquor.
- Temperature is maintained at 140-180°C and pressure at about 10atm.
- Bottom temperature is maintained at65°C

Blow down valve:-

- This valve reduces the pressure of the stream from 80 atm to 1atm before enteringblow tank.

Blow tank:-

- When hot pulp slurry is passed to the blow tank, heat is recovered in the form ofsteam.
- The chips are preheated with this recoveredsteam.
- The blow tank has high concentration of pulp and low concentration ofwater.

Screens:-

- Pulp is screened so as to remove wood knots and undigestedresidues.

Series of filters

- Pulp is filtered to separate black liquor for chemical recoveryplant.
- Black liquor is also recycled back to digester for cooling the digestedchips.
- Hot water is added to second filter for betterfiltration.

Bleaching of pulp To produce white paper, the pulp is bleached. The chemicals used to bleach pulp must be environment friendly. Bleaching with chlorine produces dioxins and other undesirable products. So, nowadays pulp is bleached with hydrogen peroxide, ozone, chlorine dioxide, oxygen etc. The objective of bleaching is to remove small fractions of lignin that remains afterdigestion.

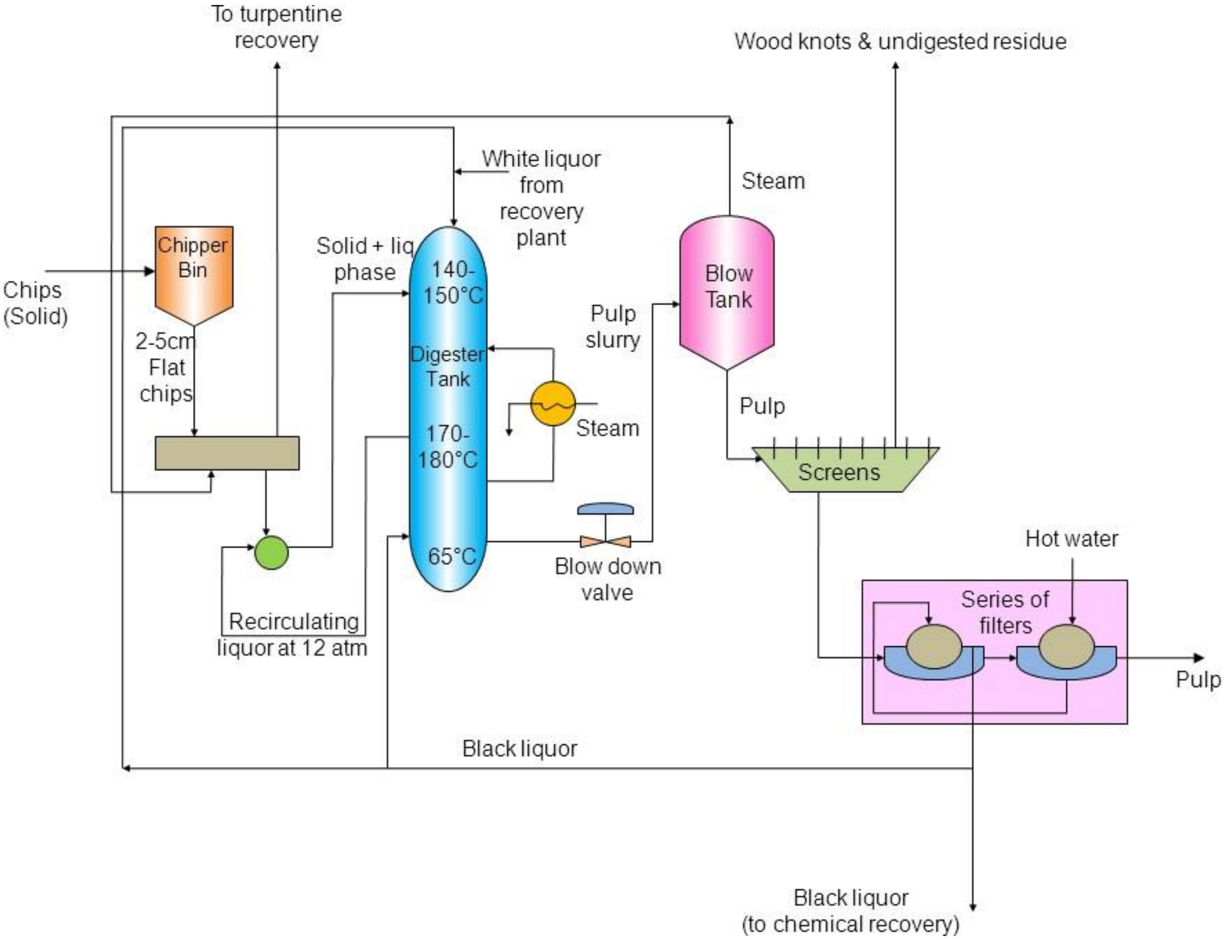


Figure 4.5 Flow sheet of manufacture of pulp by kraft process

4.4 CHEMICAL RECOVERY FROM BLACKLIQUOR

Introduction **The black liquor (lignin-rich) produced from the Sulfate pulp production contains 95-98% of digested chemicals. To reduce air and water pollution and to balance economy of operation, these chemicals should be removed before disposal.**

In chemical recovery process, black liquor is concentrated, burned and limed.

Functional role of various units

Multi effect evaporator

4.4.1 It is a series of single effectevaporators.

4.4.2 Multi-effect evaporator and disc evaporator concentrate the black liquor from 15-18% solid to 60-65%solid.

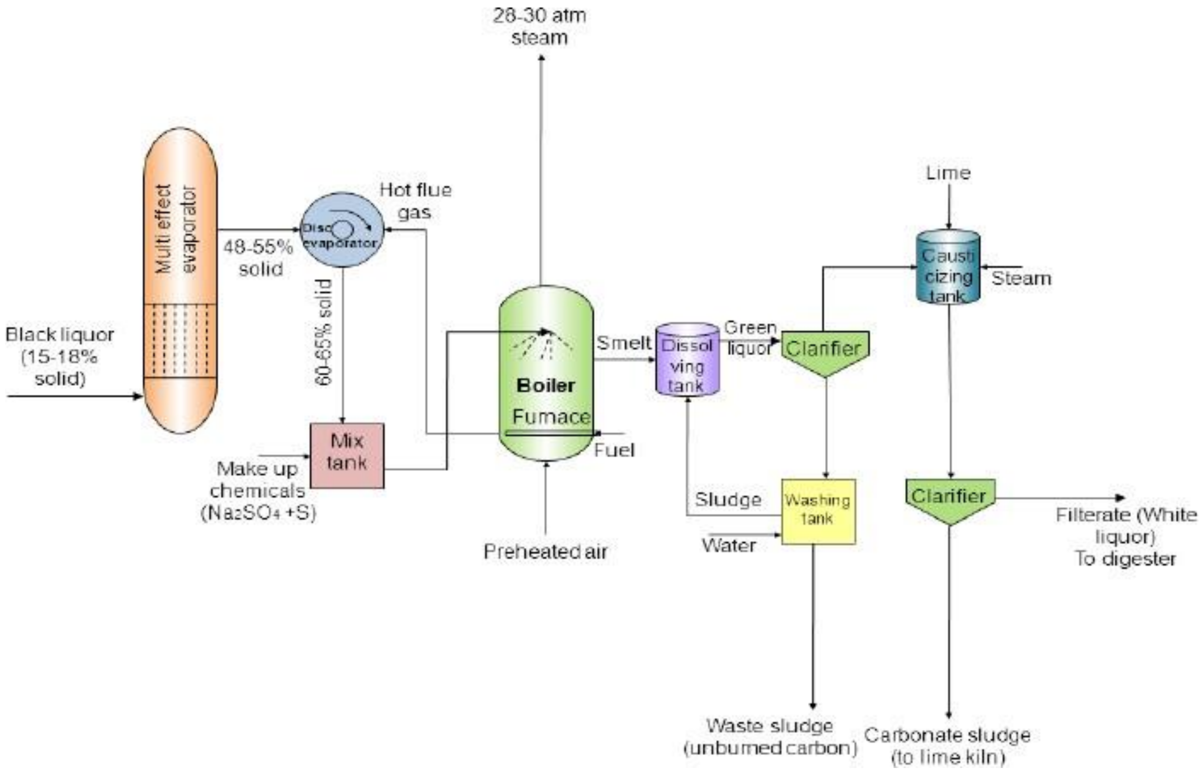


Figure4.6 Flow sheet of chemical recovery from black liquor

Mix tank

4.4.3 It is designed with two agitators to mix theproduct.

4.4.4 Make up chemicals (Na_2SO_4 + S) areadded.

Boiler

4.4.5 It produces moltenslag.

4.4.6 Here organic carbon present in black liquor isburned.

4.4.7 High pressure 28 atm to 30atm steam isproduced.

4.4.8 The reaction that takes place inside furnaceis

Na2SO4+2C□ Na2S +2CO2

Dissolving tank

4.4.9 The molten chemical smelt dissolve immediately with cold water and yield green liquor (aqueousNa2CO3).

Clarifier

4.4.10 It is used for filtering.
4.4.11 It separates calcium carbonate sludge and whiteliquor.
4.4.12 Filtering medium is monelmetal.

Washing tank

4.4.13 Impurities are washed away in this tank afterclarifying.

Causticizing tank

4.4.14 It precipitates limemud.
4.4.15 Carbonate is causticized by addingCa(OH)2

4.5 PRODUCTION OFPAPER

Paper is a sheet material made of fibers which are held together by hydrogen bonds. In wet process, fiber suspension in water is made and it is then made into sheet and dried. Paper making process is generally done on Fourdrinier machine.

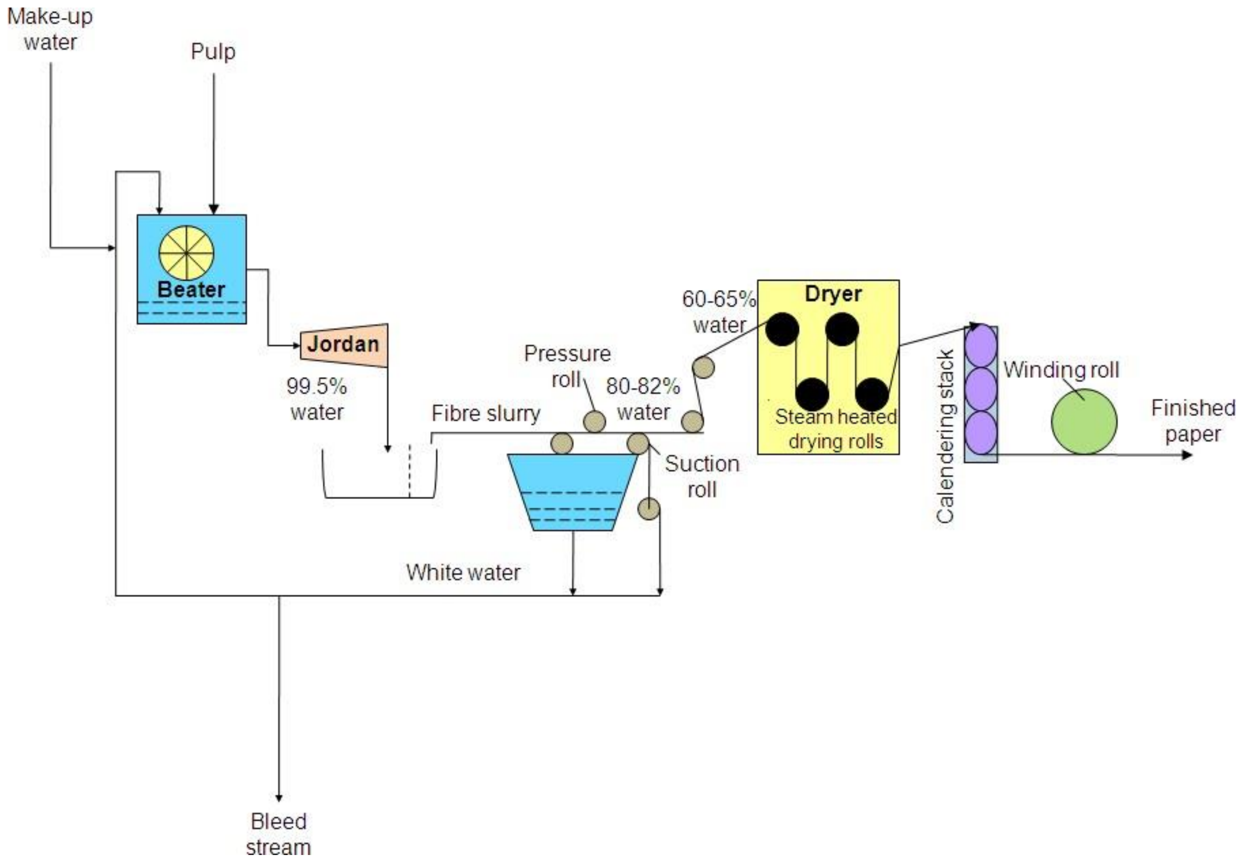


Figure 4.7 Flow sheet of production of paper

Functional role of various units

Beater

4.5.1 Beater mechanically disintegrates the pulp fibers to make paper stronger, uniform, dense, opaqueetc.

4.5.2 It consists of metal blades attached with rotatingdrum.

4.5.3 Finely ground fillers (to increase brightness, flexibility, softness and weight) and coloring agents are alsoadded.

Jordan

4.5.4 It is a conical refiner or Jordan engine.

4.5.5 Metal bars and stones are set inside.

4.5.6 Here, pulp is deformed, defibered anddispersed.

Web forming

4.5.7 99.5% water fiber slurry are made to run on an endless belt at a speed of 50m/min to 500m/min.

4.5.8 Pulp fibers are arranged into web.

4.5.9 Water is drained out bygravity.

4.5.10 Shaking motion is provided for better interlocking of fibers onmat.

4.5.11 White water is collected and it is reused to conserve water and additives and to avoid pollution.

Pressing

4.5.12 Free water is removed by pressing with pressure roll, water mark roll and suctionroll.

4.5.13 Water content is reduced to 60-65%water.

Drying

4.5.14 Additional water is removed by smoothing rolls and series of steam- heated metal drying rolls.

4.5.15 Water is reduced from 60-65% to5-6%.

Finishing

4.5.16 Here paper is passed through a series of calendaring rolls for producing smoothpaper.

4.5.17 It is wounded on a large windingroll.

4.6 MANUFACTURE OF SUGAR FROMSUGARCANE

Introduction

Sucrose is a disaccharide that occurs naturally in most fruits and vegetables. Sugar occurs in greatest quantities in sugarcane and sugar beets from which sugar is separated economically and commercially.

Chemical formula – c12H22O11 Molecular weight – 342 Density = 1.58 kg/m3 Sucrose is soluble in water but slightly soluble in methyl alcohol and ethylalcohol.

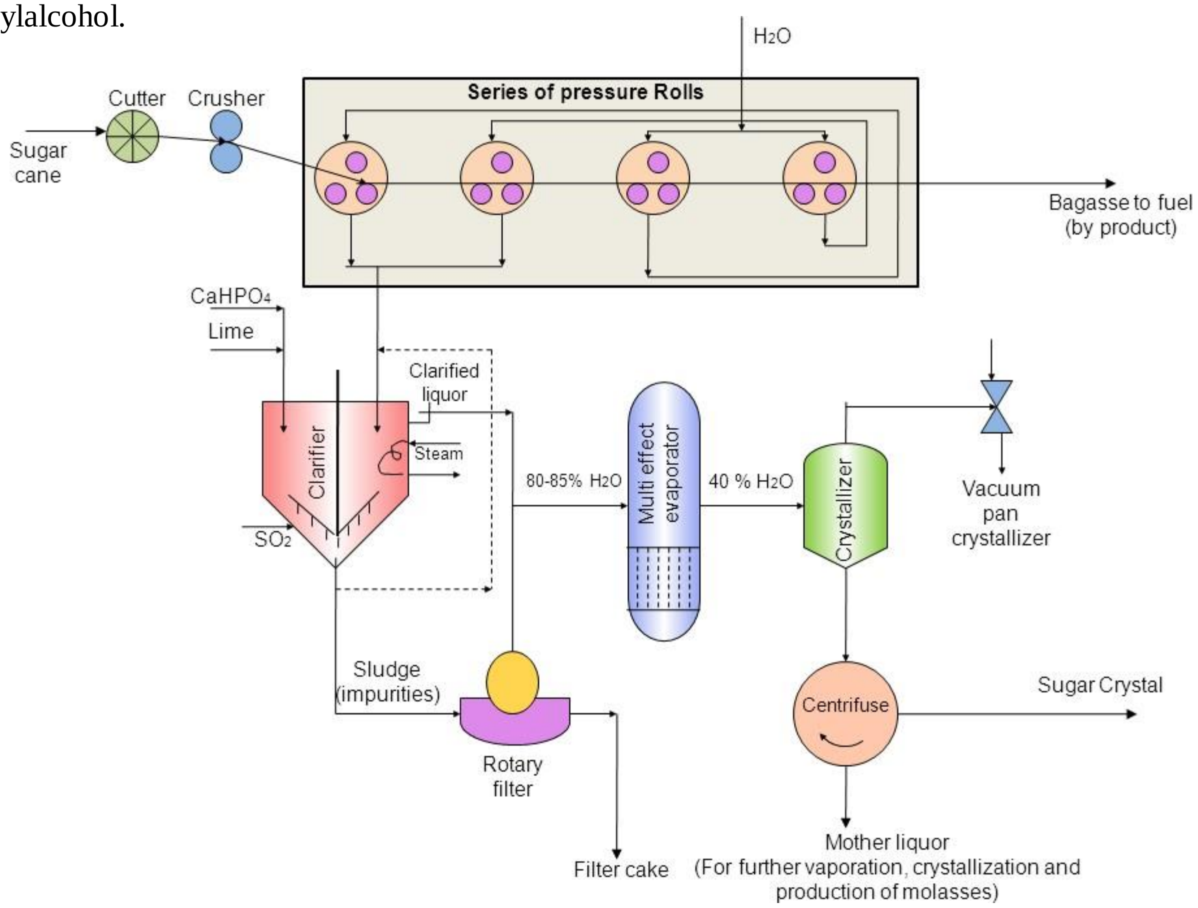


Figure 4.8 Flow sheet of manufacture of sugar from sugarcane Raw

material: Sugar cane

Functional role of various processes

Cutter

- The cutter consists of knives on a cylindrical shaft which rotate at a velocity of 400 to 500 rpm.

- The knives cut the canes into smallpieces.

Crusher

- Canes are shreddedhere.
- It consists of two rollers rotating in oppositedirection.

Series of Pressure mills

- Crushed canes are passed through four pressure mills to extractjuice.
- Each pressure mill is made up of cast ironrolls.
- Rolls are grooved and the width decreases from first roll to thelast.
- Make up water added in the third and fourth mill is recycled back to the first twomills.
- About 85-90% of juice present in cane isextracted.
- Bagasses are produced as byproduct.

Clarifier

- In general two methods of clarification are available for the manufacture of white sugar, namely, Sulfitation process and Carbonationprocess.
- The juice now comes tothickener.
- To precipitate the colloids, calcium phosphate(CaHPO4) is added followed by milk of lime.
- The milk of lime used has 9 to 10% strength and about 400mg CaO/litrealkalinity.
- Apart from maintaining pH about 7, SO2 gas also acts as a bleachingagent.
- Phosphoric acid or CO2 can also be substituted as acidifying agent depending upon the type of extractedjuice.
- At the bottom of clarifier, mud (impurities) are settled anddrained.
- Steam is used to slightly heat thejuice.

Rotary filter

- The underflow mud from the bottom of thickener is passed to a continuous rotary filter press to recover sugarsolution.
- This sugar solution if it is clear, is passed to multieffect evaporator or otherwise recycled back toclarifier.
- The filter cake produced is used forfertilizer.

Multieffect evaporator

- The clarified liquor overflows to the 3-4 forward feed multieffectevaporator.

- Here juice is concentrated from 80-85% H2O to 40% H2O to make juice readyfor crystallization.
- A vacuum of 63cm is maintained in the lasteffect.

Crystallizer

- The clarified concentrated sugar solution comes tocrystallizer.
- The sugar solution is further boiled in vacuum pans at vapor temperature of 57˚Cuntil fine cloud of crystals isseen.
- Crystallization is completed in vacuum panunit.

Centrifuge

- The mixture of crystals and syrup is calledmasscuite.
- The masscuite from crystallizer is centrifuged in basket type centrifuged to basket type to centrifuge remove mother liquor (molasses) which is abyproduct.
- The high grade sugar crystals are obtainedhere.
- The centrifuge speed is maintained at 800 to 1000rpm.

4.7 STARCH AND STARCHDERIVATIVES.

Introduction

Starch consists of a chain of D-glucopyranosyl units. It is used in the manufacture of textiles, paper, adhesives, insecticides, paints, soaps, explosives, and derivatives as dextrins, nitrostarch and corn sugar. Chemical formula- $C_6H_{10}O_5$ **Starch gets hydrolysed by acids, alkalis and enzymes giving dextrin, dextrose. Starch forms gels with water within several minutes at 60- 80˚C. The major source of starch is maizekernels.**

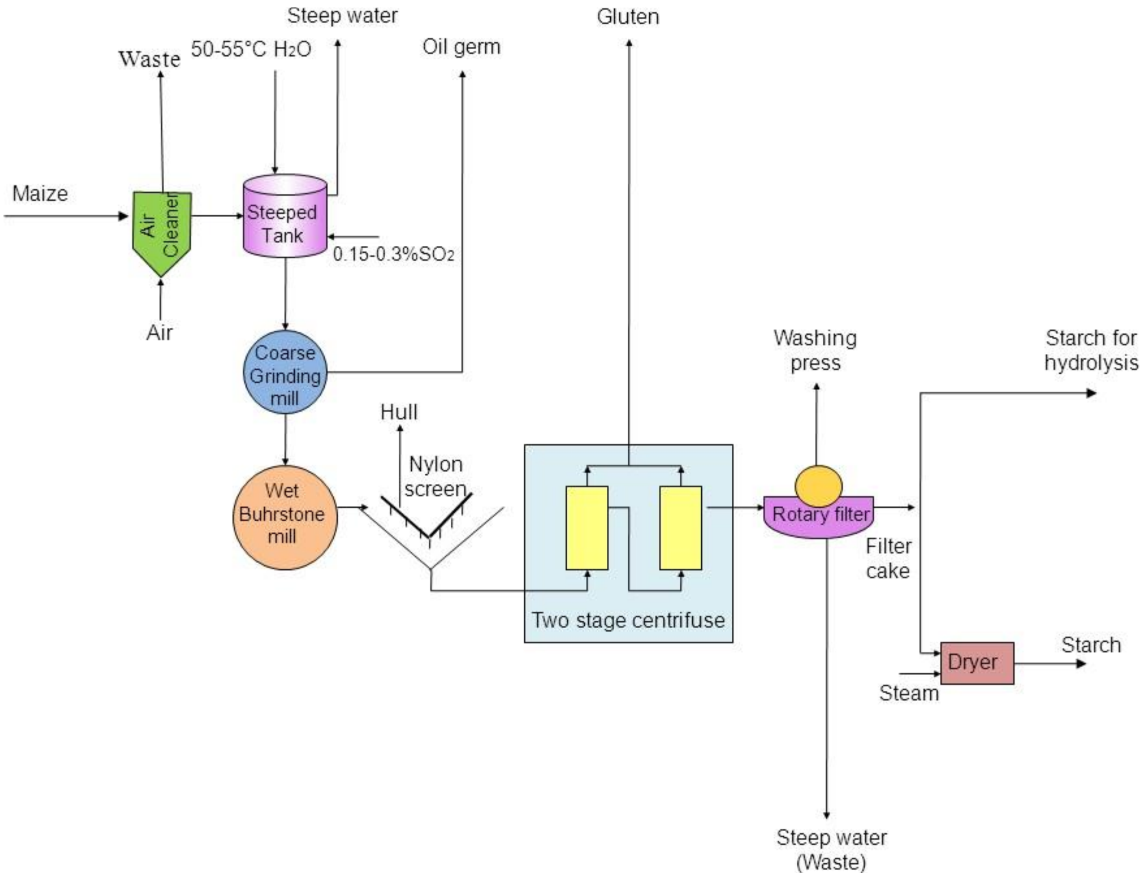


Figure 4.9 Flow sheet of manufacture of starch

Functional role of various processes

Air cleaner:-

- At first, maize kernel containing 60-65% starch is introduced in aircleaner.
- Air is passed through the bottom of cleaner.

Steeped tank:-

- Air cleaned maize kernel is passed to steeped tank to make itsoft.
- 50-55˚C water and 0.15-0.3% SO2 isadded.
- Here SO2 acts as abacteriostatic.
- Steeping is done to yield high production and quality ofstarch.
- The residence time is 40-50hours.

Grinding mill:-

- The soft grains are passed through coarse grinding mill to rupture thecells.

- The floating germ oil from the tank isremoved.

Buhrstonemill:-

- The kernel is then wet ground in buhrstonemill.
- This mill completely disrupts the cells of endosperm and release starchgranules.

Nylon screen:

- The wet ground kernel is then passed through nyloncloth.
- Water washes the starch through thescreens.
- The fibre and hulls is left over on the nylonscreen.

Two stage centrifuge:

- The gluten is water insolubleprotein.
- Gluten is a light fraction which is separated in two-stagecentrifuge.

Rotary filter:

- Water starch mixture is then passed then passed to continuous rotaryfilter.
- Starch is separated as filter cake which is of yellow colored and contains high amounts of protein.
- Other products can also be made by hydrolysis ofstarch.

Dryer:

- Starch as filter cake is dried and powdered in dryer with the introduction of steam in dryer and produced as pearlstarch.

DEXTRINMANUFACTURING

Dextrin is a carbohydrate with the same general formula as starch. Dextrins are polysaccharides and are produced by the hydrolysis of starch by heat and by acid. Their nature and chemical behavior depend upon the kind of starch from which they are produced. For commercial use dextrin is prepared by heating and drying starch and then treating this starch with HCl to produce a colorless to yellowish, tasteless and odorless powder which when mixed with water, forms a strong adhesive paste.

Typically the Littleford Day Dextrin process follows these processing steps:

1. Product (starch) is charged into the Littleford Day Ploughshare® Processor Unit. Once the plows and jacket heating are initiated, hot air drying of the starch to the proper moisture level begins.

2. After the prescribed moisture is removed and the dry starch has reached the required temperature, the Anhydrous (HCl gas) is injected onto thestarch.
3. After a predetermined reaction time and temperature the product is then ready for additional processing or for cooling anddischarging.

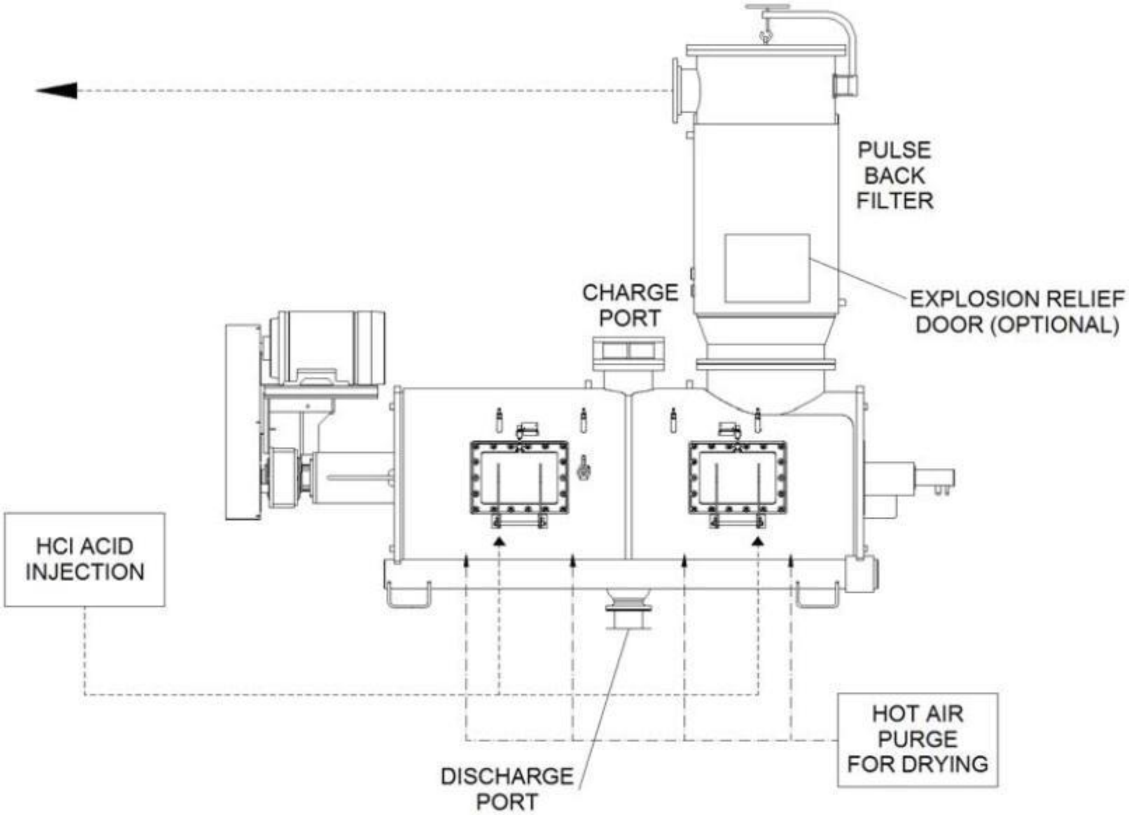


Figure 4.10 Flow sheet of manufacture of Dextrin

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SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 5 SYNTHETIC ORGANIC CHEMICALS **SCHA1305**

UNIT 5 SYNTHETIC ORGANIC CHEMICALS

Methane and synthesis gas, ethylene, acetylene and propylene. Aromatic chemicals - Benzene, toluene and xylene. Production of thermo-plastic and thermo-setting resins: polyethylene, polypropylene, and Polyvinylchloride, Polymers and their engineering applications. Polyamides and polyesters and processes for the production of natural and synthetic rubber.

5.1 INTRODUCTION

Polymer: Polymers are large chain molecules having a high molecular weight in the range of 10^3 to 10^7.These are made up of a single unit or a molecule, which is repeated several times within the chainedstructure.

Monomer : A monomer is the single unit or the molecule which is repeated in the polymer chain. It is the basic unit which makes up thepolymer.

Thermosetting Polymer : There are some polymers which, when heated, decompose, and hence, cannot be reshaped. Such polymers have a complex 3-D network (cross-linked or branched) and are called Thermosetting Polymers. They are generally insoluble in solvents and have good heat resistance quality. Thermosetting polymers include phenol-formaldehyde, urea- aldehyde, silicones and allyls.

Thermoplastic Polymer : The polymers in this category are composed of monomers which are linear or have moderate branching. They can be melted repeatedly and casted into various shapes and structures. They are soluble in solvents, but do not have appreciable thermal resistance properties. Vinyls, cellulose derivatives, polythene and polypropylene fall into the category of thermoplastic polymers.

5.2 POLYMER CLASSIFICATION

Polymers are generally classified on the basis of

i. Physical and chemical structures.

ii. Preparation methods.

iii. Physical properties.

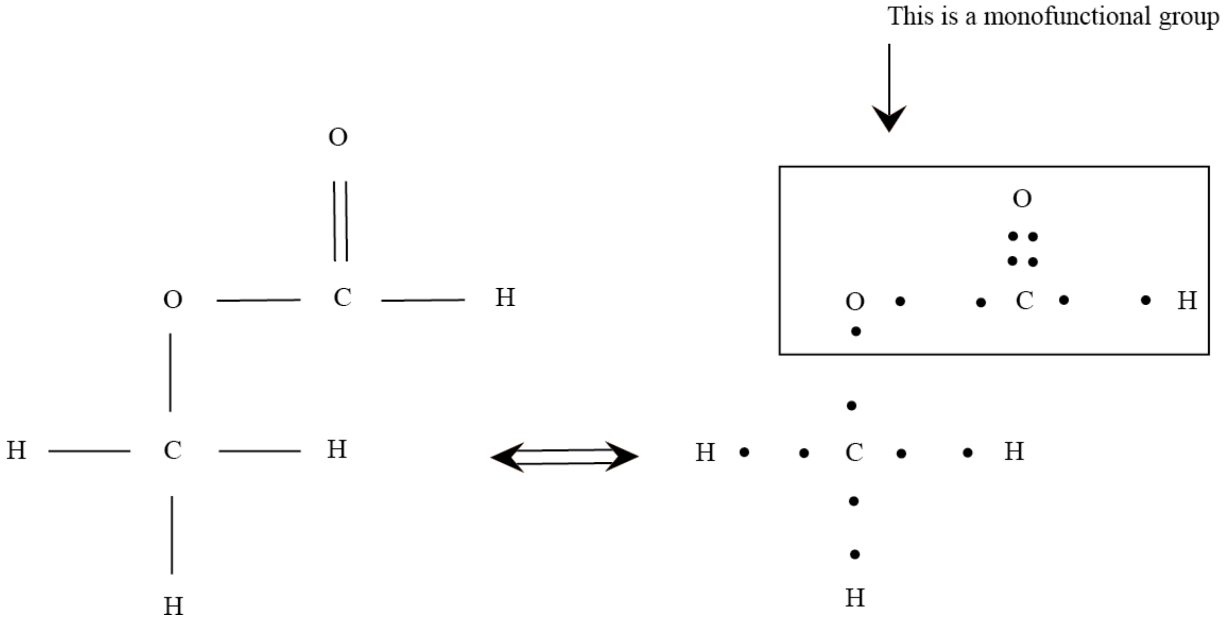
iv. Applications.

5.2.1Classification According To Physical And Chemical Structures:

1. On the basis of functionality or degree of polymerization:

The functionality of a monomer or its degree of polymerization determines the final polymer that will be formed due to the combination of the monomers. The number of reactive bonds or groups that are available for coupling will determine whether the monomer will be mono-, bi-, tri-, or polyfunctional.

a. Monofunctional or unifunctional: When a single reactive group is present in the monomer molecule, then it is termed as monofunctional or unifunctional. However a monofunctional group cannot lead to the propagation of a polymer chain. For example , in carboxylic acid, CH_3COOH, the –COOH group is the monofunctionalgroup.

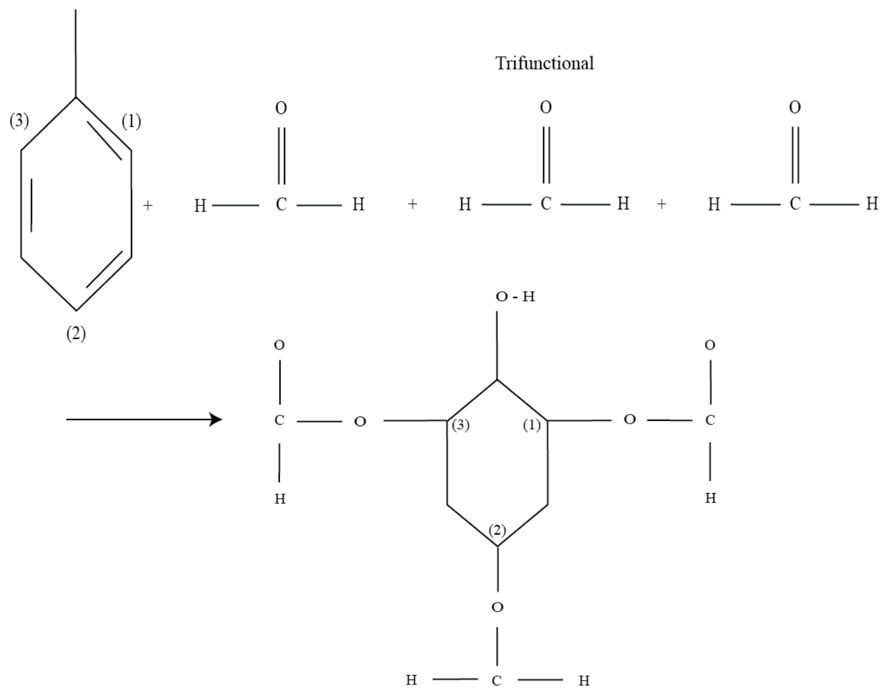


b. Bi functional : When two reactive groups are present in the monomer molecule, then it is termed as bi functional. More often than not, polymerization reaction with bi functinal groups occur when a double bond splits to couple with another double bonded monomer. If a double bonded molecule is present, then the polymer would be–

$$n\,R=R \longrightarrow -(R-R)_n-$$

c. Trifunctional : When a monomer contains three groups that are reactive, then it is termed as trifunctional. It is important to note that a trifunctional polymer may be a mixture of monofunctional and bifunctional monomerstructures.

Let us consider the reaction of phenol and formaldehyde to form trimethyl phenol.



In the figure , the three formaldehyde molecules contain three reactive groups in the form of -OH groups. These reactive groups get attached to the positions 1, 2 and 3 in the phenol molecule.

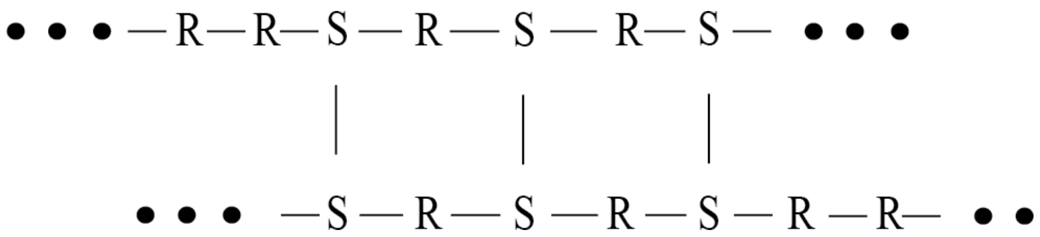
2. On the basis of physical structure :

a. Linear polymers : These polymers have a linear structure. Only bifunctional monomers can form linearpolymers.

• • • • —R—R—R—R—R—R—R—R— • • •

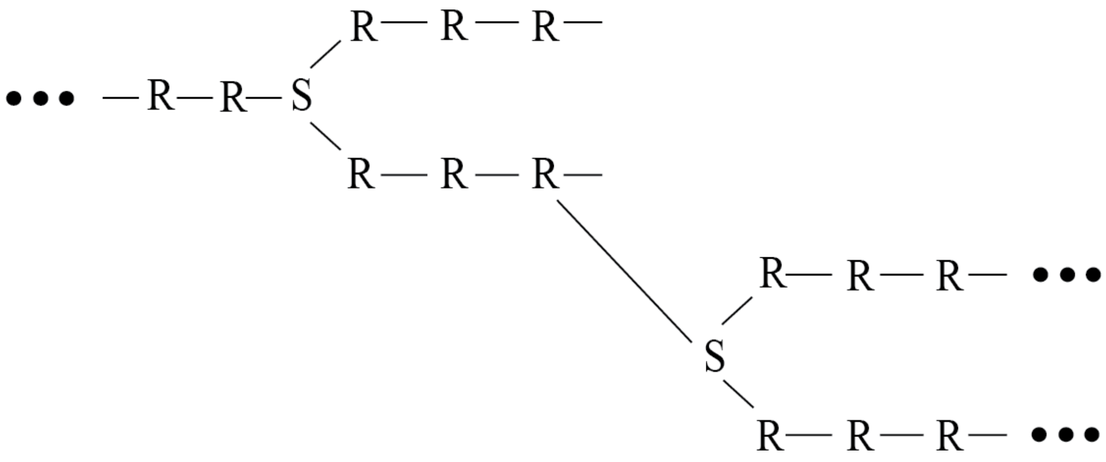
They are generally thermoplastic polymers, and except for very high molecular weight materials, they are soluble in solvents.

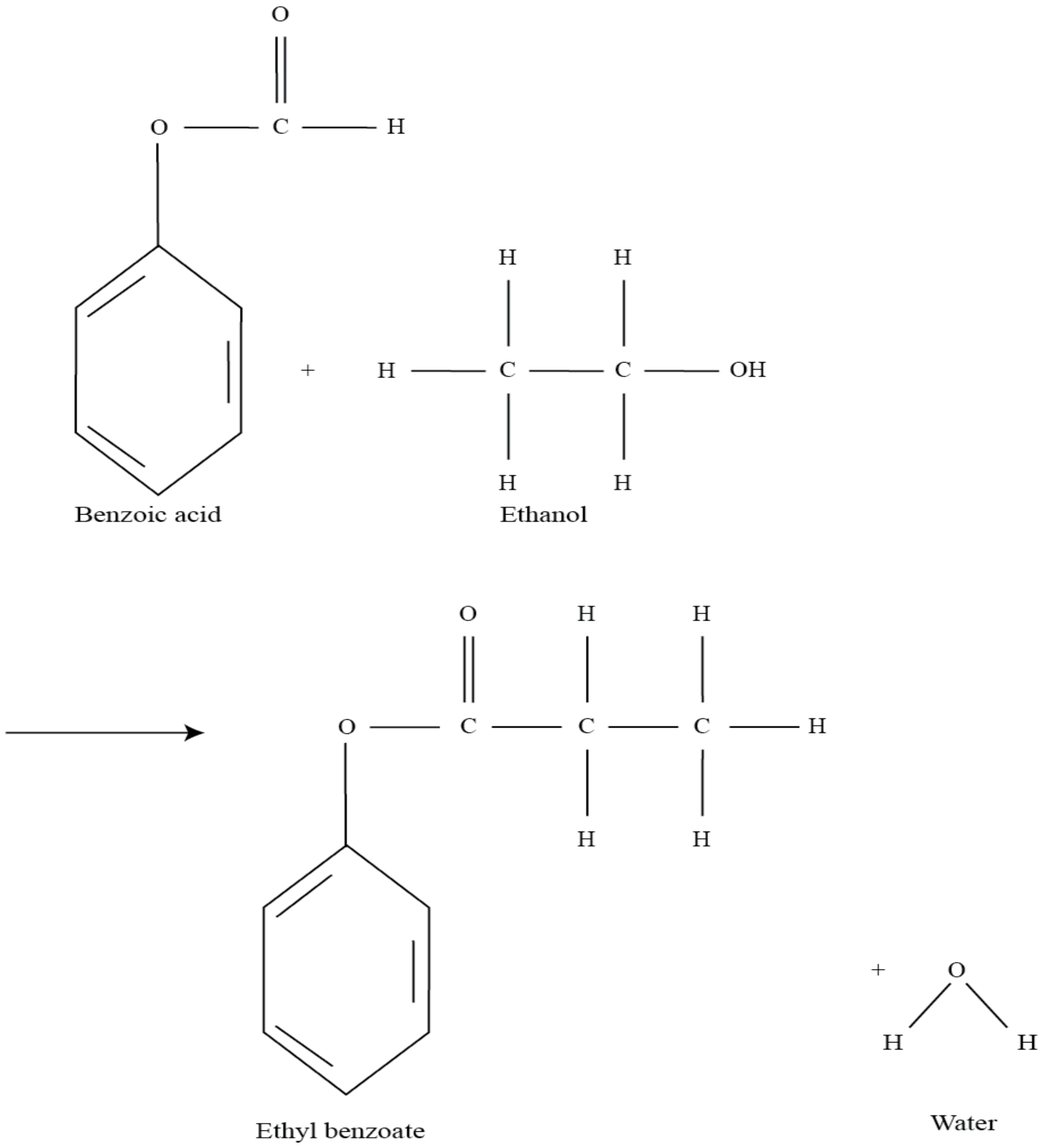
Cross –linked polymers : These polymers have a 3-D network structure. Only bi-functional and tri-functional monomers can form cross-linked polymers. Elastomeric properties are generally endowed in polymers have cross-linkage across the linearchains.



Thermosetting polymers having high thermal resistance and mechanical strength may be formed if the cross-linking among the monomer groups is extensive.

b. Branched –chain polymer : When there is no cross-linking in a polymer molecule , yet, branches arise from the parent polymer chain , then the polymer formed is called a branched – chainpolymer.





A small amount of trifunctional impurities in a bifunctional monomer may cause branching. Branching may create several physical properties in a polymer such as decrease of solubility in solvents, rise in the softening point and also the reduction in thermoplastic properties.

3. On the basis of chemical reactions :

Depending upon the basis on which monomers undergo chemical reactions to form polymers, polymers can be further subdivided.

Polycondensation Reaction : It is a stepwise process in which the monomers react by eliminating small molecules like H_2O, NH_3, CH_2O and NaCl in a repetitive manner . Indefinite growth of the polymer occurs at both ends. The condensation reaction terminates when one of the reacting molecules is completely consumed in the reaction. In general, bifunctional monomers with different functional groups undergo such reactions. One common example of a condensation reaction is the esterification reaction. Benzoic acid reacts with ethanol undergoing condensation reaction to give Ethyl benzoate, expelling one molecule of water (H_2O). The polymer formed after the reaction (in this case, ethyl benzoate) is called the condensation polymer.

Addition Reaction : These reactions occur by the formation of rapid formation of rapid chains and no elimination of small molecules occur. Such reactions generally occur among double or triple-bonded molecules, or oxo-ringcompounds.

Addition reactions can be further of three types—

i. StepReactions
ii. ChainReactions
iii. IonicReations

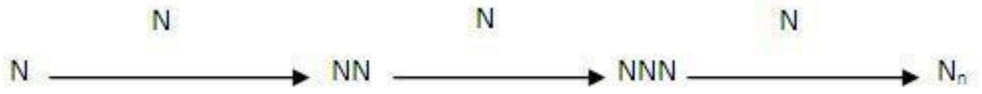
i .Step Reactions : In step reactions, a π bond is broken and two new σ bonds are formed. The substrate of an electrophilic addition reaction must have a double bond or triple bond.

ii .Chain Reactions : In chain addition reactions, the polymer is formed in a single step and within the fraction of a second. The chain kinetics occur in 4 steps – Initiation, Propagation, Transfer andTermination.
Variations of Chain Addition Reaction :

If we consider ‘M' and ‘N' be two monomeric species, then the chain addition reaction can be of the following types –

Homopolymerization

If only M and N are present,



Copolymerization

If M and N are present together,

Random type

- MM MN NNN MM N M MM NN……

Alternating type

- M N M N M N M N M………

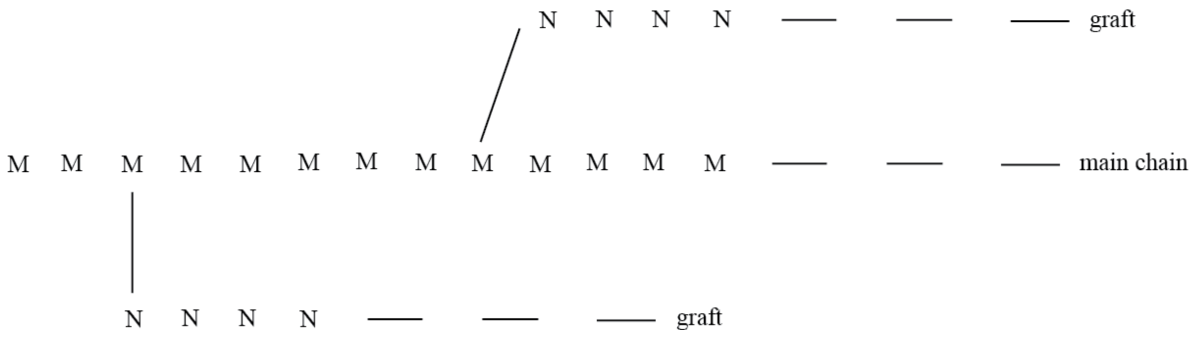
Block Polymerization

In this type, multimers resulting from straight polymerization coupled together in blocks.

— — ● M M M ● N N N N ● M M ● N N N N N ● — —

Graft Polymerization

These have a structure which differs from block polymers ; and are formed from M and N multimers.



In Graft polymerization, β – or X - radiation or chemically reactive functional groups ensue the formation of reactive radicals on the main chain or on the grafted section.

Reaction Kinetics :

Let,

A – radical source

B – monomer molecule

*- activated

B_m , B_n – growing monomer molecule chain of lengths ‘m' and ‘n'.

X – any solvent , impurity, etc. which can act as transferable energyspecies.

Initiation It is the rate – controlling step in the chain Addition Reaction. This stage is relatively slow and requires energy for breaking and forming the bonds. The energy is supplied as thermal energy or in the form of radiations (α -, β -, or ¥ - rays). However , by using a catalyst, the activation energy required can be substantiallylowered.

$$nA \xrightarrow{\text{Energy}} A^*, 2A^*, \ldots$$

Propagation These reactions occur between the already formed free radicals and an inactive monomer. With low activation energy, there is more probability of reaction or collision between the species. As a result, rapid reactions occur to attain the given degree of polymerization.

$$A^* + B \longrightarrow B^* + A$$

$$B^* + B \longrightarrow BB^*$$

$$BB^* + B \longrightarrow BBB^* \longrightarrow B^*_n$$ [B^*_n controls the degree of polymerization]

Chain Transfer Reaction

In this reaction , one radical of the multiplying chain terminates and without the loss of any number of free radicals, a new chain begins. These reactions control the degree of polymerization and the rate of branching of thepolymers.

Branching usually occurs at higher temperature, with the reaction of a multimer with a dead chain, followed by lengthening of the branch due to successive monomer addition.

$$B^*_n + B \longrightarrow B_n + B^* \quad \text{(with monomer)}$$

$$B^*_n + B_m \longrightarrow B_n + B_m^* \quad \text{(with multimer)}$$

$$B^*_n + X \longrightarrow B_n + X^* \quad \text{(with other molecules)}$$

Chain Termination

A chain terminates with the net loss of one free radical. It may occur by the collision of growing chains with coupling or disproportionation. However , if a growing chain collides with an initiation radical, undesirable impurities or the wall of the reaction vessel, then it might also terminate.

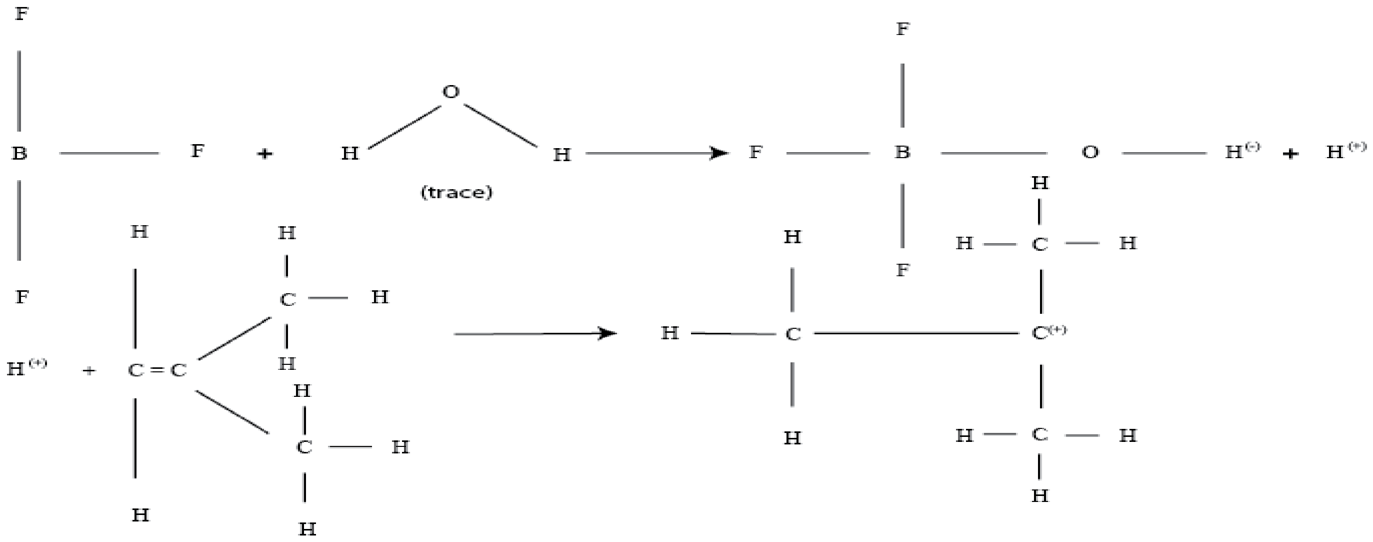
$$2\,B_m^* \longrightarrow B_{2n}$$

$$B^*_n + B_m^* \longrightarrow B_m + B_n$$

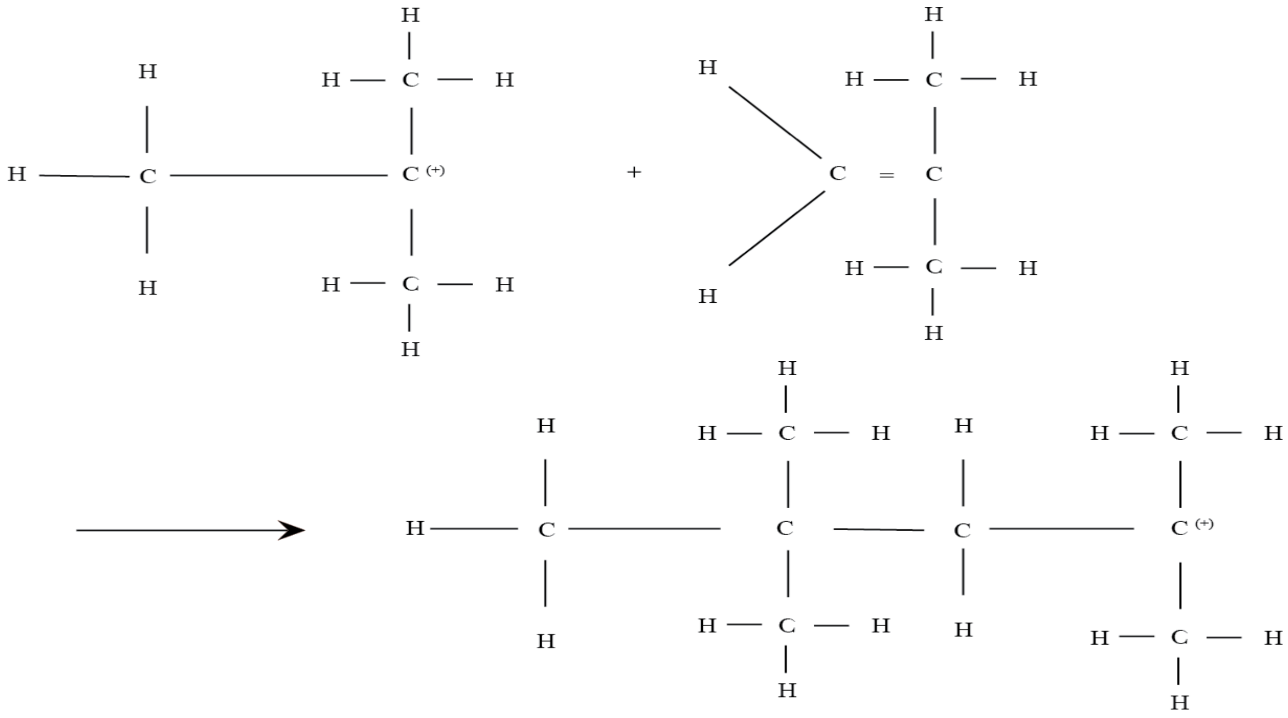
$$B^*_n + Y^* \longrightarrow B_n + Y$$

iii .Ionic Reaction :These are similar to chain addition reaction with free radicals , however ; instead of neutral, unpaired electrons, they have a positive or negative charge. A co-catalyst may be used, which is usually a trace of H_2O, which is necessary to produce ionization, as the reaction cannot occur in absolute dry conditions.An example of ionic addition reaction is the preparation of polyisobutylene with boron trifluoridecatalyst.

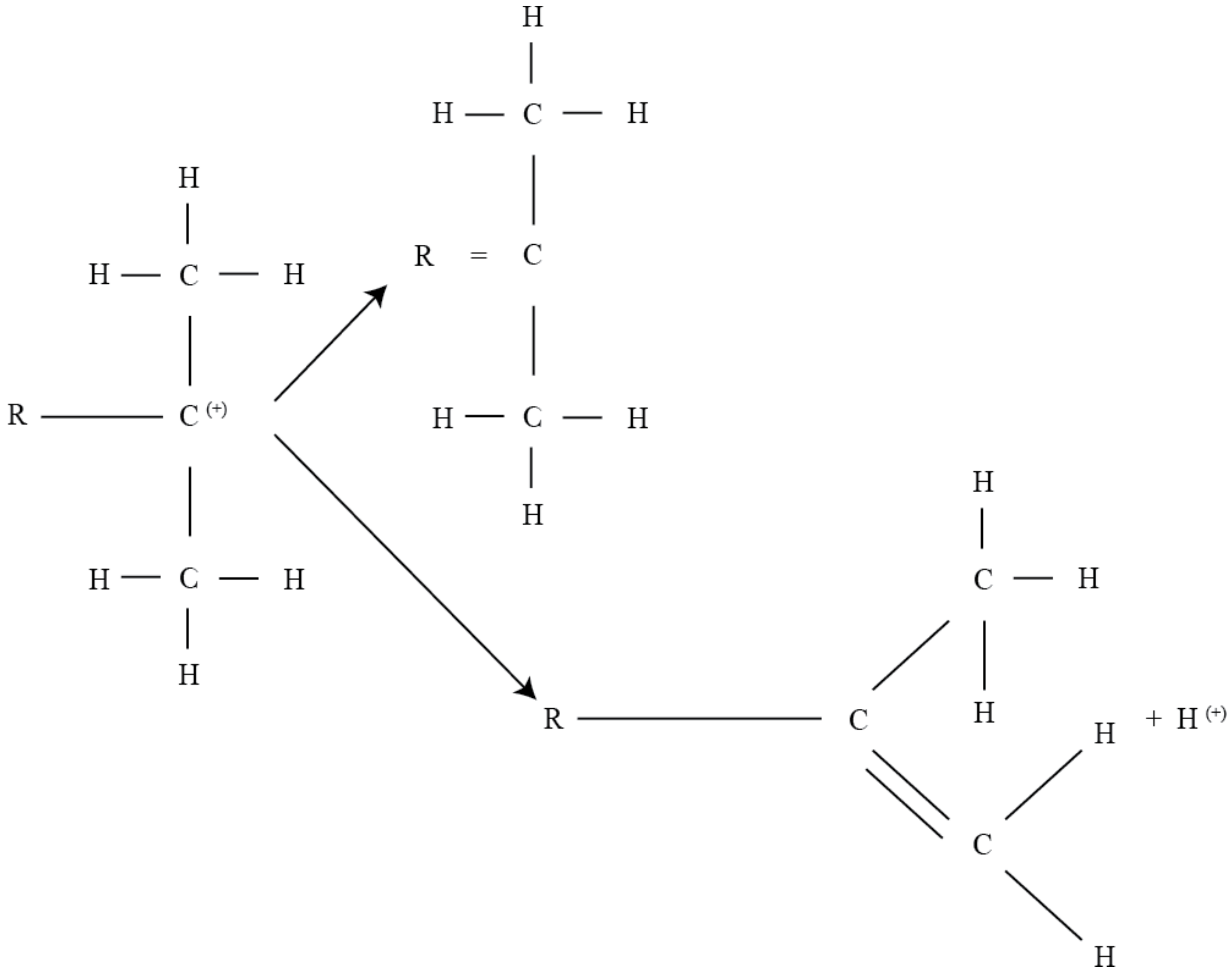
Initiation



Propagation



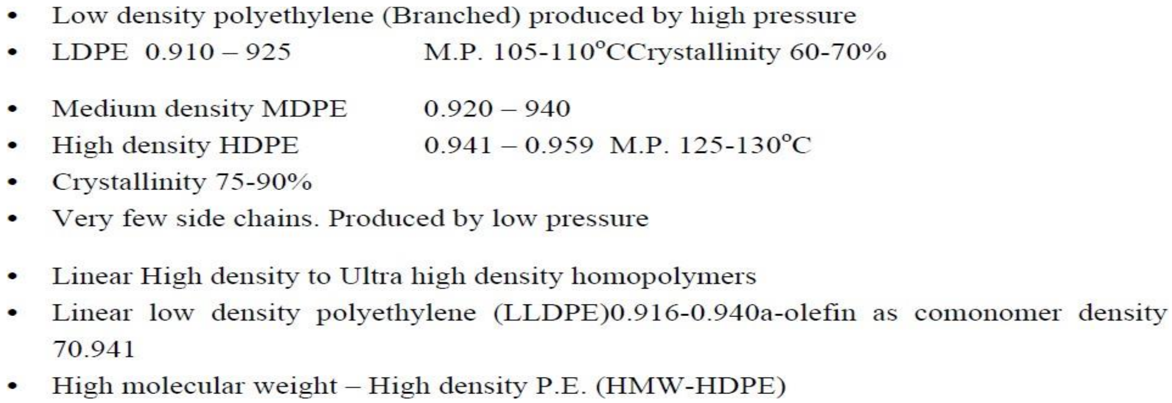
Termination



5.3 POLYETHYLENE

Polyethylene is one of the most widely used thermoplastic and its ever increasing demand is due to availability of monomer ethylene from naphtha and Gas cracker plant. First polyethylene plant in India was based on ethylene from molasses. Some of the other deriving force for fast growth and use of polyethylene are ease of processing the polymer, its relative cost, resistance to chemicals and its flexibility [Hatch &Matar, 1979]. A wide variety of polyethylene varying intensity and characteristics for wide range of application is available. Low density polyethylene (Branched) produced by high pressure.

Advantage: Low cost, excellent dielectric properties, moisture resistance, very good chemical resistance, available in food grade, processed by all thermoplastic methods.



- Low density polyethylene (Branched) produced by high pressure
- LDPE 0.910 – 925 M.P. 105-110°CCrystallinity 60-70%

- Medium density MDPE 0.920 – 940
- High density HDPE 0.941 – 0.959 M.P. 125-130°C
- Crystallinity 75-90%
- Very few side chains. Produced by low pressure

- Linear High density to Ultra high density homopolymers
- Linear low density polyethylene (LLDPE)0.916-0.940a-olefin as comonomer density 70.941
- High molecular weight – High density P.E. (HMW-HDPE)

UNIPOL Process

The process produces low density polyethylene and high density polyethylene using low pressurein gas phase. Wide range of polyethylene is produced using proprietary solid and slurry catalyst. The process produces wide range of polyethylene in a gas phase, fluidised bed reactor using proprietary solid and slurry catalyst. Gaseous ethylene, comonomer and catalyst are fed to fluidised bed reactor containing a fluidized bed of growing polymer particles operating at 25kg/cm2 and 100oC. Polymer density is easily controlled from 0.915 to 0.97 g/cm. Process flow diagram for polyethylene manufacture is given in Figure4.1

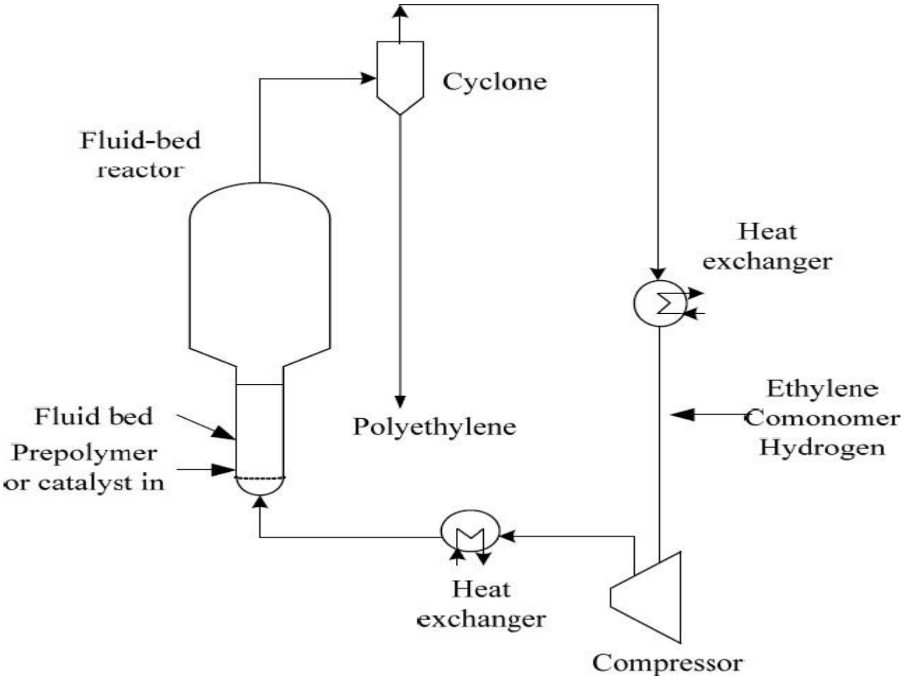


Figure 5.1: Fluidized-bed Gas Phase PE Process.

POLYPROPYLENE

Polypropylene is a low density semi-crystalline stereo-regular polymer which exists in three forms- isotactic, syndiotactic and atactic. Polypropylene was discovered in March 1954 by Professor Giulio Natta demand of polypropylene is growing at a much faster rate due to its strong demand per capita consumption of polypropylene is given in Figure4.2

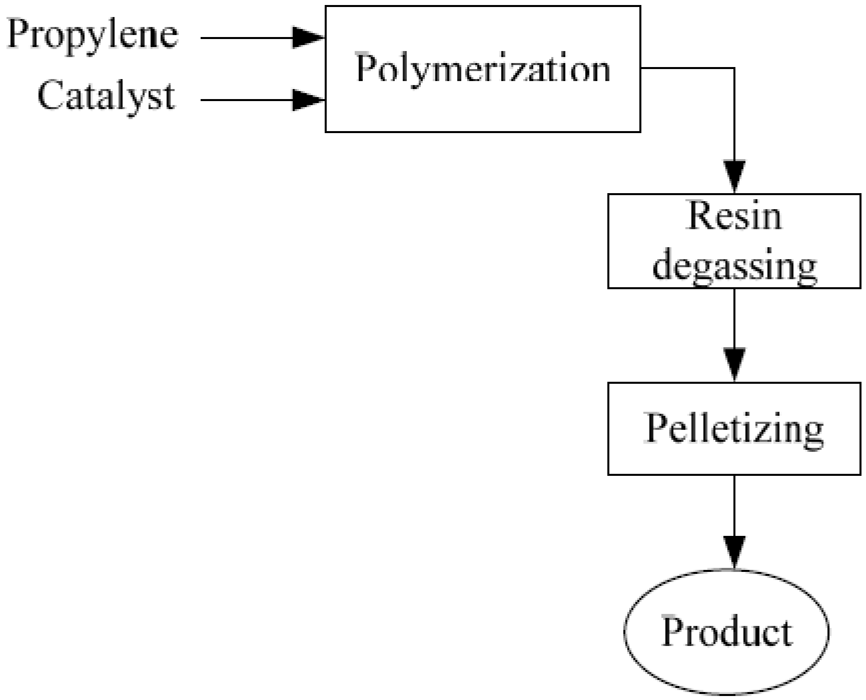


Figure 5.2: Polypropylene Process

UNIPOL Process: The process produces homopolymer, random copolymer and impact copolymer polypropylene. Polymerisation takes place in a fluidized bed reactor using slurry reactor (TiCl4 supported on MgCl2 in slurry form in mineral oil. Co-catalyst TEAL, purified propylene and ethylene incase of random PP), purified H2 and selectivity control agent is continuously fed to the reactor. Temperature 35oC and pressure 33 kg /cm2 is maintained in the reactor. Figure 4.3 illustrate the Unipol process for manufacturing of polypropylene.

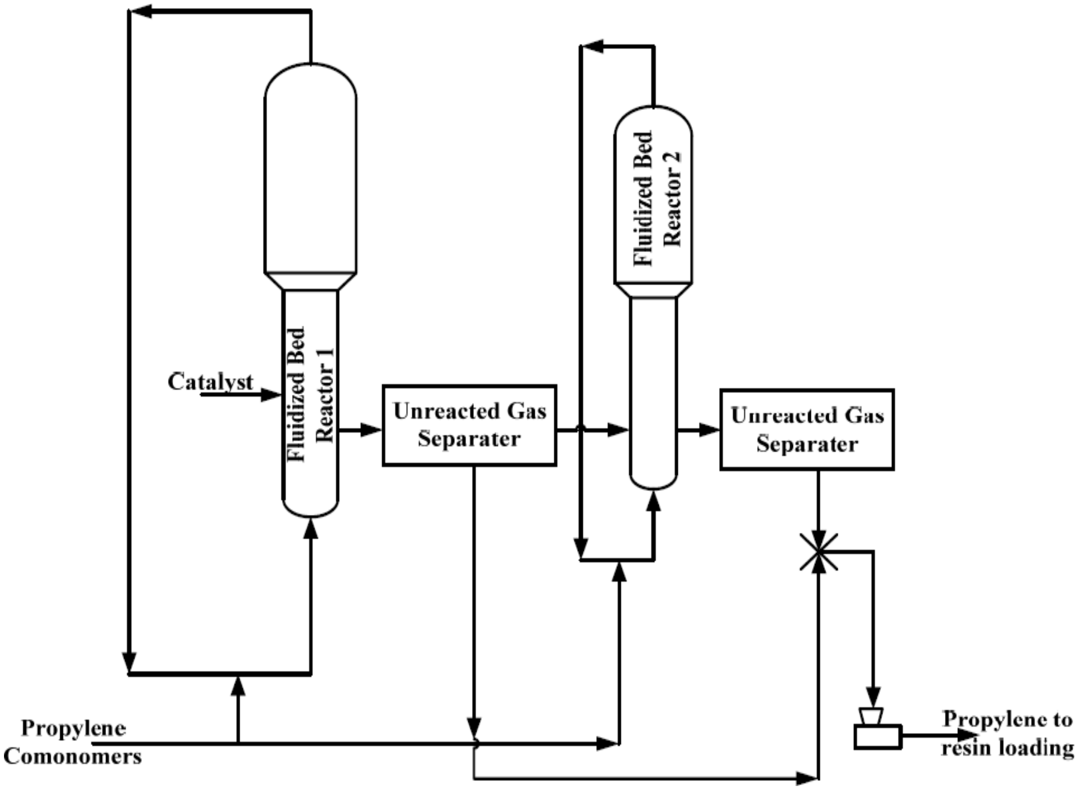


Figure 5.3: Polypropylene by Unipol process

5.4 POLYVINYLCHLORIDE

Polyvinyl chloride is second largest (after polyethylene) and most versatile of all thermoplastics. Despite various environmental issues raised time to time PVC has enjoyed onstant growth in demand because of its unique properties which include durability, ease of processing and cost effectiveness PVC has been facing innumerable challenges to its usage and growth. With use of suitable additives like stabilizer and plasticisers can be made rigid or flexible for a variety of end uses and can be processed by all types of processing methods It contains about 56.8percent chlorine and balance being hydrocarbon. A major portion of the chlorine produced in the world is used in the manufacture of PVC. The potential for growth in PVC consumption is enormous. With the addition of plasticizers, fillers, reinforcements, lubricants and stabilizer, PVC may be formulated into flexible, rigid, elastomer or foamedcompound

Process Technology for PVC

The basic monomer for manufacture of PVC is vinyl chloride which is made from either acetylene or ethylene. However, ethylene is the chief source of vinyl chloride throughout world.
Varioussourcesofethylenearenaphthagascracking,acetylenerouteandalcoholroute.Figure

4.4 illustrates the process flow diagram of PVC manufacturing. Using a free radical initiator, PVC can be made with any of four general methods of polymerisation – suspension, emulsion, bulkandsolutionpolymerisesvinylchloridemonomer.However,bulkofPVCismadeby

suspension polymerisation. Most resins produced by the suspension polymerisation are in the range of 125 - 165 microns in diameter while those produced by bulk polymerization process are in the range of 1 micron diameter Suspension polymerization of PVC has significant advantages such as low investment, large reactor technology, clean reactor wall technology, low personal requirement,environmentallysafe Vinyl chloride is copolymerized with other monomers to improve quality of the resin. When vinyl acetate is used as copolymer, polymer is more stable to light and heat than the homopolymer of vinyl chloride. With vinylidene chloride has a higher melting point than homopolymer and may be spun into afibre

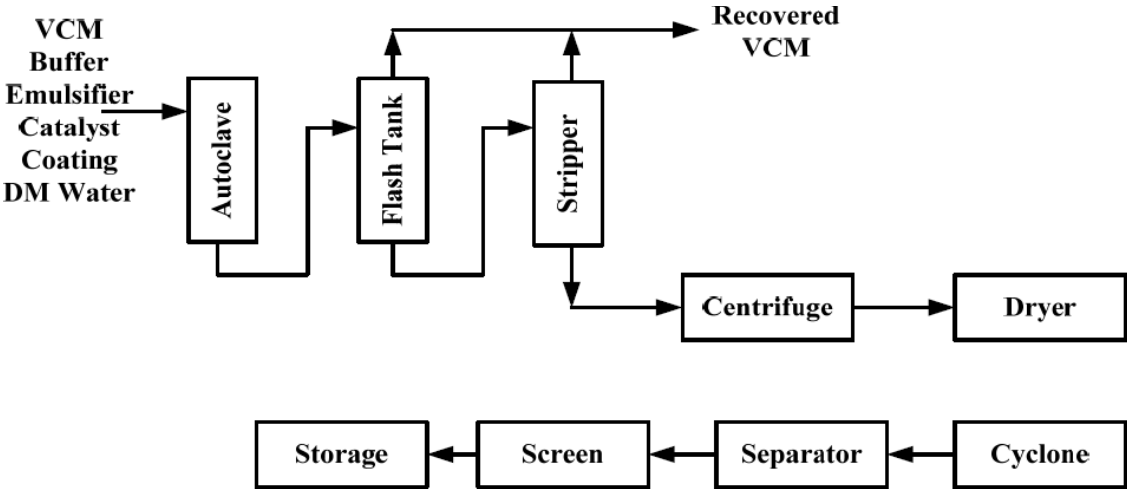


Figure 5.4: Flow Diagram for Manufacturing of PVC

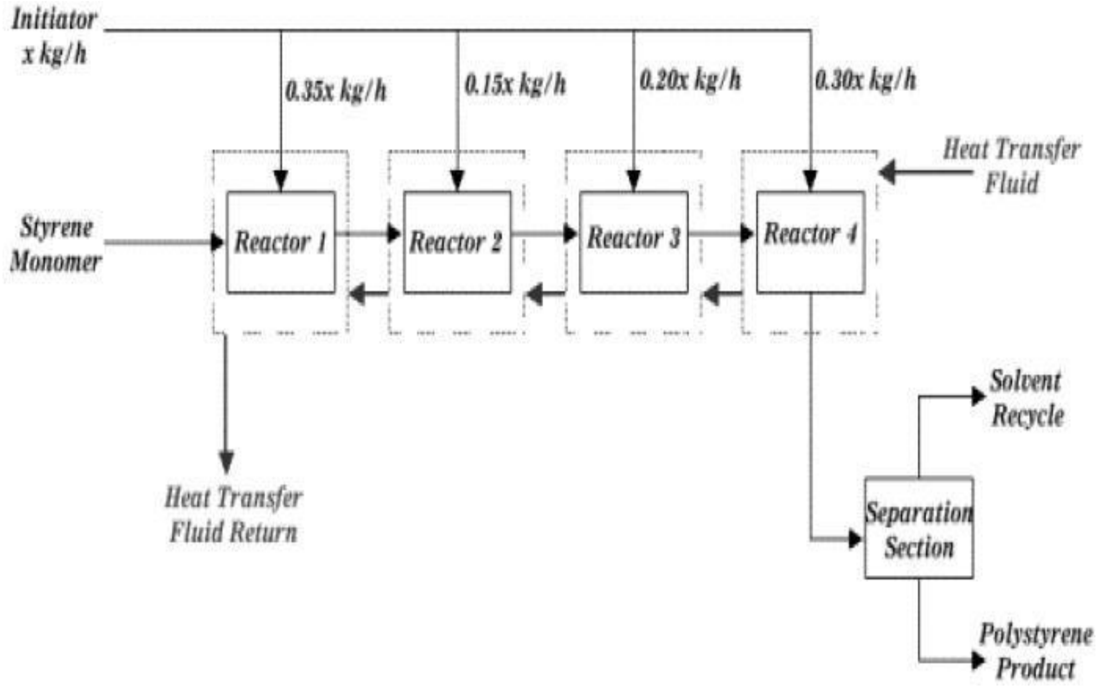
Suspension Polymerisation Process

Suspension polymerization of PVC manufacture involves dispersion of vinyl chloride monomer in water along with a suspending agent polyvinyl chloride. Polymeristion is initiated by activators at temperature around 40-70oC heat produced is continuously removed using heat transfer medium. After the polymerization is completed the suspension is transferred to degassing unit where unreacted monomer is removed, purified, condensed and recycled. Polymer is from suspension is separated by centrifuging and dried by hotair.

5.6 POLYSTYRENE

Solution (bulk) polymerization: Solution (bulk) polymerization is commonly referred to as mass polymerization in the industry. The vast majority of all polystyrene produced today is produced via this technology. The common solvents used in this process are the styrene monomer itself and ethyl benzene. The two types of mass polymerization are batch and continuous, of which continuous mass is by far the most popular. Batch mass polymerization consists of a polymerization section containing agitated vessels polymerizing up to 80% conversion in a batch method. The polymerized solution is then pumped to a batch finishing section for either devolatisation or plate and frame final polymerization and grinding. The most widelyused

process for polymerization of polystyrene today is the continuous mass process. This solution is continuously prepared in a holding vessel and will then be injected into the reactor system.



Typical feed to the first reactor would consist of 50 weight percent styrene monomer, 100 ppm water (based on styrene weight), 2000 ppm boron trifluoride (based on styrene weight), with the balance being organic solvent. The polymerization reaction gives off heat that is carried away from the reactors by jacketing them with a heat transfer fluid. The temperature of the reactants should not vary by more than 15 0 C throughout the reactor series. Temperature control is very important in this reaction because as the reaction temperature increases, the average molecular weight of the polystyrene decreases. The reaction temperature range is 40-70 0 C. Temperature can also be controlled by intermediate shell and tube heat exchangers. Monomer conversions of up to 85wt% polystyrene are obtainable in these reactors.

Figure 5.5: flow diagram for manufacturing of polystyrene 5.7 ABS (Acrylonitrile-Butadiene-Styrene)

ABS may be processed into end products by most thermoplastic processing methods such as injection and compression moulding, extrusion, blow moulding and calendering. Other operationssuchasvacuumforming,vapourmetallizing,plating,hotstampingandpaintingmay also be carried out. ABS's light weight and ability to be injection molded and extruded make it useful in manufacturing products such as drain-waste-vent (DWV) pipe systems, musical instruments (recorders, plastic clarinets, and piano movements), golf club heads (because of its good shock absorbance), automotive trim components, automotive bumper bars, medical devices for blood access, enclosures for electrical and electronic assemblies, protective headgear, whitewater canoes, buffer edging for furniture and joinery panels, luggage and protective carrying cases, small kitchen appliances, and toys, Household and consumer goods are the major applications of ABS. Keyboard keycaps are commonly made out ofABS.

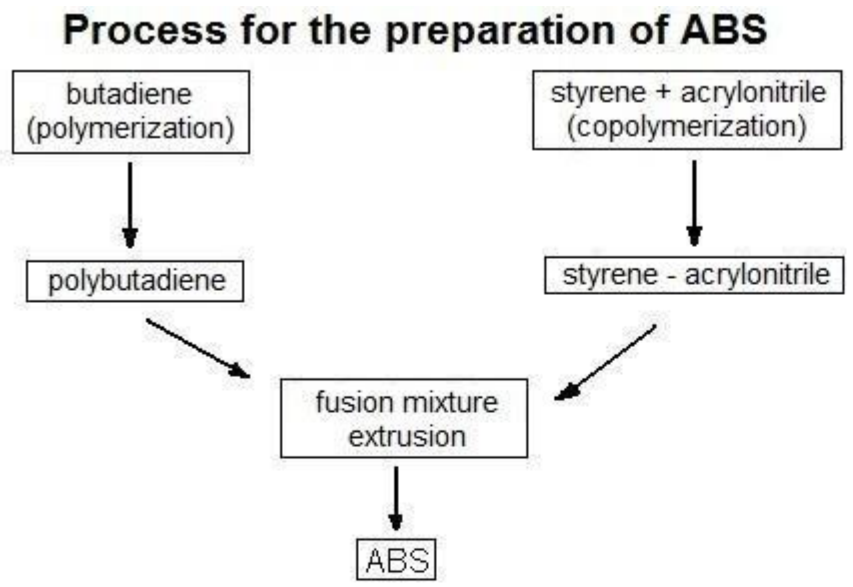


Figure 5.6: flow diagram for manufacturing of ABS

4.8 TEFLON

PTFE is one of a class of plastics known as fluoropolymers. A polymer is a compound formed by a chemical reaction which combines particles into groups of repeating large molecules. Many common synthetic fibers are polymers, such as polyester and nylon. PTFE is the polymerized form of tetrafluoroethylene.

Raw Materials

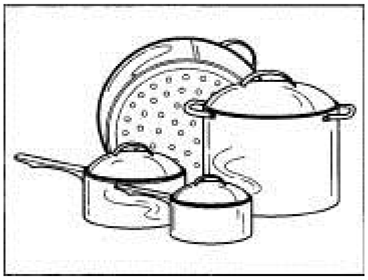
PTFE is polymerized from the chemical compound tetrafluoroethylene, or TFE.

Manufacturing Process

PTFE can be produced in a number of ways, depending on the particular traits desired for theend product. Many specifics of the process are proprietary secrets of the manufacturers. There are twomainmethodsofproducingPTFE.Oneissuspensionpolymerization.Inthismethod,the TFE is polymerized in water, resulting in grains of PTFE. The grains can be further processed into pellets which can be molded. In the dispersion method, the resulting PTFE is a milky paste which can be processed into a fine powder. Both the paste and powder are used in coating applications.

Making the TFE

STEP 1: Manufacturers of PTFE begin by synthesizing TFE. The three ingredients of TFE, fluorspar, hydrofluoric acid, and chloroform are combined in a chemical reaction chamber heated to between 1094-1652°F (590-900°C). The resultant gas is then cooled, and distilled to remove any impurities.



Teflon con be used on a wide variety of cookware.

Suspension Polymerization

- STEP 2 :The reaction chamber is filled with purified water and a reaction agent or initiator, a chemical that will set off the formation of the polymer. The liquid TFE is piped into the reaction chamber. As the TFE meets the initiator, it begins to polymerize. The resulting PTFE forms solid grains that float to the surface of the water. As this is happening, the reaction chamber is mechanically shaken. The chemical reaction inside the chamber gives off heat, so the chamber is cooled by the circulation of cold water or another coolant in a jacket around its outsides. Controls automatically shut off the supply of TFE after a certain weight inside the chamber is reached. The water is drained out of the chamber, leaving a mess of stringy PTFE which looks somewhat like gratedcoconut.

- STEP 3 :the PTFE is dried and fed into a mill. The mill pulverizes the PTFE with rotating blades, producing a material with the consistency of wheat flour. This fine powder is difficult to mold. It has "poor flow," meaning it cannot be processed easily in automatic equipment. Like unsifted wheat flour, it might have both lumps and air pockets. So manufacturers convert this fine powder into larger granules by a process called agglomeration. This can be done in several ways. One method is to mix the PTFE powder with a solvent such as acetone and tumble it in a rotating drum. The PTFE grains stick together, forming small pellets. The pellets are then dried in an oven.
- STEP 4: The PTFE pellets can be molded into parts using a variety of techniques. However, PTFE may be sold in bulk already pre-molded into so-called billets, which are solid cylinders of PTFE. The billets may be 5 ft (1.5 m) tall. These can be cut into sheets or smaller blocks, for further molding. To form the billet, PTFE pellets are poured into a cylindrical stainless steel mold. The mold is loaded onto a hydraulic press, which is something like a large cabinet equipped with weighted ram. The ram drops down into the mold and exerts force on the PTFE. After a certain time period, the mold is removed from the press and the PTFE is unmolded. It is allowed to rest, then placed in an oven for a final step calledsintering.
- STEP 5: The molded PTFE is heated in the sintering oven for several hours, until it gradually reaches a temperature of around 680°F (360°C). This is above the melting point of PTFE. The PTFE particles coalesce and the material becomes gel-like. Then the PTFE is gradually cooled. The finished billet can be shipped to customers, who will slice or shave it into smaller pieces, for furtherprocessing.

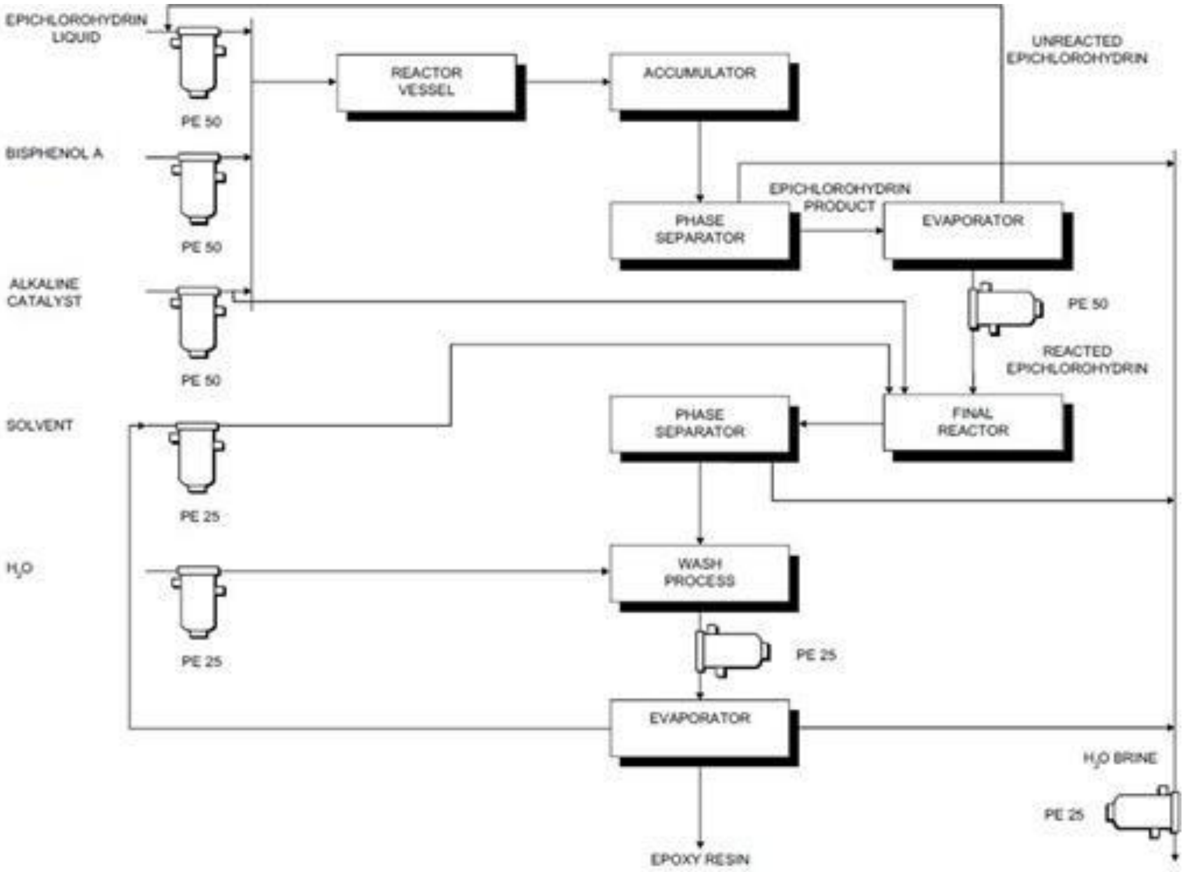
Dispersion polymerization

- STEP 6 : Polymerization of PTFE by the dispersion method leads to either fine powder or a paste-like substance, which is more useful for coatings and finishes. TFE is introduced into a water-filled reactor along with the initiating chemical. Instead of being vigorously shaken, as in the suspension process, the reaction chamber is only agitated gently. The PTFE forms into tiny beads. Some of the water is removed, by filtering or by adding chemicals which cause the PTFE beads to settle. The result is a milky substance called PTFE dispersion. It can be used as a liquid, especially in applications like fabric finishes. Or it may be dried into a fine powder used to coatmetal.

5.8 EPOXYRESINS.

Most common epoxy resins are produced from a reaction between epichlorohydrin (ECH) and bisphenol-A (BPA), though the latter may be replaced by other raw materials (such as aliphatic glycols, phenol and o-cresol novolacs) to produce specialty resins. The epoxy resins can be obtained in either liquid or solid states. The two processes are similar. Firstly ECH and BPA are charged into a reactor. A solution of 20-40% caustic soda is added to thereactionvesselasthesolutionisbroughttotheboilingpoint.After the evaporation of unreacted ECH, the two phases are separated by adding an inert solvent such as methylisobutylketone (MIBK). The resin is then washed with water and the solvent is removed by vacuum distillation.The producers will add the specific additivesto create a formula that lend special properties such as flexibility, viscosity, color, adhesiveness, and fastercuring, depending on a particular application.

In order to convert epoxy resins into a hard, infusible, and rigid material, it is necessary to cure the resin with hardener. Epoxy resins can cure at practically any temperature from 5-150oC depending on the choice of curing agent. Primary and secondary amines are widely used to cure epoxy resins.



Epoxy resin manufacturing process with flow chart

5.9 PHENOLFORMALDEHYDE

Polymer Chemistry : The formation of phenol formaldehyde follows step – growth polymerization. The process can be either acid – catalysed or base – catalysed.

Base-catalysed phenol formaldehyde resins are made with formaldehyde to phenol ratio of around 1.5. Such resins are sometimes called resols, and are found in varied industrial products. Laminates are made by impregnating one or more layers of base materials like paper or cotton with phenolic resin with the application of temperature and pressure. Moreover the resins act as binding agents in brake pads, brake shoes and various other applications.

TECHNOLOGY:

The polymerization process for the manufacture of phenol formaldehyde is an exothermic one and is controlled by a batch reactor as the viscosity of the material changes rapidly.

The raw materials for the process – phenol, formaldehyde and the catalyst are mixed in a jacketed autoclave , which is also termed as a resin kettle. Inside the autoclave, the mixture is heated with steam. Water cooling and refluxing remove the excess heat of reaction. During the initial stages of the reaction , the heavy viscous resins settle as the bottom layer, with an aqueous layer on top. A combination of heat and vacuum in the resin kettle (autoclave) enables the dehydration of the reactionmixture.

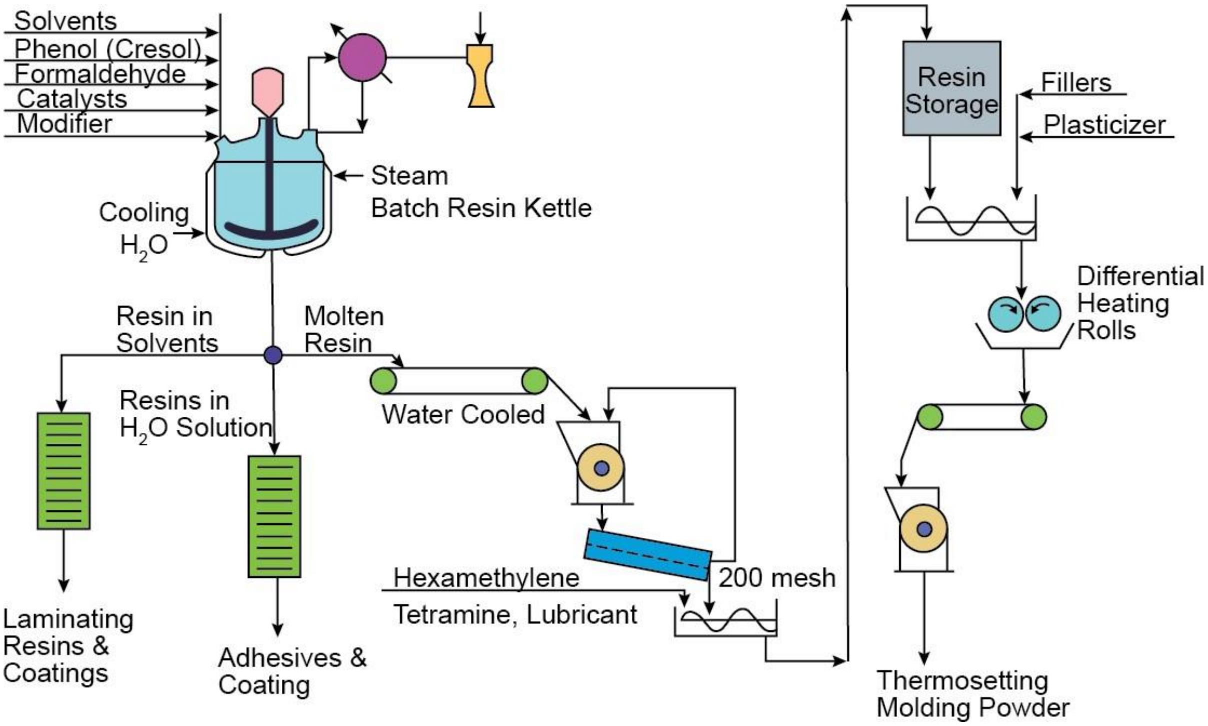


Figure 5.7: flow diagram for manufacturing of phenol formaldehyde

What isrubber?

When people talk about "rubber", they don't usually specify what kind. There are many different kinds of rubber, but they all fall into two broad types: natural rubber (latex—grown from plants) and synthetic rubber (made artificially in a chemical plant or laboratory). Commercially, the most important synthetic rubbers are styrene butadiene (SBR), polyacrylics, and polyvinyl acetate (PVA); other kinds include polyvinyl chloride (PVC), polychloroprene (better known as neoprene), and various types of polyurethane. Although natural rubber and synthetic rubbers are similar in some ways, they're made by entirely differentprocesses

Natural rubber is made from a runny, milky white liquid called **latex** that oozes from certain plants when you cut into them. (Common dandelions, for example, produce latex; if you snap off their stems, you can see the latex dripping out from them. In theory, there's no reason why we couldn't make rubber by growing dandelions, though we'd need an awful lot of them.) Although there are something like 200 plants in the world that produce latex, over 99 percent of the world's natural rubber is made from the latex that comes from a tree species called *Heveabrasiliensis*, widely known as the rubber tree. This latex is about one third water and one third rubber particles held in a form known as a colloidal suspension. Natural rubber is a polymer of isoprene (also known as 2-methylbuta-1,3-diene) with the chemical formula $(C_5H_8)n$. To put it more simply, it's made of many thousands of basic C_5H_8units (the monomer of isoprene) loosely joined to make long, tangled chains. These chains of molecules can be pulled apart and untangled fairly easily, but they spring straight back together if you release them—and that's what makes rubber elastic. and chemically quitedifferent.

Synthetic rubbers are made in chemical plants using petrochemicals as their starting point. One of the first (and still one of the best known) is **neoprene** (the brand name for polychloroprene), made by reacting together acetylene and hydrochloric acid. **Emulsion styrene-butadiene rubber (E-SBR)**, another synthetic rubber, is widely used for making vehicletires.

5.10 STYRNE BUTADIENE RUBBER(SBR)

Polymer Chemistry: The production of Styrene Butadiene Rubber (SBR) follows addition polymerization. Its glass transition temperature is approximately -55°C, but may vary with the Styrene content. It can be used extensively within the temperature range of -40 to 100°C. It may be blended with natural rubber or can be used by itself. It has good abrasion resistance properties and the addition of additives may endow it with aging stability

TECHNOLOGY:

SBR is produced by the copolymerization of Butadiene and Styrene by emulsion polymerization in 3: 1 weight ratio. The fresh and recycle monomers are purified by 20 %

aqueous caustic purification. Then the stream is continuously passed through 6 to 12 glass – lined or stainless steel reactors. The residence time in these reactors ranges from 5 to 15 hours.

Steam heating, water cooling and refrigeration are carried out in these reactors. These reactors are equipped for producing both cold and hot SBR. Cold SBR is produced at 5°C and 1 atm gage by refrigeration techniques ; whereas hot SBR is manufactured at 50°C , and 3-4 atmgage.

The polymerization product is then stripped with chemical inhibitors and the latex resulting from the reactors are collected in blow down tanks. The latex is then sent to a falling film stripper to remove the butadiene ; and the bottoms are fed to a perforated plate column where styrene is stripped out.

The monomer – free emulsion is then added with certain compounding ingredients in blend tanks. The latex is coagulated to rubber. The crumbs of rubber float onto shaker screens where the catalyst , emulsifiers and other solubles are removed by the action with wash water. The crumbs are dried in continuous belt dryers with hot air and are subsequently pressed into bales.

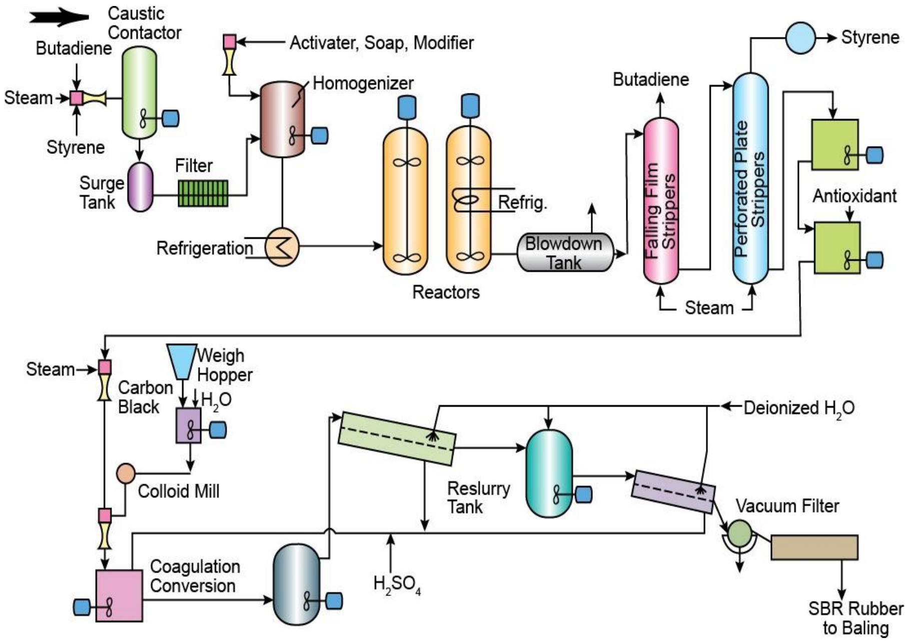


Figure 5.8 : flow diagram for manufacturing of styrne butadiene rubber (sbr)

5.11 POLYBUTADIENE

Stream of steam cracker is major source of butadiene. Other routes for butadiene manufacture are

- Catalytic dehydrogenation of butenes
- Catalytic dehydrogenation of butane

With the availability of butadiene from cracker plant, manufacture of polybutadiene has increased significantly in recent years. Polybutadiene is made by free radical emulsions, alkali methyl solution and transition metal coordination solution processes. Most processes are based on solution process. Large volume use of polybutadiene rubber has been primarily in blend with other polymers. Blend with SBR or natural rubber has improved crack resistance. Cracking and abrasion resistance is verygood.

It is characterized with high abrasion and crack resistance, better resistance to heat degradation and blowouts, good hysteresis properties, large scale use in tyre tread, modification of plastics,conveyor& V-belts, sports goods, foot wear material, 90 percent in tyre industry.

POLYISOPRENE

Polyisoprene is one of the most well known natural elastomers derived from the sap of the heavea tree. However, synthetic polyisoprne is made by polymerization of isoprene. Isoprene is recovered from the C5 fraction of naphtha cracker. Isoprene can be also made

Isoprene polymerisation is carried out in an inert hydrocarbon solvent (aliphatic solvents). Basic steps in manufacture of polystyrene are – raw material preparation and purification, polymerisation, catalyst deactivation and removal, solvent recovery, polymer drying. Polymerisation catalysts are either of the coordination (Zeigler) or alkyl lithium types. Coordination catalysts are trialkyl aluminium/titanium tetrachloride. Often polymerisation short stops and anti oxidant is added. The solvent remaining is stripped off.

Poly isoprene has good uncured track, high pure gum tensile strength, high resilience, low hysteresis, good hot tear strength. Tyre market is the major consumer of polyisoprene, a substitute of natural rubber in the tread of truck, aircraft and off the road tyres, for dipped goods, adhesive, extruded thread.

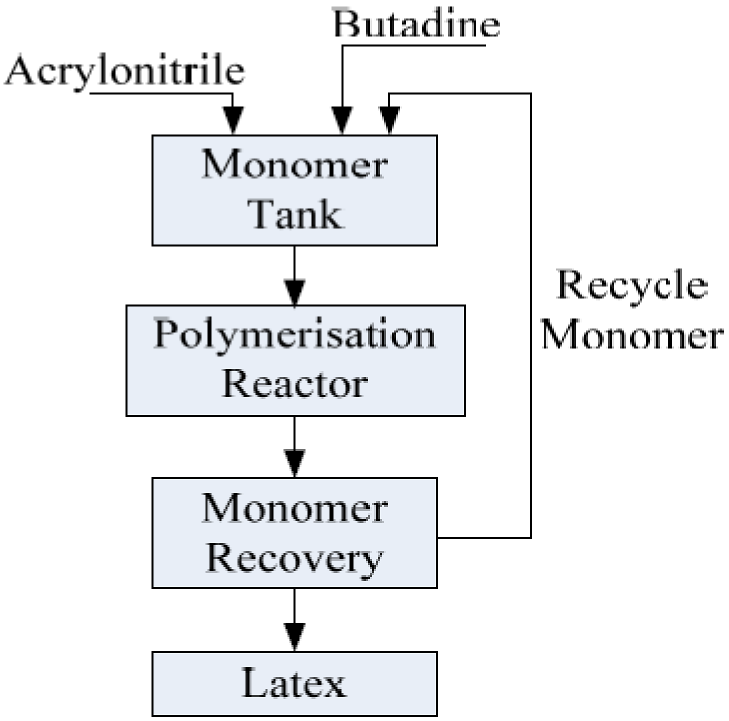


Figure 5.9 Process flow diagramme of Acrylonitrile Rubber (Nitrile rubber)

5.12 NEOPRENE (POLYCHLOROPRENE):

Chloroprene is made either via acetylene route or from butadiene. Butadiene process is commonly used.

Acetylene route involves dimerisation of acetylene to monovinyl acetylene followed by reaction of monovinyl acetylene with HCl.

Chloroprene from butadiene involves three steps

☐ Chlorination of Butadiene: Various steps involved
☐ are
☐ Chorination of Butadiene- 1,4 dichloro 2-butene and3,4-dichloro 1-
☐ butene Isomerisation of 1,4 dichloro2-butene to 3,4-dichloro 1-butene

Dehydrochlorination of 3, 4-dichloro1-butene to chloroprene in presence of caustic soda resulting in formation of chloroprene(CH2CH-CCL=CH2

Polychloroprene is made by emulsion polymerisation process using resin acid soap emulsifier. Polymerisation is carried out at 40 oC in presence of sulphur. Some of the major applicationof polychloroprene is in adhesives, transportation industry, wire and cable, construction industry, hose andbelting.

Uses : Adhesives, transportation industry (Automotive – gaskets, V-belts, shock absorber covers, wire jackets, molded seats, aviation-wire cable, gaskets, seats etc., rail brake hose, track mountings.

5.13 SILICON RUBBER(POLYSILOXANES)

Silicon elastomer are made by ring opening reaction caused by action of alkali on monomer acyclic siloxane characterised by exceptional mechanical and electrical performance under extreme temperature condition. Used in aerospace, appliances, electrical industry, construction industry, automotive industry, gaskets sealings, spark plug boots, hose, rubber rolls.

5.14 What is a RubberCompound?

Sometimes, there is a misconception that a rubber compound is one ingredient and is the same for every different polymer type. This could not be further from the truth. A rubber compound could be a combination of 3 to 15 different ingredients of thousands of different compositions andvendors.

A typical rubber formation based on parts per hundred is:

Polymer	100 phr
Filler	30 – 60 phr
Antioxidant	1 – 3 phr
Antiozonants	1 – 3 phr
Oil	5 – 30 phr
Cure	5 – 10 phr

Polymers:

The most important ingredient in a rubber compound, polymers give the bases forchemical,physicalandmoldingproperties.Typicalpolymersaredistinguishedbychemical performance and viscosity rating. An example for a Nitrile (Buna-N) compound is the amount of Acrylonitrile (ACN). The higher the ACN, the more oil resistance. These polymers are then sold with varying ACN content. The Mooney viscosity can vary to give better processing performance.

Filler:

Carbon Black is one of the most common fillers. This gives the rubber compoundphysicalstrengthanditsblackcolor.Therearevariousparticlesizesandsurface activities. Changing the particle size can increase physical properties while also increasing compression set.

White clays and Mineral fillers are used for colored compounds. This helps makes the compound white to add the desired color requested. These types of fillers are typically less reinforcing than carbon black. Blending of these fillers with carbon black helps reduce cost of the overall compound.

Antioxidant:

Antioxidants help protect the compound from high temperature while in use and while the compound is being mixed. These ingredients can absorb free radicals that can breakthe

polymers bonds and reduce service life of the compound

Antiozonants:

Themostcommonantiozonantiswax,usedtobloomoutonthesurfaceafter

molding to protect the rubber from ozone attack. A common example can be seen when purchasing new tires. The surface of a new tire will have a wax feel or show a slight haze.

Oil (processing aids):

Various oils are used to help incorporate all the dry ingredients used in the rubbercompounding.Theyalsohelptoreducetheviscosityoftheoverallcompoundtohelp

with molding. Adding more oil can also lower the hardness of the rubber. Thus, lower Shore A compounds will typically have more oil in the formulation.

Cures:

Sulfur is the most common curative for rubber compounds. Rubber polymers are just entangled hydrocarbon chains than won’t hold shape. Back in1839, Goodyeardiscovered that rubber chains can be bonded together by heating the rubber with sulfur, called vulcanization. Bonds of carbon – sulfur – carbon are formed.

Another common vulcanizing agent, peroxide creates direct bonds to the carbon chains forming carbon – carbon bonds. These bonds take more energy to break, thus typically giving higher service temperatures and low compression sets. Some polymers can only be cross-linked with peroxides

There are many other ingredients that can be used to give different properties. Because of all the combinations, not all compounds are the same. Rubber compounding is a science to assure required properties by varying the ratios of ingredients and compensating for the interactions. This is why most compounders consider their rubber formulations proprietary. It can take hundreds of variations and hours of testing to perfect the mechanical properties while maintaining goodprocessing.

5.15 VISCOSERAYON

Polymer Chemistry: The raw material for the production of Viscose rayon is wood pulp. However, the manufacturing process emits toxic effluents which have adverse environmental effects. Because of its cellulosic base , it has some properties which are similar to those of cotton and any other natural cellulosic fibres. It has moderate resistance to acids and alkalis. However, it may be damaged by relatively weak acids. Moreover, due to the inelasticity of fibers, it has poor abrasionresistance.

Technology

The raw materials used in this process are cellulose wood pulp sheets or cotton linters. These are placed in a steeping press with contact in aqueous NaOH Solution for a period of 2 – 4 hours at normal room temperature. A hydraulic ram presses out the excess alkali and the sheets are shredded to crumbs and aged for 2 – 3 days. The aging process has its direct consequence on the viscosity of the solution.

Later CS_2 is added in a rotating drum mixer over a period of 3 hours. The orange cellulose xanthate which forms is transferred to a solubilizer , wherein it is mixed into dilute caustic . The mixing of cellulose xanthate and dilute caustic yields a orange colored viscous solution which contains 7 – 8 % cellulose and 6.5 – 7 % NaOH. It is digested at room temperature for 4-5 days. Thereafter , the solution is filtered and fed to spinning machines.

The spinning is carried out in extrusion spinnerettes , which are made up of platinum or gold alloys. The orifices of these spinnerets have a diameter of 0.1 – 0.2 mm. for continuous filament yarns and of diameter 0.05 – 0.1 mm for short fibre shapes. The solution extruded from the spinnerette is contacted with an acid bath which precipitates the filaments without causing them to break or stick together. The processing treatments of washing, desulphurizing, bleaching and conditioning takes place continuously and in order after the filaments are wound on a series of plastic rolls.

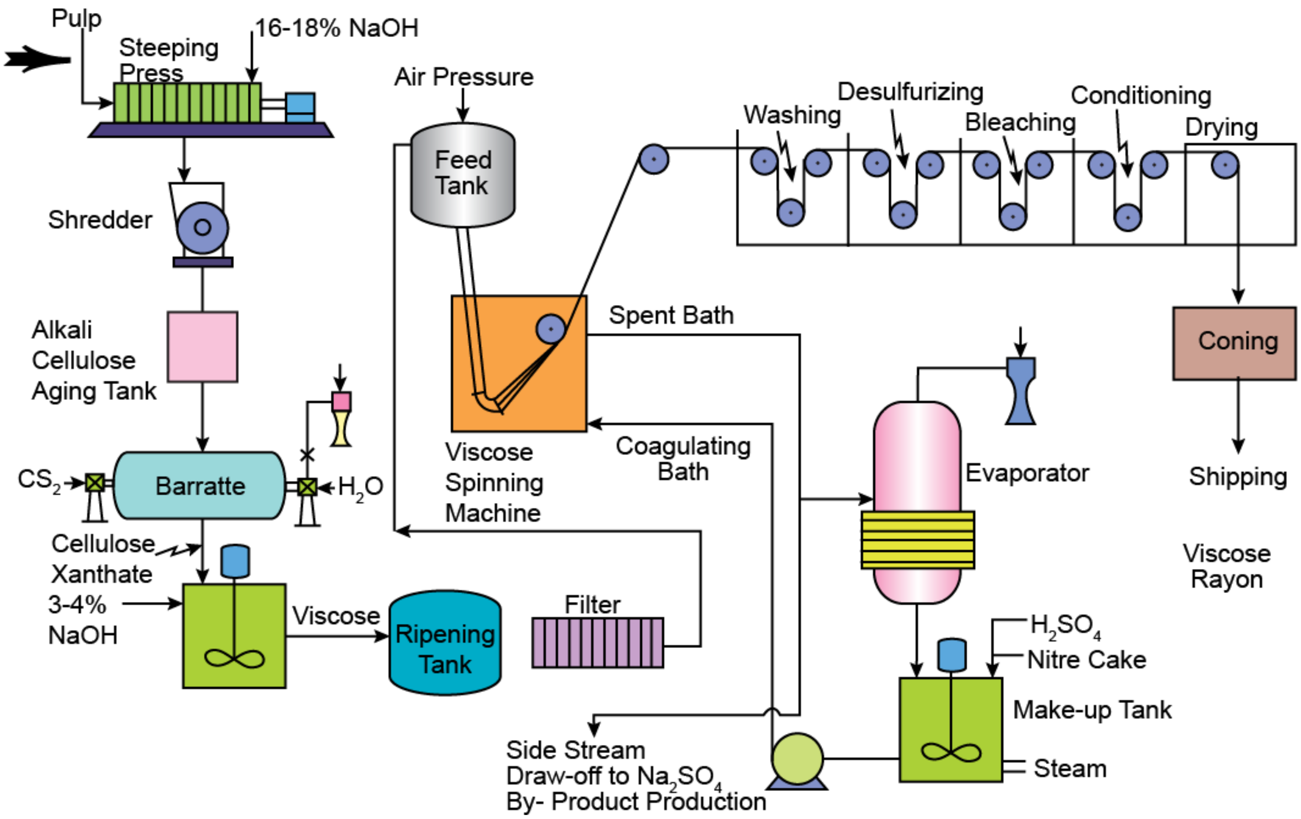


Figure 5.10 Manufacture of Viscose Rayon

5.16 NYLON

Polymer Chemistry : Nylon 66 (or 6,6 - Nylon) is a condensation polymer formed by the condensation polymerization of Adipic acid (a dibasic acid) and hexamethylene diamine (a diamine). In the nomenclature, the first number refers to the number of carbon atoms in the diamine and the second number designates the number of carbon atoms in the dibasic acid.

Nylon – 6 is a polymer of caprolactum . The number refers to the total carbon atoms in the ring, which can vary from 5 to 12. Both Nylon – 6 and Nylon – 66 have similar properties and can be used as thin films and fibres; and for extrusion and injection molding in plastics. The major difference in the physical properties of these two nylons is that the melting point of Nylon – 66 is 40 – 45°C higher than Nylon – 6. Moreover, Nylon – 66 is harder, rigid and its abrasive – resistance is lower than that of Nylon – 6.

Technology In the production of Nylon – 66, first, the amine and acid is mixed in an aqueous solution , with the pH adjusted at 7.8 to form Nylon salt. The salt is then concentrated under vacuum. It is thereafter charged to an autoclave where the rest of the water is removed. The temperature is gradually increased to 280 o C in the autoclave to complete the polymerization and the water of condensation isremoved.

The final product has a molecular weight of 12000 – 16000. It is extruded as ribbons onto chilling rolls. Then, it is sent to a chipper which produces small chips, which possesses the convenience of storage and rehandling. These chips are melted, metered through high pressure pumps. After filtration, these are passed via a melt spinnerette to produce nylon fibers. Upon cooling , these filaments harden and are wound on bobbins at a rate of 750 metres per minute or even higher. Inorder to give the fibre desirable textile properties, the threads are stretched to about 4 times its originallength.

The production of Nylon – 6 is similar to that of Nylon – 66 , the only difference being the nature of polymerization. Nylon – 6 is manufactured by the step – wise condensation of caprolactum with no net water removal. However, to maintain the thermal equilibrium between monomer and polymer at the melting and spinning temperatures is the only difficult task. Monomer retained on the fibres accounts upto 10% , so the fibres are water – washed to remove the soluble caprolactum retained.

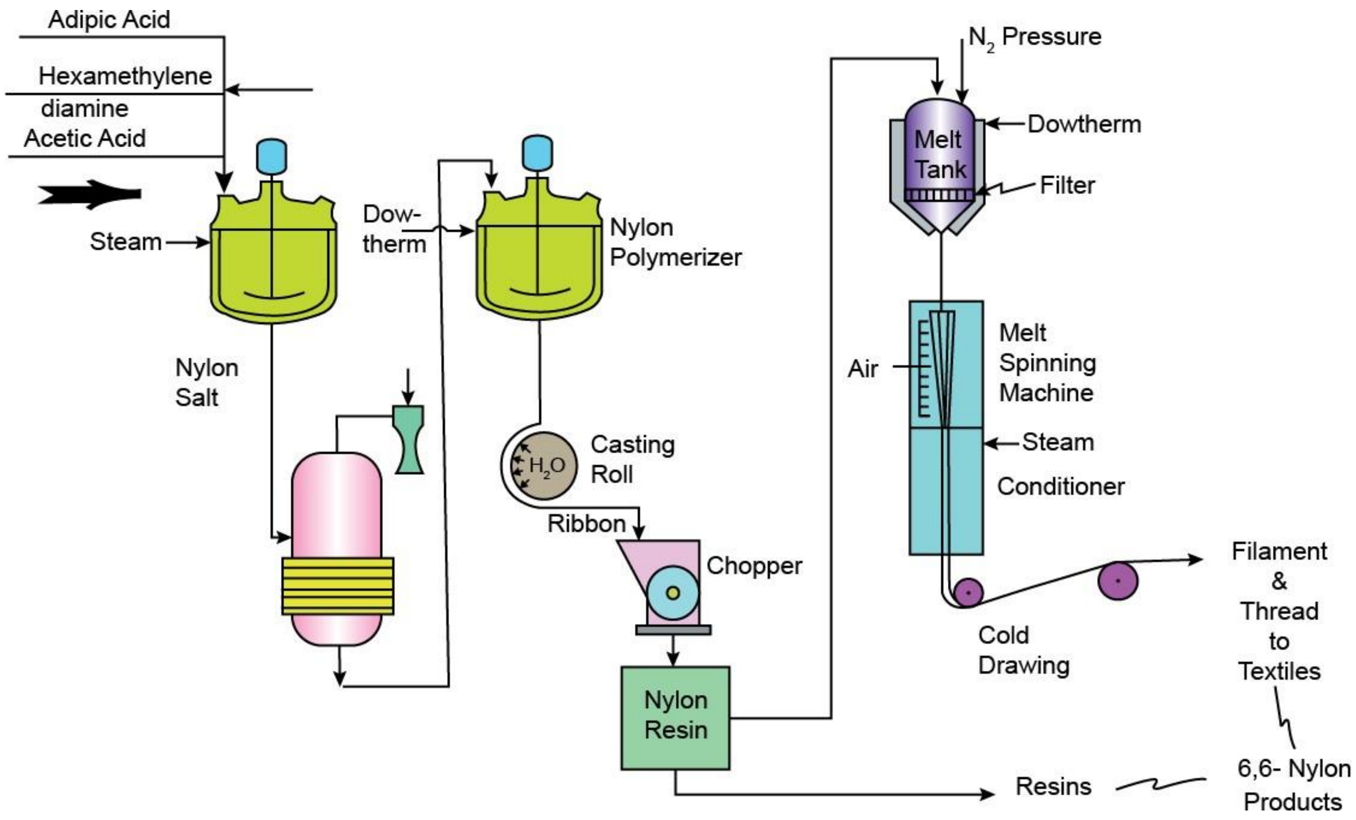


Figure 5.11 Manufacture of Nylon

5.17 CUPRAAMMONIUMRAYON:

Cupraammonium rayon is made from reaction of Cellulose with copper salt and ammonia. After bleaching celullose is added in ammonical solution of copper sulphate resulting in formation of cuprammonium cellulose which is spun into water and the yarn is washed with acid to remove traces of ammonia and dried. Process flow diagram for the manufacture of caprammoium rayon is given in Figure 5.3

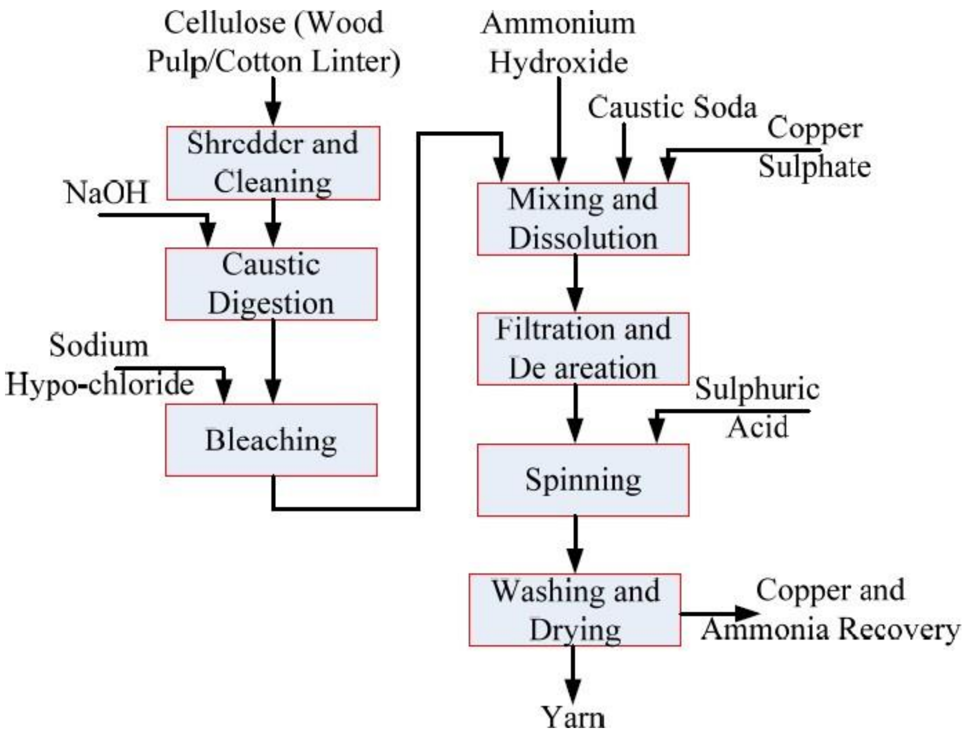


Figure 5.12 Manufacture of cupraammonium rayon

5.18 ACETATERAYON

The purified cotton linters or cellulose is fed to the acetylator containing acetic anhydride and acetic acid and conc. Sulphuric acid and acelylation is carried out at 25-30oC. The reaction mixture called acid dope is allowed for ripening for about 10-20 hrs. During reopening conversion of acetate groups takes place. After reopening, the mixture is diluted with water with continuous stirring. During the process flakes acetate rayon is precipitated which is dried and send to spinning bath where dry spinning of acetate rayon takes place by dissolving in solvent and passing troughspinnerated. The solvent is evaporates by hot air. The dope coming from the spinnerate is passed downwards to feed roller and finally to bobbin where spinning is done at higher speed.

Raw Material Purified cotton linters, wood pulp, acetic anhydride, acetic acid and sulfuric acid.
Process Steps ***Activation with Acetic Acid:*** The process involves steeping of purified cotton in acetic acid which makes. Swelling and makes cellulose more reactive

Acetylation: The pretreated cotton with acetic acid is then acetylated with excess acetic acid, acetic anhydride, with sulphuric acid to promote the reaction.

- One part of purified cellulose
- Three part of acetic anhydride
- Five parts of acetic acid
- Sulfuric acid 0.1 part (as catalyst)
- Reaction exothermic
- Temperature 20 oC for the first hour
- 25-30^{o}C for the next 7-8 h

Hydrolysis of Triacetate: The triacetate formed is hydrolysed to convert triacetate to diacetate. The resultant mixture is poured in water to precipitate the cellulose acetate

DP 350-400

2.35 – 2.4 acetyl groups per anhydro glucose unit.

Spinning: Secondary acetate is dissolved in acetone, fitered, dearerated and passed through spinerrate in hot air environment, which evaporates the solvent.

Economical Production

- Low cost and availability of acetic acid and acetic anhydride
- Recovery of acetic acid
- Recovery of acetone

Process flow diagram for the manufacture of acetate Rayon is given in Figure 5.4

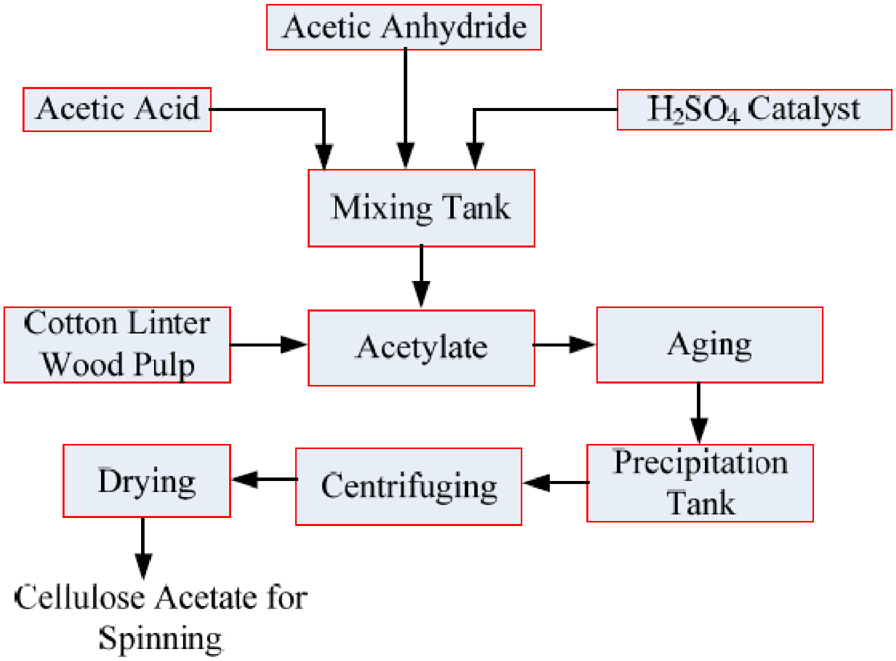


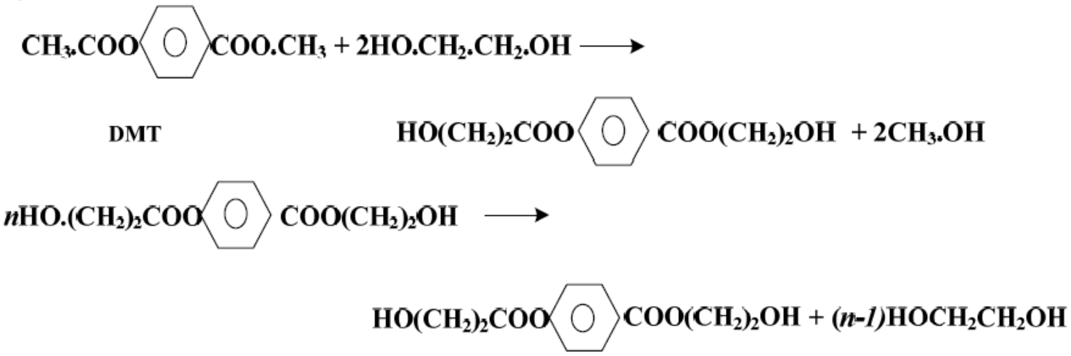
Figure 5.13 Manufacture of acetate rayon

5.21 POLYETHYLENE TEREPHTHALTE(POLYESTER)

Polyethylene Terephthalate (PET) from DMT

PET from DMT is made by transesterification route by reaction of dimethyl terephthalate with ethylene glycol followed by poly-condensation. Polyester through trans esterification route was more common earlier due to non-availability of purified terephthalic acid. During transesterification, methanol obtained as by product. Figure 5.5 describes the manufacturing process of polyester from DMT.

Polyester form DMT Routes



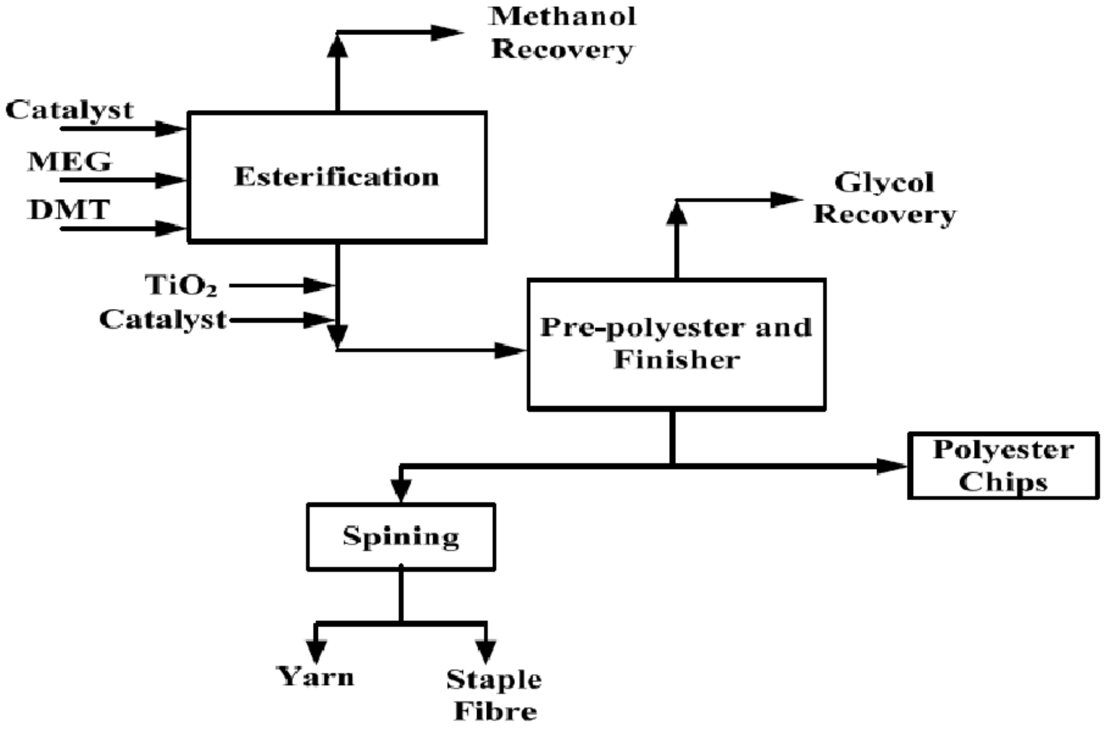


Figure 5.14Manufacture of polyester

5.22 ACRYLICFIBRE

Acrylic fibres are third largest class of synthetic fibre after polyester and nylons.

Process Technology

Manufacturing process shown in Figure 5.6 The manufacturing process can be broadly divided into two parts:

Polymerisation: Polymerisation includes copolymer composition, catalyst system, polymerisation reaction and monomer recovery. Major polymerisation processes are bulk polymerisation, suspension polymerisation, emulsion polymerisation and solution polymerisation. Most of the acrylic polymers manufactured for fiber grade are made through suspension polymerisation that gives high percentage of conversion, better product whiteness, shorter residence time and easy control of polymerisation. Emulsion polymerization is used incase of modified acrylic fibre. Inorganic compounds such as persulphate, chlorates or hydrogen peroxide are used as radical generators. Redox initiation is normaaly used in production of acrylic fibre. The most common redox system consist of ammonium or potassium persulphate (oxidizer), sodium bisulphate (reducing agent) and ferric or ferrous ion(catalyst)

Spinning: Spinning includes solution/dope preparation, spinning techniques and finishing operation including after treatment, cutting and bailing.

Dry Spinning: In dry spinning of acrylic fibre dimethyl formamide (DMF) is used. The DMF spin dope contains the polymer in the DMF, thermal stabilizers, delustrant. It passed through spinnerate placed at top of the solvent removal tower. The DMF evaporated by circulating inert gas through tower at about 300-35 oC to remove the solvent

Wet Spinning: In wet spinning sodium thiocyanate are commonly used as solvent. Wet spinning fiber is spun into a liquid bath containing a solvent non-solvent mixture called coagulant. Nonsolvent is usually water. The fibre emerging from spin bath are washed and dried followed by cutting andbailing.

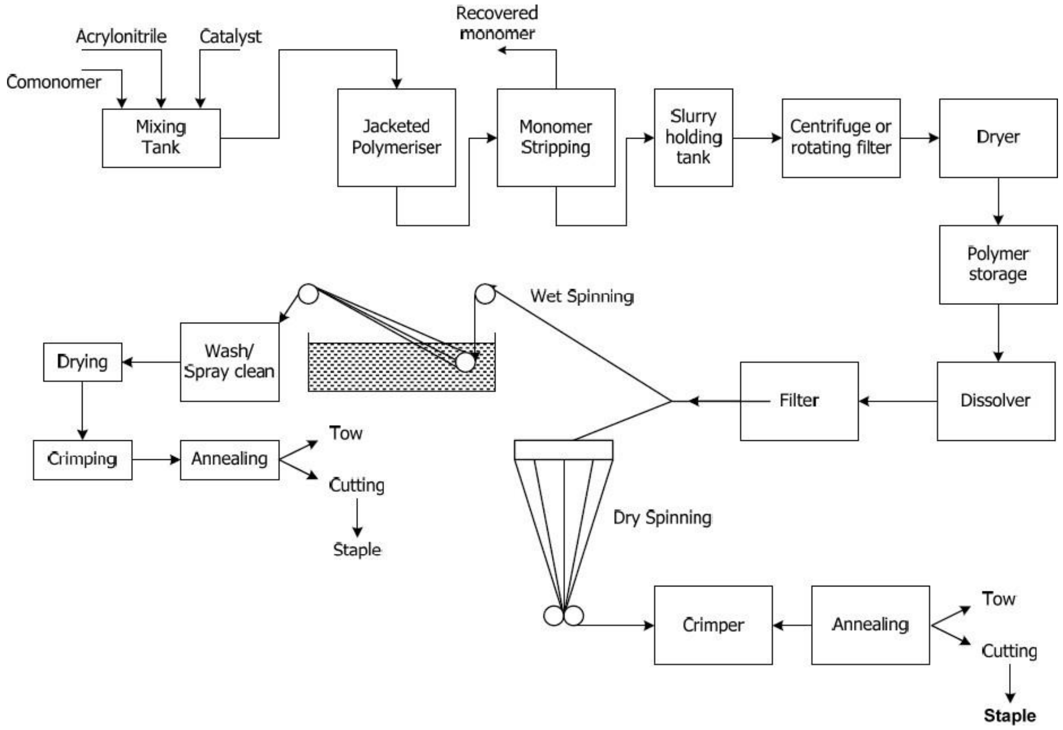


Figure 5.15Manufacture of acrylic fibre

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