



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

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SCHOOL OF BIO AND CHEMICAL ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – Chemical Process Technology – SCH1304

I. INTRODUCTION-CHLORO ALKALI INDUSTRIES

BASIC PRINCIPLES CHEMICAL PROCESSES, UNIT PROCESSES AND UNIT OPERATIONS

Chemical processes usually have three interrelated elementary processes

Transfer of reactants to the reaction zone

Chemical reactions involving various unit processes

Separation of the products from the reaction zone using various unit operations Processes may involve homogeneous system or heterogeneous systems. In homogeneous system, reactants are in same phase-liquid, gases or solids while heterogeneous system include two or more phases; gas liquid, gas-solid, gas-gas, liquid-liquid, liquid solid etc. Various type reactions involve maybe reversible or irreversible, endothermic or exothermic, catalytic or non-catalytic. Various variables affecting chemical reactions are temperature pressure, composition, catalyst activity, catalyst selectivity, catalyst stability, catalyst life, the rate of heat and mass transfer. The reaction may be carried out in batch, semi batch or continuous. Reactors may be batch, plug flow, CSTR. It may be isothermal or adiabatic. Catalytic reactors may be packed bed, moving bed or fluidised bed. Along with knowledge of various unit processes and unit operation following information are very important for the development of a process and its commercialization [Austin,1984] Basic Chemical data: Yield conversion, kinetics

Material and energy balance, raw material and energy consumption per tone of product, energy changes

Batch vs Continuous, process flow diagram

Chemical process selection: design and operation, pilot plant data, Equipment required, material of construction

Chemical Process Control and Instrumentation

Chemical Process Economics: Competing processes, Material and, Energy cost, Labour, Overall Cost of production

Market evaluation: Purity of product and uniformity of product for further processing Plant Location

Environment, Health, Safety and Hazard

Construction, Erection and Commissioning

Management for Productivity and creativity: Training of plant personals and motivation at all levels

Research, Development and patent Process

Intensification

Chemical process is combination of unit processes and Unit operation. Unit process involves principle chemical conversions leading to synthesis of various useful product and provide basic information regarding the reaction temperature and pressure, extent of chemical conversions and yield of product of reaction nature of reaction whether endothermic or exothermic, type of catalyst used. Unit operations involve the physical separation of the products obtained during various unit processes. Various chemical reactions and its application in process industries are given in Table

NITRATION

Nitration involves the introduction of one or more nitro groups into reacting molecules using various nitrating agents like fuming, concentrated, aqueous nitric acid mixture of nitric acid and sulphuric acid in batch or continuous process. Nitration products find wide application in chemical industry as solvent, dyestuff, pharmaceuticals, explosive, chemical intermediates. Typical products: TNT, Nitrobenzene, m-dinitrobenzene, nitroacetanilide, alpha nitronaphthalene, nitroparaffins

Table 1.1 : Unit Processes in Chemical Process Industries

Alkylation and Hydro delkylation	Decomposition
Acylation	Fermentation
Ammonoxidation	Halogenation
Amination by reduction	Hydsogenation
Amination	Hydrohenatlysis
Aromatisation	Hydroformylation
Amination by ammonalysis	Hydro lysis

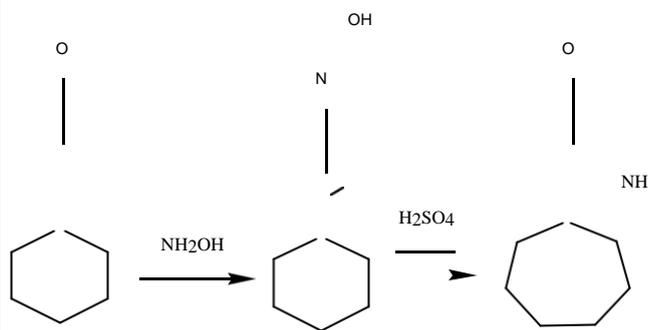
Calcination	Hydration
Carbonation	Hydroammonolysis
Causticisation	Isomerisation
Chlorination and Oxy chlorination	Neutralisation
Condensation	Nitration
Biomethanation	Methanation
Carbinisation	
Disproportionation	Oxidation and partial oxidation
Cracking; Thermal, steam cracking, catalytic cracking	Pyrolysis
Dehydration	Polymerisation: Addition and condensation Chain growth and step growth, Bulk, Emulsion, suspension, solution, Radical and coordination polymerisation
Dehydrogenation	Reduction
Dimerisation and coupling	Reforming: Steam reforming Catalytic reforming
Gasification of coal and biomass	Sulphidation
Desulphurisation and hydro desulphurisation	Sulphonation
Electrolysis	Sulphation
Etherification	Xanthation
Esterification and Trans Esterification	

Table 1.2: Important Chemical Reaction and their Application in Chemical Process Industries

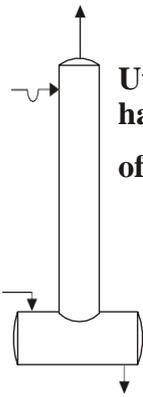
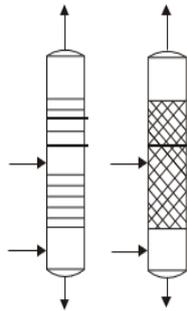
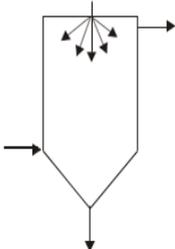
Reaction	Description
Fisher-Tropsch (FT) Process	The Fisher-Tropsch process produce a variety of hydrocarbons (alkanes: $C_nH_{(2n+2)}$) by involves a series of chemical reaction. $(2n+1) H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$

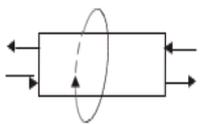
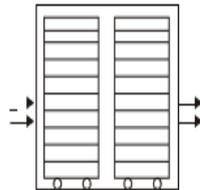
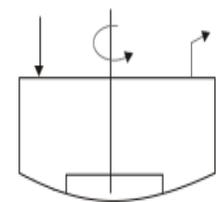
	FT process is used for synthesis of alkanes.
Friedel-Crafts reactions	<p>In this reaction attach substituent's to an aromatic ring. Two main types of Friedel-Crafts reaction are acylations reaction and alkylation reactions, both proceeding by electrophilic aromatic substitution.</p> $ \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_5 \\ \text{---} \\ \text{C} \\ \text{---} \\ \text{R} \end{array} \xrightarrow[\text{reflux anhydrous conditions}]{\text{RCl, AlCl}_3 \text{ catalyst}} \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_5 \\ \text{---} \\ \text{C} \\ \text{---} \\ \text{R} \end{array} $ <p>Friedel-Crafts process used in alkylation reactions.</p>
Oxosynthesis Reactions	<p>In this process Isomeric mixture of normal- and iso-aldehydes get produces by utilizing syngas (CO and H₂) and olefinic hydrocarbons as reactants. It is exothermic process, this process thermodynamically favorable at ambient pressure and temperatures. This reaction also called as hydroformylation reaction.</p> $\text{RCH}=\text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{CHO} + \text{R}(\text{CH}_3)\text{CHCHO}$ <p>Oxosynthesis used for production of alcohols.</p>
Hofman Process	<p>In this process, organic reaction of primary amide converts into a primary amine with one fewer carbon atom.</p> $ \begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{NH}_2 \end{array} \xrightarrow[\text{NaOH}]{\text{Br}_2} \begin{array}{c} \text{O} \\ \\ \text{R}-\text{C} \\ \\ \text{N} \end{array} + \text{H}_2\text{O} + \text{-CO}_2 $ <p>Hofman process typical examples are conversion of aliphatic amides to aliphatic amines and aromatic amides to aromatic amines.</p>
Free-Radical Reaction	<p>Any chemical reaction involving free radicals, generally radical generated from radical initiators such as peroxide or azo bis compounds. Radical reactions are chain reactions with chain initiation, propagation and termination steps. Free radical reactions are used many organic synthesis and polymerization reactions</p>
Beckmann rearrangement	<p>Beckmann rearrangement is acid catalyzed rearrangement of an oxime to an amide, which developed by German chemist Ernst Otto. A typical</p>

example of Beckmann rearrangement is synthesis of caprolactam from cyclohexanone. Caprolactam is monomer for nylon 6.



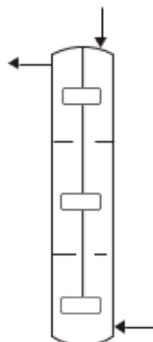
Process Equipment Symbols

<i>Unit Operation</i>	<i>Schematic Representation</i>	<i>Comments</i>
<p>1. Distillation</p> <p>(a) Batch</p>		<p>Utilized for intermittent operation and handling small volumes of feed and product</p>
<p>(b) Continuous Fractionator</p>		<p>Suitable for high volume continuous separation of complex mixtures eg. petroleum fraction</p>
<p>2. Drying of Solids</p> <p>(a) Spray Drier</p>		<p>Employed for large capacity operation on liquid feed to give powdered, spherical, free flowing product ;used in production of pigments, detergents, synthetic resins and misc inorganic salts</p>

Unit Operation	Schematic Representation	Comments
(b) Rotary Drier		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 Drier		Best suited to drying pastes or powders in trays; also used to dry pottery, lumber, leather, etc., in sheet shaped forms
3. Evaporation (a) Open Pan		Used for small batches; often of viscous mat's; such designs are easy to clean

Unit Operation	Schematic Representation	Comments
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4. Extraction
 (a) Liquid - liquid



Used to contact solvent and feed to give raffinate and extract; widely adapted to removal of naphthenes from lube oil fractions Using solvents such as furfural

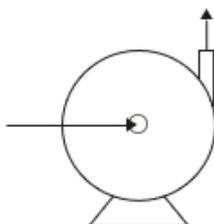
(b) Solid-Liquid (Leaching)



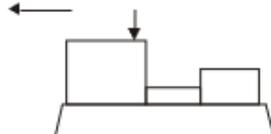
Involves removal of a solute from a Solid by means of a liquid solvent. Often used in ore treatment to Recover metal values

5. Fluid Handling

(a) Centrifugal pump



Most widely used for liquids of all types; simple in construction and maintenance

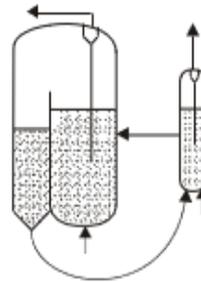
<i>Unit Operation</i>	<i>Schematic Representation</i>	<i>Comments</i>
(b) Reciprocating Pump Or Compressor		Generally used for higher pressure delivery; may be used for metering or proportioning
(c) Jet Ejector		Used for lower pressure operation or production of vacuum; steam often used as motive fluid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

Unit Operation

Schematic Representation

Comments

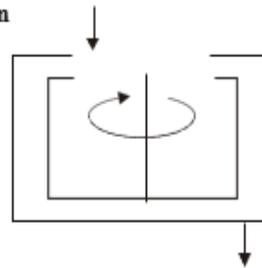
6. Fluid Bed



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

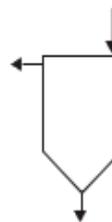
7. Fluid - Solid Separation

(a) Centrifugation



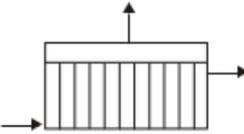
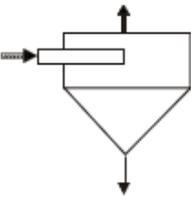
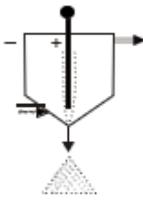
Used to separate very finely divided solids from liquid or liquids from liquid emulsions

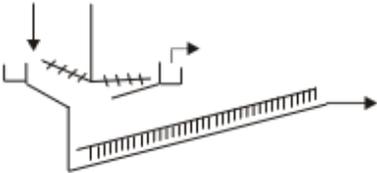
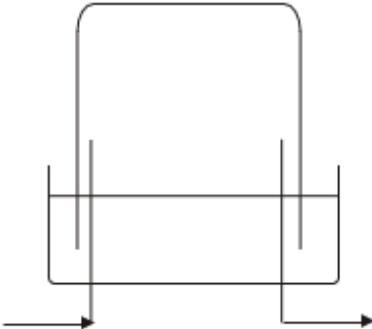
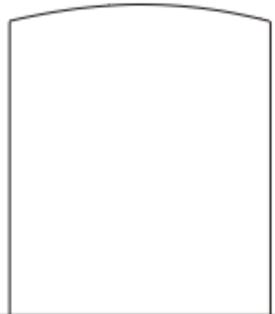
(b) Setting Tank



Simple device used to remove large particles from gas stream by simple setting in low velocity zone

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

Unit Operation	Schematic Representation	Comments
(f) Filter Press		<p>Simplest type of pressure filter; widely used; plates and fabric filter media may be made of a variety of corrosion resistant materials</p>
(g) Cyclone Separator		<p>Used to separate solid particles or liquid droplets from gases to permit product recovery or to cut down product loss and air pollution</p>
(h) Electrostatic Precipitator		<p>Used to remove fine dusts or mists suspended in gases; features high collection efficiency at wide variety of operating conditions.</p>

<i>Unit Operation</i>	<i>Schematic Representation</i>	<i>Comments</i>
(j) Thickener - Classifier		Used to separate slurry into sludges and clear liquids; used widely in mineral industries and in sewage effluent clarification
8 . Fluid Storage (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

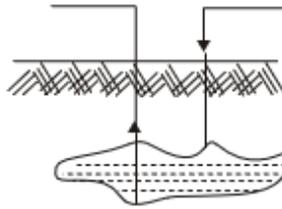
<i>Unit Operation</i>	<i>Schematic Representation</i>	<i>Comments</i>
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(c) Pressurized Spheres



Used for pressurized storage of liquified gases or high vapor pressure liquids to permit safe storage with no vapor losses

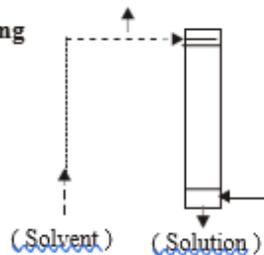
(d) Underground Caverns



Used for large volume storage of liquids or of liquified gases

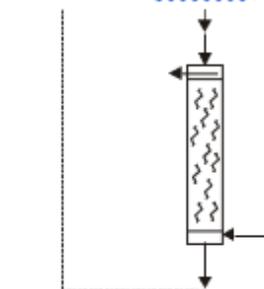
9 . Gas-Liquid Contacting

(a) Absorption

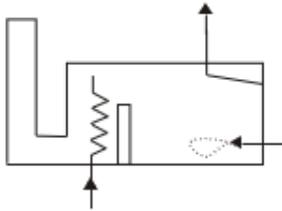
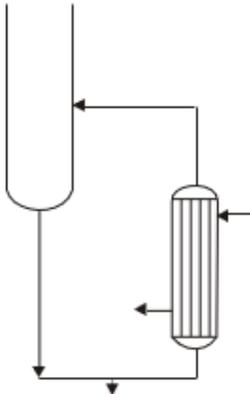
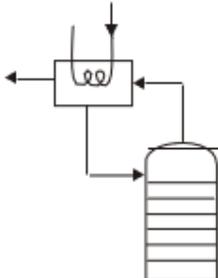


Used for taking up a soluble gas in a solvent liquid and producing a solution plus a lean exit gas ; e.g. Used in H₂S removal from hydrocarbons

(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

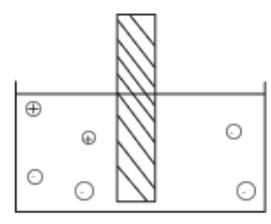
<i>Unit Operation</i>	<i>Schematic Representation</i>	<i>Comments</i>
10. Heat Exchange		
(a) Fired Heater		Used to heat petroleum fraction to distillation or cracking temperatures in direct fired tubes.
(b) Reboiler		Uses natural circulation to circulate fractionating tower bottom in heat exchange with steam, e.g., to provide necessary heat for fractionation
(c) Condenser		Usually water-cooled tubular construction to provide reflux and overhead product from fractionating column

Unit Operation	Schematic Representation	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

Unit Operation	Schematic Representation	Comments
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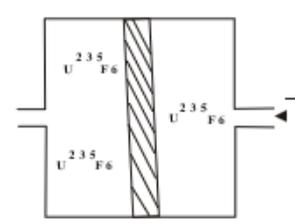
11. Membrane Separation

(a) Dialysis



Used to separate salts in sol's having widely different mole. E.g., Caustic from sugar or cellulose

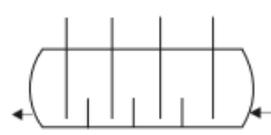
(b) Gaseous Diffusion



Uses micro porous (e.g., Ni) barriers in multistage operation to separate light (e.g., $U^{235}F_6$) from heavy (e.g., $U^{238}F_6$) components

12. Mixing

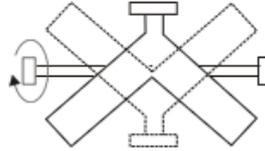
(a) Agitation



May be used for liquid - liquid or solid - solid mixing in single or multiple compartments; widely used in process industries

<i>Unit Operation</i>	<i>Schematic Representation</i>	<i>Comments</i>
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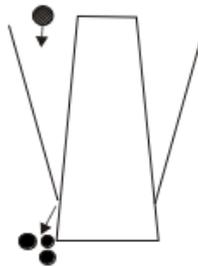
(b) Solids Blending



The device shown divides and recombines a granular mass over and over again to effect uniformity

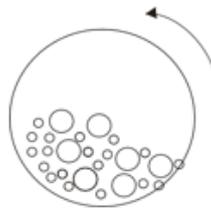
13. Size Reduction and Enlargement

(a) Crushing

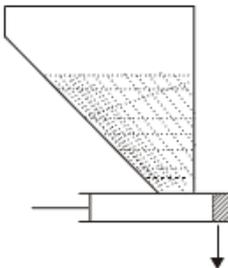
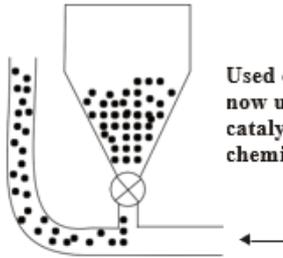
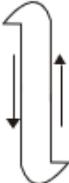


Used typically in 4:1 size reduction of hard materials from -5 to -20 mesh or -1 to -4 mesh

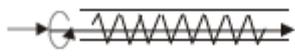
(b) Grinding



Wet or dry grinding may be carried out in presence of balls, pebbles or rods; feed may be -4 to -100 mesh and reduction ratio 10 - 15 to 1

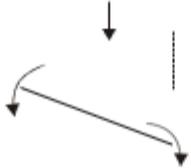
Unit Operation	Schematic Representation	Comments
(c) Pelletizing		<p>Used to make tablets from powders of Medicinals, catalysts, etc</p>
14. Solids Handling		
(a) Pneumatic Conveying		<p>Used originally for grain; now used widely for cement, catalysts, coke and powdered chemicals</p>
(b) Bucket Elevators		<p>Used for elevating materials; can be used for moving powdered or granular materials to and from storage or between reaction vessels as in moving bed catalytic processes</p>

Unit Operation	Schematic Representation	Comments
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(c) Screw conveyor  Versatile ; can be used to mix and heat or cool ; can be operated under pressure ; 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

Unit Operation	Schematic Representation	Comments
(b) Elutriation		<p>May be used to remove fines from a solid by passage of a gas to fluidize and transport the fines</p>
(c) Froth Floatation		<p>Finely ground (- 50 mesh) ores are suspend in water in presence of floating reagents (e.g., Na_2CO_3) and blow with air; desired product collects in froth.</p>
(d) Jigging		<p>One of the oldest processes used for separation of minerals from lighter gangues as a well as for separating coal from heavier contaminants</p>

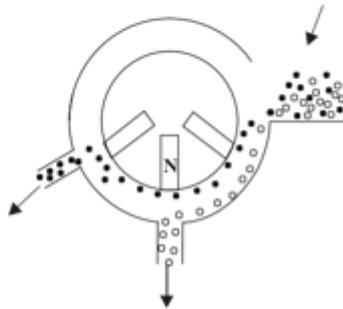
Unit Operation

Schematic Representation

Comments

(e.) Magnetic Separation

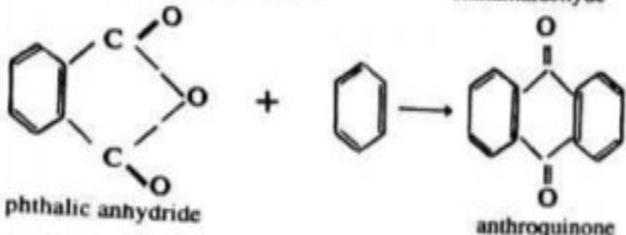
Used to remove tramp iron from feed to subsequent grinding and pulverizing steps; also used to concentrate magnetic iron ores



UNIT OPERATION AND UNIT PROCESS CONCEPTS

Table IC-1 Outline of Unit Processes

Unit Process	Typical Industry Using Process
<p>1 Alkylation</p> <p>Addition of alkyl radical ($-\text{CH}_3$) with side chain final product</p> $\text{C}=\text{C}-\text{C}-\text{C} + \text{C}-\underset{\text{C}}{\text{C}}-\text{C} \xrightarrow[\text{catalyst}]{\text{heat}} \text{C}-\underset{\text{C}}{\overset{\text{C}}{\text{C}}}-\text{C}-\underset{\text{C}}{\text{C}}-\text{C}$ <p style="text-align: center;"> 1-butylene isobutane 2,2,4-trimethylpentane or isooctane </p>	<p>Petroleum Organic chemicals</p>
<p>2 Amination by Ammonolysis</p> $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Cl} + 4\text{NH}_3 \rightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ <p style="text-align: center;"> ethylene dichloride ethylene diamine </p> $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H} + 2\text{NH}_3 \rightarrow \text{NC}\cdot(\text{CH}_2)_4\text{CN}$ <p style="text-align: center;"> adipic acid adiponitrile </p>	<p>Dyestuffs Organic chemicals Synthetic fibers</p>
<p>3 Amination by Reduction</p> $\text{CH}_3\cdot\text{CH}\cdot\text{NO}_2\cdot\text{CH}_3 + 3\text{H}_2 \rightarrow \text{CH}_3\cdot\text{CH}\cdot\text{NH}_2\cdot\text{CH}_3$ <p style="text-align: center;"> 2-nitroparaffin isopropylamine </p>	<p>Dyestuffs Organic chemicals</p>
<p>4 Ammonoxidation</p> $\text{CH}_3:\text{CH}_2\cdot\text{CH}_3 + \text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{CH}_2:\text{CH}\cdot\text{CN} + \text{H}_2\text{O}$ <p style="text-align: center;"> propylene ammonia air acrylonitrile </p>	<p>Plastics Synthetic fibers</p>
<p>5 Calcination</p> $\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2$ <p style="text-align: center;"> limestone lime </p>	<p>Cement</p>
<p>6 Carbonylation</p> $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$ <p style="text-align: center;"> methanol carbon monoxide acetic acid </p>	<p>Organic chemicals</p>
<p>7 Carboxylation</p> $\text{C}_6\text{H}_5\text{ONa} + \text{CO}_2 \xrightarrow{\text{pressure}} \text{C}_6\text{H}_5\text{COONa}$	<p>Organic chemicals</p>
<p>8 Combustion</p> $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	<p>Process heating</p>

- 9 Condensation** Synthetic perfumes
- $$\text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{CH}:\text{CHCHO} + \text{H}_2\text{O}$$
- benzaldehyde acetaldehyde cinnamaldehyde
- 
- phthalic anhydride anthroquinone
- Organic chemicals
Dyestuffs
- 10 Cracking or Pyrolysis** Petroleum
Destruction distillation
of coal
- $$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \rightarrow \text{C}-\text{C}-\text{C} + \text{C}=\text{C}-\text{C}-\text{C}$$
- 11 Cyanidation or Cyanation** Organic chemicals
- $$\text{HC}:\text{CH} + \text{HCN} \rightarrow \text{CH}_2:\text{CH}\cdot\text{CN}$$
- acetylene acrylonitrile
- 12 Cyclization** Petroleum
- $$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \rightarrow \text{C} \begin{array}{l} \diagup \text{C}-\text{C} \\ \diagdown \text{C}-\text{C} \end{array} + \text{H}_2$$
- 13 Dehydration** Organic chemicals
Inorganic chemicals
- $$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{C}:\text{CH}_2 + \text{H}_2\text{O}$$
- ethyl alcohol ethylene
- $$\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$$
- calcium hydroxide calcium oxide
- 14 Dehydrogenation** Synthetic rubber
- $$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2 \rightarrow \text{CH}_2:\text{CH}=\text{CH}:\text{CH}_2 + \text{H}_2$$
- 1-butene 1,3-butadiene
- 15 Diazotization and Coupling** Dyestuffs
- (a) $\text{R}-\text{NH}_2 + \text{HCl} + \text{HNO}_2 \rightarrow \text{R}-\text{N}_2\text{Cl} + 2\text{H}_2\text{O}$
- (b) $\text{R}-\text{N}_2^+\text{Cl}^- + \text{H}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2 \rightarrow \text{R}-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$
- 16 Disproportionation** Organic chemicals
- $$2\text{CH}_2:\text{CHCH}_3 \rightarrow \text{H}_2\text{C}:\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$$
- propylene ethylene butylene
- 17 Double Decomposition (metathesis)** Inorganic chemicals
- $$\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$$

MANUFACTURE OF SODA ASH

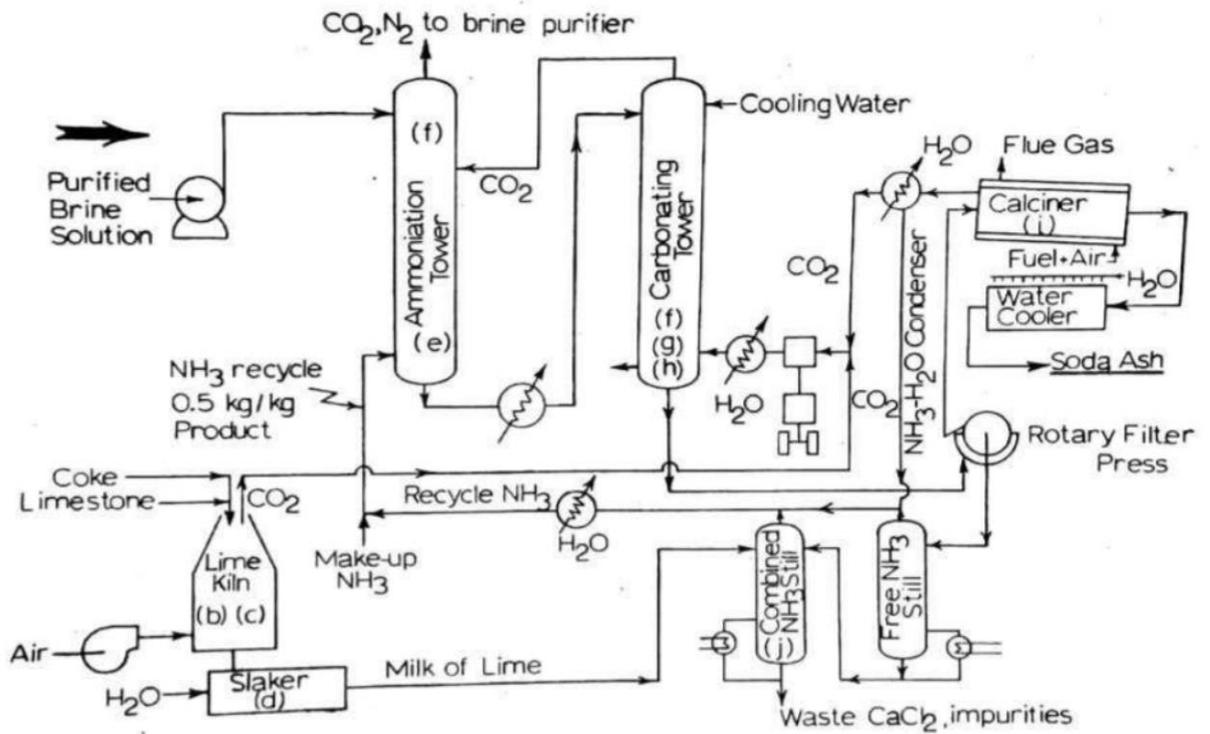


Figure 1.1 Manufacture of soda ash by Solvay process

CHLORINE -CAUSTIC SODA

Reference flow sheet: Figure 11.12

4.2.2. Electrolysis reactions

(a) Diaphragm cell type

Cell notation

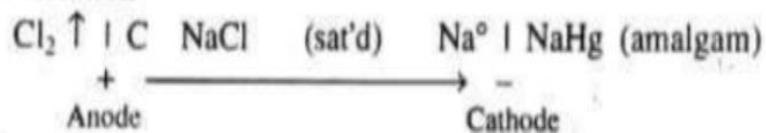


Cell reaction

- Anode : $\text{Cl}^- - e \rightarrow \frac{1}{2}\text{Cl}_2$
- Cathode : $\text{Na}^+ + \text{H}_2\text{O} + e \rightarrow \text{Na}^+ + \text{OH}^- + \frac{1}{2}\text{H}_2$
- Overall : $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2$; $\Delta H = +53.4 \text{ Kcal}$

(b) Mercury cell

Cell notation



Cell reaction

- Anode : $\text{Cl}^- - e \rightarrow \frac{1}{2}\text{Cl}_2$
- Cathode : $\text{Na}^+ + e \rightarrow \text{Na}^\circ$
 $\text{Na}^\circ + \text{Hg} \rightarrow \text{NaHg (amalgam)}$
- Denuding : $\text{NaHg} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 + \text{Hg}$
- Overall : $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2$

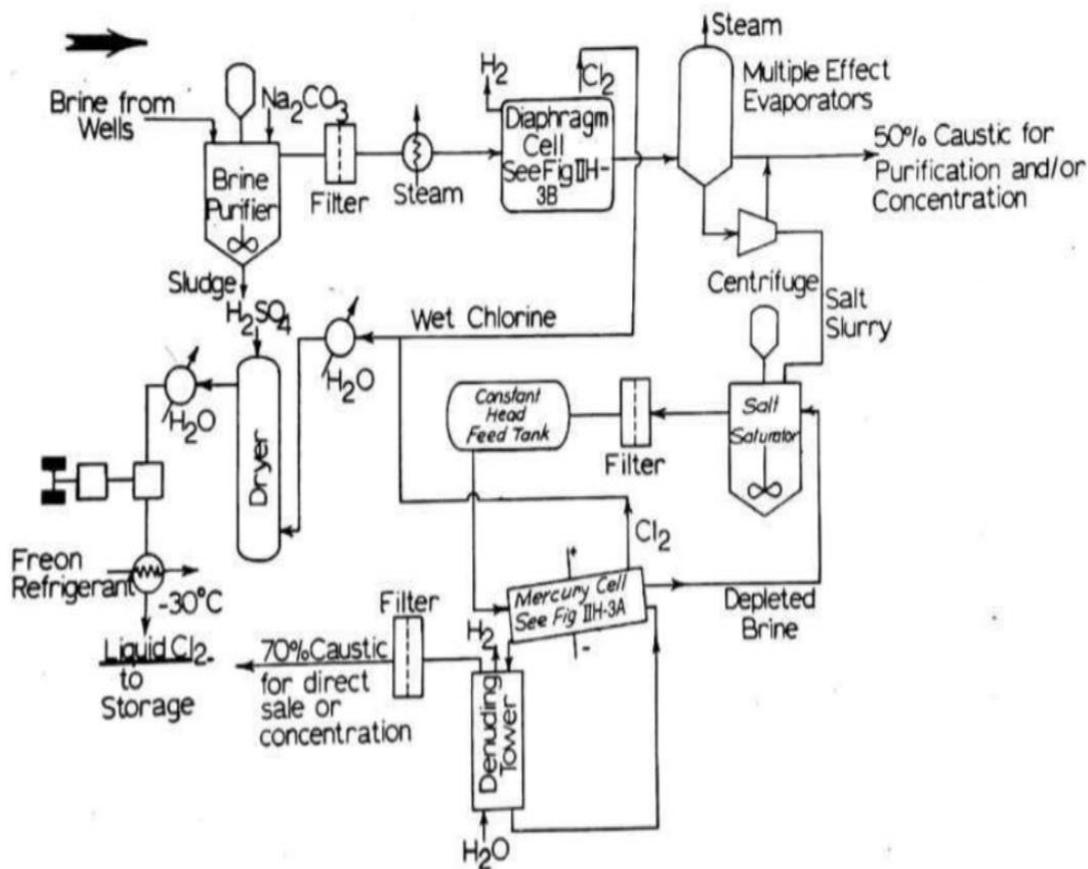


Figure 1.2 Electrolytic process for chlorine-caustic soda Production

REFERENCES

1. Gopala Rao M. and Marshall Sittig, "Dryden's Outlines of Chemical Technology", 3rd Edition, East West Press, New Delhi, 2008.
2. George T. Austin, "Shreve's Chemical Process Industries", 8th Edition, McGraw Hill International Editions, Singapore, 2002.



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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – II – Chemical Process Technology – SCH1304

II. INTRODUCTION-SULPHUR, SULPHURIC ACID AND SILICATE INDUSTRIES

SULFURIC ACID

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

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 alchemical processes.

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, $\text{Fe}_2(\text{SO}_4)_3$, which, when heated to 4800C , 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 very high.

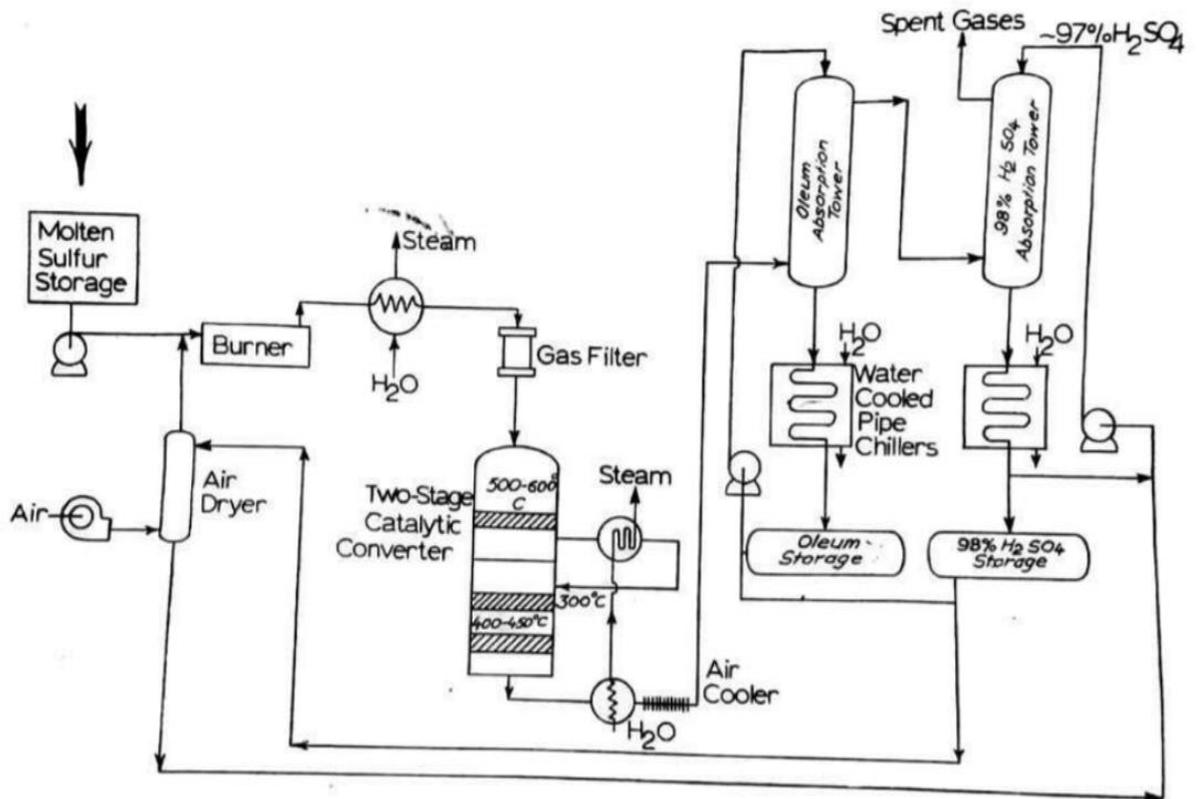


Figure 2.1 Manufacture of Sulfuric acid by contact Process

2. The contact process for sulfuric acid

Almost all sulfuric acid is manufactured by the contact process.

Raw Materials

Basis: 1000kg sulfuric acid (100%)

Sulfur dioxide or pyrite (FeS_2) = 670kg

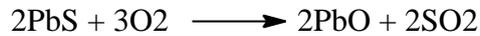
Air

= 1450-2200Nm³

Sources of raw material

The sources of sulfur and sulfur dioxide are as follows

- Sulfur from mines
- Sulfur or hydrogen sulfide recovered from petroleum desulfurization
- Recovery of sulfur dioxide from coal or oil-burning public utility stack gases
- Recovery of sulfur dioxide from the smelting of metal sulfide ores



- Isolation of SO₂ from pyrite

Reactions



ELEMENTAL SULFUR BY FRASCH PROCESS

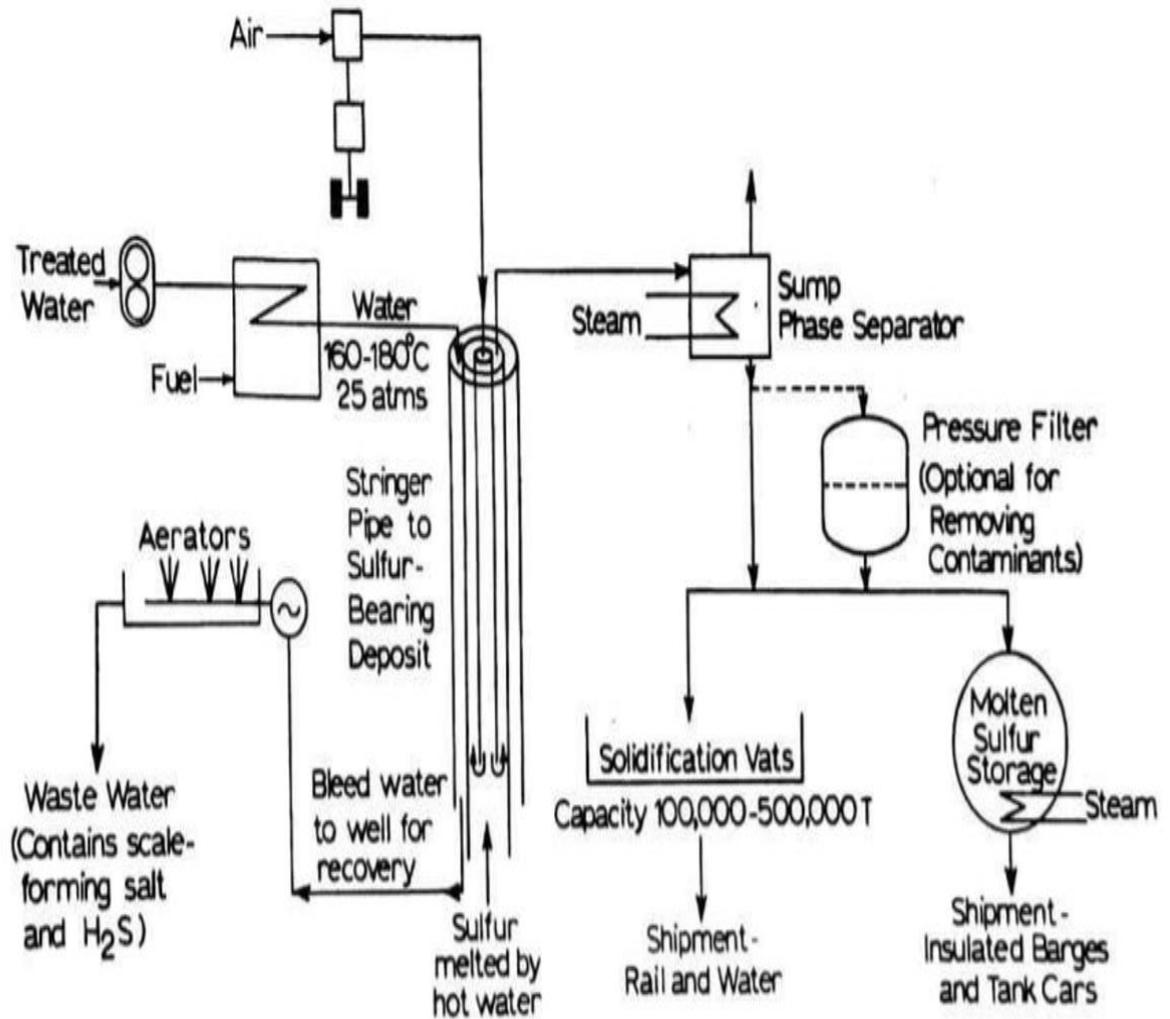


Figure 2.2 Elemental Sulfur by Frasch Process

MANUFACTURE OF PORTLAND CEMENT

Cement is broadly described as material having adhesive and cohesive property with capacity to bond the material like stone, bricks, building blocks etc. Cement is a binder, a substance that sets and hardens independently, and can bind other materials together. Cements are inorganic material that shows the cementing properties of setting and hardening when mixed with water. Cement is prepared from calcareous (Ca) material and argillaceous (Al + Si) material.

Cement has property of setting and hardening under water by virtue of chemical reaction of hydrolysis and hydration. Therefore, cements are generally divided into two types hydraulic and non-hydraulic that is on the basis of their setting and hardening pattern. Hydraulic cements harden because of hydration, chemical reactions that occur independently of the mixture's water content; they can harden even underwater or when constantly exposed to wet weather. The chemical reaction that results when the anhydrous cement powder is mixed with water produces hydrates that are not water-soluble. Non-hydraulic cements must be kept dry in order to retain their strength. Portland cement is example of hydraulic cement material while ordinary lime and gypsum plaster are consider as example of non-hydraulic cement.

Cement is used for structural construction like buildings, roads, bridges, dam etc. The most important use is the production of mortar and concrete the bonding of natural or artificial aggregates to form a strong building material that is durable in the face of normal environmental effects.

Both cement and concrete are different, because the term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a combination of a cement and aggregate.

In the last couple of decades of eighteenth century, modern hydraulic cements began to be developed due to fulfill following requirement

2. For finishing brick buildings in wet climates
3. Development of strong concretes

Hydraulic mortars for masonry construction of harbor works, etc., in contact with sea water

As the good quality building stone became expensive and construction of prestige buildings from the new industrial bricks, and to finish them with a stucco to imitate stone became the common practice. Hydraulic lime was favored for this, but the need for a fast set time encouraged the development of new cements.

James Parker developed cement from clay minerals and calcium carbonate and patented as Roman cement in 1796. It was made into a mortar with sand, set in 5–15 minutes. The success of "Roman Cement" led other manufacturers to develop competing products by burning artificial mixtures of clay and chalk.

In the first decade of nineteenth century, it was proved that the "hydraulicity" of the lime was directly related to the clay content of the limestone from which it was made first by John Smeaton and then by Louis Vicat. Vicat produce artificial cement by burning of chalk and clay into an intimate mixture in 1817. Also, James Frost produced "British cement" in a similar manner around the same time, and patented in 1822. At the same time Portland cement, was patented by Joseph Aspdin in 1824.

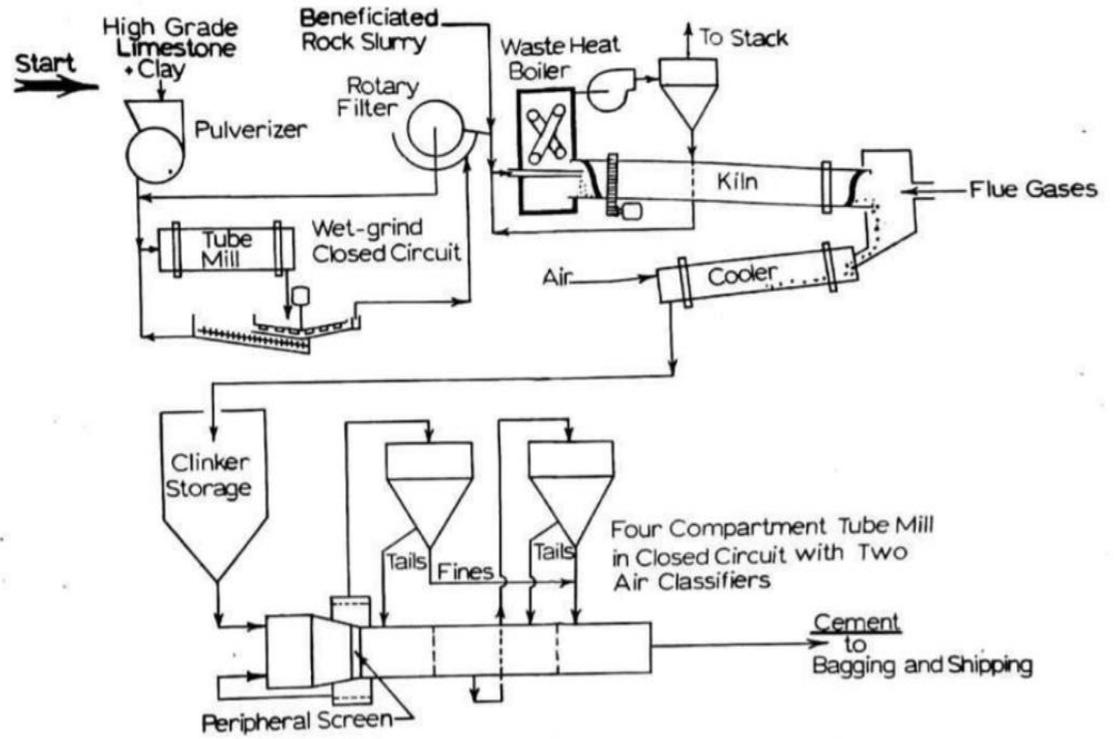


Figure 2.3 Manufacture of Portland Cement

GLASS INDUSTRIES

INTRODUCTION

When silica or quartz is heated up to 1650°C 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 manufactured which is much more stable to temperature change. The glass of various commercial qualities is prepared by heating sand or quartz along with metal oxide or carbonates.

TYPES OF GLASSES

1. Soda-lime or soft glasses

The raw materials are silica (sand), calcium carbonate and soda ash. Their approximate composition is $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$. About 90% of all glasses produced belong to soda lime glass. The low cost, low melting point soda-lime glass has resistance to devitrification 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 hard glasses

Silica (sand), calcium carbonate and potassium carbonate are the basic raw material for potash lime glass. Their approximate composition is $\text{K}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$. They possess high melting point, fuse with difficulty and have good resistance to acids, alkalis and other solvents compared 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 Flint glass

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, K_2O is used instead of sodium oxide. So, its approximate composition is $\text{K}_2\text{O} \cdot \text{PbO} \cdot 6\text{SiO}_2$. 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 fields respectively.

4. **Borosilicate glass or Pyrex glass or Jena glass**

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 following composition.

Component	SiO ₂	B ₂ O ₃	Al ₂ O ₃	K ₂ O	Na ₂ O
Percentage	80.5	13	3	3	0.5

Boron and aluminium oxides substitute Na₂O 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% Silica glass**

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% B₂O₃ and traces of other materials. This glass is then washed carefully and annealed to 12000C. 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 or clear.

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

15000C. They possess high chemical resistance to most corrosive agents. They are corroded by only HF, hot H₃PO₄ and concentrated alkaline solutions.

Uses: They are used where high temperature resistance is required and articles can be safely used at temperature up to 8000C. They are used for the constructed chemical plants, laboratory crucibles, induction furnace linings, electrical insulators.

6. 99.5% silica glass or Vitreosil

It is produced by heating SiO₂ to its melting point (1,7500C). 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 16500C, 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-silicate glass

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

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

8. Safety glass

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 the glass.

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

9. Optical or Crookes glasses

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 or Pyroceram

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.

REFERENCES

1. Gopala Rao M. and Marshall Sittig, "Dryden's Outlines of Chemical Technology", 3rd Edition, East West Press, New Delhi, 2008.
2. George T. Austin, "Shreve's Chemical Process Industries", 8th Edition, McGraw Hill International Editions, Singapore, 2002.



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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – III – Chemical Process Technology – SCH1304

CARBON DIOXIDE

INTRODUCTION

Carbon dioxide (CO₂) 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 atmospheric air.

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"

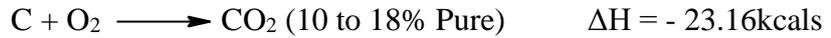
Carbon dioxide 's properties were studied by Joseph Black in 1750. He found that limestone could be heated or treated with acids to yield a gas (fixed air). He observed that gas was denser than air and supported neither flame nor animal life. Black also found that when bubbled through an aqueous solution of lime, it would precipitate calcium carbonate. Based on this phenomenon he illustrates that CO₂ 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 CO₂ at elevated pressure in 1823. While in 1834 Charles Thilorier solidifies CO₂, in pressurized container of liquid carbon dioxide.

In higher animals, the carbon dioxide travels in the blood from the body's tissues to the lungs where it is breathed out. CO₂ 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's crust is thin; and is freed from carbonate rocks by dissolution. CO₂ is also found in lakes at depth under the sea, and commingled with oil and gas deposits.

SOURCES OF CO₂

By burning of carbonaceous materials



In the production of H₂ by steam water gas 16% pure CO₂ is obtained.

- In manufacture of alcohol (ethanol) by the fermentation process. 99.9 % pure CO₂ is obtained.
- In calcinations of CaCO₃ 40% CO₂ is obtained

1000°C



MANUFACTURE

Raw materials- Coke or coal, Air

Reaction

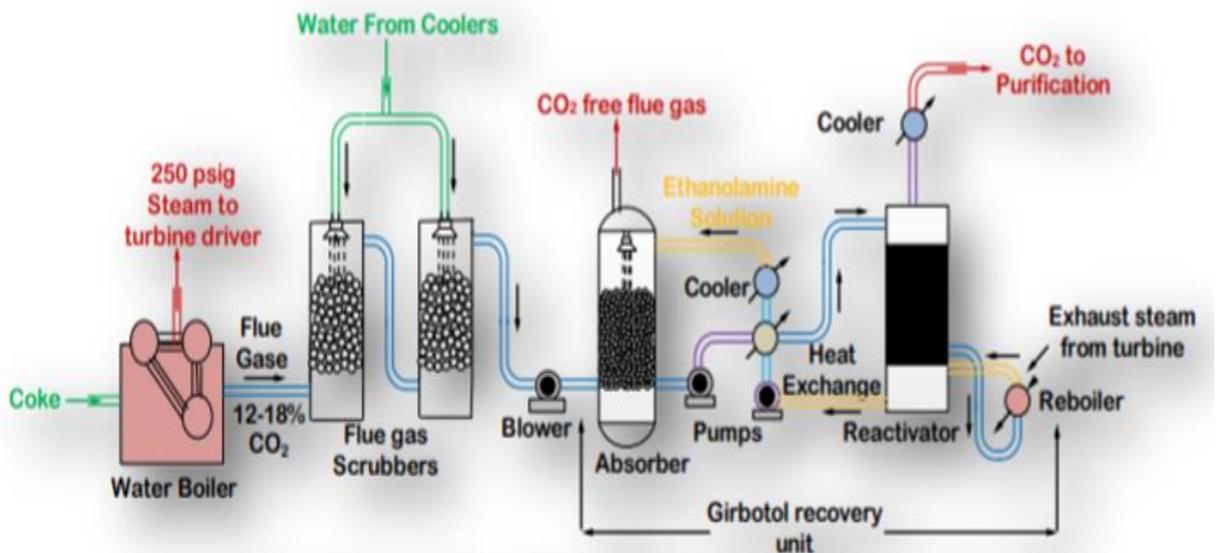


Figure 3.1 Manufacture of Carbon dioxide

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% CO₂ are taken from the boiler at 345⁰C 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 CO₂ is absorbed selectively by a solution of ethanolamine's 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 before compression.

METHODS OF RECOVERY

The processes most commonly used for recovery of carbon dioxide are

- Ethanolamine process
- Sodium carbonate process
- Potassium carbonate process

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 counter current 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 absorbing medium.

1. Girbotol amine process

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 absorption medium.



The operation are depends on the reversible nature of the above reaction. Forward reaction proceeds at low temperatures (65⁰C) 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 counter current 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 (140⁰C) 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 carbon dioxide
- Regeneration up to 100% with moderate steam consumption is possible
- Higher absorption of CO₂ in the solution
- Lower operating cost

Sodium carbonate process



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 counter current 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 and compressors.

OXYGEN AND NITROGEN

Oxygen

Oxygen (O₂) composed of two atoms of the element (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 non-metallic 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 the atmosphere.

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, and hydrogen.

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 in 1794.

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 vapours and 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.

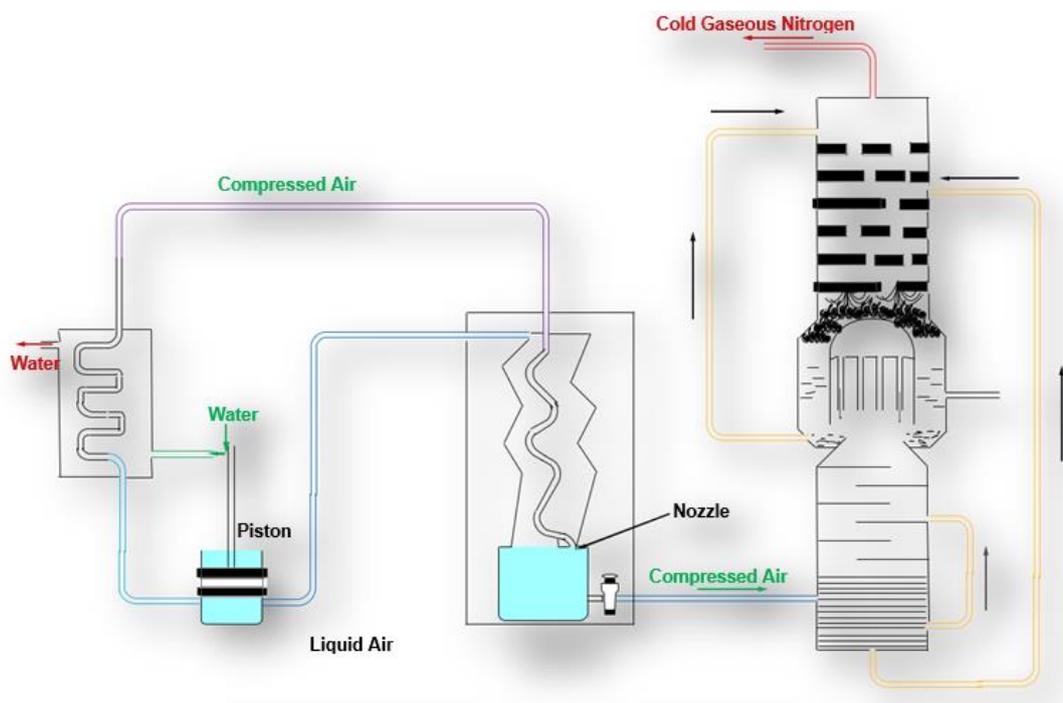


Figure 3.2 Manufacture of Oxygen and Nitrogen by Linde's Process

MANUFACTURE

Oxygen and nitrogen are usually separated by rectification of liquid air.

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.

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°C) and N₂ (-195°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 Lower column of the tower only to re-enter 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 rectification column.

ACETYLENE

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°. 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 to impurities.

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 carbon arc.

MANUFACTURE

Acetylene manufacture by following processes

From calcium carbide

From paraffin hydrocarbons by pyrolysis (Wulff process)

From natural gas by partial oxidation (Sachasse process)

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.



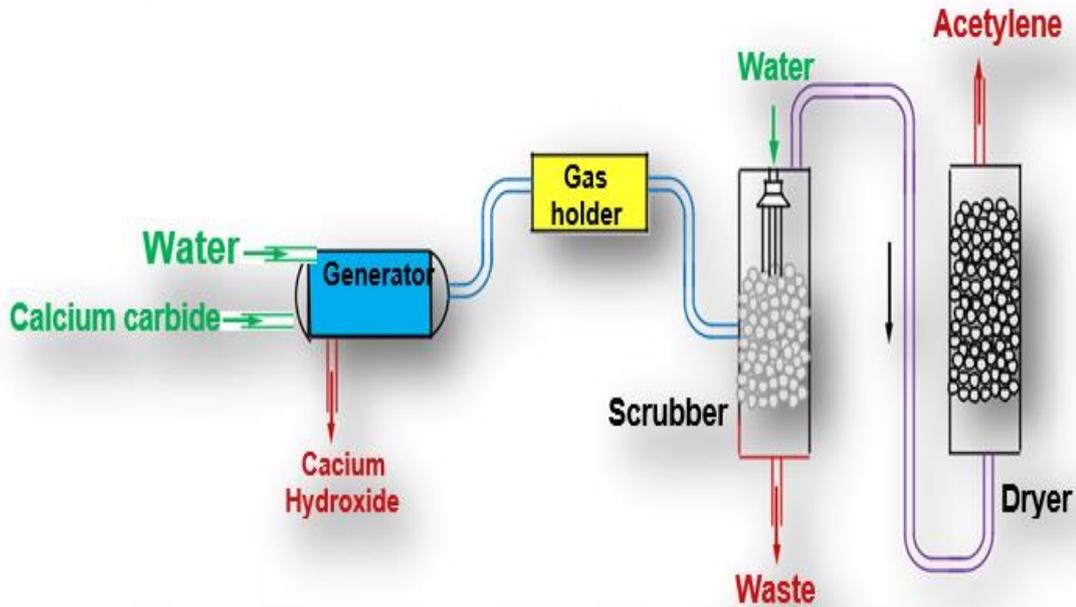


Figure:3.3 Manufacture of Acetylene

PAINT INDUSTRIES

Paints are stable mechanical mixtures of one or more pigments which impart desired colour and to protect the film from penetrating radiation, such U. V. rays. The pigments and the extenders are carried or suspended in drying oils called vehicle. Which is a film forming material, to which other ingredients are added in varying amount e .g. linseed oil, tung oil, castor oil, tall oil etc. Boiled Linseed oil is preferred to unboiled oil because it develops a good drying power and requires only two days for drying. The drying time is reduced further by adding driers to the paint. Driers act to promote the process of film formation and hardening. Thinners maintain the uniformity of the film through a reduction in the viscosity of the blend. The purpose of paint may be protective or decorative or both and can be applied on a metal or wood surface. It is applied by brushing, dipping, spraying, or roller coating.

The important varieties of paints are emulsion paints, latex paints, metallic paints, epoxy resin paints, oil paints, water paints or distempers etc.

CLASSIFICATION OF PAINTS

On the basis of their applications, paints can be classified as

a) Exterior house paints

Generally, have constituents such as pigment (ZnO, TiO₂, white lead etc.), extenders (talc, barytes, clay etc), vehicle (e.g. boiled linseed oil) and thinners (e.g. mineral spirit, naphtha etc.) Coloured pigments for light tint are also added in varying amount.

b) Interior wall paints

It is prepared by mixing pigments (e.g. white and colored pigments), vehicle (e.g. varnish or bodied linseed oil) and resins (e.g. emulsified phenol formaldehyde resins and casein)

c) Marine paints

Also known as antifouling paint and can be prepared by mixing various ingredients such as pigments (ZnO and venetian red), resin (shellac), driers (manganese lineolate), vehicle (coal tar), diluents (pine oil), toxic components (cuprous oxide and mercuric oxide) and small amount of bees wax.

d) Emulsion paints

These paints are highly durable, impermeable to dirt, resistant to washing, rapidly drying, contain water as thinner and can be easily cleaned. It contain an emulsion of alkyds, phenol formaldehyde etc.(vehicle) in water pigments and extenders are also added to get other desirable properties.

e) Chemical resistant paints

Consist of baked oleo resinous varnishes, chlorinated rubber compositions, bituminous varnishes and phenolic dispersion as chemical resistant materials in paint formulations.

f) Fire resistant paints

These paints impart a protective action on the article being coated through easy fusion of the pigments and other paint ingredients giving off fume on heating, they do not support combustion. It consist of borax, zinc borate, ammonium phosphate synthetic resins etc as anti-fire chemicals.

g) Luminous paints

Consist of phosphorescent paint compositions such as pigment (sulfides of Ca, Cd and Zn dispersed in spirit varnish), vehicle (chlorinated rubber, styrol etc.) and sensitizer for activation in UV region.

Latex paints

These paints usually contain

- **Protein dispersion:** Prepared by soyabean proteins or casein in aqueous ammonia solution for about an hour at room temperature
- **Pigments:** ZnS, TiO₂ etc dispersed in water
- **Extenders:** clay, talc, MgSiO₃, BaSO₄ etc.
- **Preservatives:** Penta chlorophenol
- **Antifoaming agent:** Pine oil
- **Plasticizer:** Tributylphosphate
- **Latex:** Prepared from a butadiene styrene copolymer in water.

Aluminum paints

Used as heat reflecting paints and consist of pigment (aluminum powder) and vehicle (spirit varnishes) and cellulose nitrate lacquers.

Metal paints

Applied on the metal surfaces or bodies for protection and decoration and are of two types

Barrier coating

Protective barrier is formed between the surface coated and its surroundings. These consist of pigment, vehicle, anticorrosive agents (e.g. zinc or chrome yellow), resins (e.g. alkyds, epoxy, polyamides, chlorinated rubbers and silicones) etc. Alkyd resists weathering of metals, epoxy and polyamides form tough film resistant to chemicals. Chlorinated rubbers resist action of soaps, detergents and strong chemicals and silicones are added as heat resistant and water repellents.

Galvanic coating

Protection is provided by self-undergoing of galvanic corrosion. e.g. Zinc coating (Galvanization) on steel. Before applying metal paints it is important to clean thoroughly the surface to be coated. Moreover, paint should be applied over a primer such as red lead by a high-pressure spray gun.

Cement paints

It is prepared by mixing white cement with colouring matter or pigments, hydrated lime and fine sand as inert filler. They are available in the form of powder of particular colour. The dispersion medium may be water or oil, depending upon the purpose of coating. Water and linseed oil are used as dispersion medium for stone/brick structure and for coating of corrugated metal surfaces respectively. Before applying cement paint a primer coat is applied which consist of a dilute solution of sodium silicate and zinc sulfate.

CONSTITUENTS OF PAINTS

Pigments are classified as follows

1. Pigments

Pigments are various inorganic or organic insoluble substances which are widely used in surface coatings. The most important properties of pigments are opacity, good covering power, mixing ability with oil, chemical inertness, non-toxicity or low toxicity, high hiding power, high tinting strength and reasonable cost. They protect the film by reflecting the destructive ultra violet light, to strengthen the film.

2. **Natural or mineral pigments:** e.g. talc mica, chalk, clays, iron ores, barytes, diatomaceous earth etc.
3. **Synthetic or chemical pigments:** e.g. white lead, zinc oxide, lithopone, titanium oxide, and many other organic and inorganic colours
4. **Reactive pigments:** Those pigments which react with drying oils or their fatty acids and form soaps are called reactive pigments. e.g. zinc oxide, red lead, titanium dioxide etc
5. **Organic dyes:** Toners (insoluble organic dyes) used directly as pigments because of their durability and colouring power. Lakes, which are organic dyes on an inorganic adsorbent (such as clay), have also been used in many colours. Para red, toluidine toner, Hansa yellow G (lemon yellow) etc. are important lakes. Clay, barite, aluminum hydroxide etc. are well known inorganic adsorbents. Both toners and lakes are ground in oil or applied like any other pigment.

Various pigments used for making paints are

- White:** White lead, titanium dioxide, zinc oxide, lithopone.
- Red:** Red lead, iron oxides, cadmium reds, rouge etc.
- Blue:** Ultramarine, cobalt blues, iron blues etc.
- Chromium oxide:** Chromium oxide, chrome green, phthalocyanine green.
- Yellow:** Litharge, lead or zinc chromates, ochre etc.
- Black:** Carbon black, lamp black, furnace black etc.
- Orange:** Basic lead chromate, cadmium orange etc.

Brown: Burnt umber, burnt sienna etc

Metallics: Copper powder, zinc dust, aluminium etc.

Metal protective pigments: Red lead, blue lead, zinc and basic lead etc.

Extenders or Fillers

They are used for decreasing the cost of paint and to supplement the pigment in increasing the covering and weathering power of the film. Extenders improve consistency, levelling and setting of the paint. E.g. Talc, china clay, gypsum, silica, barite, glass flakes, asbestos and anhydrite etc.

Film forming materials

The vehicle or film forming materials plays dual role as carriers for the pigments and as formers of protective films. Reactive oils containing olefinic unsaturation are used as vehicles. These are usually called drying and semidrying oils, depending on degree of unsaturation. E.g. Linseed oil, soyabean oil, tung oil, talc oil, castor oil, varnishes, casein, fish oil etc. These oils form a protective film through oxidation and polymerization of the unsaturated constituents of the drying oil.

Drying oil is thus a film forming component which upon exposure to oxygen has the property of drying to hard, firm, non-sticky film through oxidation involving organic peroxides as the chain initiators.

Refined linseed oil

Depending on the application, refined linseed oil may be obtained by acid treatment or alkali treatment.

In acid refining, the oil is agitated with concentrated H_2SO_4 (1% of the total oil by weight) for about an hour, and allowed to stand for about 24 hours for allowing the coagulated colouring matter and mucilage to settle down. The clear oil is carefully siphoned off and washed with water to remove excess of acid and stored after the separation of water.

In alkali treatment, the slightly warm oil is agitated vigorously with 10% NaOH and allowed for setting out the precipitate. The oil is carefully siphoned off, heated to expel moisture and finally decolourised with bleaching clay and filtering presses.

Refined linseed oil is mainly used in the manufacture of varnishers.

Boiled linseed oil

It is obtained by adding small quantities of the oxides and acetates of Co, Mn and Pb to hot linseed oil, during heating the oil thickens with darkening of colour. This change in colour is referred to as boiling. Boiled linseed oil provides durability to the paint.

The heat bodied linseed oil or stand oil

Linseed oil is heated alone at elevated temperatures. Which increase its viscosity due to partial polymerization and attain a state called as bodied. The same can also be done by exposing the linseed oil to sun light for many hours.

This oil is used mainly in making printing inks and enamels.

Blown linseed oil

It is obtained by blowing air through linseed oil to make it bodied. During blowing oxidation and polymerization take place at unsaturated positions. Blown oil undergoes hardening much faster than the heat bodied oil.

In manufacture of interior paints blown linseed oil is used.

In addition, tung oil and soyabean oil are extensively used as drying oils. When properly treated tung oil dries with extreme rapidity forming hard, dense and tough film, which is more durable and less penetrable than that formed by linseed oil.

Tung oil is used in making water proof paints. The Soyabean oil is used in making interior paints.

Driers

Initially PbO was used as a drier, but the modern driers are Co, Mn, Pb, Zn, resinoleate, linoleate and naphthenates etc. They dissolve in the hot oil and the drying time has been much reduced. They are usually mixed with hot boiled linseed oil. Too rapid drying is not desirable because of some unwanted effects, e.g, the film suffers from wrinkling.

The drier acts as catalyst and promotes the oxidation polymerization process which accelerates drying of the film. The unsaturated drying oils polymerize by reaction mechanism which involves a peroxide intermediate.

Thinners or Diluents

In order to dissolve film forming material and to thin concentrated paints for better handling as well as brushing thinner is added. It is also used to suspended pigments. Diluents or thinners may include aliphatic or aromatic naphtha fractions or many contain turpentine. Solvent such as turpentine in spite of its low volatility, maintains the fluidity of the freshly applied film for reasonable period of time.

Lacquer

Lacquer is a liquid coating composition containing the basic film forming ingredients cellulose esters or ethers and plasticizers, without or with resin. Lacquers employ aliphatic chemicals, such as ethers, esters, ketones and alcohols to provide the desired controlled volatility. By virtue of evaporation of solvent, they are also called non-convertible coating. When a pigment is added to a clear lacquer, it is called lacquer enamel or pigmented lacquer.

Anti-skinning agent

Certain anti-skinning agents are also added to the paint in order to prevent gelling and skinning of the finished product before application of the paint by brushing, spraying or dipping. e.g. Polyhydroxyphenols.

Plasticizers

Plasticizers, low melting solids or liquids of low volatility which provide elasticity to the film and thus prevent cracking of the paint. Chemically, plasticizers are mostly esters. Triphenyl phosphate, dibutylphthalate and castor oil etc are used as plasticizers.

Resins

Resins are required for water base paints contain no oils and depend on vinyl acetate, acrylic or butadiene styrene polymer resin as the film forming materials.

Varnishes are also, used in the form of natural or synthetic resins. Examples of natural resins are copal or rosin, while that of synthetic resins are urea formaldehyde, acrylate, vinyl or silicone resins. Laquers also contain nitrocellulose as the resin constituent.

Paint Formulations

Gloss Enamels (Solvent Based)		
Sr. No.	Ingredients	% by Weight
1	Titanium Dioxide (Rutile)	29.3
2	Calcium Carbonate	1.4
3	Long Oil alkyd (70% NV)	52.2
4	Mineral Turpentine Oil (MTO)	13.3
5	Dipentene	2.1
6	Methylethylketoxime	0.1
7	Cobalt octoate (6%)	0.1
8	Zirconium octoate (18%)	0.3
9	Calcium octoate (3%)	1.2

Red oxide Primer (Solvent Based)		
Sr. No.	Ingredients	% by Weight
1	Red Iron Oxide	35.9
2	Zinc Chrome	10
3	Talc	3
4	Whiting	1.5

5	Lecithin	0.4
6	Medium Oil Alkyd (70% NV)	36.4
7	Mineral Turpentine Oil (MTO)	11.4
8	Cobalt Octoate (6%)	0.4
9	Lead Octoate (18%)	1

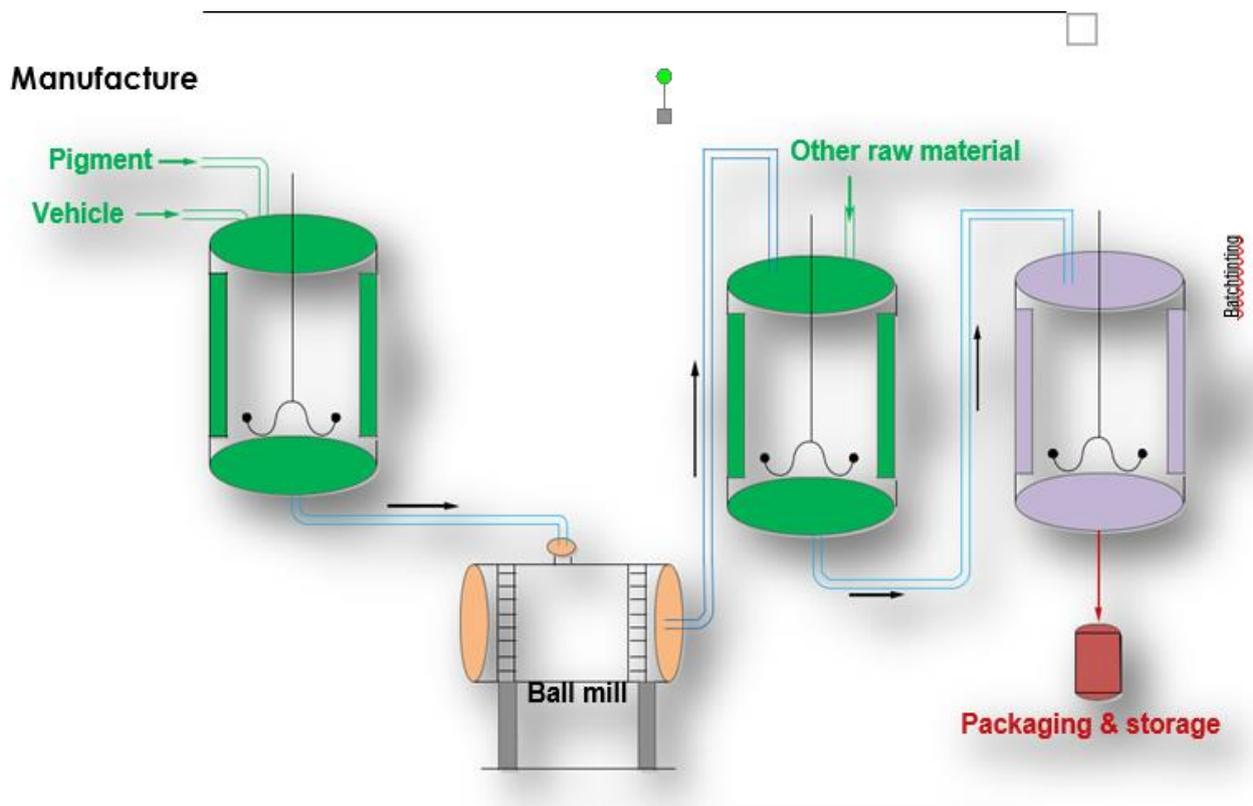


Figure:3.4 Manufacture of Paints



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DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV – Chemical Process Technology – SCH1304

NATURAL PRODCUTS

EDIBLE AND ESSENTIAL OILS

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 of glycerine, long chain fatty alcohol, sulfate and sulfonates. Oils like castor 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.

Vegetable oil extraction

Raw material: Seeds of oilseed plant

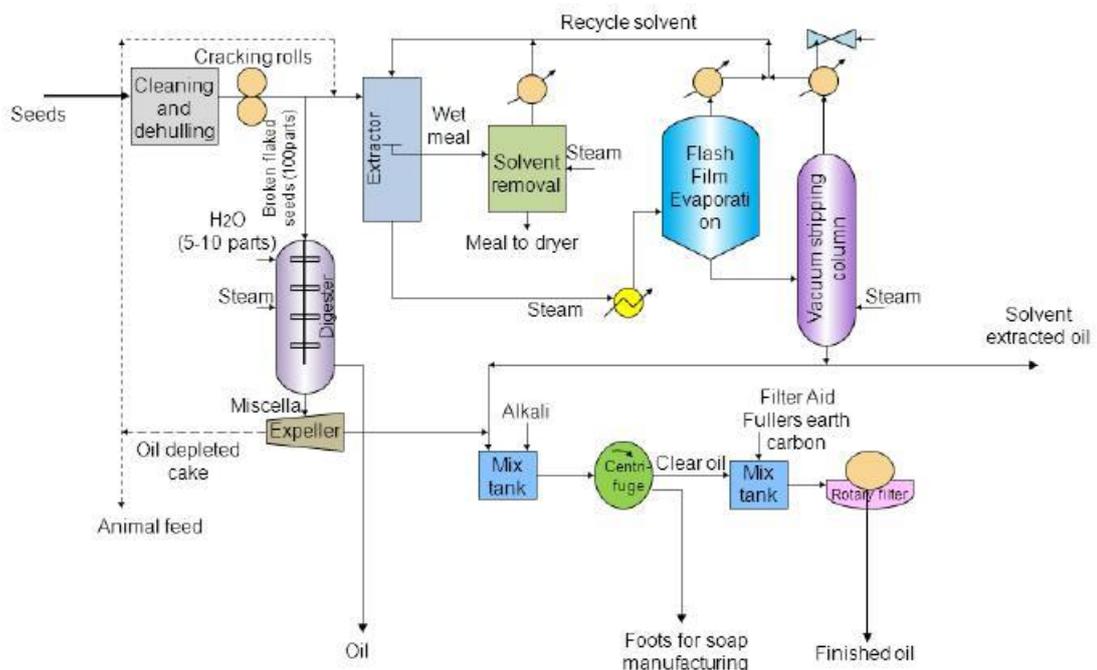


Figure 4.1 Flow sheet of vegetable oil extraction

Functional role of various processes (Figure 4.1):

Cleaner and dehulling:

Mechanical cleaning is done to remove stones and other undesirable material.

Dehulling remove hulls, dry outer covering of seed.

Cracking rolls:

Crushing rolls crush the oil seeds and gets flaked seeds

Digester:

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

Softening by means of heat and moisture is done here.

Steam is added for heating purpose.

Acid is formed by hydrolysis of ester.

The seeds get swollen up.

Expeller:

The swollen seeds are crushed under great pressure.

Cells of seeds get ruptured and oil is released.

The tapering shape ensures more application of pressure on the seeds

The oil depleted cake is either sent for solvent extraction or used as animal feed.

Oil is sent for purification.

Mix tank:

The extracted oil is treated with alkali like NaOH or Na₂CO₃ to remove fatty acids.

It also removes heavy metals, which can start oxidation of oil.

Centrifuge:

Acids are separated in centrifuge separator.

These separated acids are used as foos for soap manufacturing.

Rotary filter:

The clear oil is treated with some bleaching agent like "Fullers Earth Carbon" in filter aid before rotary filter.

Rotary drum filter is used for removal of seed particles which may be present.

This finished oil is produced.

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

Extractor:

The flaked seeds or oil extracted seeds from crushing rolls are fed on a moving bed.

Oil depleted cake is also added in extractor.

The solvent extracts oil from the seeds.

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

Solvent removal:

Steam is used to extract solvent carried by the oil seeds.

The rotating blades ensure better exposure to steam.

The solvent free meal is sent to dryer and then used as animal feed.

Solvent is collected from top and is recycled after cooling it in heat exchanger.

Flash film evaporator:

The solvent is preheated by steam.

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

The hexane is recycled back to extractor after heat recovery.

The use of flash evaporator reduces the cost of vacuum stripping column.

Vacuum stripping column:

The oil from flash evaporator is fed here.

The stripping is done by steam i.e. steam carries away the hexane.

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

Jet ejector is used here to generate vacuum.

The hexane is recycled again.

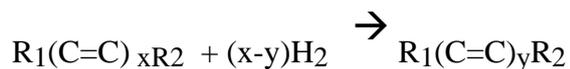
Oil produced here is either directly used or sent for purification.

Hydrogenation of oil

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)

Ni* catalyst

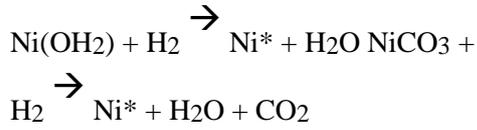


Nickel catalyst preparation:
190°C



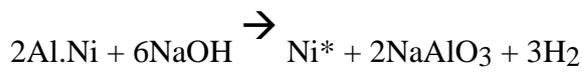
This produces a finely divided catalyst which is preferred for well-stirred hydrogenation reactors.

Nickel catalyst preparation (reduced Ni on inert catalyst support)



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

Nickel catalyst preparation



Alloy

Raney nickel

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.

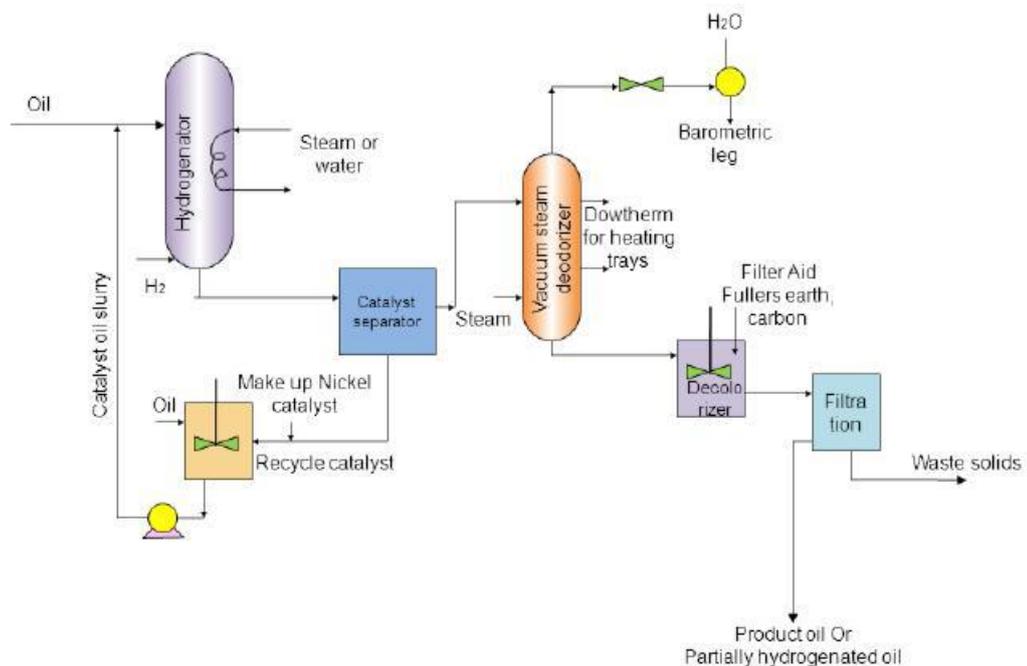


Figure 4.2 Flow sheet of hydrogenation of vegetable oil

Functional role of main units:

Hydrogenator:

- Oil is fed to the hydrogenator.
- Hydrogen, and steam is introduced in it.
- The catalyst oil slurry of concentration 5 to 15 kg per ton of oil is also put.
- The reaction is slightly exothermic so steam is sometimes turned off.

Deodorizer:

- The hydrogenated oil is now fed to vacuum steam deodorizer.
- It operates in continuous basis.

Finishing

- Oil colour is removed by treating with fuller's earth or carbon.
- It is then filtered, mixed with some vitamins.
- Now the finished oil is sent for packaging and storage.

Soaps and Detergents

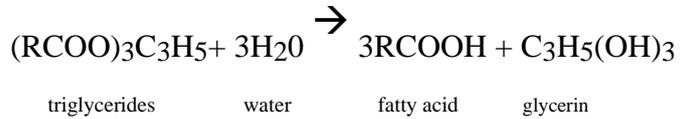
Soaps are sodium or potassium salts of fatty acid. Common fatty acids used are oleic acid, stearic acid, palmitic acid, lauric acid and myristic acid. Soaps are used for human comfort, cleanliness and for industrial use.

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 contain TiO_2 as an opacifier or as a whitener. A variety of dyes are also used to produce colour soaps.

Chemical Reactions:

Fat splitting reaction:



Saponification Reaction:

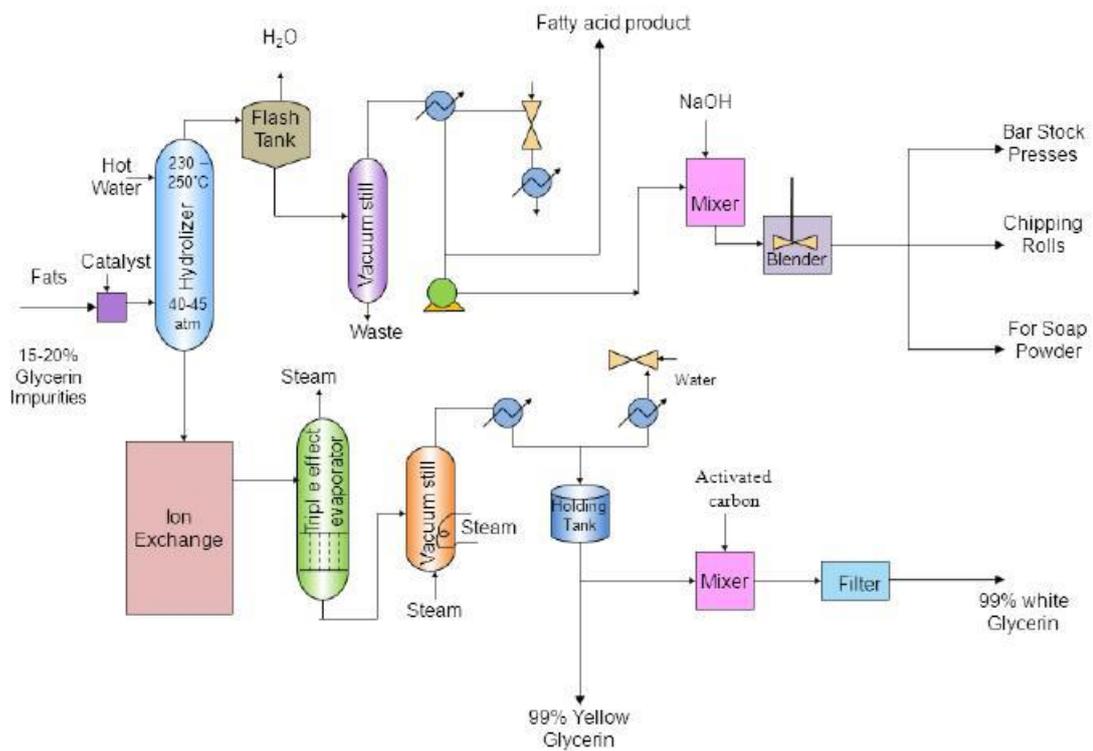
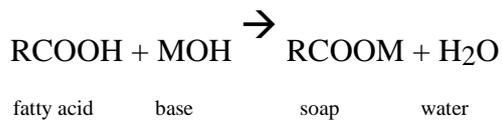


Figure 4.3 Flow sheet of manufacture of soaps, fatty acids and glycerin

Functional role of various processes

Hydrolyser

The fat and catalyst are mixed together and enter the hydrolyser.

Hot water is added here.

Intimate mixing is required for the water oil immiscible phase.

Water has 10 – 15% solubility in oil and fats.

Temperature is maintained at 230°C - 250°C and pressure at 40 – 45 atm for reaction between water and organic compound.

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

Fatty acid stream block

Flash tank:

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

Vacuum still:

The concentrated fatty acids enter a high vacuum still.

Jet ejector is used to generate vacuum in the still.

Wastes are separated from the bottom.

Fatty acid is also taken out as a marketable product.

Mixer:

Fatty acid produced from vacuum still is now pumped to mixer.

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

After mixing a viscous mass is produced.

Blender:

The viscous mass from the mixer is sent to the blender.

Ingredients like scents, anti-fungal & anti bacterial chemicals etc. is mixed in the blender.

The blender removes the solid mass which is then sent to:

Chipping rolls: to manufacture soap strips.

Spray dryer: To get soap powder (used in manufacture of liquid soaps).

Bar Press Stock: To press and cut the viscous mass into bars of soap.

Glycerin stream block**Ion Exchange:**

15 – 20% glycerin along with impurities from the hydrolyser goes for ion exchange.

Here salt and colour is removed from glycerin.

Triple effect evaporator:

The product stream from ion exchanger is sent to triple effect evaporator.

The glycerin solution is concentrated in evaporator.

Vacuum still:

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

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

Mixer:

For removing color, yellow glycerin is treated with activated carbon in mixer.

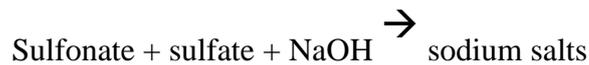
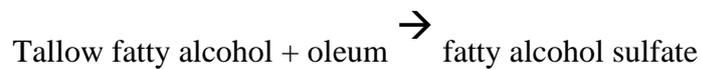
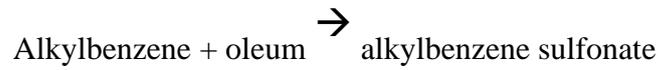
Filter:

Activated carbon is separated from the solution.

99% white glycerin is produced. The yield is 30 – 35kg per ton of soap produced.

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 or sulfonate.

General method to make synthetic detergents:

Preparation of wood pulp by sulfate (kraft) process

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

Pulping means disintegration of bulky fibrous material to small fibres.

There are mainly three modes of production of pulp:

Mechanical

Chemical

Semi chemical

Sulfate (Kraft) Pulping Process

Most popularly used process.

This is an alkaline process.

Na₂SO₄ is added to the cooking liquor. So its common name is sulfate process.

The presence of sodium sulfide makes bleaching of pulp easier and the paper produced has better strength.

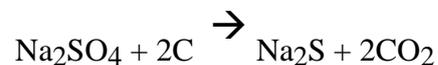
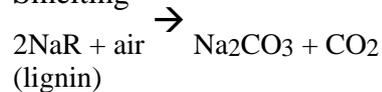
Chemical reactions involved

Digestion (hydrolysis and solubilization of lignin)



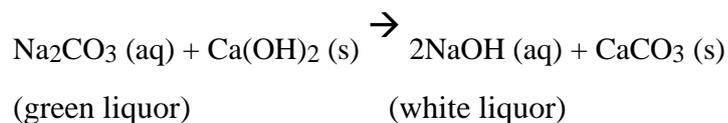
Chemical recovery from black liquor

Smelting



(from R) (white liquor)

(b) Causticizing



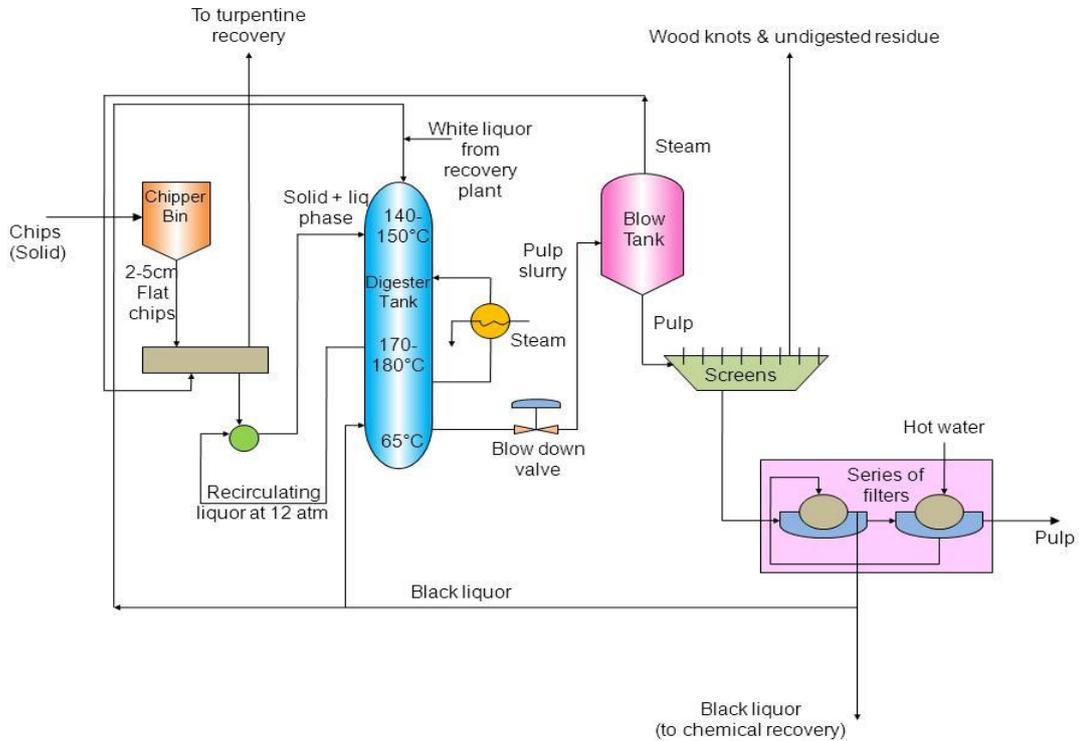
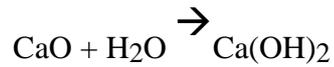
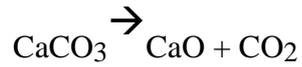


Figure 4.4 Flow sheet of manufacture of pulp manufacture

Functional role of various processes

Chipper bin:-

Chips are fed in this device.

Cut logs are conveyed to the chipper where rotary disks with heavy knives reduce the wood to size 2-5cm flat chips.

Size reduction is done to maximize penetration of process chemicals.

Digester tower:-

Continuous digester tower is 25 – 30m tall.

Chips are preheated with volatilizing turpentine and non-condensable gases.

For controlling digestion temperature, cooking liquor is withdrawn as side streams and circulated through heat exchanger.

Digestion is done to free lignin and other non-cellulosic content.

Cooking time is about one and a half hours at 170°C.

To avoid mechanical weakening of fibres, digested chips are cooled with recycled black liquor.

Temperature is maintained at 140-180°C and pressure at about 10 atm.

Bottom temperature is maintained at 65°C

Blow down valve: -

This valve reduces the pressure of the stream from 80atm to 1atm before entering blow tank.

Blow tank:-

When hot pulp slurry is passed to the blow tank, heat is recovered in the form of steam.

The chips are preheated with this recovered steam.

The blow tank has high concentration of pulp and low concentration of water.

Screens:-

Pulp is screened so as to remove wood knots and undigested residues.

Series of filters

Pulp is filtered to separate black liquor for chemical recovery plant.

Black liquor is also recycled back to digester for cooling the digested chips.

Hot water is added to second filter for better filtration.

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 after digestion.

Chemical recovery from black liquor and production of Paper

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.

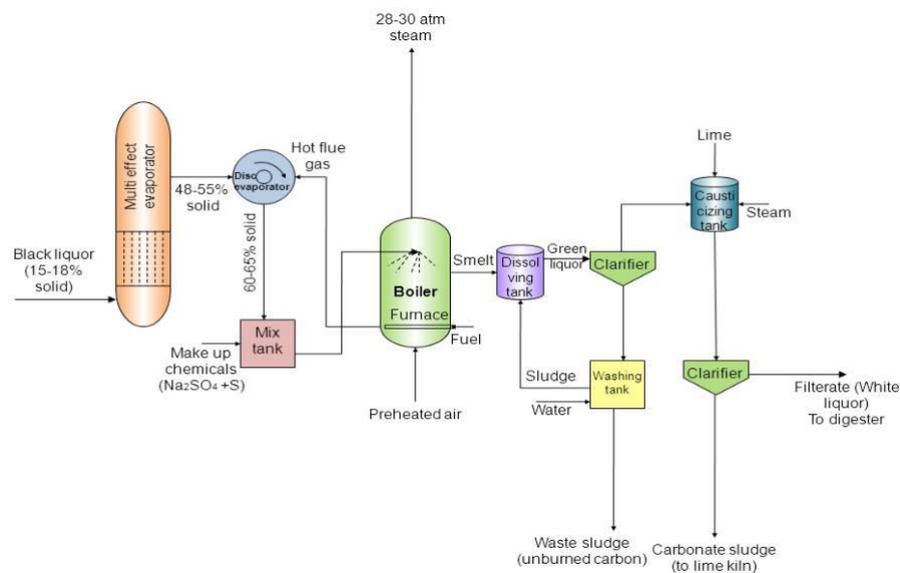


Figure 4.4 Flow sheet of chemical recovery from black liquor

Functional role of various units

Multi effect evaporator

- It is a series of single effect evaporators.
- Multi-effect evaporator and disc evaporator concentrate the black liquor from 15-18% solid to 60-65% solid.

Mix tank

- It is designed with two agitators to mix the product.
- Make up chemicals (Na₂SO₄ + S) are added.

Boiler

- It produces molten slag.
- Here organic carbon present in black liquor is burned.
- High pressure 28 atm to 30atm steam is produced.
- The reaction that takes place inside furnace is

$$\text{Na}_2\text{SO}_4 + 2\text{C} \rightarrow \text{Na}_2\text{S} + 2\text{CO}_2$$

Dissolving tank

- The molten chemical smelt dissolve immediately with cold water and yield green liquor (aqueous Na_2CO_3).

Clarifier

- It is used for filtering.
- It separates calcium carbonate sludge and white liquor.
- Filtering medium is monel metal.

Washing tank

- Impurities are washed away in this tank after clarifying.

Causticizing tank

- It precipitates lime mud.
- Carbonate is causticized by adding $\text{Ca}(\text{OH})_2$

Production of Paper

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.

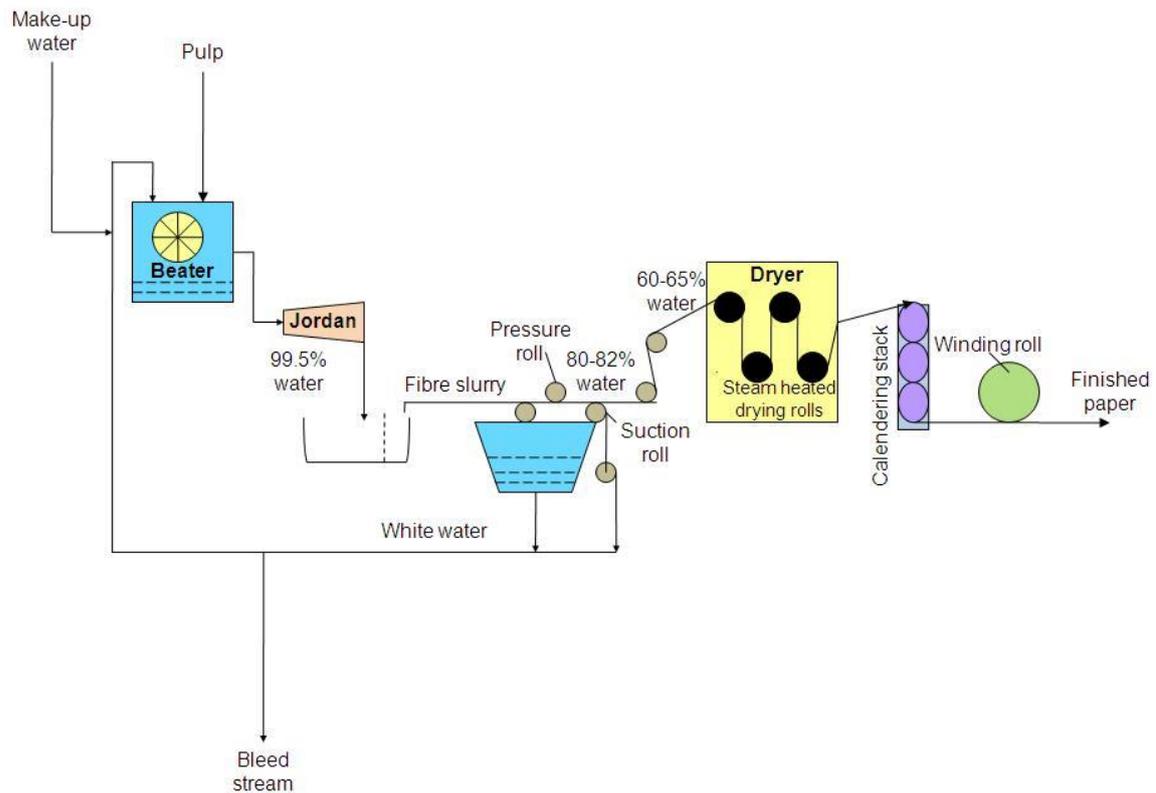


Figure 4.5 Flow sheet of production of paper

Functional role of various units

Beater

- Beater mechanically disintegrates the pulp fibers to make paper stronger, uniform, dense, opaque etc.
- It consists of metal blades attached with rotating drum.
- Finely ground fillers (to increase brightness, flexibility, softness and weight) and coloring agents are also added.

Jordan

- It is a conical refiner or Jordan engine.

- Metal bars and stones are set inside.
- Here, pulp is deformed, defibered and dispersed.

Web forming

- 99.5% water fiber slurry are made to run on an endless belt at a speed of 50m/min to 500m/min.
- Pulp fibers are arranged into web.
- Water is drained out by gravity.
- Shaking motion is provided for better interlocking of fibers on mat.
- White water is collected and it is reused to conserve water and additives and to avoid pollution.

Pressing

- Free water is removed by pressing with pressure roll, water mark roll and suction roll.
- Water content is reduced to 60-65% water.

Drying

- Additional water is removed by smoothing rolls and series of steam-heated metal drying rolls.
- Water is reduced from 60-65% to 5-6%.

Finishing

- Here paper is passed through a series of calendaring rolls for producing smooth paper.
- It is wounded on a large winding roll.

References:

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984