SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – I – PROCESS AND SEPARATION IN CHEMICAL INDUSTRY – SCH 1314

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

In order to improve productivity and make the process cost effective and for improving overall economy, compact , safe, energy efficient and environmentally sustainable plant, process intensification has become very important and industry is looking beyond the traditional chemical engineering.

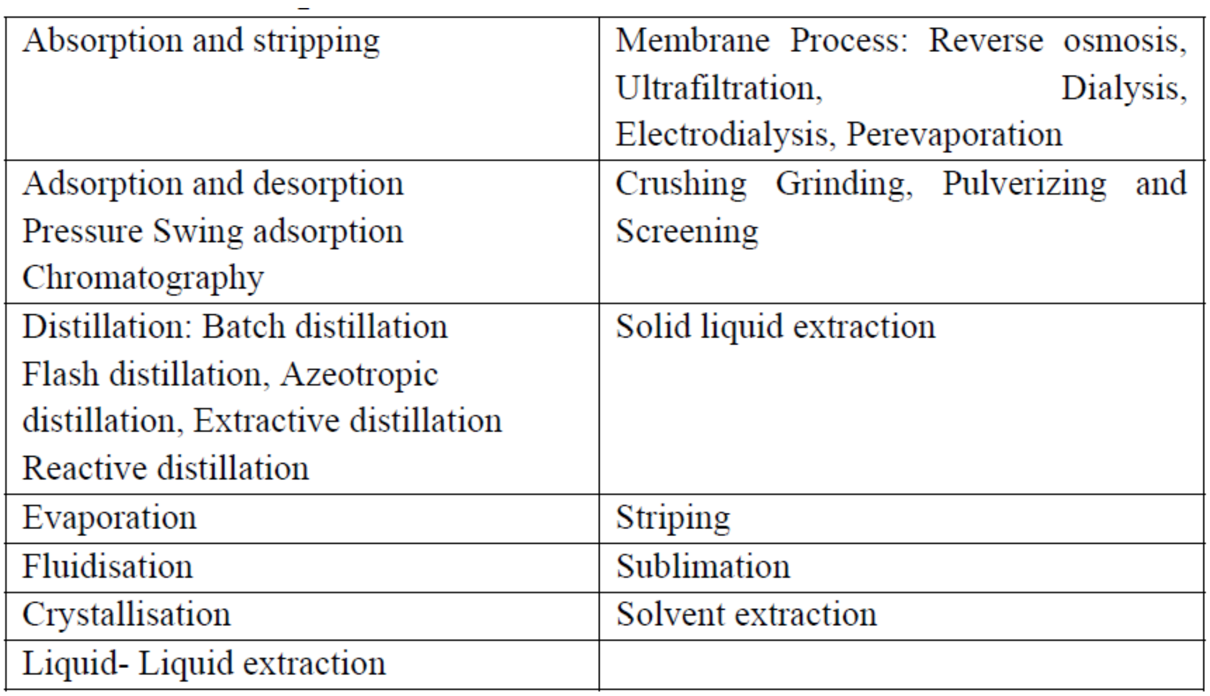
UNIT PROCESSES AND UNIT OPERATIONS IN CHEMICAL PROCESS INDUSTRIES

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 unit processes in chemical industries are given in Table

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	Hydroammonalysis
Causticisation	Isomerisation
Chlorination and Oxy chlorination	Neutralistion
Condensation	Nitration
Biomethhanation	Methanation
Carbinisation	
Disproportination	Oxidation and partial oxidation
Cracking; Thermal, steam cracking, catalytic cracking	Pyrolysis
Dehydration	Polymeristion: Addition and condensation Chain growth and step growth,Bulk, Emulsion, suspension, solution, Radical and coordination polymeristion
Dehydrogenation	Reduction
Ditozitation and coupling	Reforming: Steam reforming Catalytic reforming
Gasification of coal and biomass	Sulphidation
Desulphurisation and hydro desulphurisation	Sulphonatiomn
Electrolysis	Sulphation
Etherification	Xanthation
Estertification and Trans Estrerificartion	

UNIT OPERATIONS IN CHEMICAL INDUSTRIES

Unit operations are very important in chemical industries for separation of various products formed during the reaction.



Absorption and stripping	Membrane Process: Reverse osmosis, Ultrafiltration, Dialysis, Electrodialysis, Perevaporation
Adsorption and desorption Pressure Swing adsorption Chromatography	Crushing Grinding, Pulverizing and Screening
Distillation: Batch distillation Flash distillation, Azeotropic distillation, Extractive distillation Reactive distillation	Solid liquid extraction
Evaporation	Striping
Fluidisation	Sublimation
Crystallisation	Solvent extraction
Liquid- Liquid extraction	

DISTILLATION

Distillation has been the king of all the separation processes and most widely used separation technology and will continue as an important process for the foreseeable future . Distillation is used in petroleum refining and petrochemical manufacture Distillation is the heart of petroleum refining and all processes require distillation at various stages of operations.

MEMBRANE PROCESSES

Membrane processes have emerged one of the major separation processes during the recent years and finding increasing application in desalination, wastewater treatment and gas separation and product purification. Membrane technology is vital to the process intensification strategy and has continued to advance rapidly with the development of membrane reactors, catalytic membrane reactor, membrane distillation, membrane bioreactors for wide and varied application .

ABSORPTION

Absorption is the one of the most commonly used separation techniques for the gas cleaning purpose for removal of various gases like H_2S, CO_2, SO_2 and ammonia. Cleaning of solute gases is achieved by transferring into a liquid solvent by contacting the gas stream with liquids that offers specific or selectivity for the gases to be recovered. Unit operation and is mass transfer phenomena where the solute of a gas is removed from being placed in contact with a nonvolatile liquid solvent that removes the components from the gas. Solvent: Liquid applied to remove the solute from a gas stream. Solute: Components to be removed from entering streams.

CRYSTALLIZATION PROCESS

Crystallization processes are used in the petroleum industry for separation of wax. The process involves nucleation, growth, and agglomeration and gelling. Some of the applications of crystallization is in the separation of wax, separation of p-xylene from xylenes stream. Typical process of separation of p-xylene involves cooling the mixed xylene feed stock to a slightly higher than that of eutectic followed by separation of crystal by centrifugation or filtration.

LIQUID –LIQUID EXTRACTION

Liquid –liquid extraction has been commonly used in petroleum and petrochemical industry for separation of close boiling hydrocarbons. Some of the major applications are:

☐ Removal of sulphur compound from liquid hydrocarbons

☐ Recovery of aromatics from liquid hydrocarbon

☐ Separation of butadiene from C_4 hydrocarbons

☐ Extraction of caprolactam

☐ Separation of homogenous aqueous azeotropes

☐ Extraction of acetic acid

☐ Removal of phenolic compounds from waste water

☐ Manufacture of rare earths

☐ Separation of asphaltic compounds from oil

☐ Recovery of copper from leach liquor

☐ Extraction of glycerides from vegetable oil Some of the important property of a good solvent

☐ High solvent power/capacity

☐ High selectivity for desired component

☐ Sufficient difference in boiling points of the solvent and the feed for effective separation

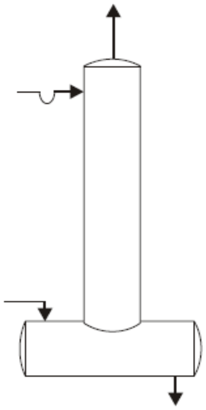
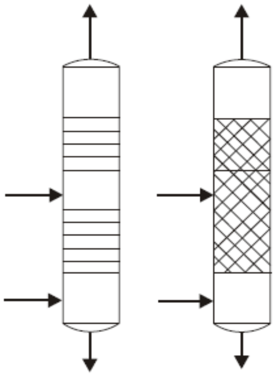
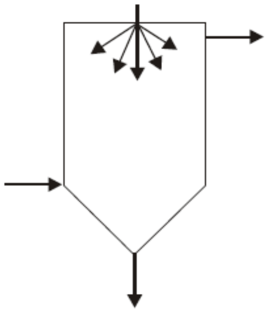
☐ Low latent heat of evaporation an specific heat to reduce utility requirement

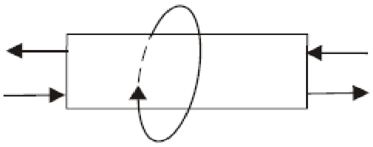
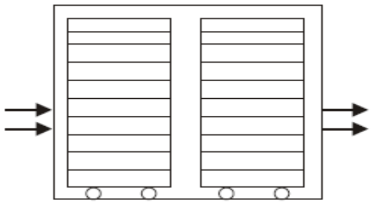
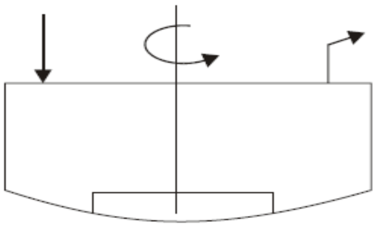
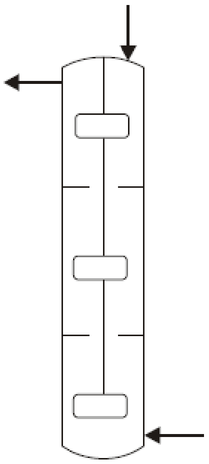
☐ high thermal an chemical stability

☐ Low melting point

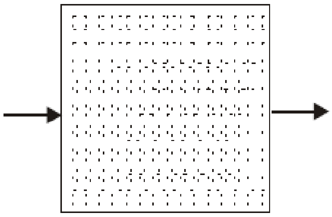
☐ Relatively inexpensive

Process Equipment Symbols

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

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 Driver		**Best suited to drying pastes or powders in trays ; also used to dry pottery, lumber, leather, etc., In sheet shaped forms**
3.Evaporation **(a) Open Pan**		**Used for small batches ; often of viscous mat's ; such designs are easy to clean**
4. Extraction **(a) Liquid - liquid**		**Used to contact solvent and feed to give raffinate and extract ; widely adapted to removal of napthenes from lube oil fractions Using solvents such as furfural**

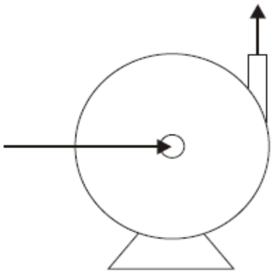
(b) Solid-Liquid (Leaching)



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

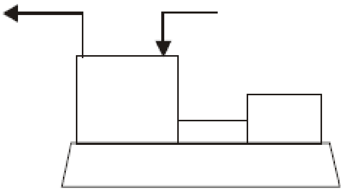
5.Fluid Handling

(a)Centrifugal pump



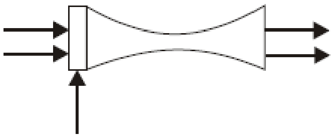
Most widely used for liquids of all types ; simple in construction and maintenance

(b) Reciprocating Pump Or Compressor



Generally used for higher pressure delivery ; may be used for metering or proportioning

(c) Jet Ejector



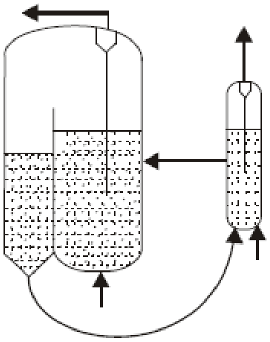
Used for lower pressure operation or production of vacuum ; steam often used as motive fluid

6. Fluid - Solid Contacting

(a) Fixed Bed

Most widely used type of catalytic rector ; used with precious metal catalysts to minimize attrition losses ; catalyst usually in form of pellets

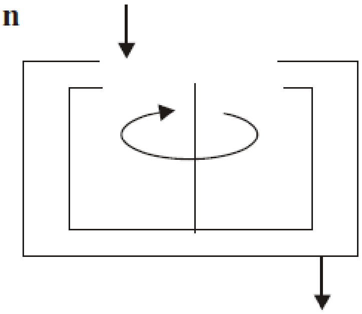
6 . Fluid Bed



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

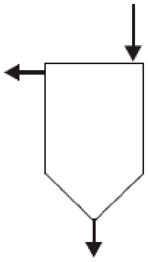
7. Fluid - Solid Separation

(a) Centrifugation



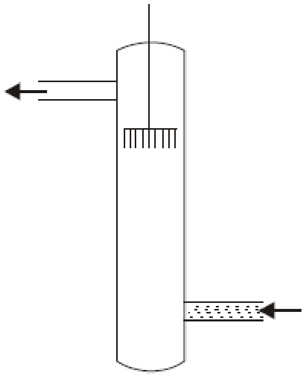
Used to separate very finely divided solids from liquid or liquids from liquid emulsions

(b) Setting Tank



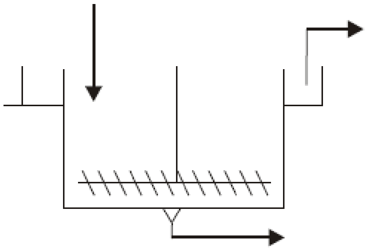
Simple device used to remove large particles from gas stream by simple setting in low velocity zone

(c) Wet Scrubber



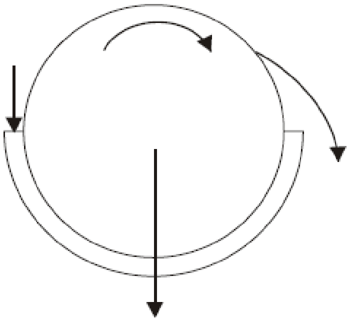
Effective means of removing suspended particles from gas stream by contact with liquid shower

(d) Crystallizer



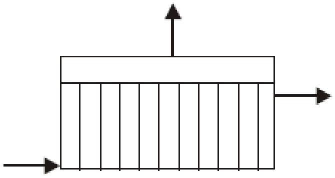
Hot, nearly-saturated solutions are stirred and cooled to effect nucleation and crystal growth ; widely used with inorganic salts.

(e) Filter (Rotary)



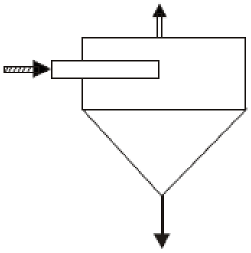
Vacuum applied to interior of drum pulls filtrate out of cake; used to separate minerals from slurries, pulp fibers from water, etc.

(f) Filter Press



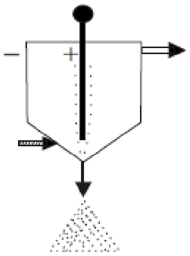
Simplest type of pressure filter; widely used ; plates and fabric filter media may be made of a variety of corrosion resistant materials

(g) Cyclone Separator



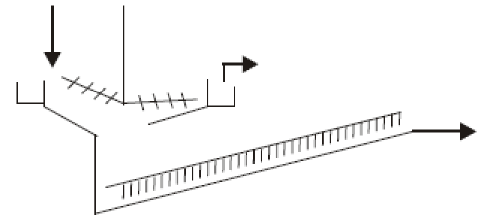
Used to separate solid particles or liquid droplets from gases to permit product recovery or to cut down product loss and air pollution

(h) Electrostatic Precipitator



Used to remove fine dusts or mists suspended in gases ; features high collection efficiency at wide variety of operating conditions.

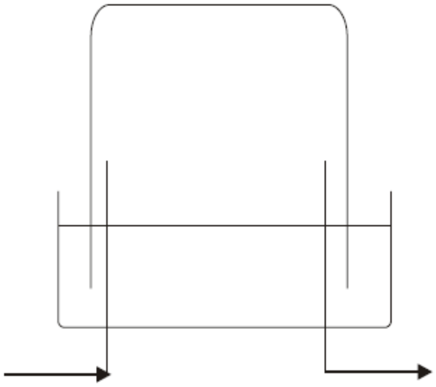
(j) Thickener - Classifier



Used to separate slurry into sludges and clear liquids ; used widely in mineral industries and in sewage effluent clarification

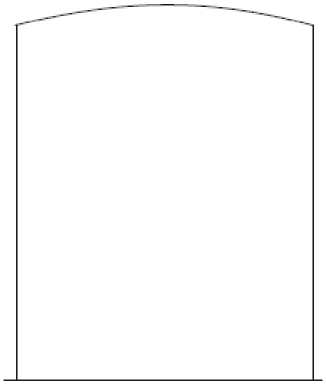
8 . Fluid Storage

(a) Gas Holders



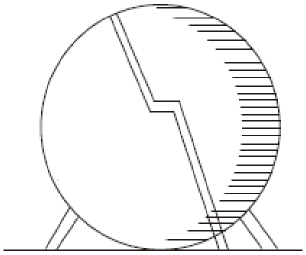
Used for low pressure storage of gases at constant pressure using liquid seal (usually water)

(b) Tanks



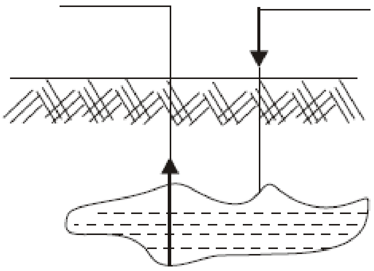
Widely used for storage of liquids of all types , usually at atmospheric pressure ; may have floating roof

(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

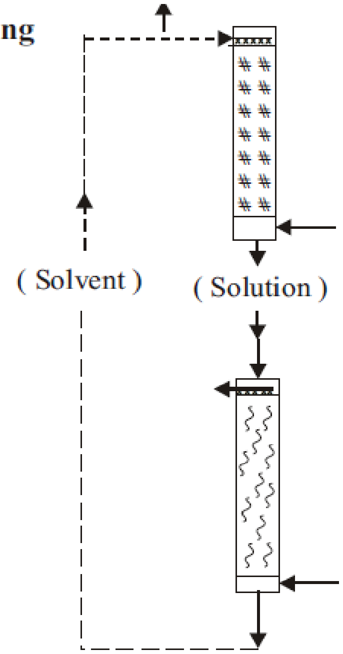


Used for large volume storage of liquids or of liquified gases

9 . Gas-Liquid Contacting

(a) Absorption

(b) Stripping

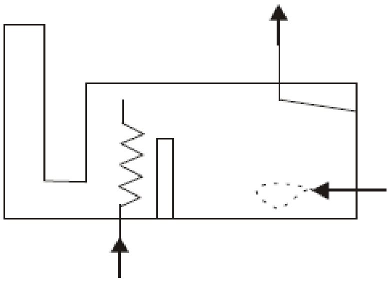


(a) Used for taking up a soluble gas in a solvent liquid and producing a solution plus a lean exit gas ; *e.g.,* Used in H_2S removal from hydrocarbons

(b) 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

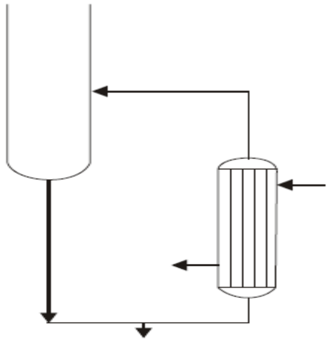
10. Heat Exchange

(a) Fired Heater



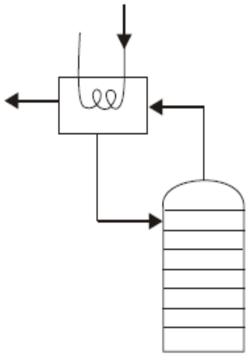
Used to heat petroleum fraction to distillation or cracking temperatures in direct fired tubes.

(b) Reboiler



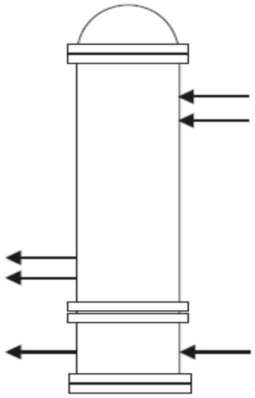
Uses natural circulation to circulate fractionating tower bottom in heat exchange with steam , *e.g.*, to provide necessary heat for fractionation

(c) Condenser



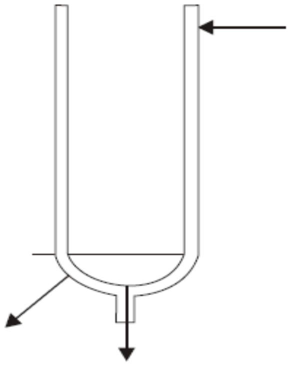
Usually water-cooled tubular construction to provide reflux and overhead product from fractionating column

(d) Shell And Tube Exchanger



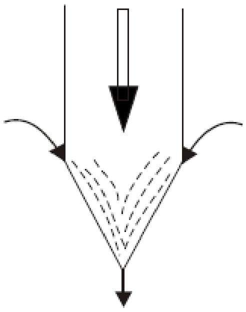
Common type of device for process heat exchange

(e) Jacketed Kettle



Common construction for reaction kettles ; water or brine may be used for cooling ; hot water, oil or Dowtherm for heating

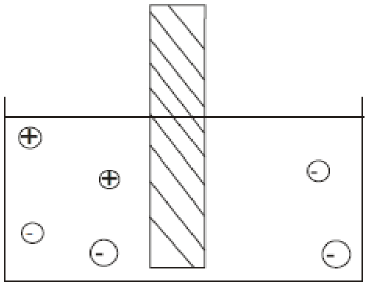
(f) Direct Mixing (Quenching)



Features intimate contact of coolant fluid (*e.g.,* water) with process gases to give quick quench, *e.g.,*in hydrocarbon pyrolysis to acetylene

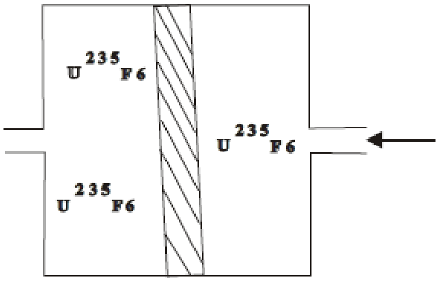
11. Membrane Separation

(a) Dialysis



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

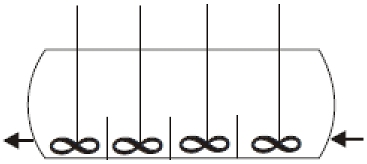
(b) Gaseous Diffusion



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

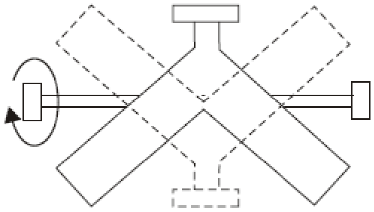
12. Mixing

(a) Agitation



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

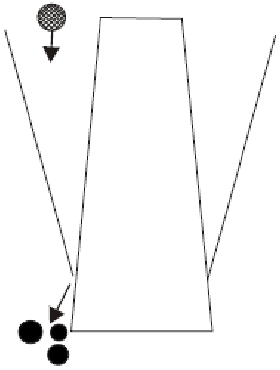
(b) Solids Blending



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

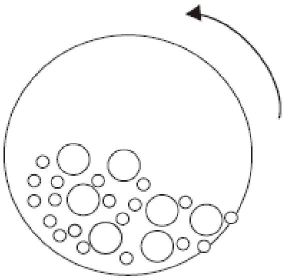
13.Size Reduction and Enlargement

(a) Crushing



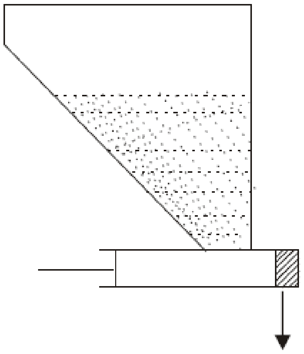
Used typically in 4:1 size reduction of hard materials from -5 to -20 mesh or -1 to -4 mesh

(b) Grinding



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

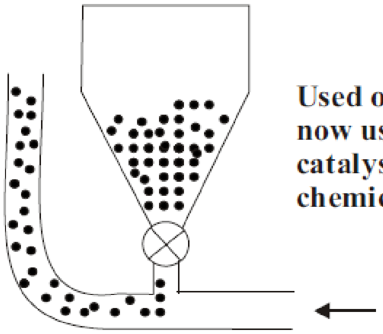
(c) Pelletizing



Used to make tablets from powders of Medicinals, cata- Catalysts, etc

14. Solids Handling

(a) Pneumatic Conveying



Used originally for grain; now used widely for cement, catalysts, coke and powdered chemicals

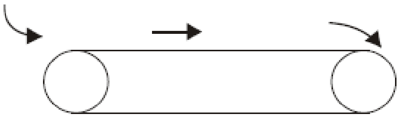
(b) Bucket Elevators

Used for elevating materials; can be used for moving powdered or granular mat’ls to and from storage or between reaction vessels as in moving bed catalytic processes

(c) Screw conveyor

Versatile ; can be used to mix and heat or cool ; can be operated underpressure ; useful for powders or sticky material.

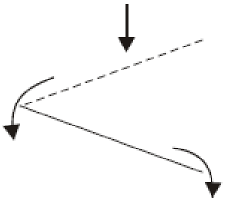
(d) Belt Conveyor



Can be used to handle large volumes over long distances economically ; used near horizontal ; belting may be fabric or rubber

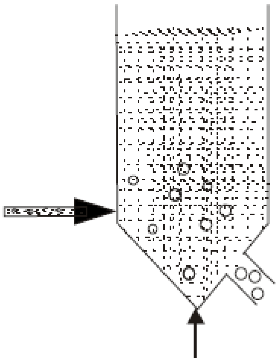
15. Solid / Solid Separation

(a) Screening



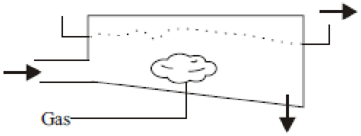
Wire , plastic or fabric screens are used to separate solids of varying sizes

(b) Elutriation



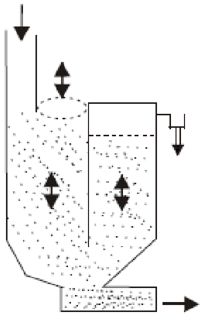
May be used to remove fines from a solid by passage of a gas to fluidize and transport the fines

(c) Froth Floatation



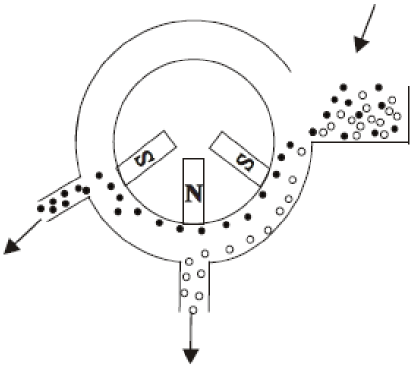
Finely ground (- 50 mesh) ores are suspend in water in presence of floating reagents (e.g.., RCOONa) and blow with air ; desired product collects in froth.

(d) Jigging



One of the oldest processes used for separation of minerals from lighter gangues as a well as for separating coal from heavier contaminants

(e) Magnetic Separation



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

Raw Materials

Human insulin is grown in the lab inside common bacteria. *Escherichia coli* is by far the most widely used type of bacterium, but yeast is also used.

Researchers need the human protein that produces insulin. Manufacturers get this through an amino-acid sequencing machine that synthesizes the DNA. Manufacturers know the exact order of insulin's amino acids (the nitrogen-based molecules that line up to make up proteins). There are 20 common amino acids. Manufacturers input insulin's amino acids, and the sequencing machine connects the amino acids together. Also necessary to synthesize insulin are large tanks to grow the bacteria, and nutrients are needed for the bacteria to grow. Several instruments are necessary to separate and purify the DNA such as a centrifuge, along with various chromatography and x-ray crystallography instruments.

The Manufacturing Process

Synthesizing human insulin is a multi-step biochemical process that depends on basic recombinant DNA techniques and an understanding of the insulin gene. DNA carries the instructions for how the body works and one small segment of the DNA, the insulin gene, codes for the protein insulin. Manufacturers manipulate the biological precursor to insulin so that it grows inside simple bacteria. While manufacturers each have their own variations, there are two basic methods to manufacture human insulin.

Working with human insulin

- 1 The insulin gene is a protein consisting of two separate chains of amino acids, an A above a B chain, that are held together with bonds. Amino acids are the basic units that build all proteins. The insulin A chain consists of 21 amino acids and the B chain has 30.
- 2 Before becoming an active insulin protein, insulin is first produced as preproinsulin. This is one single long protein chain with the A and B chains not yet separated, a section in the middle linking the chains together and a signal sequence at one end telling the protein when to start secreting outside the cell. After preproinsulin, the chain evolves into proinsulin, still a single chain but without the signaling sequence. Then comes the active protein insulin, the protein without the section linking the A and B chains. At each step, the protein needs specific enzymes (proteins that carry out chemical reactions) to produce the next form of insulin.

STARTING WITH A AND B

- 3 One method of manufacturing insulin is to grow the two insulin chains separately. This will avoid manufacturing each of the specific enzymes needed. Manufacturers need the two mini-genes: one that produces the A chain and one for the B chain. Since the exact DNA sequence of each chain is known, they synthesize each mini-gene's DNA in an amino acid sequencing machine.
- 4 These two DNA molecules are then inserted into plasmids, small circular pieces of DNA that are more readily taken up by the host's DNA.
- 5 Manufacturers first insert the plasmids into a non-harmful type of the bacterium *E. coli.* They insert it next to the *lacZ* gene. LacZ encodes for 8-galactosidase, a gene widely used in recombinant DNA procedures because it is easy to find and cut, allowing the insulin to be readily removed so that it does not get lost in the bacterium's DNA. Next to this gene is the amino acid methionine, which starts the protein formation.
- 6 The recombinant, newly formed, plasmids are mixed up with the bacterial cells. Plasmids enter the bacteria in a process called transfection. Manufacturers can add to the cell’s DNA ligase, an enzyme that acts like glue to help the plasmid stick to the bacterium's DNA.
- 7 The bacteria synthesizing the insulin then undergo a fermentation process. They are grown at optimal temperatures in large tanks in manufacturing plants. The millions of bacteria replicate roughly every 20 minutes through cell mitosis, and each expresses the insulin gene.
- 8 After multiplying, the cells are taken out of the tanks and broken open to extract the DNA. One common way this is done is by first adding a mixture of lysozome that digest the outer layer of the cell wall, then adding a detergent mixture that separates the fatty cell wall membrane. The bacterium's DNA is then treated with cyanogen bromide, a reagent that splits protein chains at the methionine residues. This separates the insulin chains from the rest of the DNA.
- 9 The two chains are then mixed together and joined by disulfide bonds through the reduction-reoxidation reaction. An oxidizing agent (a material that causes oxidization or the transfer of an electron) is added. The batch is then placed in a centrifuge, a mechanical device that spins quickly to separate cell components by size and density.

- 10 The DNA mixture is then purified so that only the insulin chains remain. Manufacturers can purify the mixture through several chromatography, or separation, techniques that exploit differences in the molecule's charge, size, and affinity to water. Procedures used include an ion-exchange column, reverse-phase high performance liquid chromatography, and a gel filtration chromatography column. Manufacturers can test insulin batches to ensure none of the bacteria's *E. coli* proteins are mixed in with the insulin. They use a marker protein that lets them detect *E. coli* DNA. They can then determine that the purification process removes the *E. coli* bacteria.

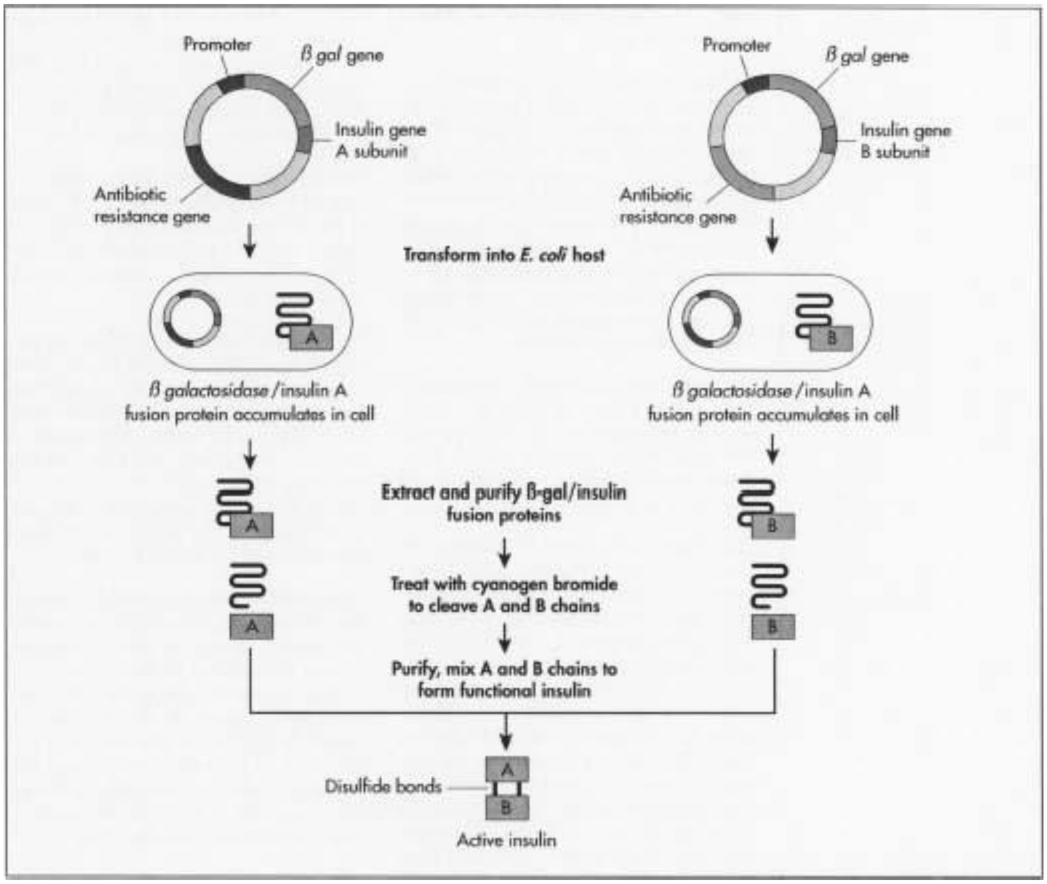
PROINSULIN PROCESS

- 11 Starting in 1986, manufacturers began to use another method to synthesize human insulin. They started with the direct precursor to the insulin gene, proinsulin. Many of the steps are the same as when producing insulin with the A and B chains, except in this method the amino acid machine synthesizes the proinsulin gene.
- 12 The sequence that codes for proinsulin is inserted into the non-pathogenic *E. coli* bacteria. The bacteria go through the fermentation process where it reproduces and produces proinsulin. Then the connecting sequence between the A and B chains is spliced away with an enzyme and the resulting insulin is purified.
- 13 At the end of the manufacturing process ingredients are added to insulin to prevent bacteria and help maintain a neutral balance between acids and bases. Ingredients are also added to intermediate and long-acting insulin to produce the desired duration type of insulin. This is the traditional method of producing longer-acting insulin. Manufacturers add ingredients to the purified insulin that prolong their actions, such as zinc oxide. These additives delay absorption in the body. Additives vary among different brands of the same type of insulin.

Analog insulin

In the mid 1990s, researchers began to improve the way human insulin works in the body by changing its amino acid sequence and creating an analog, a chemical substance that mimics another substance well enough that it fools the cell. Analog insulin clumps less and disperses more readily into the blood, allowing the insulin to start working in the body minutes after an injection. There are several different analog insulin. Humulin insulin does not have strong bonds with other insulin and thus, is absorbed quickly. Another insulin analog, called Glargine, changes the chemical structure of the protein to make it have a relatively constant release over 24 hours with no pronounced peaks.

Instead of synthesizing the exact DNA sequence for insulin, manufacturers synthesize an insulin gene where the sequence is slightly altered. The change causes the resulting proteins to repel each other, which causes less clumping. Using this changed DNA sequence, the manufacturing process is similar to the recombinant DNA process described.



Manufacturing steps for insulin.

Quality Control

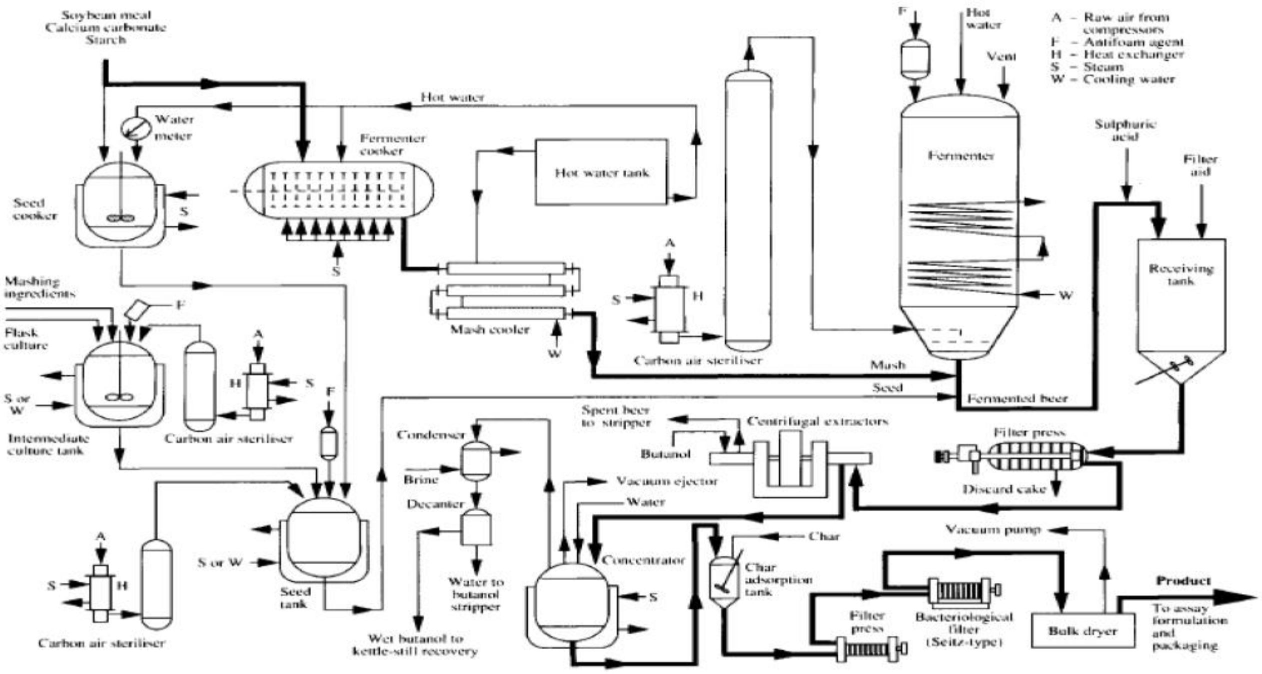
After synthesizing the human insulin, the structure and purity of the insulin batches are tested through several different methods. High performance liquid chromatography is used to determine if there are any impurities in the insulin. Other separation techniques, such as X-ray crystallography, gel filtration, and amino acid sequencing, are also performed. Manufacturers also test the vial's packaging to ensure it is sealed properly. Manufacturing for human insulin must comply with National Institutes of Health procedures for large-scale operations. The United States Food and Drug Administration must approve all manufactured insulin.

Purification. Processes for purification are highly selective and separate the product from impurities with similar properties. Typical unit operations are chromatography, ultrafiltration and fractional precipitation.

Final isolation. The final purity required depends on the product application. Crystallisation, followed by centrifugation or filtration and drying, are typical operations used for high-quality products such as pharmaceuticals.

Process Flow Diagrams

Because of the complexity of large-scale manufacturing processes, communicating information about these systems requires special methods. Flow diagrams or flow sheets are simplified pictorial representations of processes and are used to present relevant process information and data. Flow sheets vary in complexity from simple block diagrams to highly complex schematic drawings showing main and auxiliary process equipment such as pipes, valves, pumps and bypass loops.



ETHANOL

India is amongst two largest sugar producing countries in the world and converts the molasses from sugar plant to alcohol. India is fourth largest producer of ethanol in the world and second largest in Asia. India produces about 2.75 billion liters alcohol annually. The demand for potable alcohol has been ever increasing. Today 95 percent of ethanol is produced by fermentation and only 5percent is produced from petroleum feed stock by ethylene route

Ethanol has become one of the important products as alternative feedstock for large number of organic chemicals and fuel. Ethanol is an oxygenated fuel that contains 35percent oxygen, which reduces particulate and NOx emissions from combustion. Alcohol is now being used for potable liquor, as chemical feed stock, as solvent and as oxygenates. Process manufacturing of alcohol is shown in fig Various routes for manufacture of ethanol are:

☐ Alcohol from Fermentation of molasses

☐ Alcohol from Lignocelluloses biomass

☐ Alcohol from starchy feed stocks

☐ Petrochemical route via Catalytic hydration of ethylene and Ethylene etherification and hydrolysis

Fermentation of Molasses

Molasses is the residue left after extraction of crystallized sugar and is one of the major byproducts of the sugar industry. Ethyl alcohol is made from molasses by fermentation process utilizing yeast enzymes. A typical distillery consist of

☐ Molasses handling

☐ Fermentation feeding system

☐ Preparation of yeast inculam, propagation of yeast

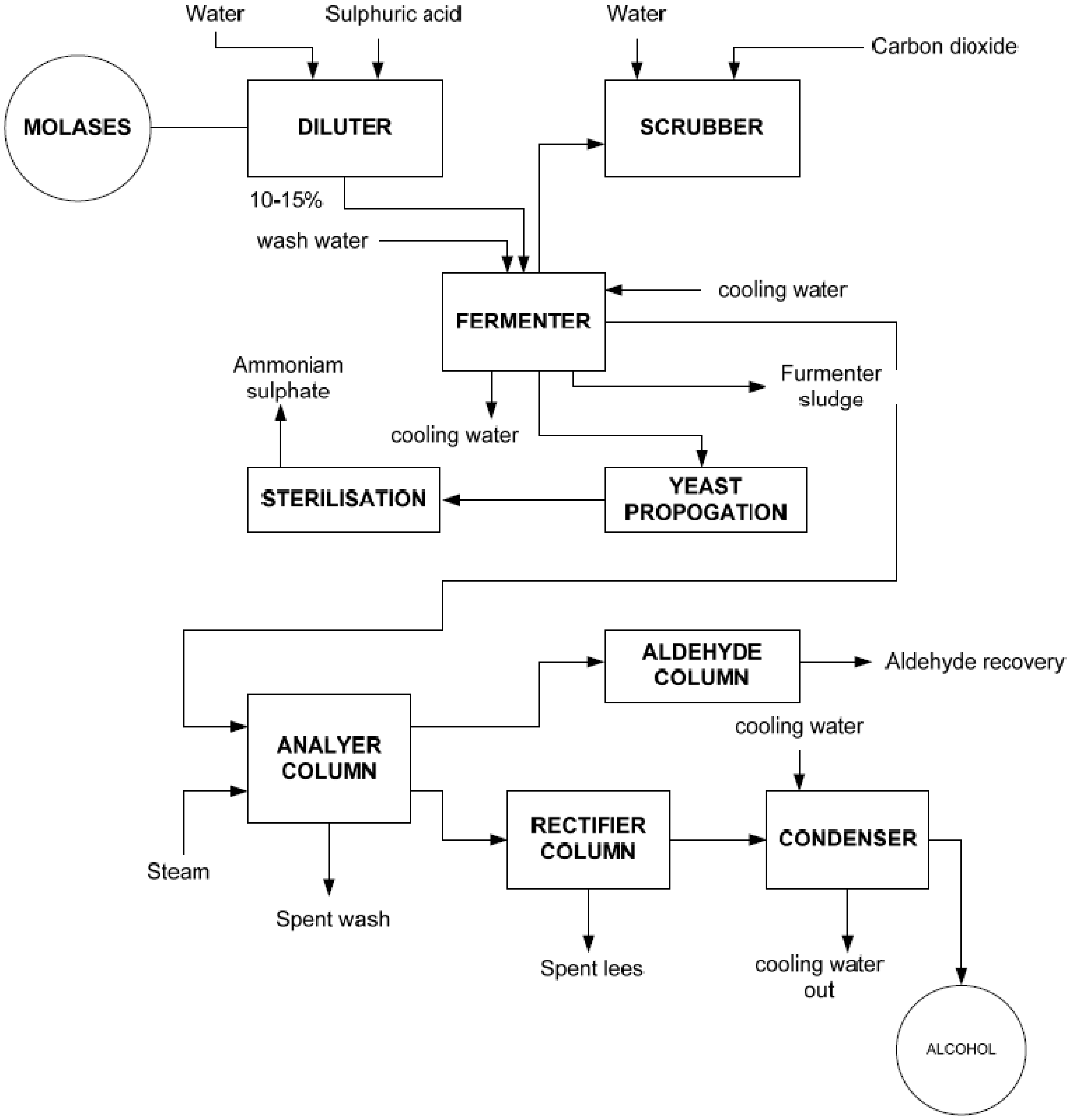
☐ Fermentation

☐ Distillation of dilute alcohol for removal of impurities

☐ Concentration of the dilute alcohol to rectified spirit and absolute alcohol

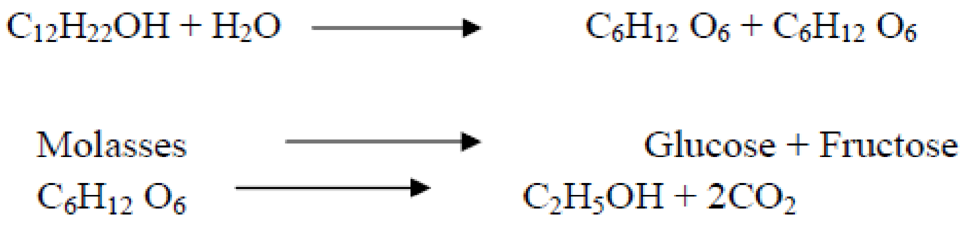
Molasses handling involves weighing of the molasses and pumping of molasses to the molasses tank from which the measured quantity of molasses is transferred to the fermenter. Preparation of yeast inculam, propagation of yeast: Yeast material is prepared in water cooled yeast vessels by inoculating molasses with yeast and then transferred to aerated yeast activation vessel to allow time for yeast cell multiplication Fermentation involves fermentation of fermentable sugars by microorganism and formation of alcohol and other by-products. Yeast (Saccharomyces cerevisiae) is commonly used for the fermentation of glucose to ethanol. After the fermentation alcohol of 7-8percent strength is obtained. Fermentation is exothermic process and heat is generated. Removal of heat is necessary to maintain the temperature in fermenter. High temperature lowers the alcohol productivity. Nutrients are added to the fermented intermittently depending upon the requirement. Sulphuric acid is added to adjust the pH of fermenter liquid. Excess foaming in the fermenter is controlled by antifoam solution. During the normal operation treated yeast cells recovered from the fermented wash are recycled from the yeast treatment system to activation vessel and after that transfer to the fermenter

After fermentation is completed, the dil. liquor ((8-10percent alcohol) is preheated and pumped to the beer still where the alcohol 50-60percent) and other volatiles like aldehydes are distilled off from the top and send to the aldehyde column for separation of aldehydes and other low boiling impurities. The residue from the bottom of the beer column is known as slops or tillage are discharged and treated for recovery of energy or concentrated and used. Alcohol drawn from side stream of the aldehyde column is sent to rectifying column. The azeotrop alcohol containing alcohol about 95-96percent alcohol is taken as top side stream from the rectifying column.



Process of Manufacturing of Ethanol

Alcohol recovery: this section involves the recovery of alcohol from the fermentation section to minimize the possible losses of alcohol along with generated CO2 and sludge from fermented. Typical reactions involved are

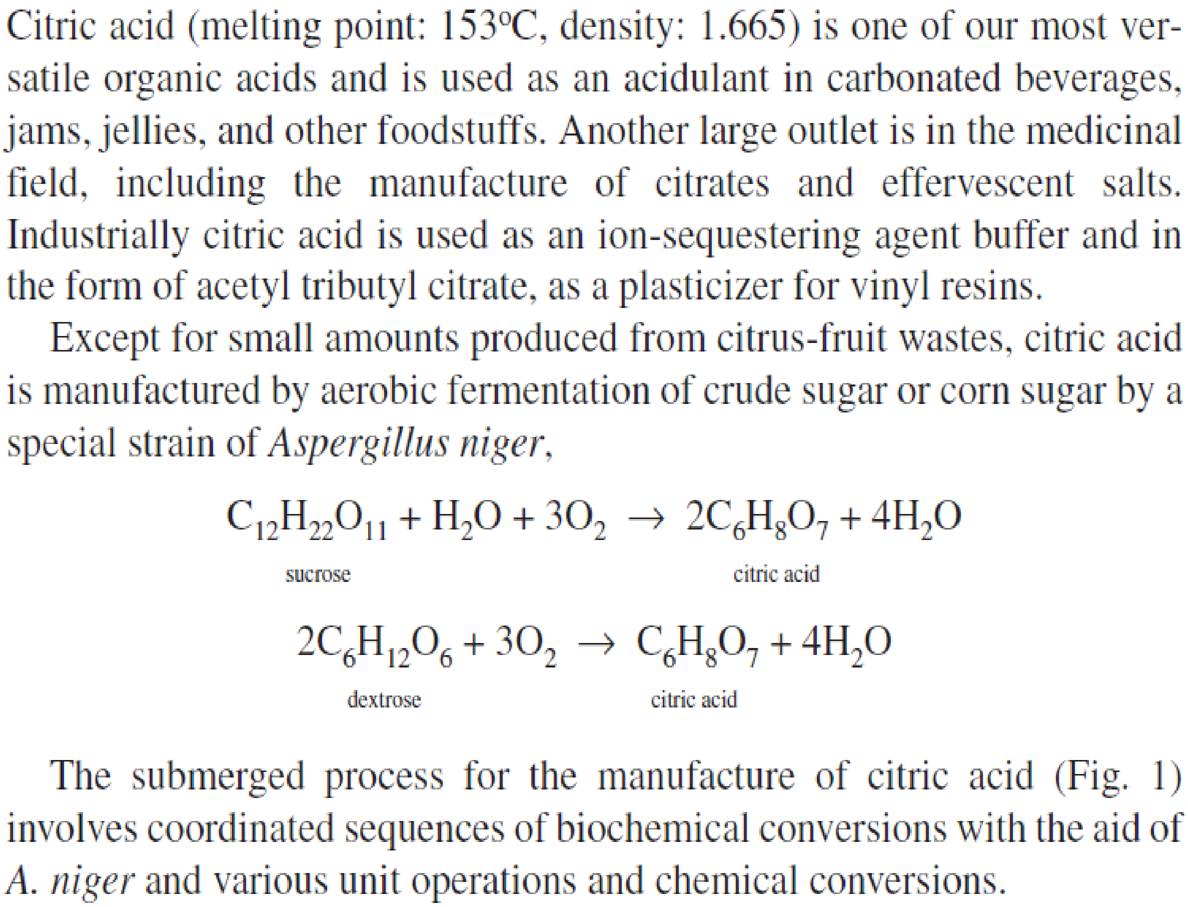


$$C_{12}H_{22}OH + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\text{Molasses} \longrightarrow \text{Glucose + Fructose}$$

$$C_6H_{12}O_6 \longrightarrow C_2H_5OH + 2CO_2$$

CITRIC ACID



Citric acid (melting point: 153°C, density: 1.665) is one of our most versatile organic acids and is used as an acidulant in carbonated beverages, jams, jellies, and other foodstuffs. Another large outlet is in the medicinal field, including the manufacture of citrates and effervescent salts. Industrially citric acid is used as an ion-sequestering agent buffer and in the form of acetyl tributyl citrate, as a plasticizer for vinyl resins.

Except for small amounts produced from citrus-fruit wastes, citric acid is manufactured by aerobic fermentation of crude sugar or corn sugar by a special strain of *Aspergillus niger*,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O + 3O_2 \rightarrow \underset{\text{citric acid}}{2C_6H_8O_7} + 4H_2O$$

$$\underset{\text{dextrose}}{2C_6H_{12}O_6} + 3O_2 \rightarrow \underset{\text{citric acid}}{C_6H_8O_7} + 4H_2O$$

The submerged process for the manufacture of citric acid (Fig. 1) involves coordinated sequences of biochemical conversions with the aid of *A. niger* and various unit operations and chemical conversions.

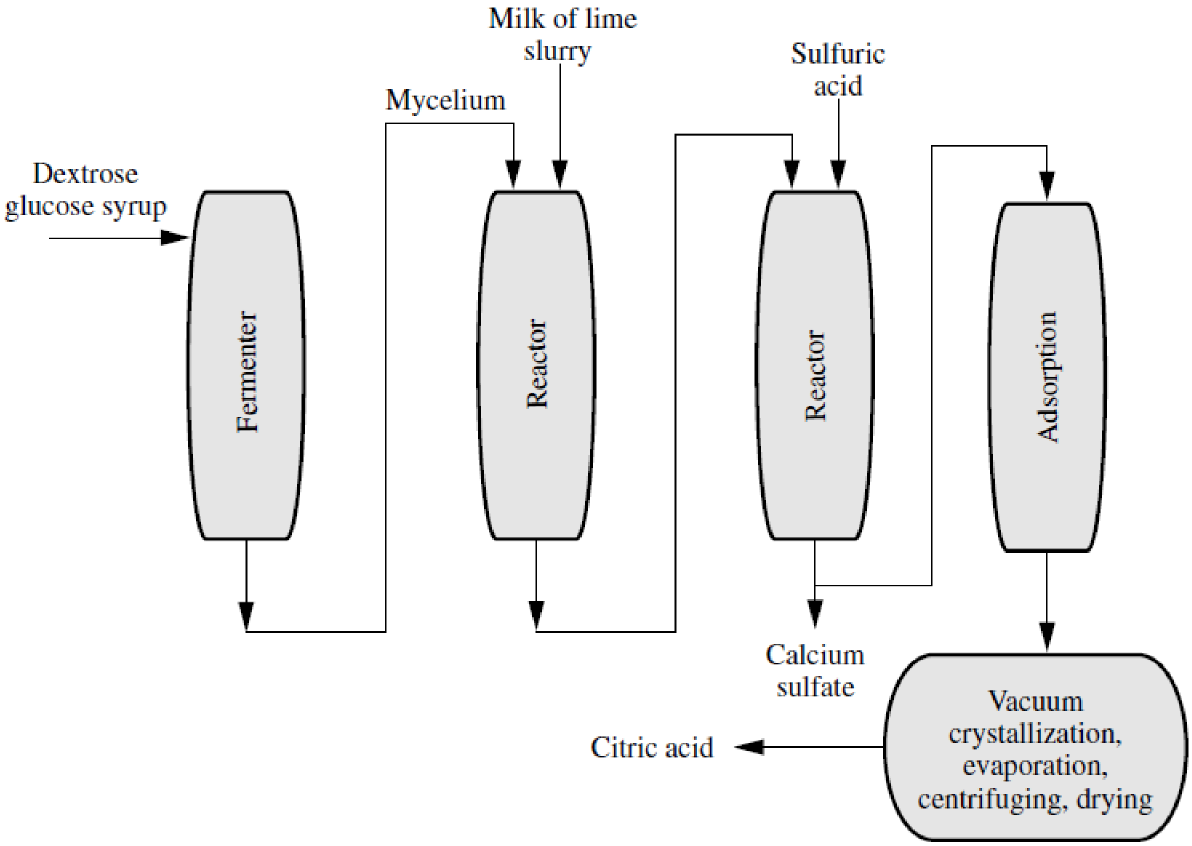


FIGURE 1 Manufacture of citric acid.

Urea

Urea (H_2NCONH_2, carbamide; melting point: 135ºC, density: 1.3230) is a colorless crystalline solid, somewhat hygroscopic, that sublimes unchanged under vacuum at its melting point and decomposes above the melting point at atmospheric pressure, producing ammonia (NH_3), isocyanic acid (HNCO), cyanuric acid [$(HNCO)_3$], biuret ($H_2NHCONHCONH_2$), and several other minor products. Urea is very soluble in water (being a component of urine), soluble in alcohol, and slightly soluble in ether.

There are several approaches to the manufacture of urea, but the principal method is that of combining carbon dioxide with ammonia to form ammonium carbamate (Figs. 1 and 2):

$$CO_2 + 2NH_3 \rightarrow NH_2COONH_4$$

This exothermic reaction is followed by an endothermic decomposition of the ammonium carbamate:

$$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

Both are equilibrium reactions. The formation reaction goes to virtual completion under usual reaction conditions, but the decomposition reaction is less complete. Unconverted carbon dioxide and ammonia, along with undecomposed carbamate, must be recovered and reused.

In the process, a 2:1 molar ratio of ammonia and carbon dioxide (excess ammonia) are heated in the reactor for 2 hours at 190ºC and 1500 to 3000 psi (10.3 to 20.6 MPa)to form ammonium carbamate, with most of the heat of reaction carried away as useful process steam. The carbamate decomposition reaction is both slow and endothermic. The mix of unreacted reagents and carbamate flows to the reactor-decomposer. The reactor must be heated to force the reaction to proceed. For all the unreacted gases and undecomposed carbamate to be removed from the product, the urea must be heated at lower pressure (400 kPa). The reagents are reacted and

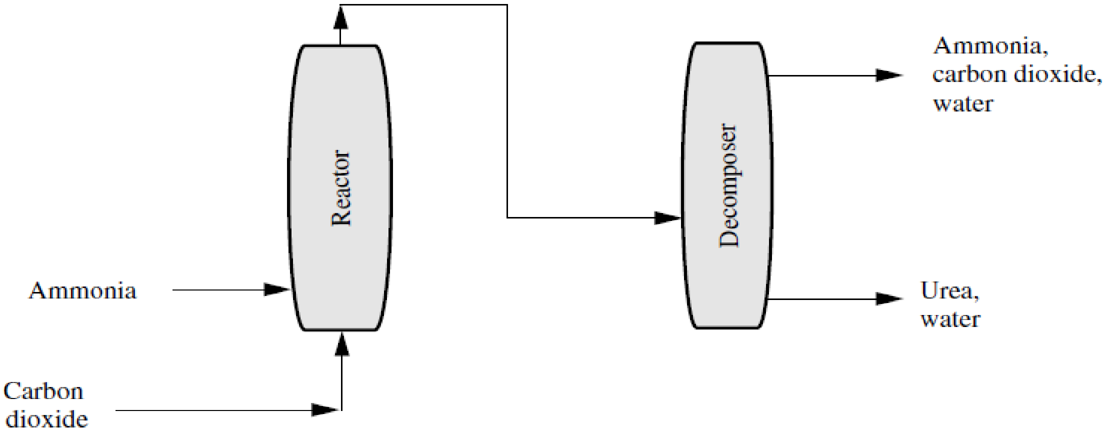


FIGURE 1 Once-through process for urea manufacture.

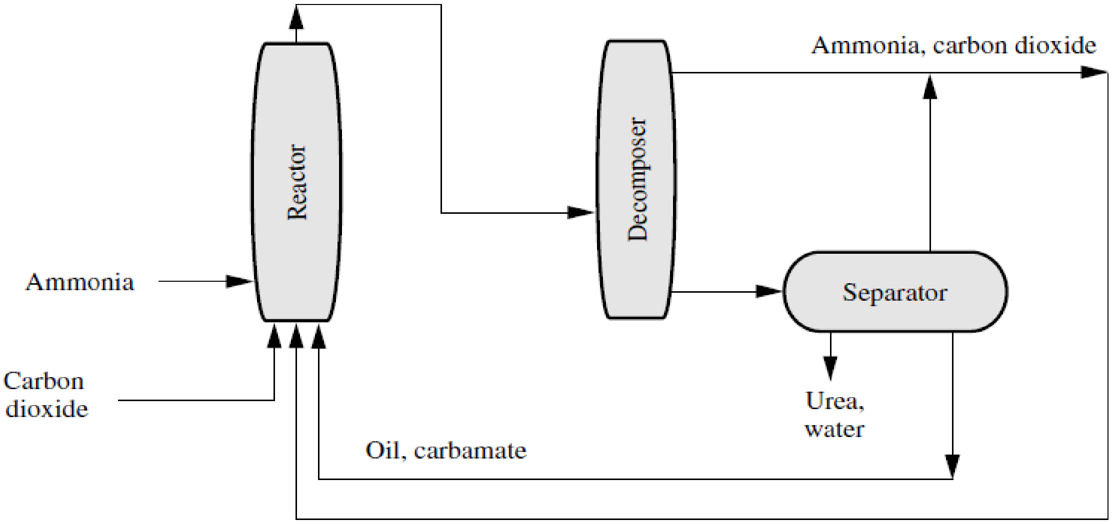


FIGURE 2 Recycle process for urea manufacture.

pumped back into the system. Evaporation and prilling or granulating produce the final product.

The mixture formed is approximately 35% urea, 8% ammonium carbamate, 10% water, and 47% ammonia. It is cooled to 150°C and the ammonia is distilled at 60°C. The residue from the ammonia still enters the crystallizer vessel at 15°C. More ammonia is removed by vacuum. The resulting slurry is centrifuged. All excess nitrogenous materials are combined and processed into liquid fertilizer, which contains a mixture of all these materials.

The corrosive nature of the reactants usually requires the reaction vessels to be lined with lead, titanium, zirconium, silver, or stainless steel. In the second step of the process, only about one-half of the ammonium carbamate is dehydrated in the first pass. Thus, the excess carbamate, after separation from the urea, must be recycled to the urea reactor or used for other products, such as the production of ammonium sulfate [$(NH_4)_2SO_4$].

Urea is used as a solid fertilizer, a liquid fertilizer and miscellaneous applications such as animal feed, urea, formaldehyde resins, melamine, and adhesives. Presently, the most popular nitrogen fertilizer is a urea-ammonium nitrate solution. Urea-formaldehyde resins have large use as a plywood adhesive. Melamine-formaldehyde resins are used as dinnerware and for extra-hard surfaces (Formica®). The melamine is synthesized by condensation of urea molecules.

As a fertilizer, urea is a convenient form for fixed nitrogen and has the highest nitrogen content (46% by weight) available in a solid fertilizer. It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard. It dissolves readily in water and leaves no salt residue after use on crops and can often be used for foliar feeding.

Urea is also used as a protein food supplement for ruminants, in melamine production, and as an ingredient in the manufacture of pharmaceuticals (e.g., barbiturates), synthetic resins, plastics (urethanes), adhesives, coatings, textile antishrink agents, and ion exchange resins. It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid, and pthalocyanines.

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – II – PROCESS AND SEPARATION IN CHEMICAL INDUSTRY – SCH 1314

MATERIAL BALANCES

Material balances are important first step when designing a new process or analyzing an existing one. They are almost always prerequisite to all other calculations in the solution of process engineering problems.

Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed. Thus, you cannot, for example, specify an input to a reactor of one ton of naphtha and an output of two tons of gasoline or gases or anything else. One ton of total material input will only give one ton of total output, i.e. total mass of input = total mass of output.

A material balance is an accounting for material. Thus, material balances are often compared to the balancing of current accounts. They are used in industry to calculate mass flow rates of different streams entering or leaving chemical or physical processes.

General Material Balance Equation

A balance (or inventory) on a material in a system (a single process unit, a collection of units, or an entire process) may be written in the following general way:

Input	+	**Generation**	–	**Output**	–	**Consumption**	=	**Accumulation**
(enters Through System boundaries)		(produced within system boundaries)		(leaves through system boundaries)		(consumed within system)		(buildup within system)

This general balance equation may be written for any material that enters or leaves any process system; it can be applied to the total mass of this material or to any molecular or atomic species involved in the process.

Steady -state operation: Under steady-state, the values of all variables associated with the process do not change with time. That is, at any given location in the process, the values of temperature, pressure, composition, flow rates, etc. are independent of time. The general balance equation may be simplified according to the process at hand. For example, by definition, the accumulation term for steady-state continuous process is zero. Thus the above equation becomes:

Input + Generation = Output + Consumption

For physical process, since there is no chemical reaction, the generation and consumption terms will become zero, and the balance equation for steady-state physical process will be simply reduced to:

Input = Output

Differential balances: The terms in a differential material balance are expressed as **rates**; that is, rate of input (e.g. moles/s, kg/s), rate of generation, rate of output, and rate of accumulation. Differential balances are applied to continuous processes.

Integral balances: These usually apply to batch processes. The terms in a batch material balance are expressed as **amounts** (molar or mass). Input is the amount placed into the system initially at the start of the process. The process is then sealed while the reaction/transformation of the input materials takes place. At the end, the process is opened and the contents are removed: output is the amount removed at this stage, including products and any unconverted reactants. Generation/consumption are the amounts produced/consumed during the time between the start and the end of the process. Accumulation is the amount left behind in the process (this is zero if all materials are removed).

Degree of Freedom Analysis

Recall: If you have N unknown variables (such as flowrates, compositions) whose value you need to solve for, you will need exactly N independent equations relating these variables (“number of independent equations = number of unknowns”).

Independent equations: equations are independent if none of them can be derived from the others. For example, not one of the set of equations can be obtained by adding or subtracting multiples of the others.

Degrees of freedom, $n_{\text{df}} = n_{\text{unknowns}} - n_{\text{indep eqns}}$

If, for a given problem,

$\boldsymbol{n_{\text{df}} = 0}$: A numerical value for each unknown can be obtained. The problem is solvable.

$\boldsymbol{n_{\text{df}} > 0}$: The problem is underspecified (underdetermined). There is not enough information (i.e. not enough independent equations) to provide a solution.

$\boldsymbol{n_{\text{df}} < 0}$: The problem is overspecified (overdetermined). The problem is mathematically and possibly physically inconsistent.

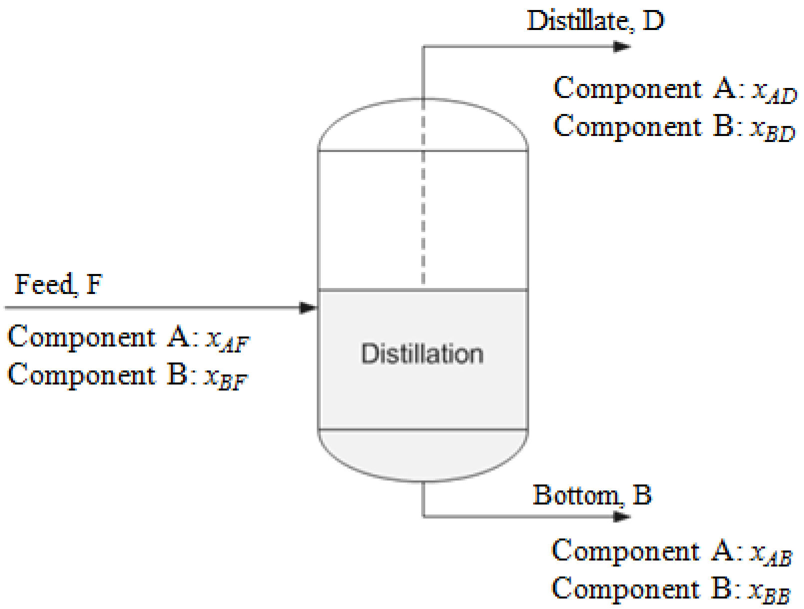
Procedure for Material Balance Calculations

In material balance problems, you will usually be given a description of a process, the values of several process variables, and a list of quantities to be determined. In order to be trained on using a systematic procedure to solve material balance problems, you are advised to follow the steps summarized below:

1. Read and understand the problem statement.
2. Draw a sketch of the process and specify the system boundary
3. Place labels (symbols, numbers, and units) on the diagram for all of the known flows, materials, and compositions.
4. Obtain any data you know are needed to solve the problem but are missing.
5. Choose a basis.
6. Determine the number of variables whose values are unknown (the unknowns), the number of independent equations and carry out a degree-of-freedom analysis.
7. Write down the equations to be solved in terms of the knowns and unknowns.
8. Solve the equations and calculate the quantities asked for in the problem.
9. Check your answer(s).

Material Balance around distillation column

Consider a steady-state distillation process,



Since the process is at steady-state condition and no chemical reaction is involved, the material balance equation becomes

Input = Output

This balance equation can be applied to:

1. The total mass entering and leaving the process – Overall Balance
2. Mass of individual component entering and leaving the process – Component Balance.

Total Mass (Overall Material Balance)

$$F = D + B$$

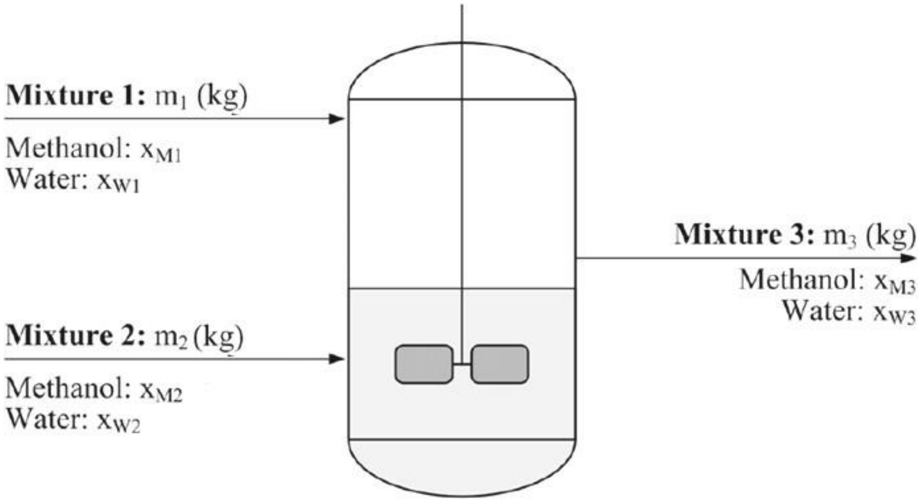
Component A Balance

$$m_{A1} = m_{A2} + m_{A3} \quad Fx_{AF} = Dx_{AD} + Bx_{AB}$$

Component B Balance

$$m_{B1} = m_{B2} + m_{B3} \quad Fx_{BF} = Dx_{BD} + Bx_{BB}$$

Material Balance for Mixing Process



Material Balances (Steady-State, Non-Reactive Process): Total Balance:

$$m_1 + m_2 = m_3$$

Methanol-Balance:

$$m_1x_{M1} + m_2x_{M2} = m_3x_{M3}$$

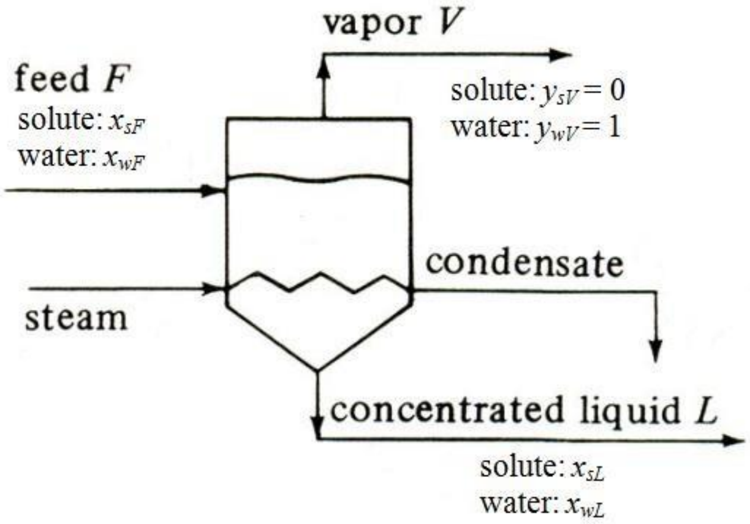
Water-Balance:

$$m_1x_{W1} + m_2x_{W2} = m_3x_{W3}$$

Physical Constraint (applied to mixture 3):

$$x_{M3} + x_{W3} = 1.00$$

Material Balance for Evaporation Process



Material Balances (Steady-State, Non-Reactive Process): Total Balance:

$$F = V + L$$

Solute Balance:

$$Fx_{sF} = Vy_{sV} + Lx_{sL}$$

Since $y_{sV} = 0$, the above equation becomes

$$Fx_{sF} = Lx_{sL}$$

Solvent (Water) Balance:

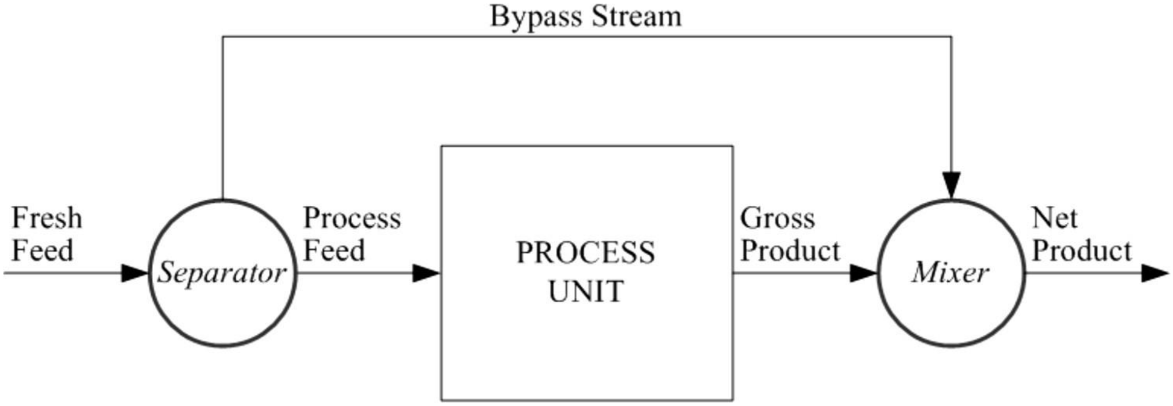
$$Fx_{wF} = Vy_{wV} + Lx_{wL}$$

Multiple Unit Processes

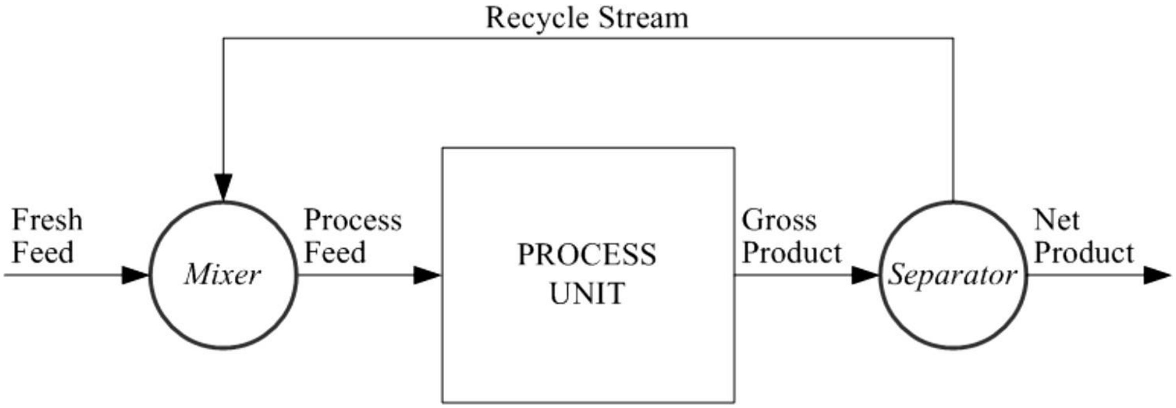
When an interconnected network of process units is involved in a material balance calculation, one typically has to make balances on individual process units, combinations of several units, as well as the overall, multiple unit system in order to arrive at the solution. Balances that are taken on the overall system, which do not involve any *internal* process streams, are referred to as overall balances. For each subsystem (e.g. a single unit, a combination of units), as well as the total process, a degree of freedom analysis will apply. You may need to solve the balances on one subsystem first in order to determine values of variables needed to solve balances on another.

Bypass, Recycle & Purge

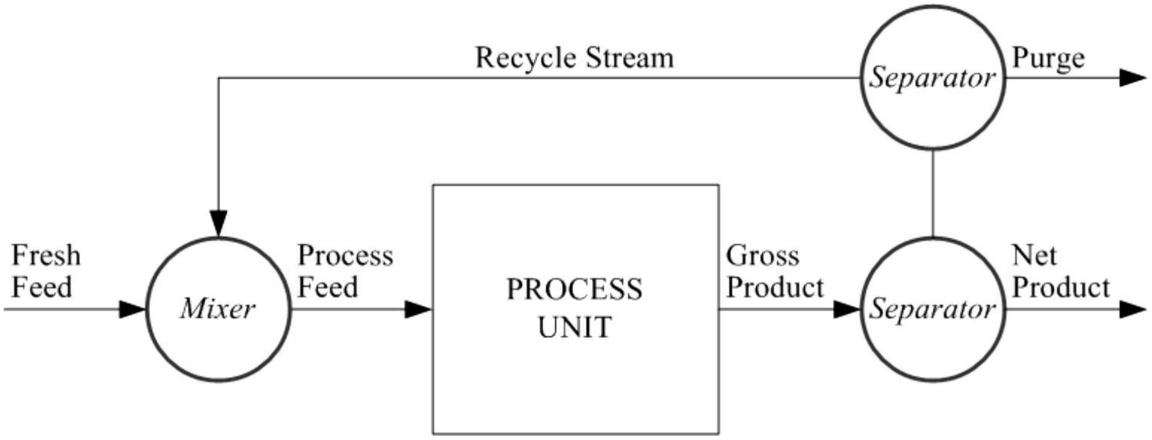
When a part of a process stream is fed forward into a later stage of the process, the stream is being “bypassed.” Bypass is useful, for example, for decreasing the extent of conversion of input materials or for providing improved control over stream temperatures.



Recycle stream is a term denoting a process stream that returns material from downstream of a process unit back to the process unit. When a part of a process stream is fed back into an earlier stage of the process, the stream is said to be “recycled.” Recycle is often used to increase the rates of conversion of a reactant. By passing a reactant molecule through the process several times, its chances to react and convert to product are increased. Other reasons to recycle part of a stream include recovery of valuable materials, such as catalysts, improved temperature control over a process, and decreased waste of working (carrier) fluid.



Purge stream is a stream bled off to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream.



SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES
DEPARTMENT OF CHEMISTRY

UNIT – III – PROCESS AND SEPARATION IN CHEMICAL INDUSTRY – SCH 1314

Fundamentals of Separation Processes

In most of the chemical engineering systems, separation processes are integral part of the entire process flowsheet. If we consider a reactive system, where, certain products are of primary interest, separation units are either put in the upstream or downstream. In such a system, the reactor is the heart of the system. It may happen that the reactants are gaseous and should be devoid of moisture. In such cases, a separation unit must be present as an upstream unit. On the other hand, if a particular product is kept in mind, a separation unit must be placed at the downstream of the flowsheet. There may be processes, where, the separation is the only objective. For example, if we consider a treatment process of an industrial effluent, separation is the only process that is involved. There may be a number of separation processes involved in a system. In an effluent treatment process, there are three steps, namely, primary, secondary and tertiary treatment processes. All these processes are primarily separation processes. Primary treatment processes include coagulation, flocculation, etc. Secondary treatment processes are mainly oxidation ponds, etc. Tertiary treatment processes involve adsorption, membrane separation, etc. In food and juice processing industries, separations are primary stages of operation. Most of the pharmaceutical industries have separation units as integral parts in the downstream or they are the main units. In milk processing separation processes are primary.

Most of the separation processes involve, either separation of solutes from the solvent or, separation of a mixture of solutes. It may be noted that the components those need to be separated are in a mixture naturally. In order to effect separation, one has to put either energy or an extra material from outside to disturb stability. This is equivalent to the concept of exceeding the activation energy of separation by an external agent (agent may be energy or matter). This point can be elaborated by some examples. Consider a case of separation of salt from sea water. In this system, thermal energy is added to the system and water is evaporated leaving behind the salts. Consider another case of separation of charged colloidal particles which are stable in a solution. In such systems, a coagulant, like potassium alum or ferric chloride or calcium oxide (selection depends upon the operating pH) is added. These coagulants are generally of opposite charges of the colloids. These colloids get themselves attached to the coagulants by electrostatic attractive forces and the whole assembly becomes heavier and settles down. In this case, we add an external agent (a matter i.e., coagulant) to effect separation. This can be schematically presented in Fig.1.1.

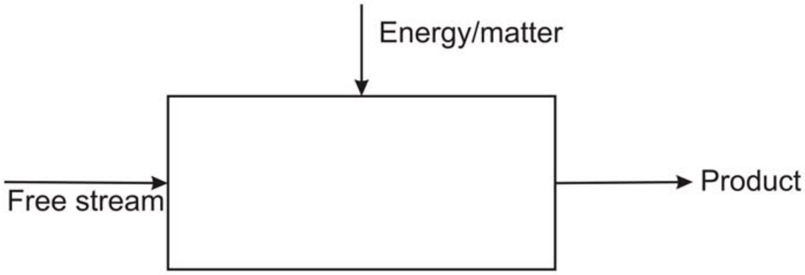


Fig.1.1: Schematic of a separation process

Various Separation processes and Identification of novel separation processes

As discussed in the earlier chapter, the separation processes are divided in equilibrium and rate governed separation process. In equilibrium governed separation processes, the product phases are in equilibrium with the inlet phases. In rate governed separation processes, difference of rate of physical transport of species brings the separation. Some of the specific separation processes under these two categories are elaborated below.

Equilibrium governed processes

Four popular and quite common equilibrium governed separation processes are described.

Distillation

Distillation is based on the differences in boiling points of the constituents in a mixture. The component having the lower boiling point will go to the vapor phase earlier, leaving behind the other component in the residual mixture. In this process, external heating is required to heat up the system. Therefore, the top vapor phase is condensed and is rich in one component and the residual liquid phase is rich in other component. This is known as flash distillation. In another process, a part of the condensed stream from the top is recycled down the column. This is known as reflux. In this case, there is intimate mixing of the liquid stream coming down and vapor going up. This operation is carried out in counter current fashion and this enhances the efficiency of the process. This is generally used for separation of aqueous mixture of various organic solvents, like, toluene, benzene, acetone, ethyl benzene, etc.

Absorption

In this process, a vapor in an inert gas is absorbed in a liquid stream. The vapor is soluble in the liquid. The liquid stream rich in solubilized vapor components is separated by distillation or some other suitable techniques. The liquid can be recovered and reused in the process itself. An example is removal of ammonia from ammonia – water mixture using water as solvent. Removal of carbon di oxide from a mixture of air and carbon dioxide using a solvent like primary or secondary or tertiary amines is another example. Typically this operation is carried out in counter current manner to enhance the efficiency of this process. Sometimes, the packed beds or staged beds like trays are used to have better mixing during the transfer process. It may be mentioned that absorption is a bulk phenomena, i.e., the gaseous solutes are transported to the bulk of the liquid stream. It may be noted that to effect separation, a matter is introduced in the system.

Adsorption

Separation of solutes by transporting it from gaseous or liquid streams on a solid surface is known as adsorption. As opposed to absorption it is a surface phenomenon. The solute is fixed on the solid surface only. Typically, the solid surface is specific for a particular component present in the feed stream. For example, in a liquid stream having organic as well as inorganic components, the organics are preferentially adsorbed on the surface of activated carbon. Typically, in a bed, the adsorbent particles are kept and the fluid is pumped through the system for intimate mixing. In the process, the solute is transferred to the solid phase. After sometime, the solid phase is completely saturated and the transfer of species becomes extremely slow due to lack of driving force. In such case, the bed has to be replaced by new adsorbents or the bed has to be regenerated by a suitable washing protocol. It may be noted, that a reasonably lower particle size of adsorbents provides sufficient surface area for separation. Removal of organics from an aqueous mixture using activated carbon is an example of adsorption. It may be noted that to effect separation, a matter is introduced in the system.

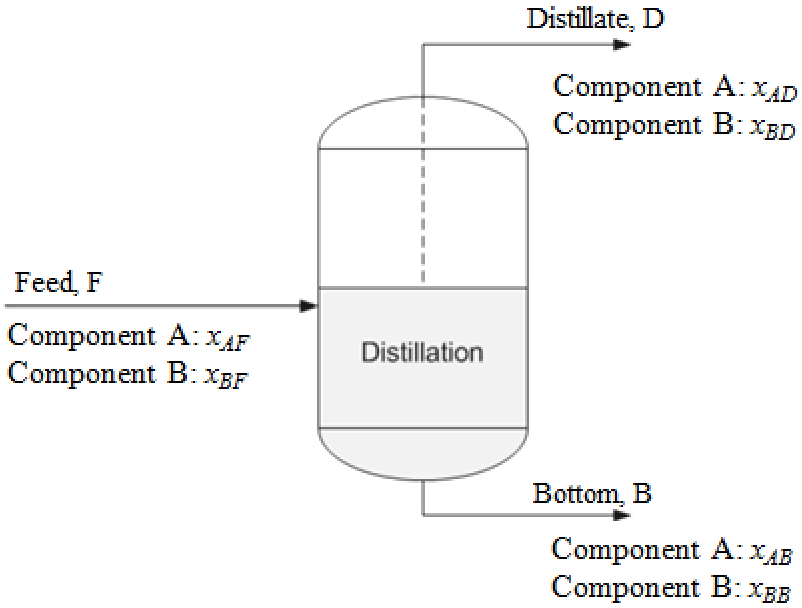
Drying

In drying, water vapours from a solid material are removed by using a vapor stream to an acceptable small limit. Generally, it is carried out by applying thermal energy as compared to introduction of a matter in case of absorption or adsorption. The process efficiency depends on the temperature, relative humidity and other thermo physical properties of the drying vapor as well as the temperature and other thermo-physical properties of the solid.

APPLICATIONS OF MATERIAL BALANCE

Material Balance around distillation column

Consider a steady-state distillation process,



Since the process is at steady-state condition and no chemical reaction is involved, the material balance equation becomes

Input = Output

This balance equation can be applied to:

1. The total mass entering and leaving the process – Overall Balance

2. Mass of individual component entering and leaving the process – Component Balance.

Total Mass (Overall Material Balance)

$$F = D + B$$

Component A Balance

$m_{A1} = m_{A2} + m_{A3}$ $Fx_{AF} =$

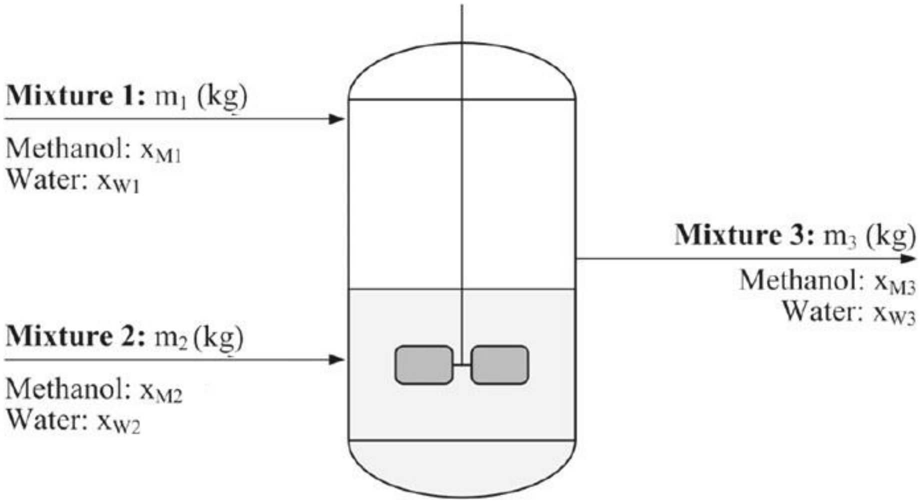
$Dx_{AD} + Bx_{AB}$

Component B Balance

$m_{B1} = m_{B2} + m_{B3}$ $Fx_{BF} =$

$Dx_{BD} + Bx_{BB}$

Material Balance for Mixing Process



Material Balances (Steady-State, Non-Reactive Process): Total Balance:

$$m_1 + m_2 = m_3$$

Methanol-Balance:

$$m_1x_{M1} + m_2x_{M2} = m_3x_{M3}$$

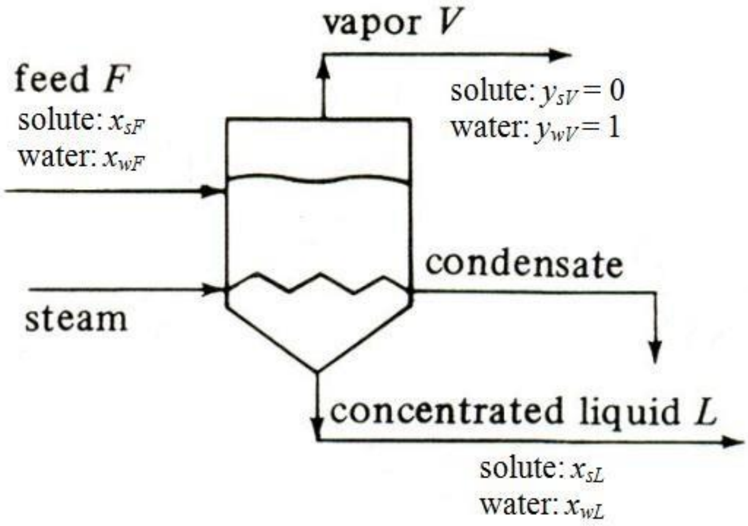
Water-Balance:

$$m_1x_{W1} + m_2x_{W2} = m_3x_{W3}$$

Physical Constraint (applied to mixture 3):

$$x_{M3} + x_{W3} = 1.00$$

Material Balance for Evaporation Process



Material Balances (Steady-State, Non-Reactive Process): Total Balance:

$$F = V + L$$

Solute Balance:

$$Fx_{sF} = Vy_{sV} + Lx_{sL}$$

Since $y_{sV} = 0$, the above equation becomes

$$Fx_{sF} = Lx_{sL}$$

Solvent (Water) Balance:

$$Fx_{wF} = Vy_{wV} + Lx_{wL}$$

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES
DEPARTMENT OF CHEMISTRY

UNIT – IV – PROCESS AND SEPARATION IN CHEMICAL INDUSTRY – SCH 1314

Unit 4

Heat capacity (*C*)

Heat capacity or thermal capacity is the measurable physical quantity that characterizes the amount of heat required to change a body's temperature by a given amount. In the International System of Units (SI), heat capacity is expressed in units of joules per kelvin.

Derived quantities that specify heat capacity as an intensive property, independent of the size of a sample, are the molar heat capacity, which is the heat capacity per mole of a pure substance, and the specific heat capacity, often simply called specific heat, which is the heat capacity per unit mass of a material.

The units for the specific heat capacity are $[C]$= J/kg.K.

The units for molar heat capacity, $[C_{mol}]$= J/mol.K

Heat capacity per unit volume and has SI units $[s] = \frac{\mathrm{J}}{\mathrm{m}^3 \cdot \mathrm{K}}$

Heat of Reaction

The Heat of Reaction (also known and Enthalpy of Reaction) is the change in the enthalpy of a chemical reaction that occurs at a constant pressure. It is a thermodynamic unit of measurement useful for calculating the amount of energy per mole either released or produced in a reaction. Since enthalpy is derived from pressure, volume, and internal energy, all of which are state functions, enthalpy is also a state function.

Introduction

ΔH, or the change in enthalpy arose as a unit of measurement meant to calculate the change in energy of a system when it became too difficult to find the ΔU, or change in the internal energy of a system, by simultaneously measure the amount of heat and work exchanged. Given a *constant pressure*, the change in enthalpy can be measured as

$$\Delta H=q$$

See section on enthalpy for a more detailed explanation.

The notation ΔH^o or ΔH^orxn then arises to explain the precise temperature and pressure of the heat of reaction ΔH. The standard enthalpy of reaction is symbolized by ΔH^o or ΔH^orxn and can take on both positive and negative values. The units for ΔH^o are kilo Joules per mole, or kj/mol.

ΔH and ΔH°_{rxn}

- Δ = represents the change in the enthalpy; (ΔH products -ΔH reactants)
    - a positive value indicates the products have greater enthalpy, or that it is an endothermic reaction (heat is required)
    - a negative value indicates the reactants have greater enthalpy, or that it is an exothermic reaction (heat is produced)
- ^{o} = signifies that the reaction is a standard enthalpy change, and occurs at a preset pressure/temperature
- rxn = denotes that this change is the enthalpy of reaction

The Standard State: The standard state of a solid or liquid is the pure substance at a pressure of 1 bar (105 Pa) and at a relevant temperature.

The ΔH^orxn is the standard heat of reaction or standard enthalpy of a reaction, and like ΔH also measures the enthalpy of a reaction. However, ΔH^orxn takes place under "standard" conditions, meaning that the reaction takes place at 25º C and 1 atm. The benefit of a measuring ΔH under standard conditions lies in the ability to relate one value of ΔH^o to another, since they occur under the same conditions.

- v_p= stoichiometric coefficient of the product from the balanced reaction
- v_r= stoichiometric coefficient of the reactants from the balanced reaction
- ΔH°_f= standard enthalpy of formation for the reactants or the products

To calculate the standard enthalpy of reaction the standard enthalpy of formation must be utilized. Another, more detailed, form of the standard enthalpy of reaction includes the use of the standard enthalpy of formation ΔH°_f:

$$\Delta H^{\ominus}=\sum \Delta vp \Delta H^{\ominus} f(\mathit{products})-\sum \Delta vr \Delta H^{\ominus} f(\mathit{reactants})$$

with

- v_p= stoichiometric coefficient of the product from the balanced reaction
- v_r= stoichiometric coefficient of the reactants from the balanced reaction
- ΔH°_f= standard enthalpy of formation for the reactants or the products

Since enthalpy is a state function, the heat of reaction depends only on the final and initial states, not on the path that the reaction takes. For example, the reaction $A \rightarrow BA \rightarrow B$ goes through intermediate steps (i.e. $C \rightarrow DC \rightarrow D$), but A and B remain intact.

$$\begin{array}{c} A \rightarrow C \\ C \rightarrow D \\ \underline{D \rightarrow B} \\ A \rightarrow B \end{array}$$

Therefore, one can measure the enthalpy of reaction as the sum of the ΔH of the three reactions by applying Hess' Law.

Heat Formation

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess’s law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 ^{o}C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The corresponding relationship is

$$\text{elements} \rightarrow \text{compound} \ \Delta H_{rxn} = \Delta H_f$$

For example, consider the combustion of carbon:

$$C(s)+O2(g)\longrightarrow CO2(g)$$

then

$$\Delta Hrxn=\Delta Hf[CO2(g)]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta Hf<0\Delta Hf<0$ if heat is released when elements combine to form a compound and $\Delta Hf>0\Delta Hf>0$ if heat is absorbed.

Heat of Combustion

In efforts to reduce gas consumption from oil, ethanol is often added to regular gasoline. It has a high-octane rating and burns more slowly than regular gas. This "gasohol" is widely used in many countries. It produces somewhat lower carbon monoxide and carbon dioxide emissions, but does increase air pollution from other materials.

Heat of Combustion

Many chemical reactions are combustion reactions. It is often important to know the energy produced in such a reaction so we can determine which fuel might be the most efficient for a given purpose. The **molar heat of combustion** (He) is the heat released when one mole of a substance is completely burned.

Typical combustion reactions involve the reaction of a carbon-containing material with oxygen to form carbon dioxide and water as products. If methanol is burned in air, we have:

$$\mathrm{CH3OH+O2\rightarrow CO2+2H2OHe=890kJ/mol}$$

In this case, one mole of oxygen reacts with one mole of methanol to form one mole of carbon dioxide and two moles of water.

It should be noted that inorganic substances can also undergo a form of combustion reaction:

$$\mathrm{2Mg+O2\rightarrow 2MgO}$$

In this case there is no water and no carbon dioxide formed. These reactions are generally not what we would be talking about when we discuss combustion reactions.

Heat of Mixing.

The enthalpy of mixing (or heat of mixing or excess enthalpy) is the enthalpy liberated or absorbed from a substance upon mixing. When a substance or compound is combined with any other substance or compound the enthalpy of mixing is the consequence of the new interactions between the two substances or compounds. This enthalpy if released exothermically can in an extreme case cause an explosion.

Enthalpy of mixing can often be ignored in calculations for mixtures where other heat terms exist, or in cases where the mixture is ideal. The sign convention is the same as for enthalpy of reaction: when the enthalpy of mixing is positive, mixing is endothermic while negative enthalpy of mixing signifies exothermic mixing. In ideal mixtures the enthalpy of mixing is null. In non-ideal mixtures the thermodynamic activity of each component is different from its concentration by multiplying with the activity coefficient.

Heat Exchangers

In any process industry, we need to transfer heat for different operations (like cooling, heating, vaporizing, or condensing) to or from various fluid streams in various equipment like condensers, water heaters, re-boilers, air heating or cooling devices etc., where heat exchanges between the two fluids. In a chemical process industry, the heat exchanger is frequently used for such applications. A heat exchanger is a device where two fluids streams come into thermal contact in order to transfer the heat from hot fluid to cold fluid stream.

In this chapter, we will discuss about the technical analysis of the heat exchangers along with the method for predicting heat exchanger performance and operational parameters. Moreover the discussion on heat exchanger size will also be discussed. However, we will not discuss the economics (though discuss the heat exchanger size) of the heat exchanger. We will consider that the heat transfer will primarily be taken by conduction and convection only. We will describe the commonly used heat exchangers and their important characteristics.

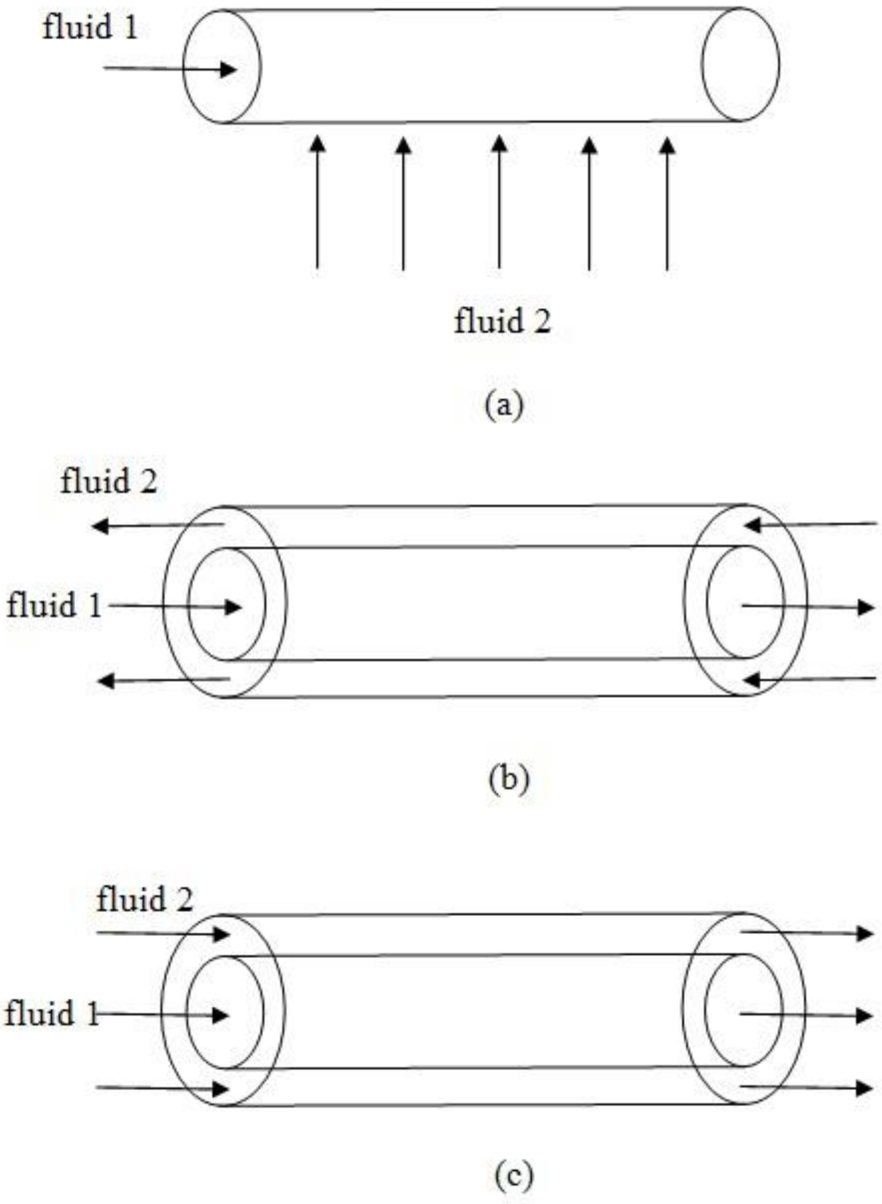
In general heat exchangers may be categorized into two general classes depending on the relative orientation of the flow direction of the two fluid streams. If the two streams cross one another in space, usually at right angles, the heat exchangers are known as cross flow heat exchanger as shown in the fig.1(a).

In the second class of heat exchanger the two streams move in parallel direction in space. The usual shell and tube heat exchanger or concentric pipe exchanger or double tube exchanger is the most frequently used exchanger in the class. Two situations may arise when the fluid flow in the parallel direction, one in which the fluids flow in same direction and the other in which the fluids flow in opposites direction. “Parallel –flow” or “Co-current flow” is used when the flow is in same direction and counter current is used when the fluid flow is in the opposite direction.

Before understanding the principle of heat exchanger we would first understand it from the point of construction.

Elements of shell and tube heat exchanger

We will discuss shell and tube heat exchanger as they or the most commonly used heat exchangers in the chemical process industries. Schematic of a typical shell and tube heat exchanger is shown in fig.2.



(a)

(b)

(c)

Fig.1: Orientation of fluid stream in heat exchanger (a) cross flow (b) counter current flow (c) parallel flow

The heat exchanger as shown in fig.2 consists of a bundle of tubes properly secured at either ends in tube sheets. The tube sheets are drilled plates into which the tubes are fixed up using different technique to have leak proof joints. The entire tube bundles shown in the fig.3 is placed inside a closed shell, which seals around the tube sheet periphery to form the two immiscible zones for hot and cold fluids are shown in fig.4.

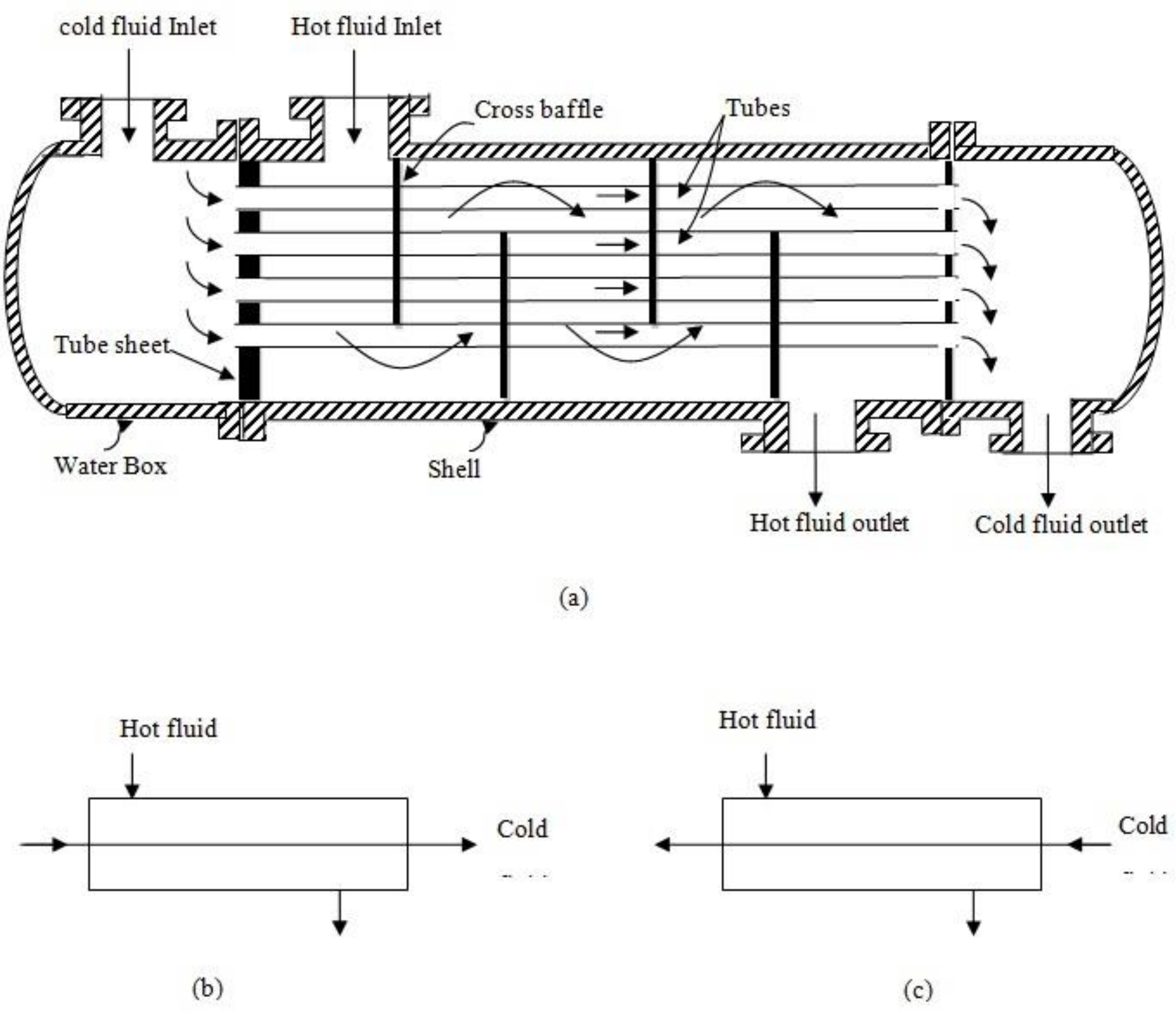


Fig.2: A schematic of (a) one-shell pass, one tube pass heat exchanger; (b) parallel flow; and (c) counter flow

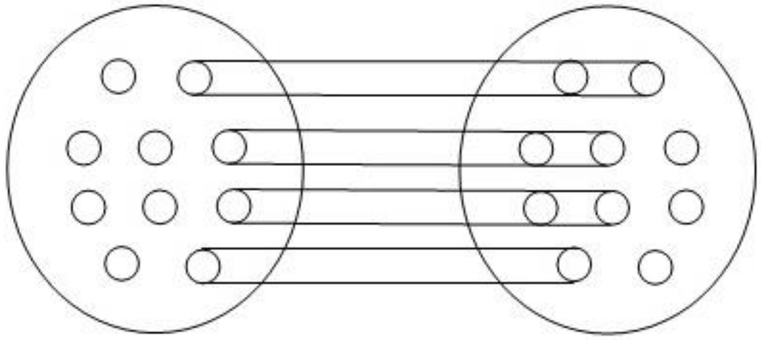


Fig. 3 Tube bundle fitted in two sheets

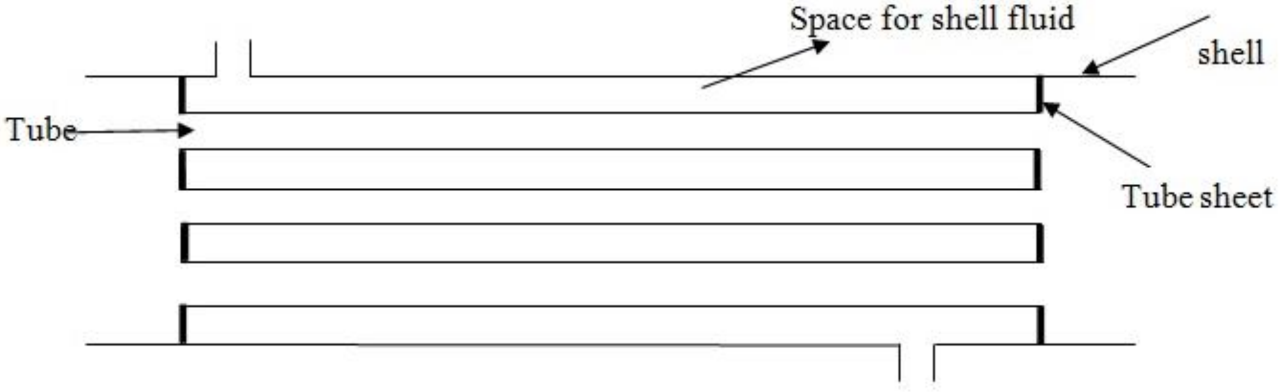


Fig.4: Tube bundle inside a shell

One fluid flows through the tubes while the other fluid flows around the outside of the tubes, it is the space between the tube sheets and enclosed by the outer shell.

For a thorough distribution of the shell side fluid, baffles are placed normal to the tube bundle. This baffle creates turbulence in the shell side fluid and enhances the transfer coefficients for the shell side flow.

Fig.2 shows the simplified diagram of a shell and tube heat exchanger, showing a few of the important components. Infact, the present heat exchanger used in the process industry are quite complex and have improved design such as factors for thermal expansion stresses, tube fouling due to contaminated fluids, ease of assembly and disassembly, size, weight, etc.

The heat exchanger shows in fig.2 is having one shell and one tube pass since both the shell and tube side fluid make a single traverse through the heat exchanger. Thus, this type of shell-and-tube heat exchangers is designated as 1-1 exchanger. If we desire to pass the tube fluid twice, then it is designated as 1-2 exchangers. Similarly, if there are 2 shell pass and 4 tube pass, the designation will be 2-4 exchanger. The number of pass in tube side is done by the pass partition plate. A pass particular plate or pass divider as shown in fig.5. The shell side pass can be creator by a flat plate as shown in fig.6.

The three most common types of shell-and-tube exchangers are (1) fixed tubesheet design, (2) U-tube design, and (3) floating-head type. In all three types, the front-end head is stationary while the rear-end head can be either stationary or floating depending on the thermal stresses in the shell, tube, or tubesheet, due to temperature differences as a result of heat transfer. The exchangers are built in accordance with three mechanical standards that specify design, fabrication, and materials of unfired shell-and-tube heat exchangers. Class R is for the generally severe requirements of petroleum and related processing applications. Class C is for generally moderate requirements for commercial and general process applications. Class B is for chemical process service. The exchangers are built to comply with the applicable ASME Boiler and Pressure Vessel Code, Section VIII (1998), and other pertinent codes and/or standards. The TEMA standards supplement and define the ASME code for heat exchanger applications. In addition, state and local codes applicable to the plant location must also be met. The TEMA standards specify the manufacturing tolerances for various mechanical classes, the range of tube sizes and pitches, baffling and support plates, pressure classification, tubesheet thickness formulas, and so on, and must be consulted for all these details. In this book, we consider only the TEMA standards where appropriate, but there are other standards, such as DIN 28 008. Tubular exchangers are widely used in industry for the following reasons. They are custom designed for virtually any capacity and operating conditions, such as from high

CLASSIFICATION OF HEAT EXCHANGERS FIGURE

(a) Shell-and-tube exchanger (BEM) with one shell pass and one tube pass; (b) shell and-tube exchanger (BEU) with one shell pass and two tube passes. vacuum to ultrahigh pressure [over 100 MPa (15,000 psig)], from cryogenics to high temperatures [about 11008C (20008F)] and any temperature and pressure differences between the fluids, limited only by the materials of construction. They can be designed for special operating conditions: vibration, heavy fouling, highly viscous fluids, erosion, corrosion, toxicity, radioactivity, multi-component mixtures, and so on. They are the most versatile exchangers, made from a variety of metal and nonmetal materials (such as graphite, glass, and Teflon) and range in size from small [0.1 m2 (1 ft^2) to supergiant [over 105 m^2 (106 ft^2)] surface area. They are used extensively as process heat exchangers. in the petroleum-refining and chemical industries; as steam generators, condensers, boiler feed water heaters, and oil coolers in power plants; as condensers and evaporators in some air-conditioning and refrigeration applications; in waste heat recovery applications with heat recovery from liquids and condensing fluids; and in environmental control

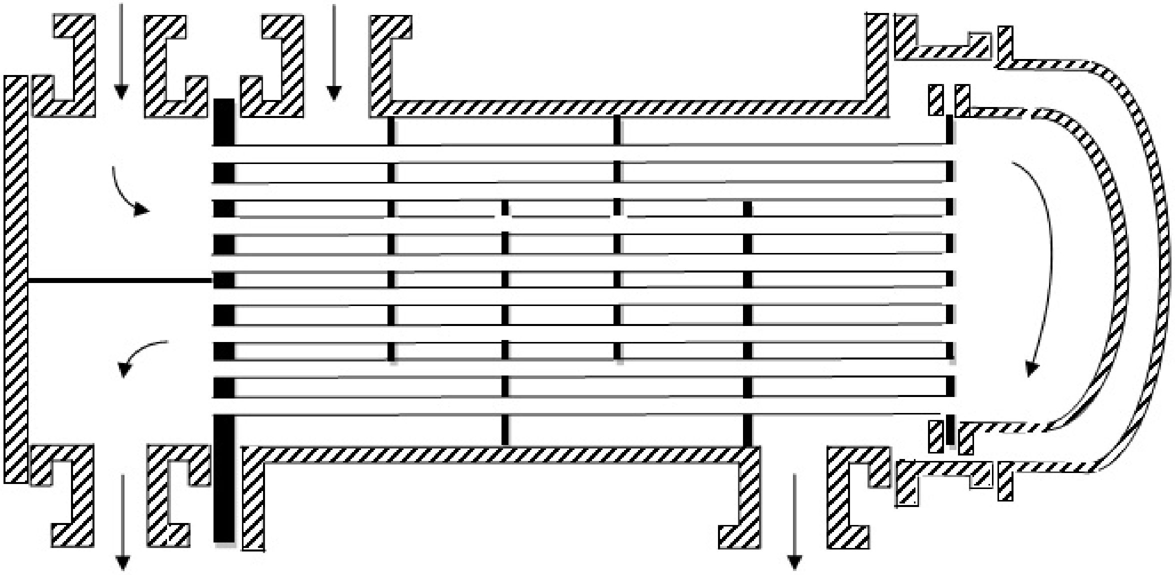


Fig. 5: 1-2 exchanger showing pass partition plate

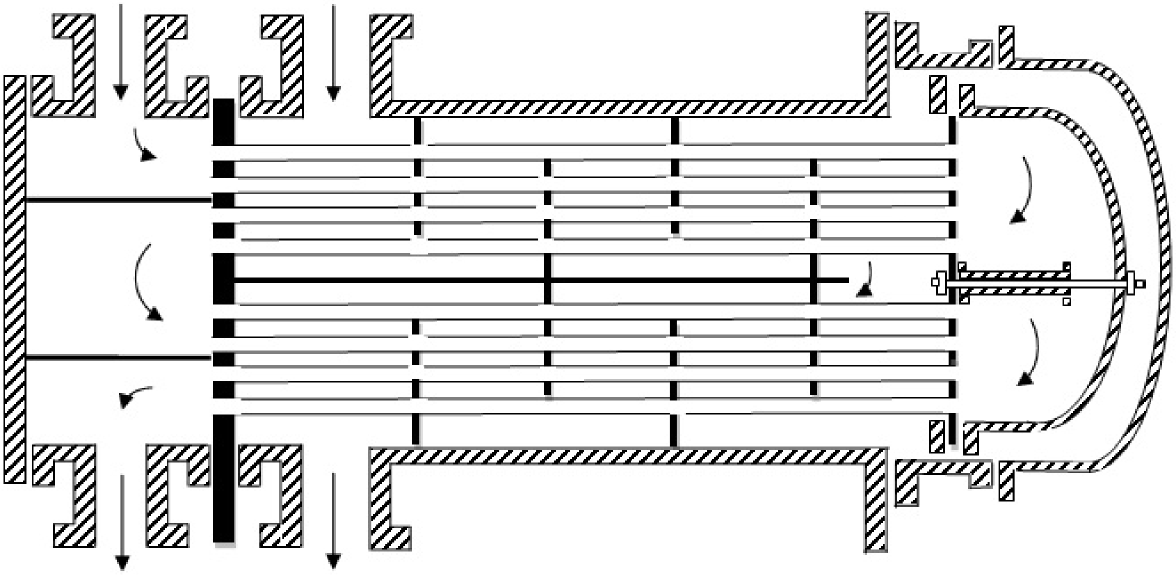
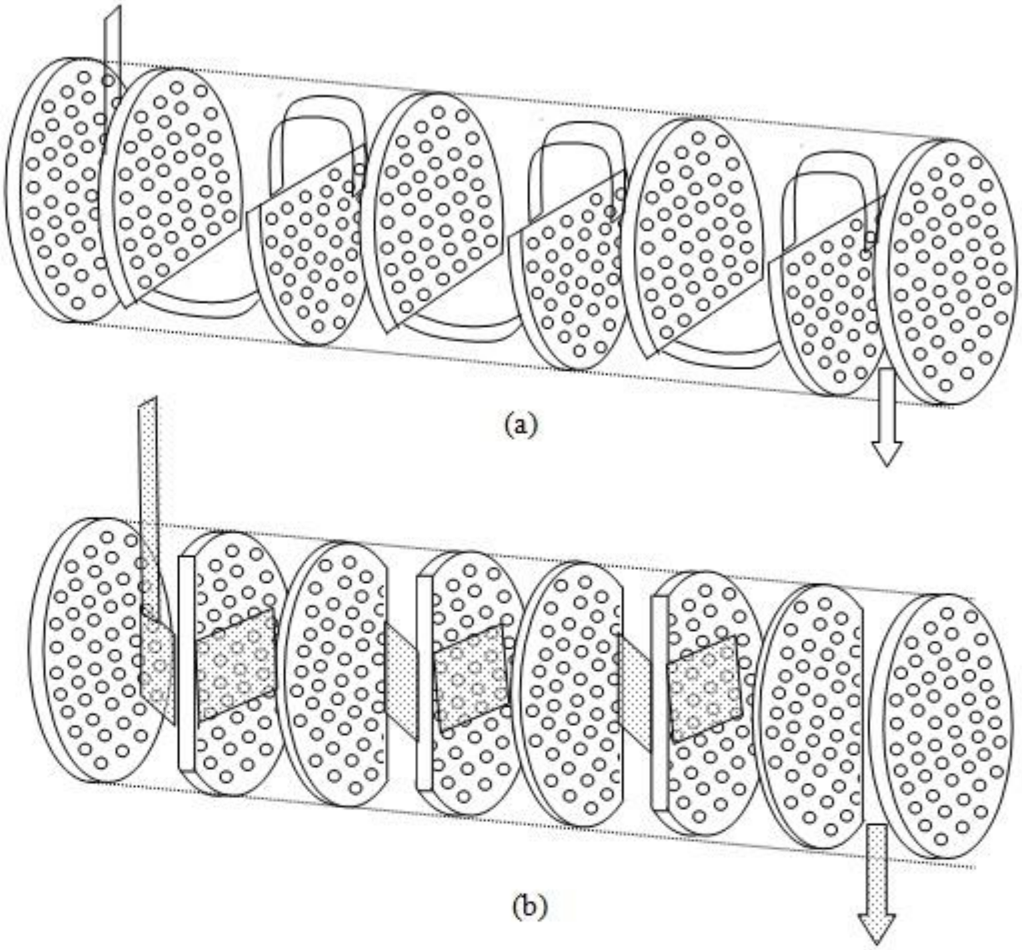


Fig 6: 2-4 exchanger showing shell and tube passes

It can be understood that for a given number of tubes; the area available for flow of the tube side fluid is inversely proportional to the number of passes. Thus, on increasing the pass the area reduces and as a result the velocity of fluid in the tube increases and henceforth the Reynolds number increases. It would result in increased heat transfer coefficient but at the expense of high pressure drop. Generally, even numbers of tube passes are used for the multi-pass heat exchangers.

Figure 2 shows some baffles. These baffles (or shell-side baffles) are a metal plate usually in the form of the segment of a circular disc having holes to accommodate tubes. Shell-side baffles have two functions. The first is to create turbulence in the shell side fluid by changing the flow pattern parallel or cross flow to the tube bundles and thus increases the shell side heat transfer coefficient. The second major function of these baffles is to support the tube all along its length otherwise the tube may bend. Moreover, these baffles may have horizontal or vertical cuts (segmental baffle) as shown in fig.7.



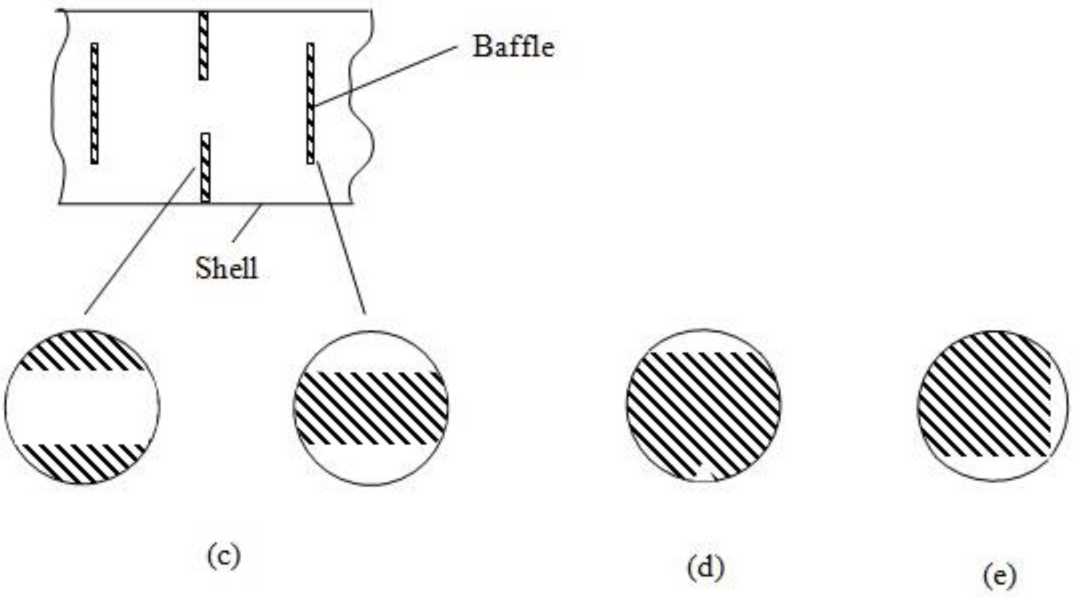


Fig.7: Baffles; (a) horizontal cut baffles; (b) Vertical cut baffles; (c, d and e)the shaded region show the baffle area

The cut portion of the baffle, which is called baffle window, provides the area for flow of the shell fluid. The baffle window area ranges from 15% to 50%. At 25% cut segmental baffle means that the area of the cut-out portion is 25% of the area of the baffle. The spacing between the baffles is an important aspect. A larger baffles spacing reduces the shell side pressure drop but at the same time decreases the turbulence and heat transfer coefficient. Smaller baffle spacing increases the turbulence and heat transfer coefficient. However, the pressure drop may increase significantly, thus the advantage attained due to the higher heat transfer coefficient may be nullified. Therefore baffle spacing is selected considering the allowable shell side pressure drop and the heat transfer coefficient desired. A rule of thumb is that the minimum spacing of segmental baffles is one by fifth of the shell diameter or 5 cm, whichever is larger.

Evaporation

Evaporation is the vaporization of a liquid. Chemical process industries, in general, use evaporator for the vaporization of a solvent from a solution. We have already discussed the heat transfer for boiling liquids in early chapter. However, the evaporation is so important operation in chemical process industry that it is considered an individual operation. In this chapter we will focus on the evaporation with an objective to concentrate a solution consisting of a non-volatile solute and a volatile solvent. If we continue the evaporation process, the residual mater will be solid, which is known as drying. However, our aim is not to dry but to concentrate the solution, moreover, we will also not deal with the crystallization, in which the evaporation leads to formation of crystal in the solution. It is suggested that reader should learn the difference between evaporator, drying and crystallization.

Types of evaporator

Natural circulation evaporator

In this category the main evaporators are,

1. Calandria type or short tube evaporator
2. Long tube vertical evaporator

As the name indicates, the circulation of the solution is natural and the density difference derives it. The solution gets heat up and partially vaporized as it flows up the tubes. The heated liquid flows up because of the density difference. Vapor-liquid disengagement occurs above the tube. Thick liquor comes down from this down comer and withdrawn from the bottom. The natural-circulation evaporators may be used if the solution is quite dilute. In the dilute solution the natural circulation will be at sufficient speed. It may also be used when the solution does not have suspended solid particles. As the solution stays in the tube for larger time, the solution should not be heat sensitive.

The Calandria type or short-tube evaporators have short tubes as compared to the long tube evaporators. The short-tube evaporation uses circulation and solution flows many times in the evaporators. However, in case of the long tube evaporator the flow is once through.

Forced circulation evaporator

Natural circulation evaporators have many limitations (as mentioned earlier) through they are economical as compared to forced circulation evaporator. A forced circulation evaporator has a tubular exchanger for heating the solution without boiling. The superheated solution flashes in the chamber, where the solution gets concentrated. In forced circulation evaporator horizontal or vertical both type of design is in- practice. The forced circulation evaporators are used for handling viscous or heat sensitive solution.

Falling film evaporator

Highly heat sensitive materials are processed in falling film evaporators. They are generally once-through evaporator, in which the liquid enters at the top, flows downstream inside the heater tubes as a film and leaves from the bottom. The tubes are heated by condensing steam over the tube. As the liquid flows down, the water evaporates and the liquid gets concentrated. To have a film inside of the tube, the tube diameter is kept high whereas the height low to keep the residence time low for the flowing liquid. Therefore, these evaporators, with non-circulation and short resistance time, handle heat sensitive material, which are very difficult to process by other method. The main problem in falling film evaporator is the distribution of the liquid uniformly as a thin film inside the tube.

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE
www.sathyabama.ac.in

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – V – PROCESS AND SEPARATION IN CHEMICAL INDUSTRY – SCH 1314

Membrane separation:

Membrane separations represent a new type of unit operation. The membrane acts as a semi permeable barrier and separation occurs by the membrane controlling the rate of movement of various molecules between two liquid phases, two gas phases, or a liquid and a gas phase. The two fluid phases are usually miscible and the membrane barrier prevents actual, ordinary hydrodynamic flow.

Classification of membrane processes

- Gas diffusion: The rates of gas diffusion depend on the pore sizes and the molecular weights. We may have molecular, transition, and Knudsen diffusion regions depending on the relative sizes of pore and gas molecule.
- Microfiltration (MF): This refers to membranes that have pore m. It is used to□diameters from 0.1 to 10 filter suspended particulates, bacteria or large colloids from solution.
- Ultrafiltration (UF): This refers to membranes having pore diameters in the range 20-1000 A o . It can be used to filter dissolved macromolecules, such as proteins and polymers, from solution. Reverse osmosis (RO): The membrane pores are in the range of 5-20 A o in diameter, which are within the range of the thermal motion of the polymer chains.
- Dialysis

Membrane modules:

The practical equipment where the actual membrane-based separation occurs is known as membrane modules. The basic aim of development of these modules is to provide maximum membrane area in relatively smaller volume, so that the permeate flux i.e., the productivity of the system is maximum.

These membrane modules are of four types,
(i) plate and frame module,
(ii) hollow fiber module,
(iii) spiral wound and
(iv) tubular modules.

Plate and frame modules

The heart of plate-frame module is the support plate that is sandwiched between two flat sheet membranes. The membranes are sealed to the plate, either gaskets with locking devices, glue or directly bonded. The plate is internally porous and provides a flow channel for the permeate which is collected from a tube on the side of the plate. Ribs or grooves on the face of the plate provide a feed side flow channel. The feed chanel can be a clear path with chanel heights from 0.3 to 0.75 mm. The higher channel heights are necessary for high viscosity feeds; reduction in power consumption of 20 to 40% can be achieved by using a 0.6 mm chanel compared to a 0.3 mm chanel. Alternatively, retentate separator screens (20 or 50 mesh polypropelyne) can be used. Commercial plate-frame units are usually horizontal with the membrane plates mounted vertically. They can be run with each plate in parallel plates in two or three series.

Tubular modules

In such modules, the membrane is cast on the inside surface of a porous tube. Tubular membranes operate in tangential, or cross-flow, design where process fluid is pumped along the membrane surface in a sweeping type action. The feed solution is pumped through the center of the tube at velocities as high as 6 m/s. These cross-flow velocities minimize the formation of a concentration polarization layer on the membrane surface, promoting high and stable flux and easy cleaning, especially when the objective is to achieve high suspended solids in the MF, UF or NF concentrate. Permeate is driven through the membrane to be directed out of the system or back into the process depending on the application. There are many advantages in tubular membrane configurations. Besides their rugged construction, they have a distinct advantage of being able to process high suspended solids, and concentrate product successfully and repeatedly to relatively high end point concentration levels without plugging. A common objective of an end-of-pipe waste treatment UF system is to reduce waste volume as much as possible to reduce concentrate hauling costs. For juice clarification applications, tubular membrane systems produce the greatest yields and the highest final suspended solids concentration levels. Tubular MF, UF and NF systems do not require significant prefiltration. Some tubular products have the ability to be mechanically cleaned with spongeballs. Spongeballs can be used in process, and are also used to enhance chemical cleaning by reducing time and cleaning chemicals. Tubular membranes are ideally suited to treatment of metalworking oily waste, wastewater minimization and recovery from industrial processes, juice clarification, treatment of pulp and paper industry waste, etc. Tubular membranes typically have life upto 2 to 10 years.

Hollow fiber module

In hollow fiber module, lots of hollow fibers (each fiber is a tubular module) are kept in a large pipe. Geometry allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption. Hollow fiber membranes can be designed for circulation, dead end and single pass operation. Some of the many hollow fiber membrane filtration applications include, potable water treatment, juice clarification, wine filtration, dairy processing, etc. The advantages of such modules include reduction in space requirement, lowering in labor cost, lowering in chemical cost, delivery of high quality product water, etc. Hollow fiber membranes offer the unique benefits of high membrane packing densities, sanitary designs and, due to their structural integrity and construction, can withstand permeate back pressure thus allowing flexibility in system design and operation. Most hollow fiber products are available in (i) 1" diameter laboratory test cartridges ranging up to 10" diameter for commercial products, (ii) Standard commercial cartridge lengths of 25", 43", 48", 60" and 72", (iii) Nominal separation ranges from 0.2 micron down to 1,000 MWCO, (iv) Fiber inside diameters from 0.02"(.5mm) up to 0.106"(2.7mm), (v) Various materials of construction including polysulfone and polyacrylonitrile. The following figure (Fig. 3.5c) shows some hollow fiber cartridges of 5, 8 and 10” diameter with endcaps. Benefits of hollow fiber membranes include (i) controlled flow hydraulics, (ii) tangential flow along the membrane surface limits membrane fouling, (iii) membranes can be backflushed to remove solids from the membrane inside surface, thus extending the time between two chemical cleaning cycles, (iv) high membrane packing density resulting in high throughput, (v) modular in structure so that future extension of the plant becomes easier.

Spiral wound module

In spiral wound membrane, membrane is cast as a film onto flat sheet. Membranes are sandwiched together with feed spacers (typical thickness 0.03 to 0.1 inch) and permeate carrier. They are sealed at each edge and wound up around a perforated tube. The module diameter ranges from 2.5 to 18 inch and length varies from 30 to 60 inch.

Driving forces in membrane separation processes:

Separation in membrane is the result of differences in the transport rates of chemical species through it. Transport rate is determined by the driving force acting on individual components, their mobility, concentration of solute in membrane phase, etc.. Mobility : Depending on solute size and structure of membrane. Concentration : Chemical compatibility of solute & interface material.

Fouling of membrane:

Fouling of membrane is of two types reversible and irreversible.

Reversible fouling: It can be washed away by adopting an appropriate cleaning protocol, like membrane washing. After cleaning, membrane permeability is restored. Concentration polarization is reversible fouling.

Irreversible fouling: In this case, membrane pores are blocked permanently and they cannot be removed, even after proper washing. Permeability is lost permanently.

Fouling results in a continuous decline in membrane permeation rate, an increased rejection of low molecular weight solutes and eventually blocking of flow channels. On start-up of a process, a reduction in membrane permeation rate to 30–10 per cent of the pure water permeation rate after a few minutes of operation is common for ultrafiltration. Such a rapid decrease may be even more extreme for microfiltration. This is often followed by a more gradual decrease throughout processing. Fouling is partly due to blocking or reduction in effective diameter of membrane pores, and partly due to the formation of a slowly thickening layer on the membrane surface.

The extent of membrane fouling depends on the nature of the membrane used and on the properties of the process feed. The first means of control is therefore careful choice of membrane type. Secondly, a module design which provides suitable hydrodynamic conditions for the particular application should be chosen. Process feed pretreatment is also important. The type of pretreatment used in reverse osmosis for desalination applications . In biotechnological applications pretreatment might include prefiltration, pasteurisation to destroy bacteria, or adjustment of pH or ionic strength to prevent protein precipitation. When membrane fouling has occurred, backflushing of the membrane may substantially restore the permeation rate. This is seldom totally effective however, so that chemical cleaning is eventually required. This involves interruption of the separation process, and consequently time losses due to the extensive nature of cleaning required. Thus, a typical cleaning procedure might involve: flushing with filtered water at 35–50 .C to displace residual retentate; recirculation or back-flushing with a cleaning agent, possibly at elevated temperature; rinsing with water to remove the cleaning agent; sterilisation by recirculation of a solution of 50–100 ppm of chlorine for 10–30 minutes (600–1800s) at (293–303 K) (20–30 .C); and flushing with water to remove sterilising solution. More recent approaches to the control of membrane fouling include the use of more sophisticated hydrodynamic control effected by pulsated feed flows or non-planar membrane surfaces, and the application of further perturbations at the membrane surface, such as continuous or pulsated electric fields.

What is membrane?

A membrane may be defined as “an interphase separating two phases and selectively controlling the transport of materials between those phases”. A membrane is an interphase rather than an interface because it occupies a finite, though normally small, element of space.

What is mean by membrane separation?

The use of thin barriers (membranes) between miscible fluids for separating a mixture; a suitable driving force across the membrane, for example concentration or pressure differential, leads to preferential transport of one or more feed components.

Separations of liquids and gases are commonly accomplished using membrane separation methods which include dialysis, reverse osmosis, and ultrafiltration Hybrid and more exotic membrane methods that have also proven effective are electrodialysis, helium separation through glass, hydrogen separation through Palladium and alloy membranes, immobilized solvent and liquid-surfactant membranes.

Permeation of liquids and gases through polymeric membranes occurs where a constituent passes through the membrane by diffusion and sorption by the fluid on the other side of the membrane. The driving force is achieve either by pressure or concentration difference across the membrane.

Membranes modules can be configured in three ways

1. single stage feed and bleed
2. multistage feed and bleed
3. continuous single pass as shown in figures

Principle of Operation

When a solution and water are separated by a semi-permeable membrane, the water will move into the solution to equilibrate the system. This is known as osmotic pressure If a mechanical force is applied to exceed the osmotic pressure (up to 700 psi), the water is forced to move down the concentration gradient i.e. from low to high concentration. Permeate designates the liquid passing through the membrane, and retentate (concentrate) designates the fraction not passing through the membrane.

Advantage of membrane over other process

- A higher overall liquid removal rate is achieved by prevention of the formation of an extensive filter cake.
- The process feed remains in the form of mobile slurry suitable for further processing.
- The solids content of the product slurry may be varied over a wide range.
- It may be possible to fractionate particles of different sizes.

Limitation of membrane processes

The specification and the characteristics of the feed is important in membrane process, cleaning of membranes at regular interval is necessary, concentration polarization, membrane fouling are the two usual phenomena in membranes

Example for membrane separation process

Some of the membrane processes are dialysis, reverse osmosis, ultrafiltration, and electrodialysis.

Membrane materials for various application

Initially most of the membranes were cellulosic in nature. These are now being replaced by polyamide, polysulphone, polycarbonate and a number of other advanced polymers. These synthetic polymers have improved chemical stability and better resistance to microbial degradation. Membranes have most commonly been produced by a form of phase inversion known as immersion precipitation.

Uses of membrane separation

In general, membrane separation techniques are especially useful in separating:

- Mixtures of similar chemical compounds,
- Mixtures of thermally unstable components (since no heating is needed), and In conjunction with conventional separation methods (such as using membranes to break azeotropic mixtures before feeding them)
- proteins can be separated in whey for the production of whey protein concentrate (WPC)
- milk can be concentrated prior to cheese making at the farm level apple juice and wine can be clarified.
- waste treatment and product recovery is possible in edible oil, fat, potato, and fish processing
- fermentation broths can be clarified and separated
- whole egg and egg white ultrafiltration as a pre concentration prior to spray

Distinguish between osmosis & reverse osmosis

When two solutions of differing concentrations of dissolved materials are separated by a semi-permeable membrane, the liquid component will tend to flow from the lower to the more highly concentrated side. In a sense, the concentration difference will tend to equilibrate across the membrane. This process is called osmosis.

If the liquid on the more concentrated side is maintained at a higher pressure, however, this process can be reversed: the solvent will flow from the concentrated side to the less concentrated side. Since the membrane blocks the passage of the dissolved waste constituents, the concentrated solution becomes even more concentrated. This process is called reverse osmosis.

What is ultra-filtration?

Ultrafiltration (UF) is a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure.

Electro dialysis

A ionic mobility under the influence of an electric field through the anionic and cationic membranes is known as electrodialysis. Charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations. Electrodialysis membranes are comprised of polymer chains - styrene-divinyl benzene made anionic with quaternary ammonium groups and made cationic with sulphonic groups. 1-2V is then applied across each pair of membranes. Some applications are

- Cheese whey demineralization
- Brackish water desalination
- Nitrate removal for drinking water
- Food/sugar products desalting
- Tartaric wine stabilization
- NaCl removal from amino acid salts
- Acid removal from organic product
- Conversion of organic salts into acid and base
- Desalting of amines.
- De-acidification of fruit juices
- Metals removal from ethylene glycol

Ion exchange.

The ion exchange is the exchange of equivalent numbers of similarly charged ions, between an immobile phase, which may be a crystal lattice or a gel, and a liquid surrounding the immobile phase. If the exchanging ions are positively charged, the ion exchanger is termed cationic,and anionic if they are negatively charged. The rate at which ions diffuse between an exchanger and the liquid is determined, not only by the concentration differences in the two phases, but also by the necessity to maintain electroneutrality in both phases.

Ion exchange is not a membrane process but it is used for product of protein isolates of higher concentration than obtainable by membrane concentration. Fractionation may also be accomplished using ion exchange processing. It relies on inert resins (cellulose or silica based) that can adsorb charged particles at either end of the pH scale. The design can be a batch type, stirred tank or continuous column. The column is more suitable for selective fractionation. Whey protein isolate (WPI), with a 95% protein content, can be produced by this method. Following adsorption and draining of the deproteined whey, the pH or charge properties are altered and proteins are eluted. Protein is recovered from the dilute stream through UF and drying. Selective resins may be used for fractionated protein products or enriched in fraction allow tailoring of ingredients.

Application examples of ion exchange membrane

- Production of High Purity Chemicals
- Production of Ultra Pure Water
- Battery Diaphragm
- Recovered developing solution.
- Food and pharmaceutical
- Demineralization of Cheese Whey
- Demineralization of Organic Acids and Amino Acids
- Desalination of Soy-Sauce
- Stabilization of Wine
- Demineralization, Deacidification of Fruit Juice
- Demineralization of Natural Extract

<u>Environmental conservation</u>

- Desalination of Leachate
- Removal of Nitrate from Under-Ground Water

Others

- * Production of Salt from Sea water

- * Production of Drinking Water from Brackish Water

- * Desalination of Deep Sea Water

- * Acid Recovery from Waste Acid

- * Recovery of Valuable Metals

- * Recovery of Acid from Pickling Waste

Principles of ion exchange

The ion-exchange solids first used were porous, natural or synthetic minerals containing silica, the zeolites, such as the mineral Na20.AI20s.4Si02.2H20, for example. Positively charged ions (cations) of a solution which are capable of diffusing through 'the pores will exchange with the Na+ ions of such a mineral, and the latter is therefore called a cation exchanger. For example,

$$Ca^{++} + Na_2R \rightarrow CaR + 2Na^{+}$$

where R represents the residual material of the zeolite. In this manner "hard" water containing Ca^{++} may be softened by contact with the zeolite, the less objectionable Na+ replacing the C^{++} in solution and the latter becoming immobilized in the solid. The reaction is reversible, and after saturation with Ca^{++} the zeolite may be regenerated by contact with a solution of salt,

$$CaR + 2NaCl \rightarrow Na_2R + CaCl_2$$

Later certain carbonaceous cation exchangers were manufactured by treating substances such as coal with reagents such as fuming sulfuric acid, and the like. The resulting exchangers can be regenerated to a hydrogen form, HR, by treatment with acid rather than salt. Thus, hard water containing $Ca(HCO_3)_2$ would contain H_2CO_s after removal of the Ca^{++} by exchange, and since the carbonic acid is readily removed by degasification procedures, the total solids content of the water may be reduced in this manner. Early applications of ion exchangers using these principles were largely limited to water- softening problems.

synthetic, insoluble polymeric resins containing sulfonic, carboxylic, .or phenolic groups can be considered as consisting of an exceedingly large anion and a replaceable or exchangeable cation. These make exchanges of the following type possible,

$$Na^{+} + HR \leftrightarrow NaR + H^{+}$$

and different cations will exchange with the resin with different relative ease. The Na^+ immobilized in the resin may be exchanged with other cations or with H+, for example, much as one solute may replace another adsorbed upon a conventional adsorbent. Similarly synthetic, insoluble polymeric resins containing amine groups and anions may be used to exchange anions in solution. The mechanism of this action is evidently not so simple as in the case of the cation exchangers, but for present purposes it may be considered simply as an ion exchange. For example,

$$RNH_3OH + Cl^- \leftrightarrow RNH_3CI + OH^-$$

$$H^+ + OH^- \rightarrow H_20$$

where RNH_3 represents the immobile cationic portion of the resin. Such resins may be regenerated by contact with solutions of sodium carbonate or hydroxide. The synthetic ion-exchange resins are available in a variety of formulations of different exchange abilities, usually in the form of fine, granular solids or beads,]6 to 325 mesh. The individual beads are frequently nearly perfect spheres.

Ion exchange resins

Ion-exchange operations are essentially chemical reactions between an electrolyte in solution and an insoluble electrolyte with which the solution is contacted. The mechanisms of these reactions and the techniques used to bring them about resemble those of adsorption so closely that for most engineering purposes ion exchange may be simply considered as a special case of adsorption.

There are two general types of ion exchange resins: those that exchange positive ions, called cation resins, and those that exchange negative ions, called anion resins. A cation is an ion with a positive charge. Common cations include Ca , Mg , Fe, and H . A cation resin is one that exchanges positive ions. An anion is an ion with a negative charge. Common anions include Cl , SO , and OH . An anion resin is one that exchanges negative ions. Chemically, both types are similar and belong to a group of compounds called polymers, which are extremely large molecules that are formed by the combination of many molecules of one or two compounds in a repeating structure that produces long chains. A mixed-bed demineralizer is a vessel, usually with a volume of several cubic feet, that contains the resin. Physically, ion exchange resins are formed in the shape of very small beads, called resin beads, with an average diameter of about 0.005 millimeters. Wet resin has the appearance of damp, transparent, amber sand and is insoluble in water, acids, and bases. Retention elements or other suitable devices in the top and bottom have openings smaller than the diameter of the resin beads. The resin itself is a uniform mixture of cation and anion resins in a specific volume ratio depending on their specific gravities. The ratio is normally 2 parts cation resin to 3 parts anion resin. In some cases, there may be chemical bonds formed between individual chain molecules at various points along the chain.

Such polymers are said to be cross-linked. This type of polymer constitutes the basic structure of ion exchange resins. In particular, cross-linked polystyrene is the polymer commonly used in ion exchange resins. However, chemical treatment of polystyrene is required to give it ion exchange capability, and this treatment varies depending on whether the final product is to be an anion resin or a cation resin. All of the resin, except the exchangeable ion, is inert in the exchange process.

Osmosis And Reverse Osmosis

When two solutions of differing concentrations of dissolved materials are separated by a semi-permeable membrane, the liquid component will tend to flow from the lower to the more highly concentrated side. In a sense, the concentration difference will tend to equilibrate across the membrane. This process is called osmosis.

If the liquid on the more concentrated side is maintained at a higher pressure, however, this process can be reversed: the solvent will flow from the concentrated side to the less concentrated side. Since the membrane blocks the passage of the dissolved waste constituents, the concentrated solution becomes even more concentrated. This process is called reverse osmosis.

Reverse osmosis (RO) designates a membrane separation process, driven by a pressure gradient, in which the membrane separates the solvent (generally water) from other components of a solution. The membrane configuration is usually cross-flow. With reverse osmosis, the membrane pore size is very small allowing only small amounts of very low molecular weight solutes to pass through the membranes. It is a concentration process using a 100 MW cutoff, 700 psig, temperatures less than 40°C with cellulose acetate membranes and 70-80°C with composite membranes.

Reverse osmosis is often used to remove dissolved organics and metals where concentrations are less than 300 parts per million. However, special care and testing must be performed to assure that the wastes don't dissolve or clog the membrane. Low solubility salts are also prone to precipitate on the membrane surface.

Electrodialysis

Ions in aqueous solution can be separated using a direct current electrical driving force on an ion-selective membrane. Electrodialysis usually uses many thin compartments of solution separated by membranes that permit passage of either positive ions (cations) or negative ions (anions) and block passage of the oppositely charged ion.

Cation-exchange membranes are alternatively stacked with anion-exchange membranes placed between two electrodes. The solution to be treated is circulated through the compartments and a direct current power source is applied. All cations gravitate toward the cathode (negatively terminal) and transfer through one membrane,

while anions move in the opposite direction, thereby concentrating in alternative compartments.

Electrodialysis is commonly used to recover spent acid and metal salts from plating rinse. It obviously is not effective for non-polar solutions. Electrodialysis is used for demineralization of milk products and whey for infant formula and special dietary products. Also used for desalination of water.

Principles of operation:

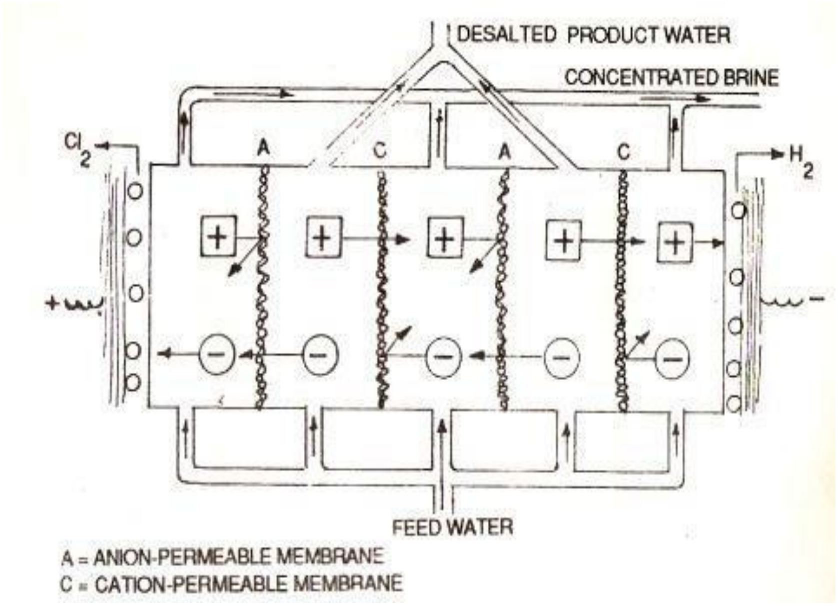
Under the influence of an electric field, ions move in an aqueous solution. The ionic mobility is directly proportioned to specific conductivity and inversely proportioned to number of molecules in solution. ~3-6 x 102 mm/sec.Charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations.Electrodialysis membranes are comprised of polymer chains - styrene-divinyl benzene made anionic with quaternary ammonium groups and made cationic with sulphonic groups. 1-2V is then applied across each pair of membranes.

Electrodialysis process:

Anion and cation exchange membranes are arranged alternately in parallel between an anode and a cathode (see schematic diagram). The distance between the membranes is 1mm or less.

APPLICATIONS OF ELECTRODIALYSIS:

- Cheese whey demineralization
- Brackish water desalination
- Nitrate removal for drinking water
- Food/sugar products desalting
- Tartaric wine stabilization
- NaCl removal from amino acid salts
- Acid removal from organic product
- Conversion of organic salts into acid and base (bipolar membrane ED)
- Desalting of amines.
- De-acidification of fruit juices
- Metals removal from ethylene glycol



Categories of membrane separation

Membrane separation processes are classified under different categories depending on the materials to be separated and the driving force applied:

(1) In ultrafiltration, liquids and low-molecular-weight dissolved species pass through porous membranes while colloidal particles and macromolecules are rejected. The driving force is a pressure difference.

(2) In dialysis, low-molecular-weight solutes and ions pass through while colloidal particles and solutes with molecular weights greater than 1000 are rejected under the conditions of a concentration difference across the membrane.

(3) In electrodialysis, ions pass through the membrane in preference to all other species, due to a voltage difference.

(4) In reverse osmosis, virtually all dissolved and suspended materials are rejected and the permeate is a liquid, typically water.

(5) For gas and liquid separations, unequal rates of transport can be obtained through nonporous membranes by means of a solution and diffusion mechanism. Pervaporation is a special case of this separation where the feed is in the liquid phase while the permeate, typically drawn under subatmospheric conditions, is in the vapor phase.

(6) In facilitated transport, separation is achieved by reversible chemical reaction in the membrane. High selectivity and permeation rate may be obtained because of the reaction scheme. Liquid membranes are used for this type of separation.

Ultrafiltration

Suspended materials and macromolecules can be separated from a waste stream using a membrane and pressure differential, called Ultrafiltration. This method uses a lower pressure differential than reverse osmosis and doesn't rely on overcoming osmotic effects. It is useful for dilute solutions of large polymerized macromolecules where the separation is roughly proportional to the pore size in the membrane selected. Ultrafiltration membranes are commercially fabricated in sheet, capillary and tubular forms. The liquid to be filtered is forced into the assemblage and dilute permeate passes perpendicularly through the membrane while concentrate passes out the end of the media. This may prove useful for the recovery and recycle of suspended solids and macromolecules.

Ultrafiltration (UF) designates a membrane separation process, driven by a pressure gradient, in which the membrane fractionates components of a liquid as a function of their solvated size and structure. The membrane configuration is usually cross-flow. In UF, the membrane pore size is larger allowing some components to pass through the pores with the water. It is a separation/ fractionation process using a 10,000 MW cutoff, 40 psig, and temperatures of 50-60°C with polysulfone membranes. In UF milk, lactose and minerals pass in a 50% separation ratio; for example, in the retentate would be 100% of fat, 100% of protein, 50% of lactose, and 50% of free minerals.

Excellent results have been achieved in textile finishing applications and other situations where neither entrained solids that could clog the filter nor dissolved ions that would pass through are present. Membrane life can also be affected by temperature, pH, and fouling.

Microfiltration (MF) designates a membrane separation process similar to UF but with even larger membrane pore size allowing particles in the range of 0.2 to 2 micrometers to pass through. The pressure used is generally lower than that of UF process. The membrane configuration is usually cross-flow. MF is used in the dairy industry for making low-heat sterile milk as proteins may pass through but bacteria do not. Please click above link for a schematic diagram of these membrane processes.

Uses of membrane separation

The use of thin barriers (membranes) between miscible fluids for separating a mixture; a suitable driving force across the membrane, for example concentration or pressure differential, leads to preferential transport of one or more feed components.

Separations of liquids and gases are commonly accomplished using membrane separation methods which include dialysis, reverse osmosis, and ultrafiltration Hybrid and more exotic membrane methods that have also proven effective are electrodialysis, helium separation through glass, hydrogen separation through Palladium and alloy membranes, immobilized solvent and liquid-surfactant membranes. Permeation of liquids and gases through polymeric membranes occurs where a constituent passes through the membrane by diffusion and sorption by the fluid on the other side of the membrane. The driving force is achieve either by pressure or concentration difference across the membrane.

In general, membrane separation techniques are especially useful in separating:

- Mixtures of similar chemical compounds,
- Mixtures of thermally unstable components (since no heating is needed), and In conjunction with conventional separation methods (such as using membranes to break azeotropic mixtures before feeding them)
- proteins can be separated in whey for the production of whey protein concentrate (WPC)
- milk can be concentrated prior to cheese making at the farm
- waste treatment and product recovery is possible in edible oil, fat, potato.