

CHEM: 602-Industrial Chemistry

CHEM – 602 Industrial Chemistry (Cr.03)

Chemical processes i.e. unit operations, unit process, Chemical process control and instrumentation, Safety; Hazards such as fire or toxic materials. Research and development, Important modern industries, their chemistry and technology, like pharmaceutical, polymer, paper, petroleum, oil, fats and waxes, water conditioning, flavors and food additives, sugar and starch, steel, soap and detergent etc.

Recommended Books

Kent, J.A. Riegel's Handbook of Industrial Chemistry, CBS Publishers and Distributors, New Delhi, (1997).

Smith, R., Chemical Process Design, McGraw Hill Book Co. New York, (1995).

Instructor : Prof. Dr. Ashraf Shaheen

Unit Process and Unit operation

Unit processes are also referred to as chemical conversions. In simple terms, the **process** which involves chemical changes are known as **Unit Processes**. Together with **unit operations** (physical conversions), **unit processes** (chemical conversions) form the basic building blocks of a chemical manufacturing **process**.

Define Unit Operation

In [chemical engineering](#) and related fields, a **unit operation** is a basic step in a [process](#). Unit operations involve bringing a physical change such as separation, crystallization, evaporation, filtration etc. For example, in milk processing, [homogenization](#), [pasteurization](#), chilling, and [packaging](#) are each unit operations which are connected to create the overall process. A process may have many unit operations to obtain the desired product.

UNIT OPERATIONS AND PROCESSES

- Waste water treatment is any operation / process or combinations of operations and processes that can reduce the objectionable properties of waste water and render it less dangerous.
- Waste water treatment is a combination of physical, chemical and biological processes.
- Methods of treatment in which application of physical forces predominate, are known as unit operations.
- Methods of treatment in which chemical or biological activities are involved , known as unit processes.

Difference between Unit operation and Unit process

- The chemical process is a combination of unit processes and Unit operation. Hence the Difference between Unit operation and Unit process as follows.

Unit process

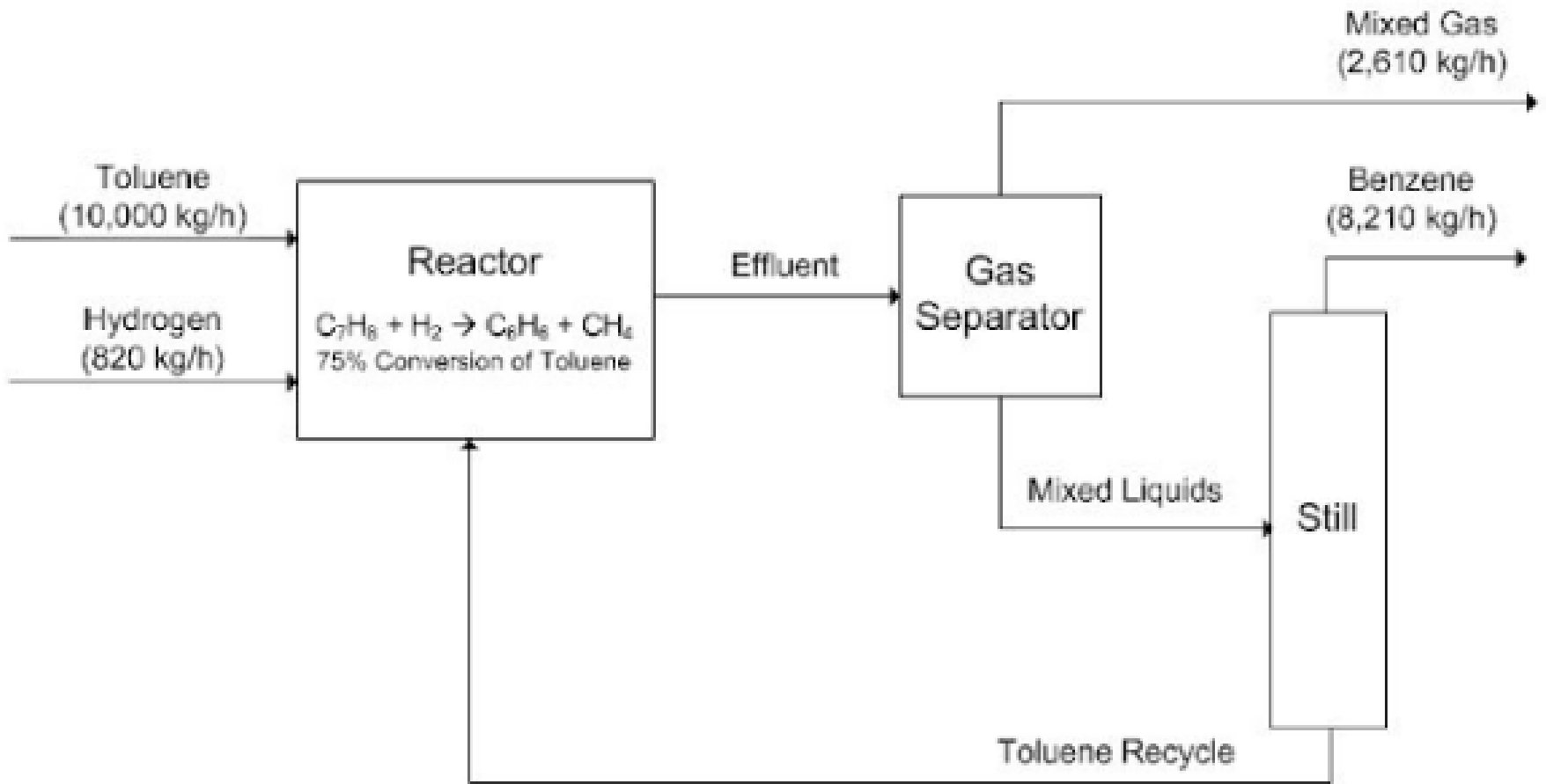
The unit process involves a chemical change or sometimes it referred to as chemical changes along with physical change leading to the synthesis of various useful product

- It also provides basic information regarding the reaction temperature and pressure, the extent of chemical conversions and yield of product of the reaction, nature of reaction whether endothermic or exothermic, type of catalyst used.
- Example: hydrogenation, oxidation, nitration, etc

Unit operations

The operations carried out in the chemical process industry involving physical changes in the materials handled or in the system under consideration are called Unit operations

- Hence unit operations involve the physical separation of the products obtained during various unit processes.
- It is very important in chemical industries for separation of various products formed during the reaction.
- Individual operations have common techniques and are based on the same principles.



Above figure shows the unit process flow diagram for the production of benzene from toluene via various unit operations which are carried out in reactor, gas separator and still

Types of unit operations are as follows

1. **Mechanical operations:**-Example:- size reduction, conveying, filtration
2. **Fluid flow operations:**- In these operations, pressure difference act as a driving force.
3. **Heat transfer:**- In these operations, temperature difference act as a driving force. Example:-
Evaporation
4. **Mass transfer:**- In these operations, the concentration difference act as a driving force. Example:-
Distillation

Table 1.2 Examples of unit operations

Agitation	Dispersion	Heat transfer
Atomization	Distillation	Humidification
Centrifuging	Evaporation	Mixing
Classification	Filtration	Pumping
Crushing	Flotation	Settling
Decanting	Gas absorption	Size reduction

Unit Process

we defined unit processes as chemical transformations or conversions. Unit processes are the core of industrial synthetic chemistry and are dominant in organic processes. We will look at some of the unit processes that we are likely to encounter in subsequent learning activities.

Unit Processes in Chemical Industry

Halogenation

A process that introduces one of the halogen atoms (F, Cl, Br and I) into an organic compounds is called halogenation. The chlorine derivatives primarily produced on an industrial scale because of greater economy in affecting their preparation. Bromine derivatives possessed certain pharmaceutical or dyeing properties and have certain advantages due to the greater ease of their preparation. The fluorine derivatives are well established in the field of refrigerants and aerosol propellants because of their stability and low boiling points.

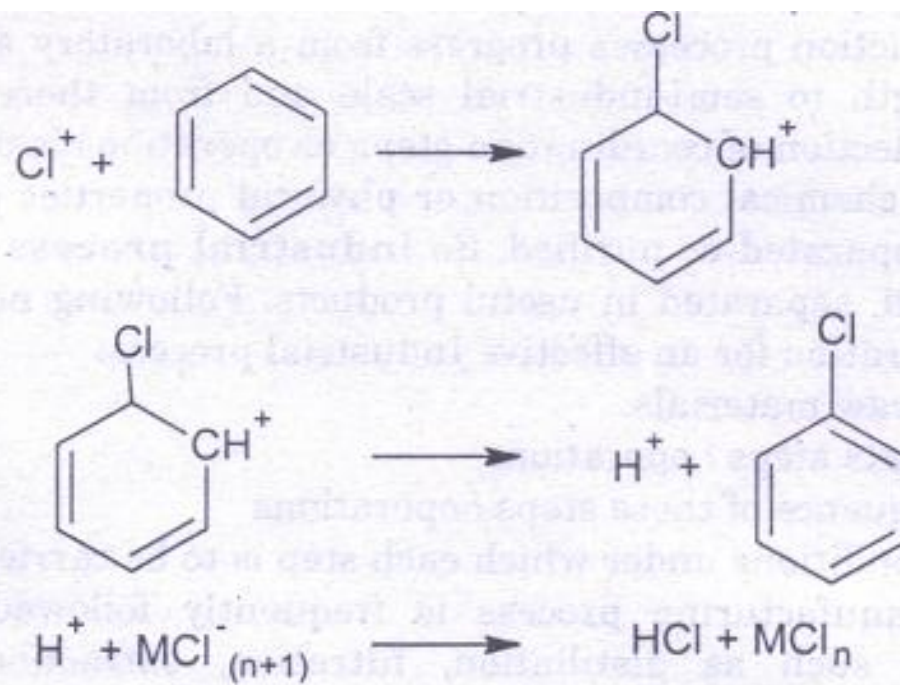
a) Substitution Procedure

In this procedure, a halogen atom replaces a hydrogen atom of an organic compound. This takes place usually at elevated temperature and is characterized by a free radical chain mechanism.



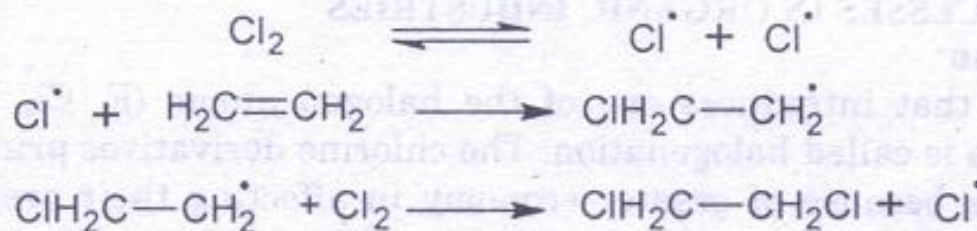
Chlorination in which carbon - carbon bonds are broken and carbon - hydrogen bonds are formed is characterized by a series of free radical reactions and usually take place at temperature greater than 500°C. Electrophilic aromatic substitution is performed with the aid of Friedel Crafts catalyst (halide salt of metal) to give halo - aromatic compounds. Metal halides are electron deficient and act as a Lewis acids.



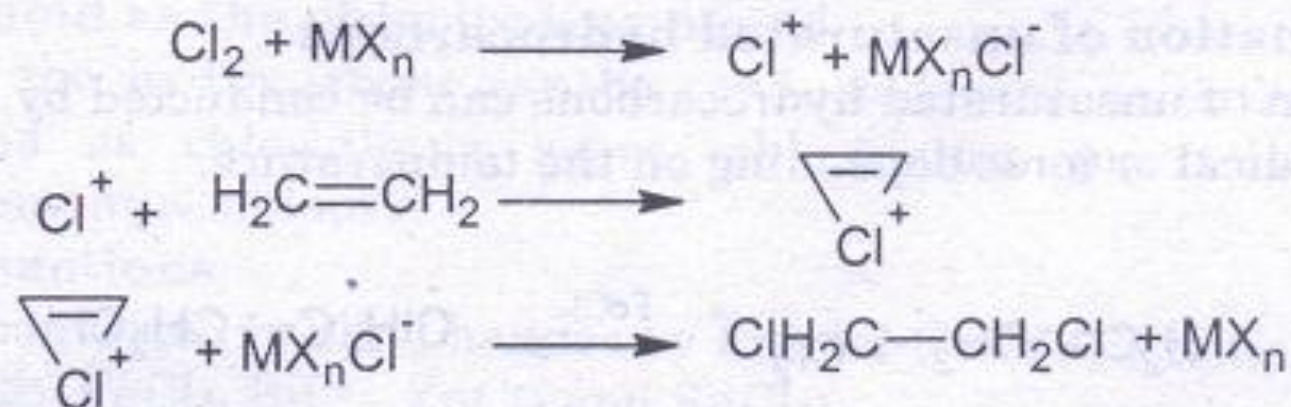


b) Addition Procedure

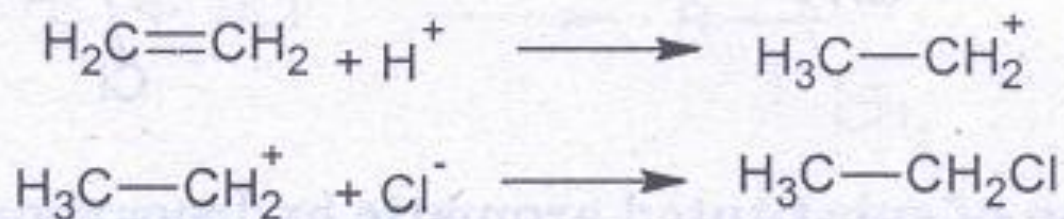
Addition of a halogen atom to an organic compound can be ionic or free radical, depending on the conditions of the reaction and particularly on the catalyst involved.



The free radical addition is a chain reaction.

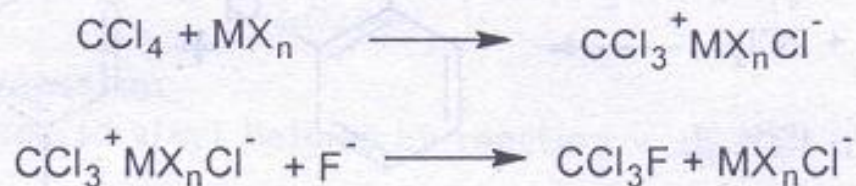


An ionic process carries out hydro chlorination.

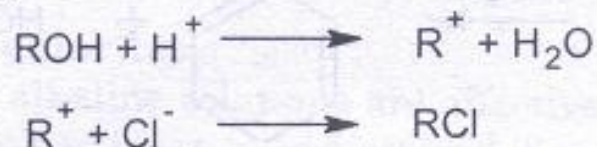


c) Replacement of groups

Halogen atom can replace certain groups such as hydroxyl or sulfonic acid group or one halogen atom can replace the other halogen atom. The replacement reaction (ionic replacement) is thought to be proceeding through ion formation. Chlorine can be replaced by fluorine. A carbonium ion is generated in the presence of a halide ion; the alkyl halide will be formed.



In case of alcohols, a strong mineral acid or a metal halide generates a carbonium ion and forms an alkyl halide.



Preparation of Chlorobenzene

Background

Monochlorobenzene is an important derivative of benzene which acts as a precursor to such chemicals as nitrochlorobenzenes and phenols. Even though the use of monochlorobenzene in agrochemicals is declining due to environmental concerns and its carcinogenic nature, it enjoys wide applications in rubber, plastics, pharmaceuticals, dyes and pigments.[1]

Controlled chlorination of benzene with chlorine in liquid phase in 20-40 deg. C gives selective conversion to monochlorobenzene in presence of a suitable metal catalyst. Commonly, Ferric Chloride and Iron raschig rings are used as the catalyst. In that case, the reported conversion (per-pass) is 75% monochlorobenzene and 22% dichlorobenzene with para and ortho derivatives in the ratio 3:2.[2] This information is used in the conversion reactor data. NRTL is the most preferred thermodynamic model used in the flowsheet.

Process Description

Dry Benzene (S-01) and Chlorine (S-02) feeds along with the recycle feed (S-07) are mixed in M-01 and heated to the reactor temperature in HE-01. They are fed to a chlorinator reactor (RC-01) which operates at 40 deg. C and maintained at atmospheric pressure. The product mixture leaving the reactor is flashed into a vapour stream (S-06) rich in hydrochloric acid (94% mol) and a liquid stream (S-05) rich in monochlorobenzene. Hydrochloric acid from S-06 is recovered with the help of a suitable solvent in an absorber and that from S-05 is scrubbed in another tower SC-01.

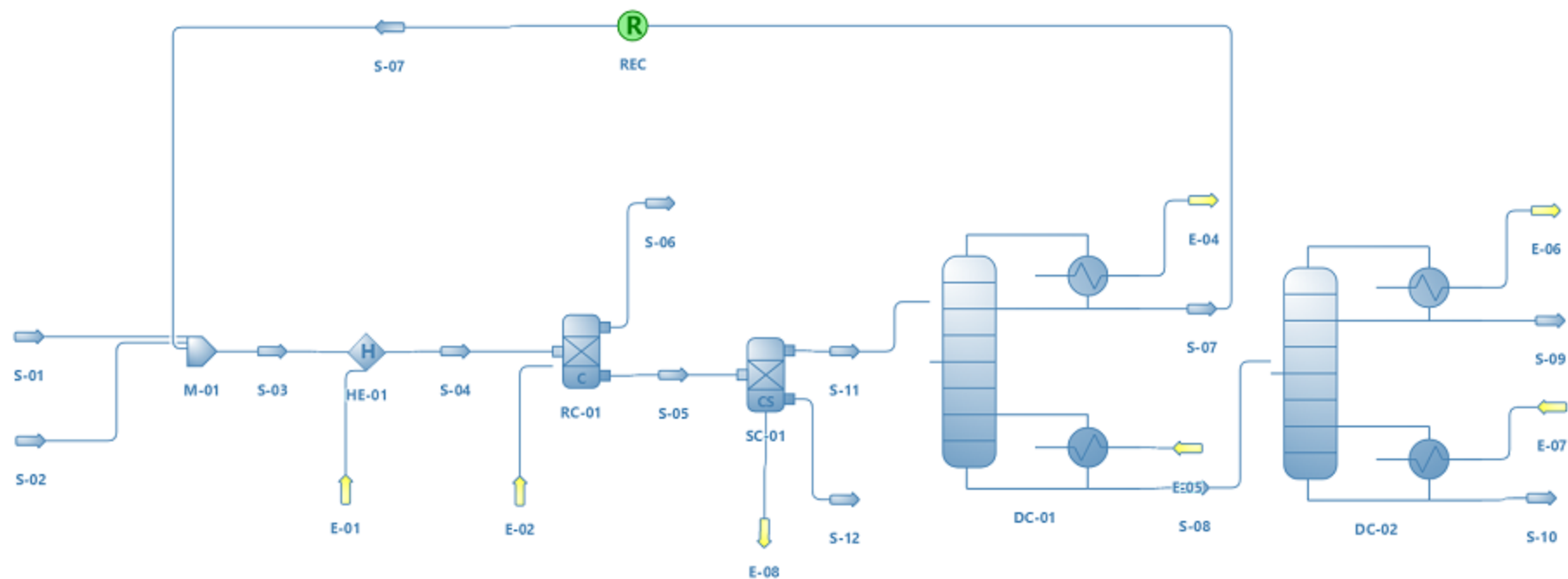


Figure 1: Flowsheet for Production of Chlorobenzene from Benzene and Chlorine

The liquid stream (S-11) leaving SC-01 is sent to benzene recovery column (DC-01) operated at atmospheric pressure where 99% of unreacted benzene is recovered in the distillate and recycled back to the chlorinator feed. The bottoms of DC-01 (S-08) are fed to chlorobenzene column (DC-02) operated at atmospheric pressure where at least 94% pure monochlorobenzene is recovered in the distillate (S-09). The bottoms (S-10) contain a mixture of dichlorobenzenes which is either subjected to higher degree of chlorination or purified depending on the process requirements.

Method

The chlorination of benzene is carried out in tall narrow iron vessels, jacketed or surface cooled to the desired operating temperature. The chlorinator is provided with a flux condenser and may have external circulation through a cooler. Ferric chloride is generally employed as catalyst. The isomeric *ortho* and *para*-dichlorobenzene accompany the principal monochloro compound. The reaction rate of benzene to chlorobenzene is approximately 8.5 times greater than for chlorobenzene to dichlorobenzene.

Dried benzene is charged to the chlorinator along with a small quantity of anhydrous ferric chloride 0.1-0.5% chlorine is bubbled into the charge through an iron distributor pipe near the base of the reactor. The chlorine feed is so controlled to keep the temperature at 55-60°C. When the density of the reaction mixture is reached at 1.28 at 15°C the current of chlorine is stopped. HCl escapes through a vent in the condensing system.

The chlorobenzene is allowed to settle and is then drawn off from a side outlet and delivered to the neutralizer. The neutralizer is a vertical steel tank occupied with a reflux condenser and a vent. The solution of caustic soda is mixed with chlorobenzene. The mixture is thoroughly agitated and charge is kept warm during this operation. When the chlorobenzene indicates a faintly alkaline, the charge is delivered to the settling tank. The charge is allowed to settle for several hours. The sludge settle out at conical base is rich in dichlorobenzene. The chlorobenzene is withdrawn through a side outlet and pumped to a storage tank that is heated to prevent crystallization of the charge.

Steam coils heat the chlorinated benzene and the vapors are drawn through a tall column to the condenser by a vacuum pump. The first fraction is benzene and water. Second fraction is impure chlorobenzene, which is recycled with the batch to be distilled. The chlorobenzene fraction is run into the separate container. The presence of *para*-dichlorobenzene in the distillate is indicated by the sudden increase in the density. The residue is principally dichlorobenzene.

For the separation of isomers of dichlorobenzene, the bottoms of the distillation column are run to a cast iron tank at 50°C and allowed to crystallize.

- The usual method is to treat the eutectic mixture at 20-25 °C. *P*-isomer is solid while *o*-isomer is oil.
- The mixture is treated with chlorosulfonic acid below 15 °C; the *o*-isomer is attacked with the formation of a sulfonyl chloride.
- The usual method for separation is sweating treatment. It involves the solidification of the mixture by cooling and then it is warmed slowly to temperature at which one or more constituents liquefy and filtered off which is predominantly *o*-isomer.

The crystals of the crude *p*-dichlorobenzene are melted and fractionally recrystallized to desired monoclinic form. The mother liquor, which is predominantly *o*-dichlorobenzene, is fractionated under vacuum.

Polymerisation

The term polymer comes from two Greek words: “polys” which means “many” and “meros” which means “parts.” A polymer is therefore a substance having hundreds or thousands of many small identical parts known as monomers, which are bonded together covalently in a chemical process known as polymerization.

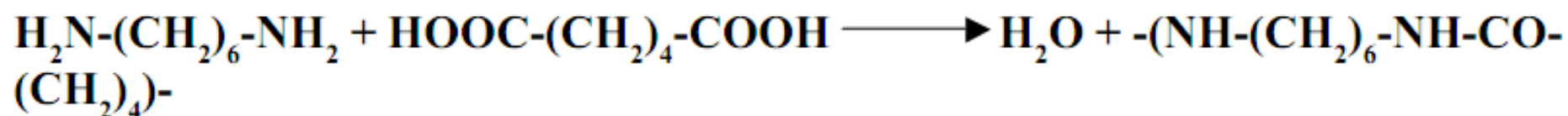
Polymerization reactions

For polymerisation to yield polymers with long chain (high polymers), the monomers must:

- Be polyfunctional i.e. contain at least two reactive groups
- Not give cyclic products by intramolecular ring closure because this will terminate polymerisation.

Polymerization reactions fall into two general classes:

1. Addition or chain polymerization involving successive stages of reaction **initiation, propagation** and **termination**. Examples of addition polymers include polyethylene, polypropylene, polyvinyl chloride and polystyrene.
2. Condensation or step-reaction polymerization. This involves condensation reaction between two polyfunctional molecules, sometimes with the elimination of a small molecule such as water. Nylon is a condensation polymer of hexamethylene diamine and adipic acid as shown in the equation below:



If one of the reactants in a step-reaction polymerization contain more than two functional groups, a cross-linked polymer is obtained.

Free radical polymerization

One of the most common and useful reactions for making polymers is free radical polymerization. It is used to make polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds. Polymers made by free radical polymerization include polystyrene, polymethylmethacrylate, polyvinyl acetate and branched polyethylene

Initiation: The whole process starts off with a molecule called an initiator. This is a molecule like benzoyl peroxide or 2,2'-azo-bis-isobutyronitrile (AIBN). The special characteristic of these molecules is that they have an ability to split in unusual way. When they split, the pair of electrons in the bond, which is broken, separates to produce two initiator fragments, each of which has one unpaired electron. Molecules like this, with unpaired electrons are called *free radicals*

The carbon-carbon double bond in a vinyl monomer, like ethylene, has a pair of electrons, which is very easily attacked by the free radical. When this happens, a new chemical bond is formed between the initiator fragment and one of the double bond carbons of the monomer molecule. This electron, having nowhere else to go, associates itself with the carbon atom, which is not bonded to the initiator fragment. This whole process, the breakdown of the initiator molecule to form radicals, followed by the radical's reaction with a monomer molecule is called the *initiation* step of the polymerization.

Propagation: This new radical reacts with another ethylene molecule in the exact same way as the initiator fragment did. A free radical is formed when this reaction takes place over and over again and the chain grows. The adding of more and more monomer molecules to the growing chain is called *propagation*.

Because we keep remaking the radical, we can keep adding more and more ethylene molecules, and build a long chain. Self-perpetuating reactions like this are called *chain reactions*.

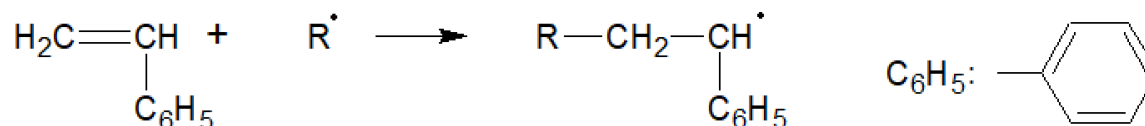
Termination: Termination is the third and final step of a chain-growth polymerization. Free radicals are unstable, and eventually they find a way to become paired without generating a new radical. Then the chain reaction will grind to a halt. This happens in several ways. The simplest way is for two growing chain ends to find each other. The two unpaired electrons then join to form a pair, and a new chemical bond joining their respective chains. This is called *coupling*. Coupling is one of two main types of *termination reaction*. Another way in which the unpaired electrons can shut down polymerization is called *disproportionation*. In disproportionation, the unpaired electron of one chain finds an electron in the carbon-hydrogen bond of the next carbon atom forming a double bond at the end of the polymer chain.

Sometimes, the unpaired electron at the end of a growing chain pairs with an electron from a carbon-hydrogen bond along the backbone of another polymer chain. This starts a new chain growing out of the middle of the main chain. This is called *chain transfer to polymer*, and the result is a *branched polymer*. It is especially a problem with polyethylene, so much that linear non-branched polyethylene cannot be made by free radical polymerization.

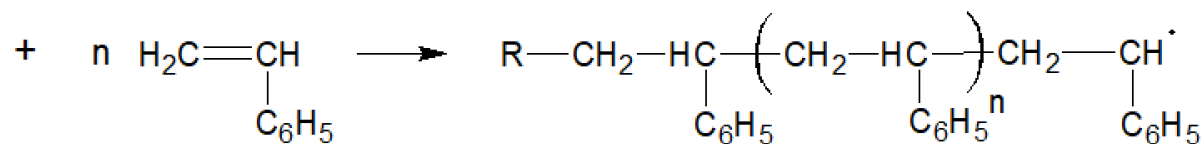
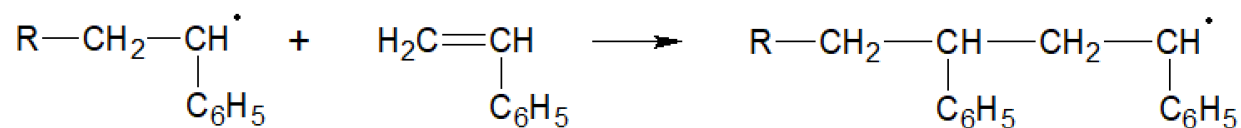
Polymerisation products are numerous with many uses and include phenolic resins, alkyl resins, polyamides, polyesters, elastic foams, silicon polymers, isocyanate polymers, epoxy resins, adhesives, coatings, polyethylene, vinyl polymers and acrylic polymers (for paint industry) to mention but a few.

Mechanism

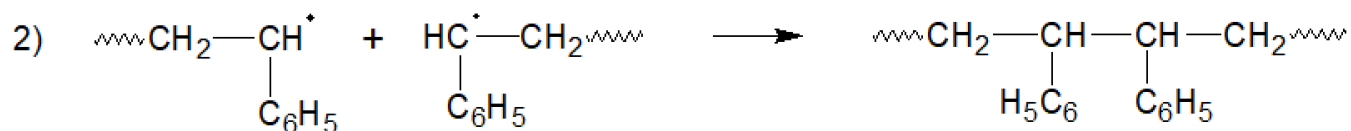
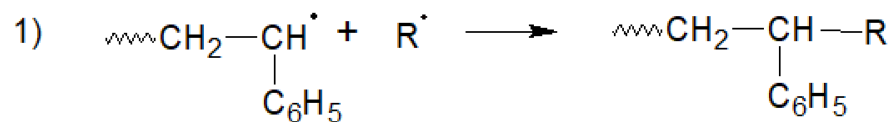
a) Initiation



b) Propagation



c) Termination

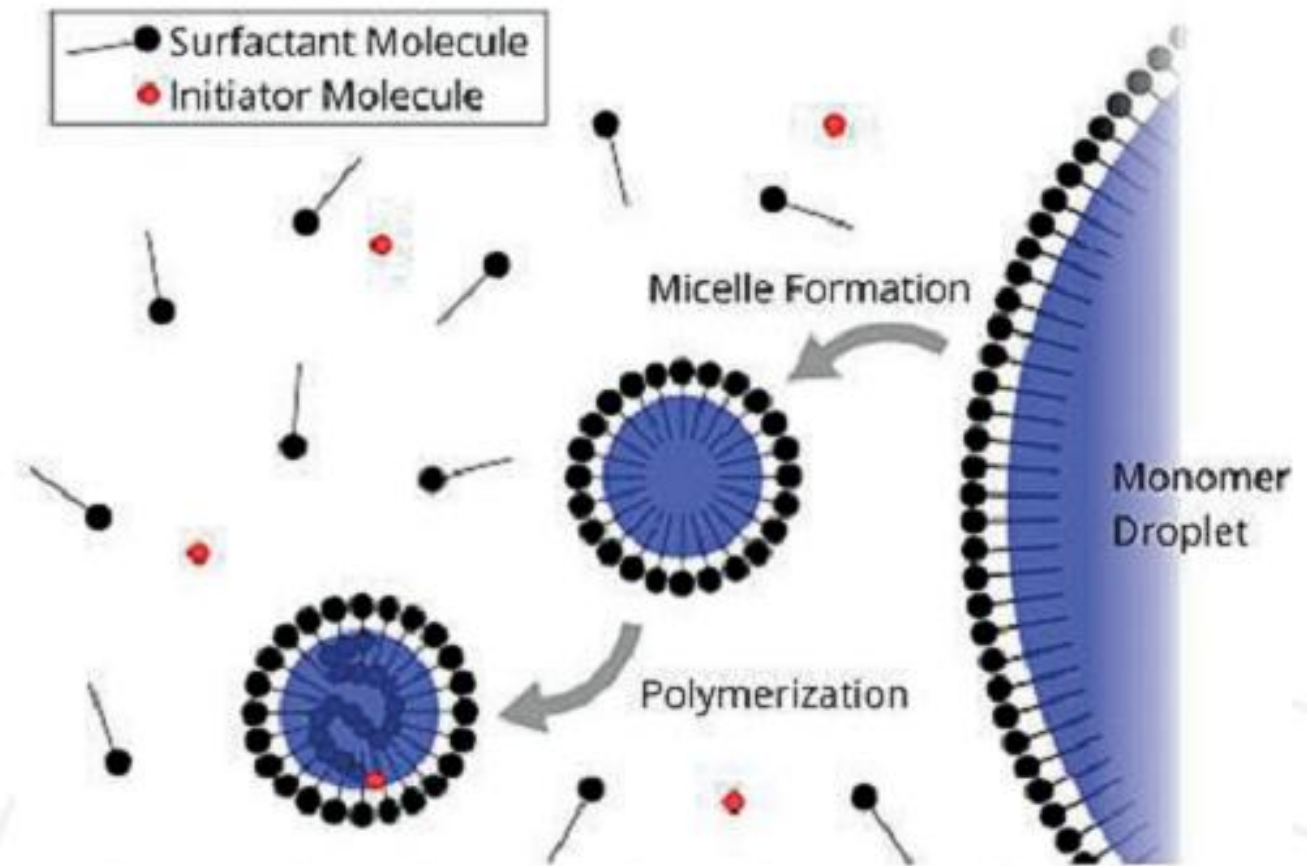


Emulsion polymerization

Emulsion polymerization is a type of free radical polymerization that usually starts with an emulsion consisting of water, monomer and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous water phase. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl celluloses, can also be used to act as emulsifiers/stabilizers. Emulsion polymerization is used to manufacture several commercially important polymers. Many of these polymers are used as solid materials and must be isolated from the aqueous dispersion after polymerization. In other cases, the dispersion itself is the end product. A dispersion resulting from emulsion polymerization is often called a latex (especially if derived from a synthetic rubber) or an emulsion (even though “emulsion” strictly speaking refers to a dispersion of a liquid in water). These emulsions find applications in adhesives, paints, paper and textile coatings. Because they are not solvent-based, they are eco-friendly.

Emulsion polymerization is a unique process involves emulsification of hydrophobic monomers by oil-in water emulsifier, then reaction initiation with either a water soluble initiator (e.g. potassium persulfate ($K_2S_2O_8$) or an oil-soluble initiator (e.g. 2,2-azobisisobutyronitrile (AIBN)) [1, 2] in the presence of stabilizer which may be ionic, nonionic or protective colloid to disperse hydrophobic monomer through aqueous solution [3, 4]. Typical polymerization monomers involve vinyl monomers of the structure ($CH_2=CH-$). These emulsion polymers find a wide range of applications such as synthetic rubbers, thermoplastics, coatings, adhesives, binders, rheological modifiers, plastic pigments [1]. Emulsion polymerization is a rather complex process because nucleation, growth and stabilization of polymer particles are controlled by the free radical polymerization mechanisms in combination with various colloidal phenomena [1]. Aside from other polymerization techniques, emulsion polymerization affords increasing molecular weight of the formed latexes through decreasing polymerization rate by either decreasing initiator concentration or lowering reaction temperature [5, 6].

Systems of emulsion polymerization involve (1) conventional emulsion polymerization, in which a hydrophobic monomer emulsified in water and polymerization initiated with a water-soluble initiator [5]. (2) Inverse emulsion polymerization [7], where organic solvents of very low polarity as paraffin or xylene used as a polymerization media to emulsify hydrophilic monomers [5], then initiation proceed with the aid of hydrophobic initiator [5]. These two polymerization types known as oil-in-water (o/w) and water-in-oil (w/o) emulsions [5]. (3) Mini emulsion polymerization involves systems with monomer droplets in water with much smaller droplets than in emulsion polymerization and characterized by monomer droplet = 50–1000 nm, surfactant concentration < critical micelle concentration (CMC), water insoluble co stabilizer as hexadecane to prevent Ostwald ripening, polymer particle size equal monomer droplet size = 50–1000 nm, and both water soluble and oil soluble initiator used [4, 8]. (4) Microemulsion polymerization with very much smaller monomer droplets, about 10–100 nm, and characterized by surfactant concentration > CMC, polymer particles = 10–50 nm, water-soluble initiator are commonly used [9, 10]. Miniemulsion, microemulsion and conventional emulsion polymerizations show quite different particle nucleation and growth mechanisms and kinetics [1]. Many articles discuss different types of emulsion polymerization found in literature [1, 11–16].



Schematic representation of emulsion polymerization.

Advantages of emulsion polymerization include:

- High molecular weight polymers can be made at fast polymerization rates
- The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the system, allowing many reaction methods to increase their rate.
- Since polymer molecules are contained within the particles, viscosity remains close to that of water and is not dependent on molecular weight
- The final product can be used as is and does not generally need to be altered or processed.

Disadvantages of emulsion polymerization include:

- Surfactants and other polymerization adjuvants remain in the polymer or are difficult to remove
- For dry (isolated) polymers, water removal is an energy-intensive process

Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer

The Smith-Ewart-Harkins theory for the mechanism of free-radical emulsion polymerization is summarized by the following steps:

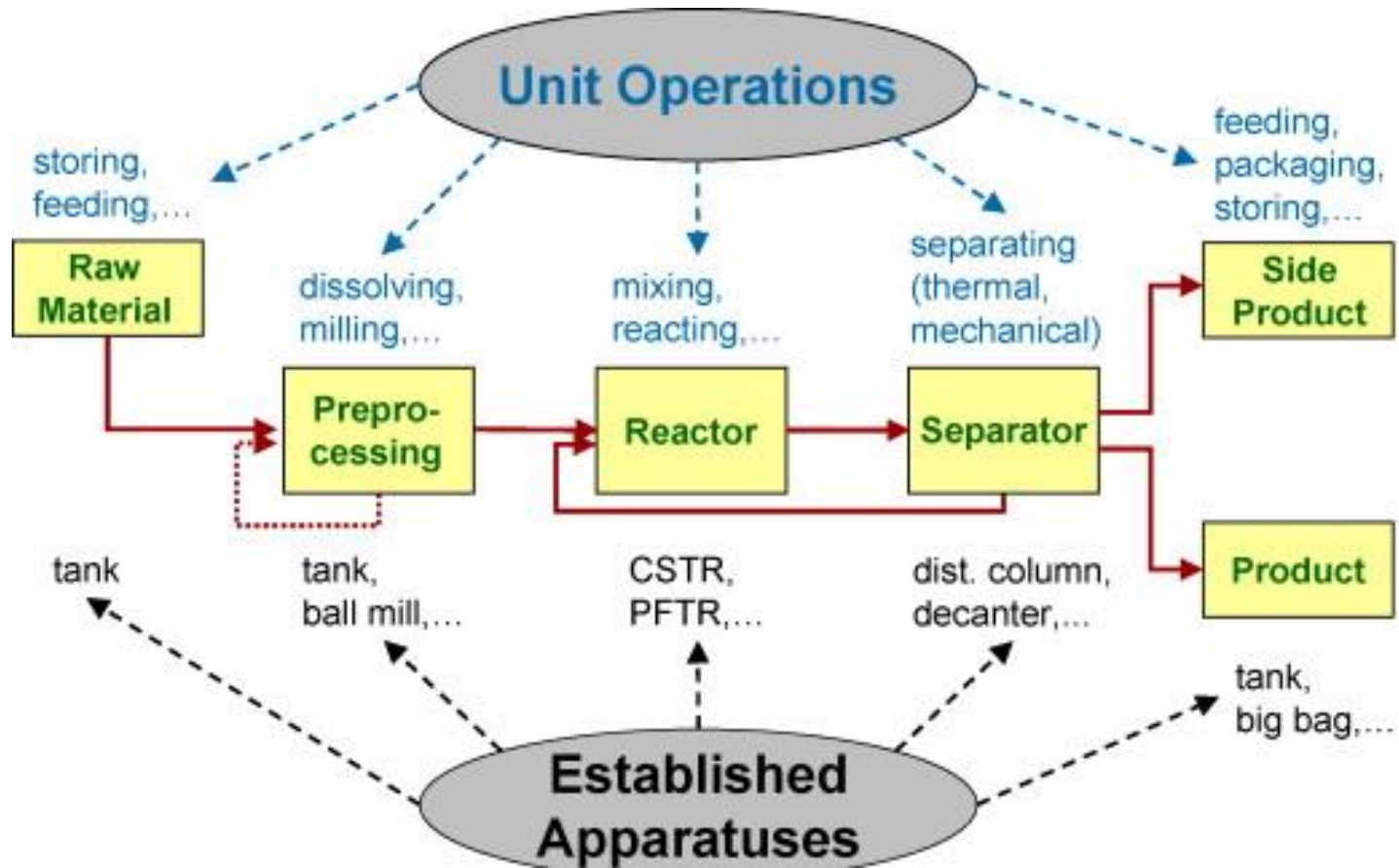
- A monomer is dispersed or emulsified in a solution of surfactant and water forming relatively large droplets of monomer in water.
- Excess surfactant creates micelles in the water.
- Small amounts of monomer diffuse through the water to the micelle.
- A water-soluble initiator is introduced into the water phase where it reacts with monomer in the micelles. This is considered Smith-Ewart Interval 1.
- The total surface area of the micelles is much greater than the total surface area of the fewer, larger monomer droplets; therefore the initiator typically reacts in the micelle and not the monomer droplet.
- Monomer in the micelle quickly polymerizes and the growing chain terminates. At this point the monomer-swollen micelle has turned into a polymer particle. When both monomer droplets and polymer particles are present in the system, this is considered Smith-Ewart Interval 2.

- More monomer from the droplets diffuses to the growing particle, where more initiators will eventually react.
- Eventually the free monomer droplets disappear and all remaining monomer is located in the particles. This is considered Smith-Ewart Interval 3.
- Depending on the particular product and monomer, additional monomer and initiator may be continuously and slowly added to maintain their levels in the system as the particles grow.
- The final product is a dispersion of polymer particles in water. It can also be known as a polymer colloid, a latex, or commonly and inaccurately as an 'emulsion'.

Emulsion polymerizations have been used in batch, semi-batch, and continuous processes. The choice depends on the properties desired in the final polymer or dispersion and on the economics of the product.

Unit Operations

we defined unit operations as physical transformations. They are very many and include size reduction, size enlargement and separation of mixtures. In this unit, we shall look at operation principles of equipment in these unit operations and their application in the chemical industry.



Size Reduction

Size reduction refers to all the ways in which particles are cut or broken into smaller pieces. The objective is to produce small particles from big ones for any of the following reasons:

1. To reduce chunks of raw materials to workable sizes e.g. crushing of mineral ore.
2. To increase the reactivity of materials by increasing the surface area.
3. To release valuable substances so that they can be separated from unwanted material.
4. To reduce the bulk of fibrous materials for easier handling.
5. To meet standard specifications on size and shape.
6. To increase particles in number for the purpose of selling.
7. To improve blending efficiency of formulations, composites e.g. insecticides, dyes, paints

Principle of Size Reduction

Most size reduction machines are based on mechanical compression or impact.

When a solid is held between two planes and pressure is applied on one plane, the solid is fractured and breaks into fragments when pressure is removed. The fragments formed are of different sizes. An example of an industrial equipment that is based on compression is a jaw crusher. Impact is the breaking up of material when it is hit by an object moving at high speed. The product contain coarse and fine particles. A ball mill is based on impact.

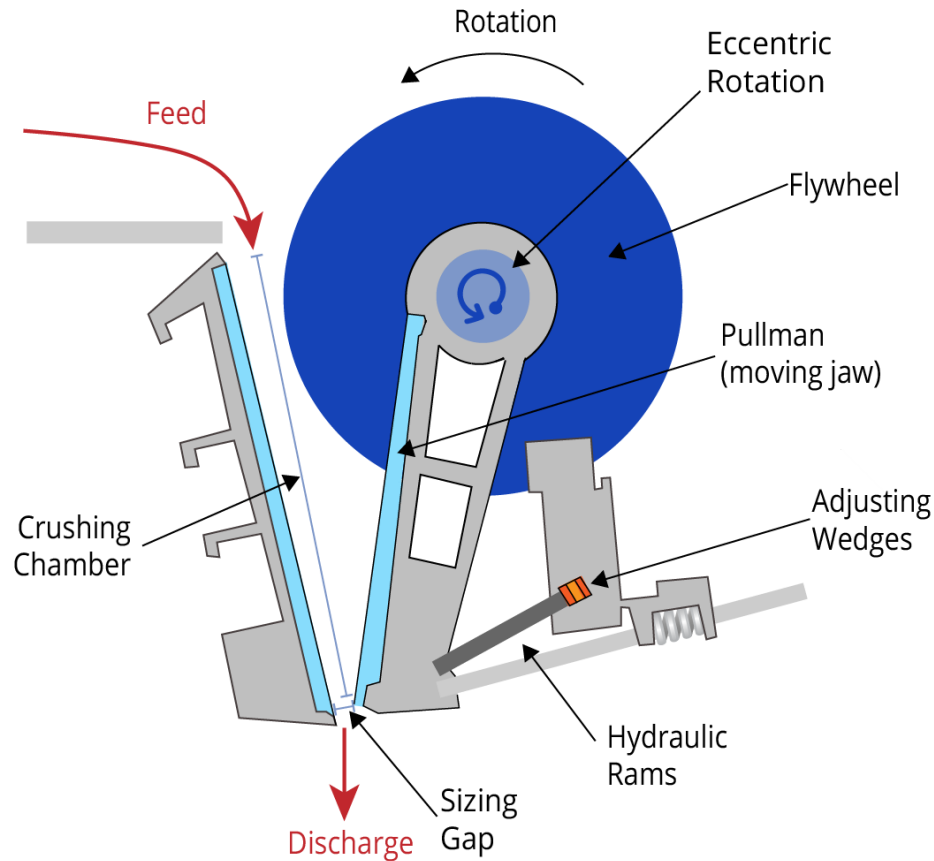
Jaw Crusher

A jaw crusher consists of a vertical fixed jaw and another swinging jaw that moves in the horizontal plane. The two jaws make $20-30^\circ$ angle between them. The swinging jaw closes about 250 to 400 times/min. Feed is admitted between the jaws. It is crushed several times between the jaws before it is discharged at the bottom opening. A jaw crusher produces a coarse product.

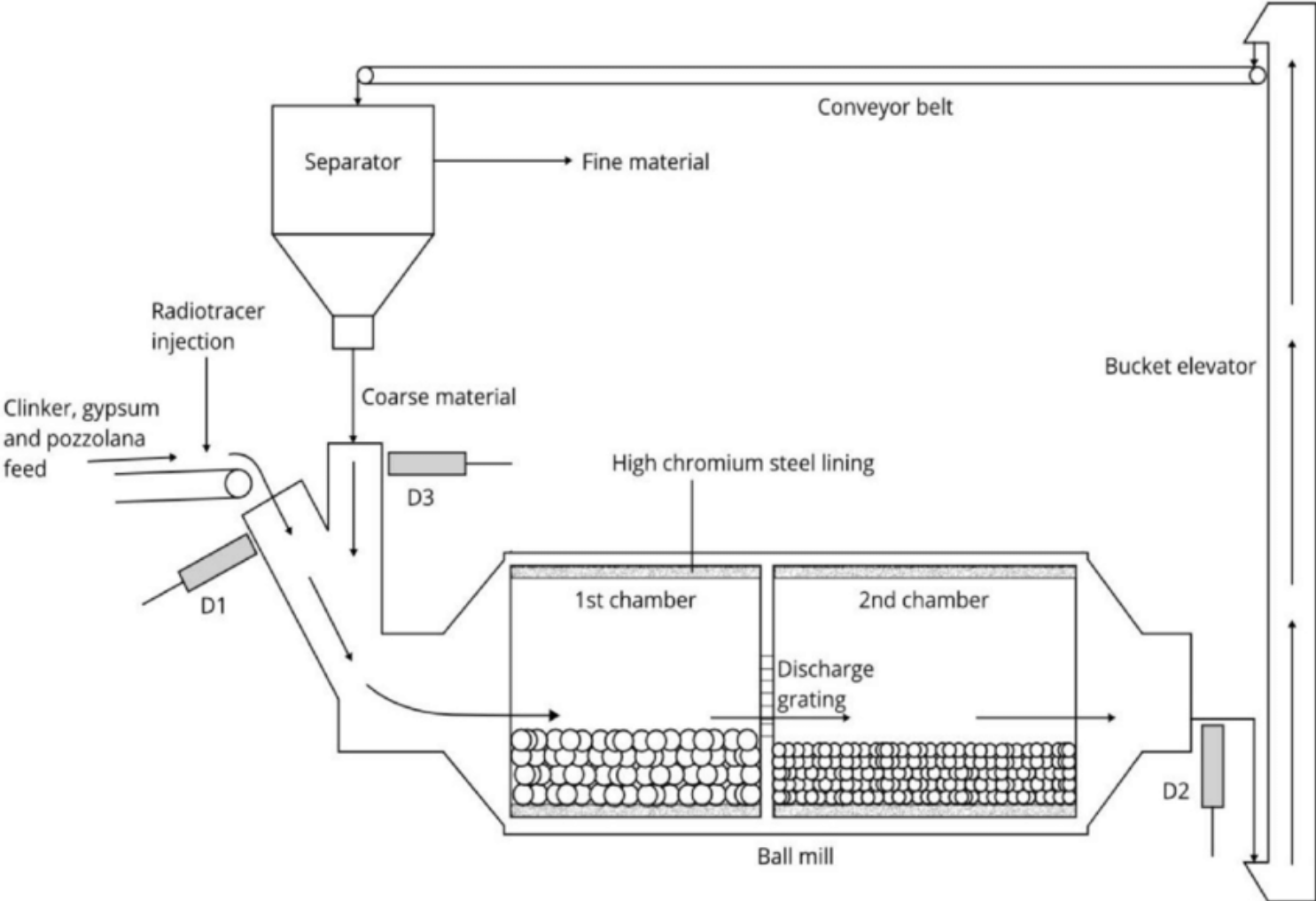
Jaw Crusher

A jaw crusher consists of a vertical fixed jaw and another swinging jaw that moves in the horizontal plane. The two jaws make 20-30° angle between them. The swinging jaw closes about 250 to 400 times/min. Feed is admitted between the jaws. It is crushed several times between the jaws before it is discharged at the bottom opening.

A jaw crusher produces a coarse product.



A Ball Mill



Construction

- ▶ Ball mill consist of a hollow cylindrical shell rotating about its axis.
- ▶ Axis of the shell horizontal or at small angle to the horizontal
- ▶ It is partially filled with balls made up of Steel,Stainless steel or rubber
- ▶ Inner surface of the shell is lined with abrasion resistant materials such as Manganese,Steel or rubber
- ▶ Length of the mill is approximately equal to its diameter
- ▶ Balls occupy about 30–50% of the volume.dia of the ball 12 mm–125 mm
- ▶ Shell is rotated through a drive gear (60–100 rpm) and large mills, shell might be in 3m in dia and 4.25 m in length.
- ▶ Operation may be batch or continuous,wet or dry...in a continuously operated ball mill outlet is normally covered with coarse screen to prevent the escape of the balls..



A ball mill is a tumbling mill generally used for previously crushed materials. It is generally used to grind material 6mm and finer, down to a particle size of 20 to 75 microns.

A ball mill is a type of grinder used to grind and blend bulk material into nanosize using different sized balls. The working principle is simple; impact and attrition size reduction take place as the ball drops from near the top of a rotating hollow cylindrical shell.

The operation of a ball mill is illustrated in Fig. 1. The mill consists of a cylinder containing a mixture of large and small steel grinding balls and the feed. When the cylinder is rotated, the rotation causes the balls to fall back into the cylinder and onto the material to be ground. The rotation is usually between 4 to 20 revolutions per minute, depending on the diameter of the mill. The larger the diameter, the slower the rotation. If the speed of the mill is too great, it begins to act like a centrifuge and the balls do not fall back, but stay on the perimeter of the mill. The point where the mill becomes a centrifuge is called the critical speed. Ball mills usually operate at 65% to 75% of the critical speed.

A ball mill is suitable for dry- or wet- milling of various material in cement, fertilizer, metallurgical industries and other industries.

Working of Ball Mill

- ▶ Material to be ground is fed from the left through a 60° cone and product is discharged through a 30° cone to the right.
- ▶ As the shell rotates the balls are lifted up on the rising side of the shell and they cascade down from near the top of the shell
- ▶ The solid particles in between balls are ground and reduced in size by impact.
- ▶ As the shell rotates the large balls segregate near the feed end and small balls segregate near the product end
- ▶ If the rate of feed is increased, coarser product will be obtained and if the speed of rotation is increased the fineness for a given capacity increases.

- ▶ During grinding, balls themselves wear and are continuously replaced by new ones so that mill contains balls of various ages and thus of various sizes
- ▶ Ball mill produces 1 to 50 ton/hr of powder of which 70 to 90 % will pass through a 200 mesh screen and energy requirement of the ball mill is about 16 kwh/ton
- ▶ In case of a batch operated mill a measured quantity of a solid to be ground is charged to the mill through the opening in the shell. The opening is closed and the mill is rotated for several hours. It is then stopped and the product is discharged

Applications

- ▶ The ball mill is used for grinding materials such as coal, pigments, and feldspar for pottery.

Grinding can be carried out in either wet or dry but the former is carried out at low speeds.

The advantages of wet grinding are less power consumption, increased capacity, no dust formation etc...

Dis advantages are high wear on the grinding medium and necessity to dry the product

Advantages of Ball Mill

- ▶ The cost of installation is low
- ▶ The cost of Production is low
- ▶ It is suitable for materials of all degree of hardness
- ▶ The grinding Medium is cheap
- ▶ Used for the grinding of explosive materials
- ▶ Suitable for both batch & continuous operations



Photograph of a ball mill in a Cement Plant.

Evaporation

It is a thermal separation or thermal concentration process. Evaporation refers to the process of heating liquid to the boiling point to remove solvent as vapor. It starts with a liquid product and ends up with a more concentrated but still liquid and pump able thick liquor as the main product and vapors are condensed and discarded. There are very few cases where the evaporated, volatile component is the main product.

“Evaporation is the process of removal of volatile solvent (mostly water) by vaporization, from an aqueous solution, suspension or emulsion consisting of non-volatile solute.”

Requirements

- Humidity of the atmosphere be less than the evaporating surface (100% relative humidity, there is no more evaporation).
- Requires a large amount of energy e.g. evaporation of one gram of water at a temperature of 100°C requires 540 calories of heat energy (600 calories at 0°C).
- The product is subjected to minimal thermal degradation.
- Liquid must be exposed to the lowest possible boiling temperature for the shortest period of time.

Principle

Most evaporators are heated by steam condensing on the metal tube. Steam is produced in large boilers, generally tube and chest heat exchanger. Usually steam is at a low pressure below 3 atm. abs. The steam temperature is the function of the steam pressure; too high steam temperature causes burn or fouling. For instance water boils at 100°C at one atmosphere and it changes with pressure. Nearly always the material to be evaporated flows inside the tubes and is at boiling temperature. Often boiling liquid is under moderate vacuum, at pressure down to about 0.05 atm. abs.; reducing the boiling temperature of the liquid increases the temperature difference between the steam and the boiling liquid. Therefore increases heat transfer rate in evaporator. The entrained liquid droplets are separated in the disengaging surface from the vapors. Vapors are condensed and discarded. The rate of evaporation is determined by both the rate of heat transfer into the product and the rate of mass transfer of vapor from the product.

Basic components of an evaporator

The basic components of a typical evaporator are

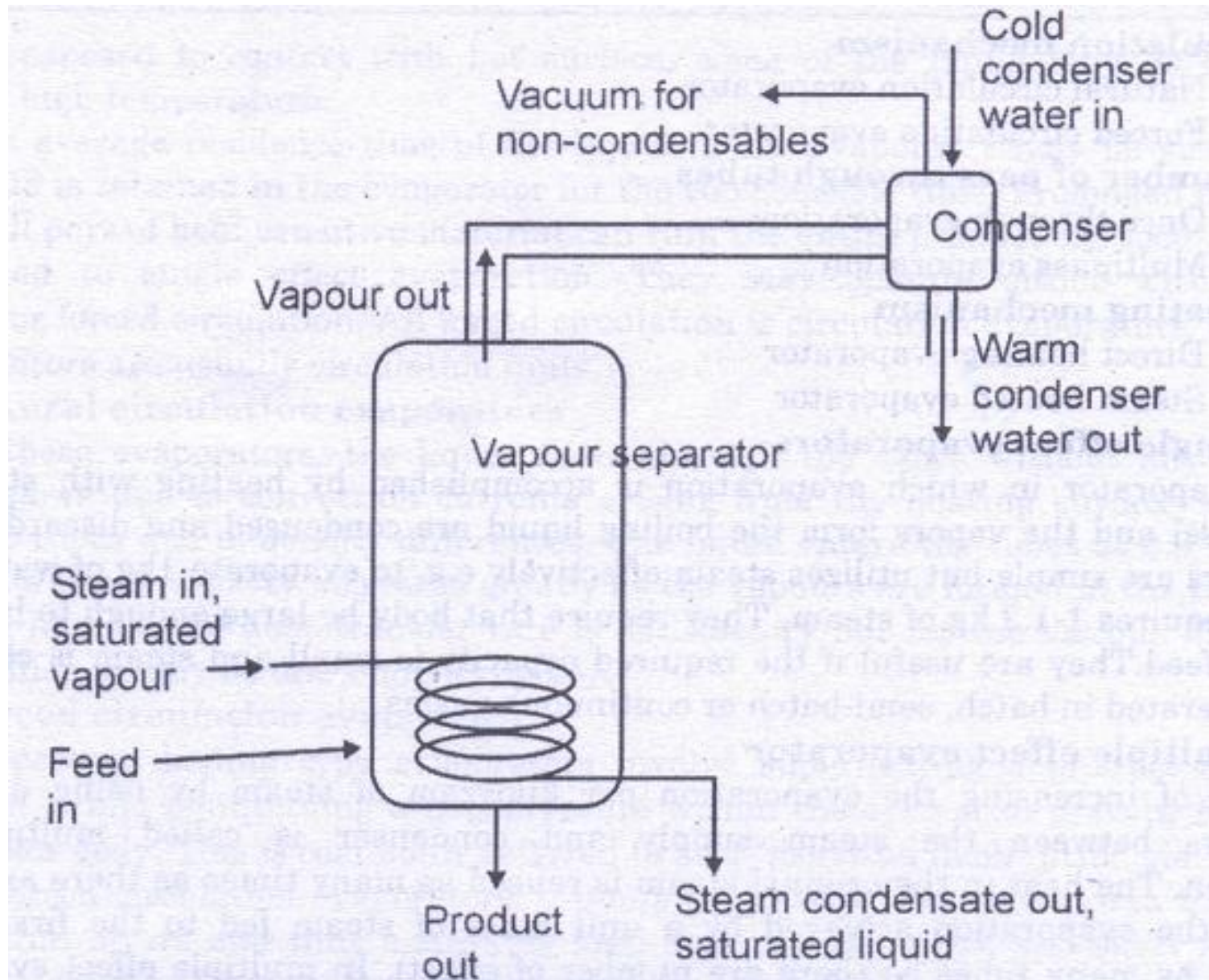
- Heat exchanger
- Vacuum
- Vapor separator
- Condenser

Heat exchanger: It is enclosed in a large chamber and transfer heat from the heating medium, usually low pressure steam to the product via indirect contact surfaces.

Vacuum: It keeps the product temperature low and the difference in temperature high.

Vapor separator: It removes the entrained solid from the vapors, channeling solid back to heat exchanger and the vapors out to the condenser.

Condenser:It may be a part of the heat exchanger but more likely a separate unit. The condenser condenses the vapors from inside the heat exchanger and may act as vacuum source.



Schematic diagram of an evaporator.

Main functions of evaporation in industry

- i. It is used to pre-concentrate foods prior to drying, freezing or sterilization e.g. fruit juice milk and coffee.**
- II. To increase the solid contents of food and to preserve it by reduction in water activity.**
- III. Removal of water provides Microbiological stability.**
- IV. Reduces deteriorative chemical reactions.**
- V. Reduces transportation and storage costs.**
- VI. Evaporation provides greater convenience for consumers such as fruit drinks for dilution, soups, tomato or garlic paste.**
- VII. Convenience for manufacture such as liquid pectin, fruit concentrates for use in ice cream or baked goods.**
- VIII. Evaporation changes the flavor or color of a food e.g. caramelized syrups for use in baked goods and sugar confectionery.**

Types of evaporators

To maintain the quality of liquids, avoid the damage to the product, exposure of the liquid to the lowest boiling temperature for the shortest period of time, energy efficiency and minimized environmental impact are the requirements during the evaporation process which results in the development of a large range of different evaporators types. Evaporators may be classified on the following bases

I. Number of effects

- Single effect evaporator
- Multiple effect evaporator

II. Circulation mechanism

- Natural circulation evaporator
- Forced circulation evaporator

III. Number of pass through tubes

- Once through evaporation
- Multipass evaporation

IV. Heating mechanism

- Direct heating evaporator
- Steam heated evaporator

I. Single effect evaporators

Evaporator in which evaporation is accomplished by heating with steam in a single vessel and the vapors from the boiling liquid are condensed and discarded. These evaporators are simple but utilize steam effectively e.g. to evaporate 1kg of water from a solution requires 1-1.3 kg of steam. They require that body be large enough to hold entire charge of feed. They are useful if the required capacity is small and steam is cheap. They may be operated in batch, semi-batch or continuous modes.

II. Multiple effect evaporator

A method of increasing the evaporation per kilogram of steam by using a series of evaporators between the steam supply and condenser is called multiple effect evaporation. The heat in the original steam is reused as many times as there are number of effect (the evaporation achieved by a unit mass of steam fed to the first effect is multiplied as many times as there are number of effect). In multiple effect evaporators, the steam is fed to first evaporator, the vapor from the first evaporator into the steam chest of second evaporator and so on and the vapor from the last evaporator is sent to the condenser. The total amount of concentration is spread over several effects. There are triple, quadruple or sextuple effect evaporators but mostly triple, quadruple and quintuple effects are concentrated in practice.

III. Once through evaporators

All the evaporation is accomplished in a single pass. The feed liquor passes through the tubes once, releases the vapor and leaves the unit as thick liquor. The ratio of evaporation to feed is limited and these are well adapted to multiple effect operation. They are especially useful for heat sensitive materials. By operating under high vacuum, the temperature of the liquid can be kept low. The thick liquor is exposed to evaporation temperature for a short time with a single phase passage through the tubes and can be quickly cooled as soon as it leaves the evaporator. Agitated film evaporators are always operated once through operation; falling film and climbing film evaporators can be operated in the same way.

IV. Circulation evaporators

The liquor passes through the tubes more than once and only a part of total evaporation occurs in one pass. A pool of liquid is held in the evaporator and the incoming feed liquor is mixed with the liquor held in the pool. A liquor mixture is passed through the tubes, unevaporated liquid is discharged from the tubes returns to the pool and the thick liquor is withdrawn from the pool. The liquor in the pool is at the maximum concentration and the liquor entering the tubes may contain several parts of thick liquor for each part of feed, its viscosity is high and heat transfer co-efficient tends to be low. They are suited for concentrating heat sensitive liquids. By operating under high vacuum, the temperature of the bulk of the liquid may be non-destructive but as the liquid is repeatedly exposed to contact with hot surface, some of the liquid may be heated to excessively high temperature.

The average residence time of the liquid in the evaporator may be short, but a part of liquid is retained in the evaporator for the considerable time. Prolonged heating of even a small part of heat sensitive material can ruin the entire product e.g. food. They are well adapted to single effect evaporation. They may operate either with natural circulation or forced circulation. All forced circulation is circulation evaporators. Climbing film evaporators are usually circulation units.

V. Natural circulation evaporators

In these evaporators, the liquor flows through the tubes without any external agency. It flows due to convection currents arising from the heating surface and flows through the tubes due to density differences. The liquid enters the tubes at 0.3-1.2m/s(1-4ft/sec) and a linear velocity increases greatly as the vapours are formed in the tubes. For non-viscous liquids, the heat transfer rate is satisfactory but for the viscous liquid, the overall co-efficient may be uneconomically low.

VI. Forced circulation evaporator

Suppressed boiling type evaporators involve superheating a product above its boiling point, while maintaining a backpressure within the system to prevent boiling in the evaporator body. This is commonly referred to as a "heat and flash" principle.

In forced circulation evaporators, a pump or scraper assembly moves the liquor, usually in thin layers and thus maintains high heat transfer rates and short residence times. The circulating liquid is heated when it flows through the heat exchanger and then partially evaporated when the pressure is reduced in the separator, cooling the liquid to the boiling temperature corresponding to this pressure.

Distillation

Distillation is the most common separation technique that separates substances by the difference in the tendency of vaporization.

Vaporization may be defined as:

'A process in which a liquid or vapour mixture of two or more substances is separated into its component fractions of desired purity, by the application (boiling) and removal (condensation) of heat.'

or

'The separation of the substances composing a mixture from the more fixed, specifically, the operation of driving off or vapour from volatile liquids or solids, by heating until it boils in a retort or still, capturing and condensing resulting the hot vapors (the products) by a cool receiver, alembic, or condenser and collecting the condensed vapours.'

Distillation was probably first used in the production of intoxicating beverages. Today, many industries i.e. petroleum refining, beverages, chemical processing, petrochemicals, and natural gas processing use refined methods of distillation for critical separation in making useful products. It involves a change of state, as of liquid to gas, and subsequent condensation.

Principle

Distillation is based on the fact that the different substances have different boiling points (the differences in the volatility) and the vapour of a boiling mixture will be richer in the more volatile components. Therefore, when vapour is cooled and condensed, the condensate will contain more volatile components while the original mixture will contain more of the less volatile material.

Separation of components from a liquid mixture via distillation depends on

- The difference in the boiling points of the individual components.
- The concentrations of the components in the liquid mixture.

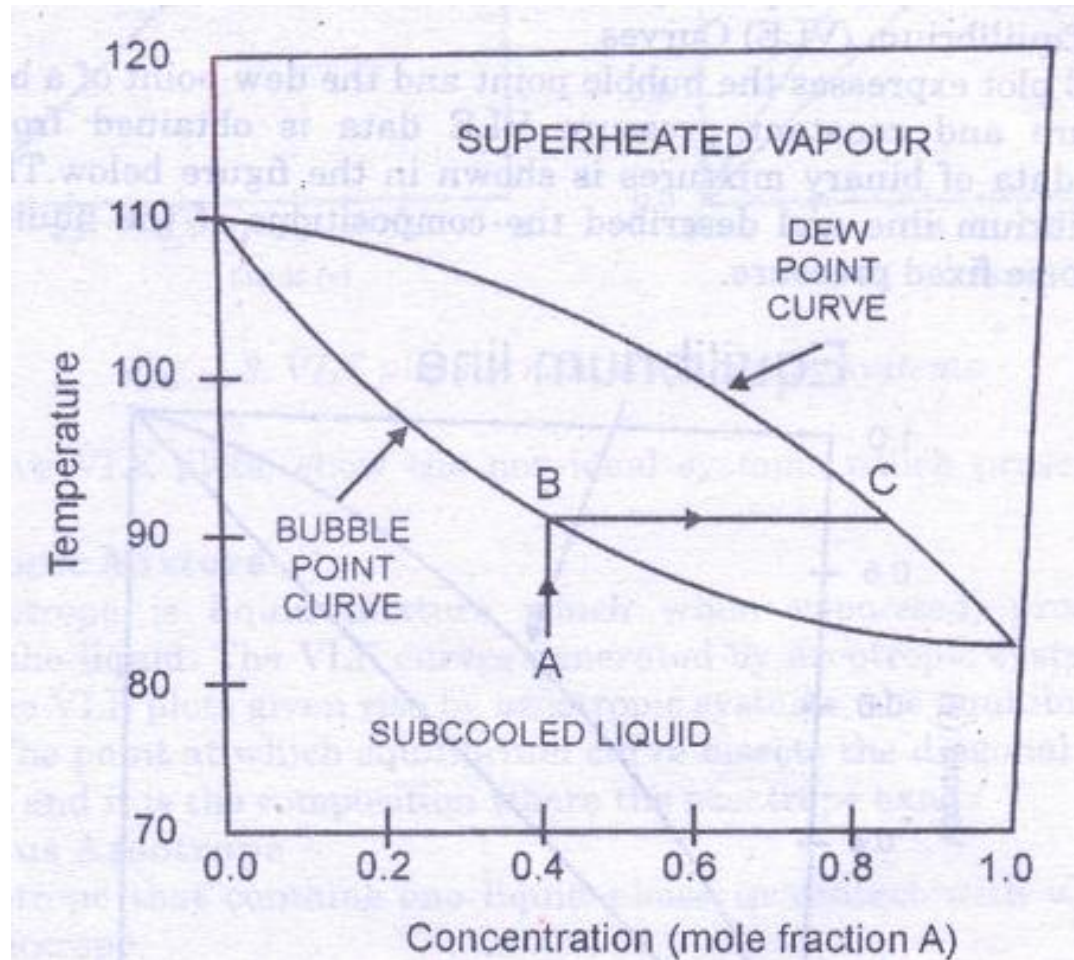
The vapour pressure characteristics of liquid mixtures i.e. liquids with high vapour pressures (volatile liquids) boil at lower temperatures hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture.

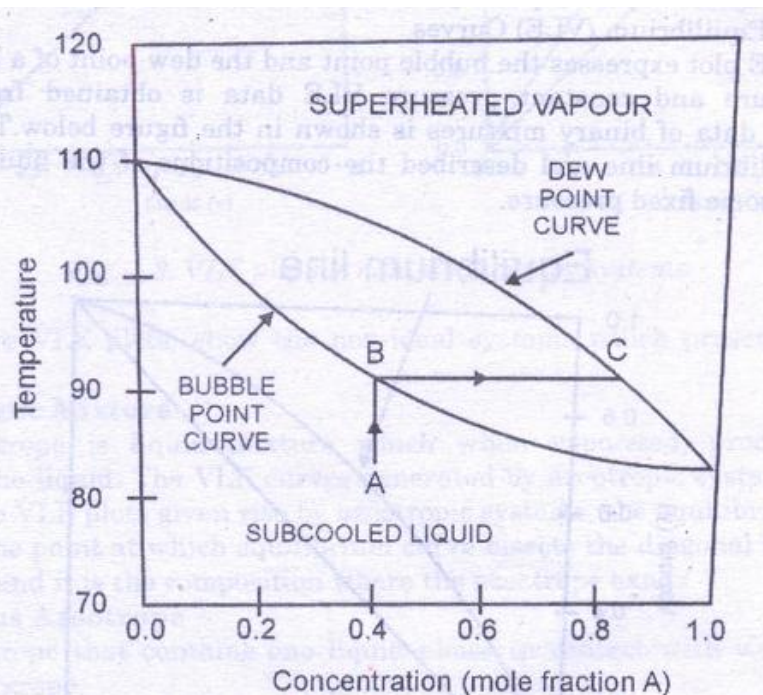
The equilibrium composition of the components in the vapour phase corresponding to the equilibrium composition in the liquid phase is predicted by the boiling point diagram.

The Boiling Point Diagram

The boiling point diagram shows the variation in the equilibrium compositions of the components in a liquid mixture with temperature at a fixed pressure.

Consider a binary liquid mixture of A and B provided that A is the more volatile component than B. The boiling point diagram is shown below.





The boiling point of A is that at which the mole fraction of A is 1. The boiling point of B is that at which the mole fraction of A is 0. The upper curve in the diagram is called the dew-point curve while the lower one is called the bubble-point curve.

- The dew-point is the temperature at which the saturated vapors start to condense.
- The bubble-point is the temperature at which the liquid starts to boil.

The region above the dew-point curve shows the equilibrium composition of the superheated vapour while the region below the bubble-point curve shows the equilibrium composition of the sub cooled liquid.

Let a sub cooled liquid with mole fraction of $A=0.4$ (point A) is heated, its concentration remains constant until it reaches the bubble-point (point B), when it starts to boil. The vapour evolved during the boiling has the equilibrium composition given by point C, approximately 0.8 mole fraction A. This is approximately 50% richer in A than the original liquid.

Azeotropic Mixture

An azeotrope is liquid mixture which when vaporized, produces the same composition as the liquid. The VLE curves generated by azeotropic systems are the most intriguing. In the VLE plots given rise by azeotropic systems, the equilibrium curves cross the diagonals. The point at which equilibrium curve bisects the diagonal line is called the azeotropic point and it is the composition where the azeotrope exists.

a) Homogeneous Azeotrope

An azeotrope that contains one liquid phase in contact with vapour is called a homogeneous azeotrope.

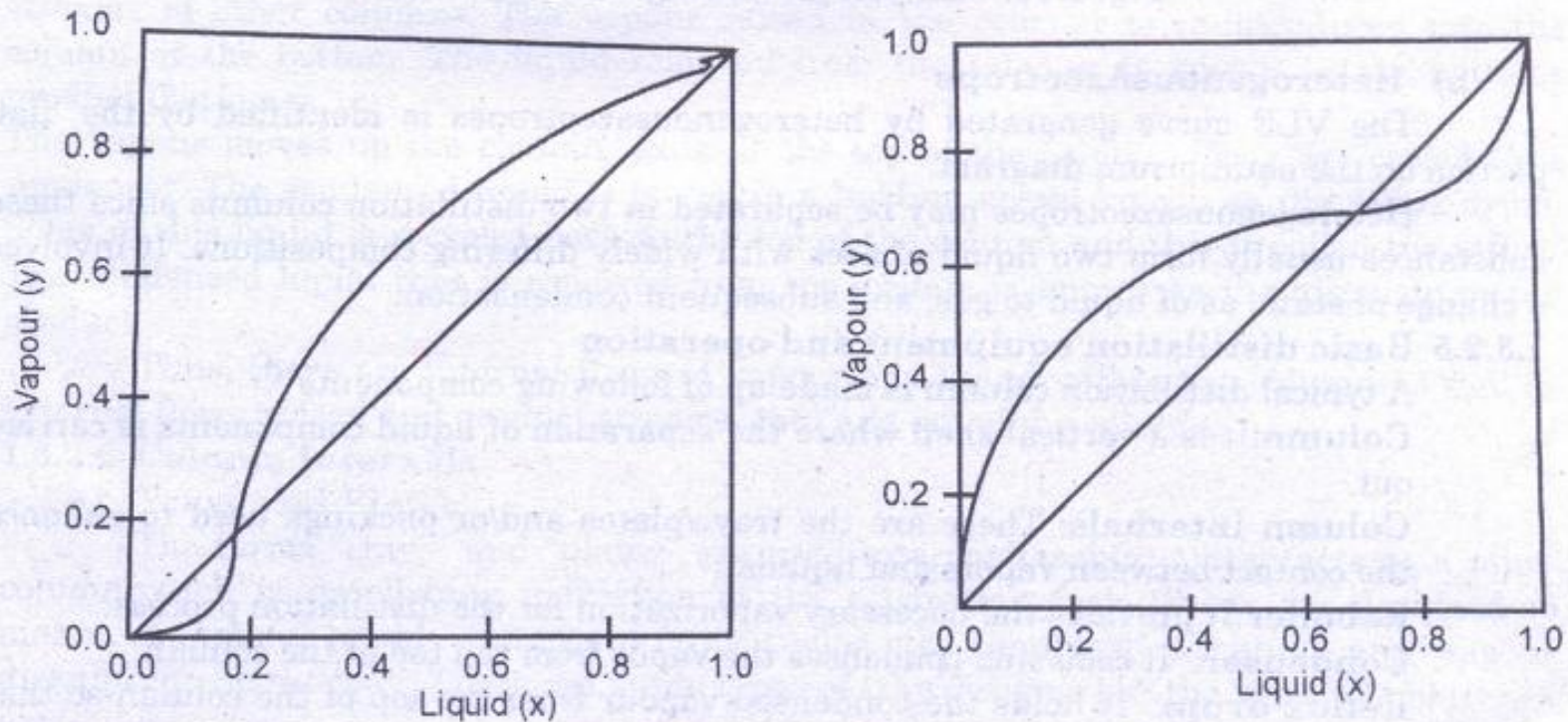
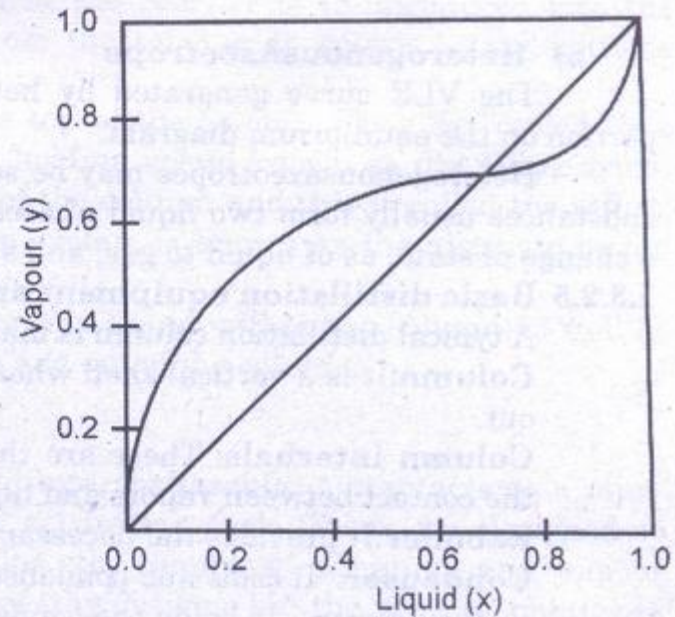
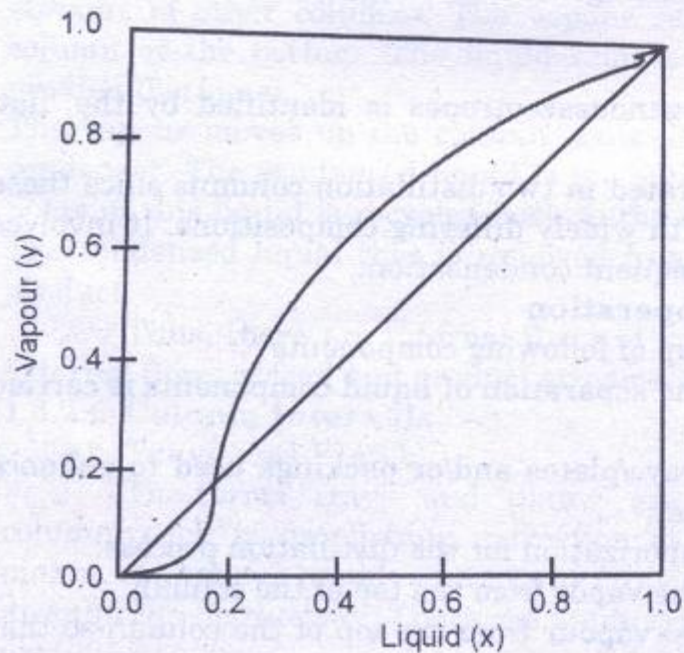


Fig 1.9. Plots for Maximum and Minimum boiling point homogeneous



The above two VLE plots are obtained from two different homogenous azeotropic systems.

- One with a minimum boiling point
- One with a maximum boiling point

A homogenous azeotrope cannot be separated by conventional distillation. However, they can be separated either:

1. By vacuum distillation, that the lower pressure can shift the azeotropic point.
2. By adding a substance to shift the azeotropic point to a more 'favourable' position.

When the additional component appears in appreciable amounts of the top of the column, the operation is called azeotropic distillation.

When the additional component appears mostly at the bottom of the column, the operation is called extractive distillation.

Heterogeneous Azeotrope

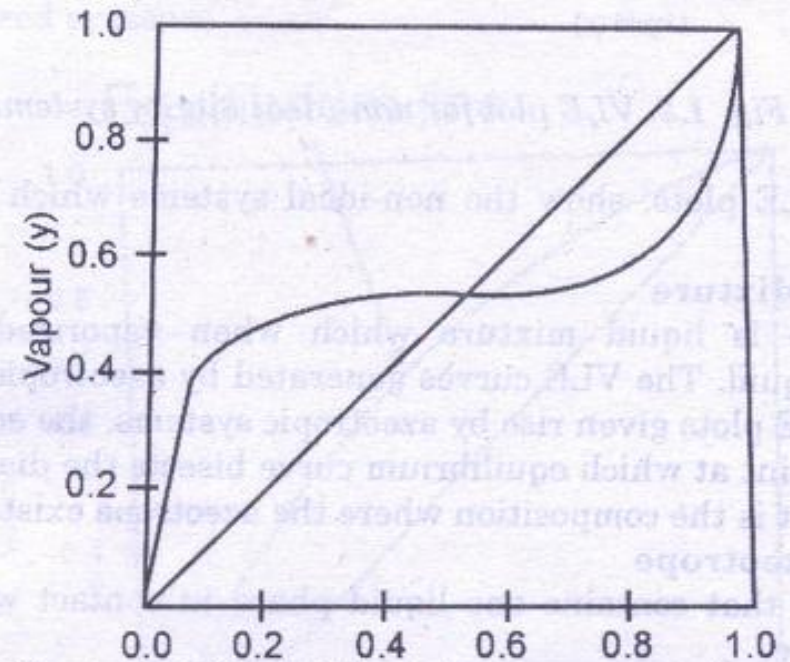


Fig. 1.10. VLE plot for heterogeneous azeotrope

b) Heterogeneous Azeotrope

The VLE curve generated by heterogeneous azeotropes is identified by the 'flat' portion on the equilibrium diagram.

Heterogeneous azeotropes may be separated in two distillation columns since these substances usually form two liquid phases with widely differing compositions. It involves a change of state, as of liquid to gas, and subsequent condensation.

Basic distillation equipment and operation

A typical distillation column is made up of following components

Column: It is a vertical shell where the separation of liquid components is carried out.

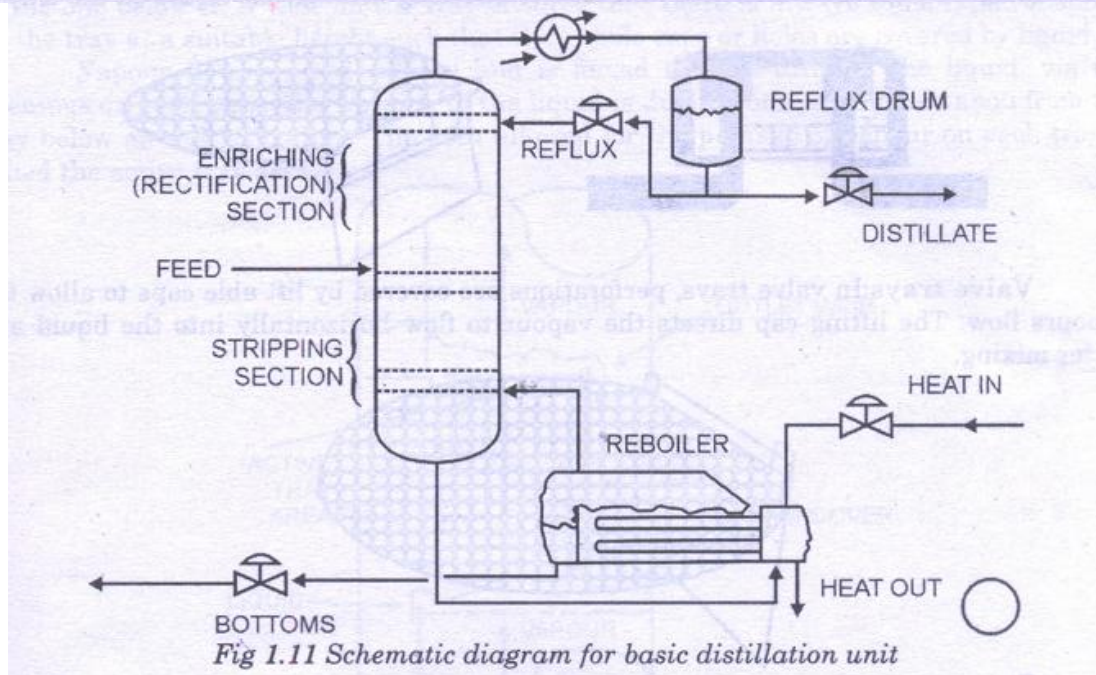
Column internals: These are the trays/plates and/or packings used to enhance the contact between vapors and liquids.

Reboiler: It provides the necessary vaporization for the distillation process.

Condenser: It cools and condenses the vapor from the top of the column.

Reflux drum: It holds the condensed vapour from the top of the column so that liquid (reflux) can be recycled back to the column.

The vertical shell (column) houses the column internals and together with the condenser and reboiler, constitutes a distillation unit. A schematic diagram of a typical distillation unit with a single feed and two product streams is shown below.



The liquid mixture to be processed is known as the feed and is introduced usually somewhere near the middle of the column to a tray known as feed tray. The feed tray divided the column into top (enriching or rectification) section and a bottom (stripping) section. The feed flows down the column where it is collected at the bottom in the reboiler.

Heat is supplied to the reboiler to generate either in the form of steam or fluid or streams of other columns. The vapour raised in the reboiler is re-introduced into the column at the bottom. The liquid removed from the reboiler is known as the bottoms product (bottoms).

The vapour moves up the column, exits at the top of the column. They are cooled by a condenser. The condensed liquid is stored in a holding vessel known as the reflux drum. Some of this liquid is recycled back to the top of the column and this is called the reflux. The condensed liquid that is removed from the system is known as the distillate or top product.

Thus, there are internal flows of vapour and liquid within the column as well as external flows of feed and product streams, into and out of the column.