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Introductory Chapter: Fractionation

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<http://dx.doi.org/10.5772/intechopen.78050>

1. Introduction

Separation processes whereby different properties are used in the separation of mixtures of different compositions are some of the most important chemical engineering processes. The mixtures to be separated may be mixtures of isotopes, molecules, polymers or cells. The different properties on which the separation process is based may be chemical or physical including such properties as chemical reactivity, solubility, molecular size, electrical charge and change-of-phase temperatures such as boiling and freezing points.

The application of separation processes ranges from such operations as water purification to refining of products and separation of raw materials. Separation processes account for 40–90% of the capital investment in industrial establishments. It has been variously estimated that the capital investment in separation equipment is 40–50% of the total for a conventional fluid processing unit [1].

There are many different separation techniques which may be broadly classified into processes of mechanical separation and separation by diffusion. Mechanical separation techniques may be based on particle size, density and electrical or magnetic mobility. Separation by diffusion includes chromatographic separation, extraction and fractionation. Of the many and varied separation processes available, fractionation plays a major part, and capital investment in fractionation equipment and processes may form a significant fraction of industrial processing investment.

Fractionation, in the most general sense, could mean any process whereby a mixture is separated into different components or fractions. Fractionation in this general sense, however, would include diverse methods and techniques that may have little in common. Such methods and techniques may be broadly grouped in four classes, namely fractionation proper, general separation, analytical separation and purification. It is important to note, however, that this is

not an exclusive classification as some methods may have characteristics belonging to more than one of these classes. Chromatography, for example, may be either analytical or separatory:

1. Fractionation proper in the restricted commonly accepted sense, sometimes referred to as thermal separation, may be defined as any physical fractional or separation process involving a phase transition in which a mixture is separated in a single run into two or more fractions with variable compositions. The mixture to be separated could be a homogeneous mixture such as a solution or a heterogeneous mixture such as a mixture of solid and liquid. The mixture to be separated may also be gaseous, liquid or solid. The fractions are separated based on differences in a specific property of the individual components such as boiling, freezing or melting points. The phase changes involved could be condensation for vapours and gases (dephlegmation), boiling and evaporation (distillation) or freezing and crystallisation (freeze distillation and solution crystallisation) for liquids, and melting or sublimation for solids. Most of these processes find application on industrial scales but some processes such as fractionation by sublimation are restricted to laboratory-scale procedures.

The general characteristics of fractionation processes may thus be summarised as follows:

1. Fractionation processes are processes of separation of mixtures of liquids, gases or solids into their components.
2. Fractional separation is based on differences in a specific property of the individual components.
3. Fractionation processes are physical processes, where phase transition is involved.
4. They are carried out in single runs.

Examples of fractionation processes include (**Table 1**):

1. Dephlegmation, where mixtures of vapours are separated by difference in their condensation point.
2. Fractional distillation, where mixtures of liquids and gases are separated by difference in boiling point.
3. Fractional freezing, where mixtures of liquids are separated by difference in freezing point.
4. Fractional melting, where mixtures of solids are separated by difference in melting point.
5. Isotope fractionation, where mixtures of isotopes are separated by difference in density during phase transition.

2. The term 'fractionation', however, may sometimes be used in a more general sense to refer to any separation process that may involve no phase change and may not therefore be classified as a fractionation process properly speaking. Such separation processes include:

2.1. Solvent or clean fractionation, where a mixture of an organic solvent and water is used to achieve clean separation.

Fractionation process	Mixture	The specific property	Area of application
Dephlegmation	Vapours	Condensation point	Oil refining
Fractional distillation	Liquids and vapours	Boiling point	Petroleum and petrochemical industries
Fractional crystallisation = fractional freezing	Partial crystallisation Liquids	Freezing point	Fractionation of food Upgrading of alternative fuels Obtaining very pure substances.
	Solution crystallisation Liquids	Solubility	
Fractional melting	Solids	Melting point	
Isotope fractionation		Density	

Table 1. Fractionation processes.

2.2. Thermal diffusion, where mixtures of gases or liquids are separated by difference in density.

2.3. Centrifugation, which is a process where substances of different densities in a heterogeneous mixture are separated by sedimentation using a centrifuge.

2.4. Gaseous diffusion, where mixtures of gases are separated by difference in molecular weight.

2.5. Chromatography where fractionation of components from a solution mixture takes place by difference in affinity between the stationary and the mobile phases.

3. The term 'fractionation' may also be used sometimes to refer to an analytical technique and not to a separation process. Examples of such use include bioassay-guided fractionation, analytical chromatography and geochemical fractionation.

Bioassay is an analytical method to determine the concentration or potency of a substance by its effect on living cells or tissues. In bioassay-guided fractionation, extracted components are separated based on differences in their physicochemical properties and biological activity. In pharmacognosy, a pure chemical agent from natural origin is isolated by bioassay-guided fractionation.

Geochemical fractionation is a laboratory procedure in which chemical extraction is used to determine fractions of metals in soils and sediments and their susceptibility to release into an aqueous environment.

4. Finally, fractionation may refer to a purification process, where a desired component is extracted from a mixture and purified as, for example, in the pharmaceutical industry, where natural and synthetic drugs are separated and purified to meet health needs. Surface Active Foam Fractionation, a new technology developed by scientists from a privately-owned Australian company, may be used to remove certain contaminants from water. In this

technology, air is introduced into the column of contaminated water through a diffuser, and the resulting bubble column rises to produce contaminant-rich foam on the water surface, which is extracted using a uniquely-designed vacuum extraction system.

Such purification processes, however, may not be considered as separation or fractionation processes per se.

Fractionation in the restricted commonly accepted sense as a separation process properly speaking is widely used in the chemical industries including food and pharmaceutical industries and in petroleum and petrochemical industries in particular. It is normally used to separate a non-usable crude mixture into separate usable fractions as, for example, in oil refineries where crude oil is fractionated into useful petroleum products such as fuels, lubricants and chemical raw materials. In biorefineries, lignocellulosic raw materials are fractionated into their polymeric and non-polymeric constituents and new routes developed for their chemical and biochemical conversion into high-value-added products.

1.1. Dephlegmation

Dephlegmation is a separation process where mixtures of vapours are separated by difference in their condensation point. In chemistry, the noble gases are separated from one another by fractionation, making use of their different condensation temperatures.

1.2. Fractional distillation

Fractional distillation is a distillation process where mixtures of liquids and gases are separated by difference in boiling point. Fractional distillation processes include topping, rectification, exhausting, stripping, vacuum distillation, stabilization and extractive distillation.

Distillation as a separation process is used in general to separate a fluid mixture of two (binary) or more (multi-component) substances into its component parts. In most cases, the components to be separated are miscible liquids with different volatilities and boiling points. This separation process is a thermal unit operation that utilizes the differences of vapour pressure to produce the separation. In this process, the vapour or liquid mixture is heated whereby the more volatile components are evaporated, condensed and allowed to drip or drip apart, that is, distil or destillare, as it was originally called in Latin. It is from this fact of 'dripping' that the name of the distillation process was derived [1].

In general, distillation is favoured over other separation techniques when large rates are desired of products that are thermally stable with a relative volatility greater than 1.2 and where no extreme corrosion, precipitation, sedimentation or explosion issues are present [2].

The pre-eminence of distillation for the separation of fluid mixtures is fundamental for both kinetic and thermodynamic reasons [3]. It may also be the most economical process for the separation and production of high-purity products. In 1992, Darton estimated the worldwide throughput of distillation columns at 5 billion tonnes of crude oil and 130 million tonnes of *petrochemicals* per year [1].

Fractional distillation is a special type of distillation, and as a separation technique, is much more effective than simple distillation and more efficient. Fractional distillation is equivalent in effect to a series of distillations, where separation is achieved by successive distillations or repeated vaporization-condensation cycles. Each vaporization-condensation cycle makes for an equilibrium stage, commonly known as a theoretical stage. A number of such theoretical stages may be required for the efficient fractionation and separation of the vapour or the liquid mixture. The McCabe-Thiele method is a graphical method that may often be used to calculate the required number of theoretical stages. These theoretical stages will then have to be converted to actual plates or an equivalent packed height depending upon the separation efficiency for a particular service. As a separation technique, fractional distillation is much more effective than simple distillation and more service [1].

In fractional distillation, the components are separated through continuous heat and mass transfer between counter-current streams of a rising vapour and a descending liquid. As in all thermal separation processes, the motive force for the separation is the drive towards thermodynamic equilibrium between the different phases (VLE or vapor liquid equilibrium). This equilibrium is continuously disturbed by the mixing of the colder descending liquid and the hotter rising vapour, where the more volatile components of the descending liquid are vaporized and the less volatile components of the rising vapour are condensed and the driving force for the separation process is thereby maintained. The concentration of the lighter components will be greater in the vapour phase and conversely the concentration of the heavier components will be greater in the liquid phase, and only in the case of pure components or azeotropic mixtures will the equilibrium composition be the same in both phases [1].

In recent years, fractional distillation has become one of the most important unit operations in chemical engineering industries. It is by far the most common specialized separation technology. In the USA, fractionators are used in 90–95% of the separations [4].

In petroleum refineries, in particular, atmospheric fractionation of crude oil, variously known as topping, is the first and the most important process of the series of oil refinery operations [5]. The crude oil feedstock, which is a very complex multi-component mixture, is separated into a number of products or fractions, with each product or fraction being composed of groups of compounds within a relatively small range of boiling points. These straight-run products or fractions are the origin of the term fractional distillation or fractionation. Fractional distillation, however, is not used in the petroleum-refining industry only, but is also used in other chemical, petrochemical, beverage and pharmaceutical industries and in natural gas-processing plants [1]. In chemistry, fractional distillation may be used for the separation of a mixture of isotopes, where the molecules of the fraction having the lower boiling point (the lighter isotopes) tend to concentrate in the vapour stream and are collected.

Fractional distillation, though widely used, is one of the most energy-intensive operations. In fact, distillation may be the largest consumer of energy in petroleum and petrochemical processing. Of the total energy consumption of an average unit, the separation steps account for about 70% and distillation alone can consume more than 50% of a plant's operating energy cost [6]. Fractional distillation accounts for about 95% of the total distillation consumption [7].

Replacing fractional distillation by other separation techniques in such industries as petroleum and petrochemical industries is, however, highly unlikely despite its energy intensiveness [1].

Extractive distillation is a special type of distillation which is used for the separation of components with similar evaporation points. Such components cannot be separated by simple distillation, because their volatility is nearly the same, causing them to evaporate at nearly the same temperature at a similar rate, making normal distillation impractical. In extractive distillation, a separation solvent is used, which is generally non-volatile, has a high boiling point and is miscible with the mixture, but does not form an azeotropic mixture. The solvent interacts differently with the components of the mixture, thereby causing their relative volatilities to change. This enables the new three-part mixture to be separated by normal distillation. The original component with the greatest volatility separates out as the top product. The bottom product consists of a mixture of the solvent and the other component, which can again be separated easily.

1.3. Fractional freezing

Fractional freezing, also known as fractional crystallisation, is a process where mixtures of liquids are separated by difference in freezing point. It was further observed, when reported data on crystallisation were analysed, that fractionation occurs according to molecular weight. Fractional crystallisation is generally used to produce ultra-pure solids or to recover valuable products from waste solutions and to concentrate liquids. In geology, a process of fractional freezing is known to occur during the metamorphism and structural change of rocks.

Fractional freezing is a simple process that does not require sophisticated equipment or complicated procedures, and it can be used on an industrial scale. Fractional freezing can be used in particular to concentrate heat-sensitive liquids, such as fruit juice concentrates, as it does not involve heating the liquid (as happens during evaporation). However, it is not always possible with this method to produce pure products or to eliminate impurities completely, elimination of impurities being dependent on the nature of these impurities. Furthermore, part of the desired component will always be lost in the discarded material.

Fractional freezing may be carried out by either of two processes, namely

1. Partial crystallisation, also called normal freezing or progressive freezing, where mixtures of liquids are separated by difference in freezing point. This is done by cooling and partial freezing of the liquid and removing the frozen material that is poorer in the desired material than the liquid portion left behind. This is sometimes known as freeze distillation because the resulting enrichment of the liquid portion parallels enrichment by true distillation, where the evaporated and re-condensed portion is richer in the desired lighter material than the liquid portion left behind.

Fractional freezing by partial crystallisation can be used as a simple method to reduce the gel point of biodiesel and other alternative diesel fuels and to increase the alcohol concentration in fermented alcoholic beverages.

The separation of a mixture of water and alcohol is a well-known example of partial crystallisation. Freezing in this case begins at a temperature significantly below 0°C. The first material to freeze is a dilute solution of alcohol in water. The frozen material, while always poorer in alcohol than the liquid, becomes progressively richer in alcohol. The liquid left behind, on the other hand, becomes increasingly richer in alcohol, and, as a consequence, further freezing would take place at progressively lower temperatures. The degree of concentration of the alcohol in the liquid will depend on the final cooling temperature. But even if the final temperature is somewhat below the freezing point of alcohol, there will still be alcohol and water mixed as a liquid, and at some still lower temperature, the remaining alcohol-and-water solution will freeze.

The best-known freeze-distilled beverages are applejack, made from hard cider, and ice beer (Eisbock). In the olden days, barrels of beer were left outside in the winter months and the formed ice, mainly composed of water, would be periodically removed, and this would continue until no more ice is formed. In effect, the presence of ethanol lowers the melting point of water in a solution of water and ethanol, and the solidified phase would contain lesser amounts of ethanol than the liquid phase which will be gradually enriched to give eventually ice beer.

In practice, while not able to produce an alcohol concentration comparable to distillation, partial crystallisation can achieve some concentration with far less effort than any practical distillation apparatus would require. The danger of freeze distillation of alcoholic beverages is that, unlike heat distillation where the methanol and other impurities can be separated from the finished product, freeze distillation does not remove them. Thus, the ratio of impurities may be increased compared to the total volume of the beverage. This concentration may cause side effects to the drinker, leading to intense hangovers and a condition known as 'apple palsy', although this term has also been used simply to refer to intoxication, especially from applejack.

Partial crystallisation may also be used to desalinate sea water which contains principally sodium chloride. Because sodium chloride lowers the melting point of water, the salt in sea water tends to be forced out of pure water while freezing. This is sometimes referred to as brine rejection.

A fractional freezing technique that permits the freezing of large quantities of solutions is the so-called slow fractional freezing. This is a costly procedure, however, that requires the use of rather expensive equipment. In one such technique, a cylinder containing the liquid is cooled where freezing of the solution starts at the bottom of the cylinder and the frozen solid rises slowly towards the surface of the cylinder. The freezing may be stopped at the desired point for the separation of the solid from the liquid. In another technique that allows better control of the freezing rate, a spherical container is used where freezing starts at the surface of the sphere and moves slowly towards its centre leaving the desired purified liquid at the centre of the sphere surrounded by the frozen solid from which it can be extracted.

2. Solution crystallisation, where chemical substances are fractionated based on difference in solubility at a given temperature. This is done by the addition of a dilute solvent to the liquid mixture and cooling and partial freezing of the liquid and removing of frozen material. If the desired dissolved substance to be separated is the most soluble substance at the specific cooling temperature, the frozen material will be poorer in that desired substance. On the other hand, the liquid portion left behind will be richer in the desired substance. The proportion of the components in the frozen

material and the liquid portion will depend on their solubility products. If the solubility products are very similar, a cascade process will be needed to effect a complete separation.

1.4. Fractional melting

Fractional melting is a fractionation process where mixtures of solids are separated by difference in melting point. This can be done by partial melting of the solid. Fractional melting may be used to desalinate sea water as sea ice, frozen salt water, when partially melted, leaves behind ice that is of a much lower salt content. Fractional melting may also be used to separate waxes into fractions of different melting points which can then be recombined.

1.5. Isotope fractionation

Isotope fractionation occurs during a phase transition as a result of the different distribution of the lighter and heavier isotopes between the liquid and vapour phases. For example, when water vapour condenses, the heavier water isotopes (^{18}O and ^2H) become enriched in the liquid phase while the lighter water isotopes (^{16}O and ^1H) tend towards the vapour phase.

Other separation processes that are referred to sometimes as fractionation processes although they do not involve in general any phase changes:

1.5.1. Clean or solvent fractionation

In clean fractionation, a mixture of an organic solvent and water is used to achieve clean separation. This fractionation process may be used for upgrading biomass feedstocks for a biorefinery by separating their three main components, viz. cellulose, hemicelluloses and lignin, into pure streams for conversion into value-added products.

1.5.2. Thermal diffusion

In thermal diffusion, natural convection is utilized in the separation of mixtures of liquids or gases by difference in density. In a region with a temperature gradient, the lighter molecules tend to concentrate in the hot parts of the region and the heavier molecules tend to concentrate in the cold parts. Moreover, hotter molecules tend to rise as a result of natural thermal convection and cooler molecules tend to fall, effecting thereby a separation between the lighter and heavier components of the mixture. As no phase change is necessarily involved in thermal diffusion, this process is not normally considered a fractionation process.

A simple form of a thermal diffusion apparatus consists of a tall vertical tube with a wire electrically heated to a specified temperature running down its centre, producing a temperature gradient between the centre and the wall of the tube. The heavier molecules tend to concentrate in the outer portions of the tube, and the lighter molecules to concentrate towards the centre. At the same time, because of thermal convection, the gas or liquid near the wire tends to rise, and the cooler outer gas or liquid tends to fall. The overall effect is that the heavier molecules collect at the bottom of the tube and the lighter at the top.

Thermal diffusion is often used for the separation of mixtures of isotopes.

1.5.3. Centrifugation

Centrifugation is a process where substances of different densities in a heterogeneous mixture are separated by sedimentation using a centrifuge. Centrifugation, however, though a separation process, may not be considered a fractionation process properly speaking as it involves no phase change.

Centrifugation is used in industrial and laboratory settings, particularly in the chemical and food industries and in biological research. Centrifugation is also the most common method used for uranium enrichment, relying on the slight mass difference between atoms of U238 and U235 in uranium hexafluoride gas. In isotope fractionation, the centrifugal force acts more strongly on the heavy molecules than on the light ones, increasing the concentration of the heavy isotopes in the outer region.

In cell fractionation, also called cell lysis, cell components are separated by difference in density while preserving individual functions of each component. With this methodology, the different individual cell components may be examined and their biochemical synthesis and capacity investigated. Cell fractionation is being increasingly applied in research activities in the pharmaceutical industry and disease investigation.

In blood fractionation, blood is separated into its three major components, plasma, buffy coat and erythrocytes. These separated components can be analysed and often further separated. In plasma protein fractionation, the inherent differences of each protein are used and the temperature or the acidity of the plasma is changed so that proteins that are normally dissolved in the plasma fluid become insoluble and can be collected by centrifugation. In cold alcohol fractionation or ethanol fractionation, which is one of the very effective ways for carrying out plasma protein fractionation, alcohol is added to the plasma with simultaneous cooling. Plasma fractionation is used in the prevention and treatment of life-threatening diseases caused by trauma, immunologic disorders and infections. It is also used in treating protein deficiency in health-care applications.

1.5.4. Gaseous diffusion

In gaseous diffusion, the difference in the rate of diffusion of gases of different molecular weight through a porous barrier is utilized to effect separation. As the rate of diffusion of a gas is inversely proportional to the square root of its mass, light atoms diffuse through a porous barrier faster than heavier atoms.

Gaseous diffusion was used in the early forties of the last century for the separation of uranium isotopes. As the difference in weight between uranium-235 and uranium-238 is slight, however, thousands of separation stages would be required to produce 99% uranium-235 from natural uranium.

1.5.5. Chromatography

Chromatography is a technique for the separation of mixtures, where the mixture to be separated is dissolved in a fluid called the mobile phase (the eluent), which carries it through a structure holding another material called the stationary phase. The mobile phase may be a

liquid (LC and capillary electrochromatography (CEC)), a gas (GC) or a supercritical fluid (supercritical-fluid chromatograph SFC). The stationary phase may be a thin layer of an adsorbent like silica gel, alumina or cellulose on a flat, inert substrate in thin layer chromatography (TLC) or a strip of chromatography paper in paper chromatography. Furthermore, the stationary phase may be as or on a plane in planar chromatography or the bed of the stationary phase may be in a tube in column chromatography.

The various components of the mixture to be separated travel at different speeds causing them to separate. Fractionation of the mixture components (the analytes or elutes) takes place by difference in affinity between the stationary and the mobile phases. Several mechanisms may be applied for the separation of the analytes such as ion exchange (in ion exchange chromatography) and size exclusion (in size exclusion chromatography, also known as gel permeation chromatography or gel filtration chromatography). In ion exchange chromatography, the analytes are separated based on their respective charges. In size exclusion chromatography, molecules are separated according to their size (or hydrodynamic diameter or volume).

Chromatography may be preparative or analytical, but only preparative chromatography is a form of separation. In chromatography, however, no phase transition is involved and even preparative chromatography may not therefore be considered a true fractionation process.

1.5.6. Other processes of separation

Other processes of separation that are mainly used for isotope separation include electromagnetism and laser separation. In electromagnetism, first used for the production of uranium-238, an ionic beam obtained from a uranium compound was passed through a magnetic field. Because the radius of the curvature of the path of the ions deflected by the beam depends on the mass of the ion, ions of different mass complete their path at different positions, and the uranium isotopes were appreciably separated. In laser separation, the isotope mixture is first vaporized and its atoms are selectively excited and ionized by an accurately tuned laser beam and the desired isotope is thus separated out.

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