14
Separations in Food Processing

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14.1
Introduction

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Separations are vital to all areas of the food processing industry. Separations usually aim to remove specific components in order to increase the added value of the products, which may be the extracted component, the residue or both. Purposes include cleaning, sorting and grading operations (see Chapter 1), extraction and purification of fractions such as sugar solutions or vegetable oils, recovery of valuable components such as enzymes or flavour compounds, or removal of undesirable components such as microorganisms, agricultural residues or radionuclides. Operations range from separation of large food units, such as fruits and vegetables measuring many centimetres, down to separation of molecules or ions measured in nanometres.

Separation processes always make use of some physical or chemical difference between the separated fractions; examples are size, shape, colour, density, solubility, electrical charge and volatility.

The separation rate is dependent on the magnitude of the driving force and may be governed by a number of physical principles involving concepts of mass transfer and heat transfer. Rates of chemical reaction and physical processes are virtually always temperature-dependent, such that separation rate will increase with temperature. However, high temperatures give rise to degradation reactions in foods, producing changes in colour, flavour and texture, loss of nutritional quality, protein degradation, etc. Thus a balance must be struck between rate of separation and quality of the product.

Separations may be classified according to the nature of the materials being separated, and a brief overview is given below.

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14.1.1 Separations from Solids

Solid foods include fruits, vegetables, cereals, legumes, animal products (carcasses, joints, minced meat, fish fillets, shellfish) and various powders and granules. Their separation has been reviewed by Lewis [1] and can be subdivided as follows.

14.1.1.1 Solid-Solid Separations

Particle size may be exploited to separate powders or larger units using sieves or other screen designs, examples of which are given in Chapter 1.

Air classification can be achieved using differences in aerodynamic properties to clean or fractionate particulate materials in the dry state. Controlled air streams will cause some particles to be fluidised in an air stream depending on the terminal velocity, which in turn is related primarily to size, but also to shape and density. Also in the dry state, particles can be separated on the basis of photometric (colour), magnetic or electrostatic properties.

By suspending particles in a liquid, particles may be separated by settlement on the basis of a combination of size and density differences. Buoyancy differences can be exploited to separate products from heavy materials such as stones or rotten fruit in flotation washing, while surface properties can be used to separate peas from weed seeds in froth flotation.

14.1.1.2 Separation From a Solid Matrix

Plant materials often contain valuable components within their structure. In the case of oils or juices, these may be separated from the bulk structure by expression, which involves the application of pressure. Alternatively, components may be removed from solids by extraction (see Section 14.4), which utilises the differential solubilities of extracted components in a second medium. Water may be used to extract sugar, coffee, fruit and vegetable juices, etc. Organic solvents are necessary in some cases, e.g. hexane for oil extraction. Supercritical CO_2 may be used to extract volatile materials such as in the decaffeination of coffee. A combination of expression and extraction is used to remove 99% of the oil from oilseeds.

Water removal from solids plays an important role in food processing (see Chapter 3).

14.1.2 Separations From Liquids

Liquid foods include aqueous or oil based materials, and frequently contain solids either in true solution or dispersed as colloids or emulsions.

14.1.2.1 **Liquid-Solid Separations**

Discrete solids may be removed from liquids using a number of principles. Conventional filtration (see Section 14.2) is the removal of suspended particles on the basis of particle size using a porous membrane or septum, composed of wire mesh, ceramics or textiles. A variety of pore sizes and geometric shapes are available and the driving force can be gravity, upstream pressure (pumping), downstream pressure (vacuum) or centrifugal force. Using smaller pore sizes, microfiltration, ultrafiltration and related membrane processes can be used to fractionate solids in true solution (see Section 14.7).

Density and particle size determine the rate of settlement of dispersed solids in a liquid, according to Stokes Law. Settlement due to gravity is very slow, but is widely used in water and effluent treatment. Centrifugation subjects the dispersed particles to forces greatly exceeding gravity which dramatically increases the rate of separation and is widely used for clarifying liquid food products. A range of geometries for batch and continuous processing are available (see Section 14.3).

14.1.2.2 **Immiscible Liquids**

Centrifugation is again used to separate immiscible liquids of different densities. The major applications are cream separation and the dewatering of oils during refining.

14.1.2.3 **General Liquid Separations**

Differences in solubility can be exploited by contacting a liquid with a solvent which preferentially extracts the component(s) of interest from a mixture. For example, organic solvents could be used to extract oil soluble components, such as flavour compounds, from an aqueous medium.

An alternative approach is to induce a phase change within the liquid, such that components are separated on the basis of their freezing or boiling points. Crystallisation is the conversion of a liquid into a solid plus liquid state by cooling or evaporation (see Section 14.6). The desired fraction, solid or liquid, can then be collected by filtration or centrifugation. Alternatively, evaporation (see Chapter 3) is used to remove solvent or other volatile materials by vapourisation. In heat-sensitive foods, this is usually carried out at reduced operating pressures and hence reduced temperature, frequently in the range 40–90 °C. Reverse osmosis (see Section 14.7) is an alternative to evaporation in which pressure rather than heat is the driving force.

Ion exchange and electrodialysis (see Sections 14.8 and 14.9) are used to separate dissolved components in liquids, depending on their electrostatic charge.

14.1.3
Separations From Gases and Vapours

These separations are not common in food processing. Removal of solids suspended in gases is required in spray drying and pneumatic conveying and is achieved by filter cloths, bag filters or cyclones. Another possibility is wet scrubbing to remove suspended solids on the basis of solubility in a solvent (see Chapter 3).

14.2
Solid-Liquid Filtration

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14.2.1
General Principles

In this method of separation the insoluble solid component of a solid-liquid suspension is separated from the liquid component by causing the latter to flow through a porous membrane, known as the *filter medium*, which retains the solid particles within its structure and/or as a layer on its upstream face. If a layer of solid particles does form on the upstream face of the medium it is known as the *filter cake*. The clear liquid passing through the medium is known as the *filtrate*. The flow of the liquid through the medium and cake may be brought about by means of gravity alone (*gravity filtration*), by pumping it through under pressure (*pressure filtration*), by creating a partial vacuum downstream of the medium (*vacuum filtration*) or by centrifugal force (*centrifugal filtration*). Once the filtration stage is complete, it is common practice to wash the cake free of filtrate. This is done to recover valuable filtrate and/or to obtain a cake of adequate purity. When filtering oil, the cake may be blown free of filtrate by means of steam. After washing, the cake may be dried with heated air.

In the early stages of a filtration cycle, solid particles in the feed become enmeshed in the filter medium. As filtration proceeds, a layer of solids begins to build up on the upstream face of the medium. The thickness of this layer and so the resistance to the flow of filtrate increases with time. The pressure drop, $-\Delta p_c$, across the cake at any point in time may be expressed as:

$$-\Delta p_c = \frac{\alpha \eta w V}{A^2}\left(\frac{dV}{dt}\right) \tag{14.1}$$

Where η is the viscosity of the filtrate, w is the mass of solids deposited on the medium per unit volume of filtrate, V is the volume of filtrate delivered in time t, A is the filter area normal to the direction of flow of the filtrate and α is

the *specific cake resistance*. α characterises the resistance to flow offered by the cake and physically represents the pressure drop necessary to give unit superficial velocity of filtrate of unit viscosity through a cake containing unit mass of solid per unit filter area.

If a cake is composed of rigid nondeformable solid particles, then α is independent of the pressure drop across the cake and is constant throughout the depth of the cake. Such a cake is known as *incompressible*. In the case of incompressible cakes, it is possible to calculate the value of α. In contrast, a *compressible* cake is made up of nonrigid deformable solid particles or agglomerates of particles. In such cakes, the value of α increases with increase in pressure and also varies throughout the depth of the cake, being highest near the filter medium. The relationship between α and $-\Delta p_c$ is often expressed as:

$$\alpha = \alpha_0(-\Delta p_c)^s \tag{14.2}$$

Where α_0 and s are empirical constants. s is known as the *compressibility coefficient* of the cake and is zero for an incompressible cake rising towards 1.0 as the compressibility increases. In the case of compressible cakes, values of α must be obtained by experiment.

The filter medium also offers resistance to the flow of the filtrate and a pressure drop, $-\Delta p_m$, develops across it. This pressure drop may be expressed as:

$$-\Delta p_m = \frac{R_m \eta}{A}\left(\frac{dV}{dt}\right)\cdots \tag{14.3}$$

Where R_m is known as the *filter medium resistance*. Values of R_m are determined experimentally. It is usual to assume that R_m is constant throughout any filtration cycle.

The total pressure drop across the cake and medium, $-\Delta p$, is obtained by adding the two pressure drops together, thus:

$$-\Delta p = -\Delta p_c - \Delta p_m = \frac{\eta}{A}\left(\frac{dV}{dt}\right)\left(\frac{\alpha w V}{A} + R_m\right) \tag{14.4}$$

or:

$$\frac{dV}{dt} = \frac{A(-\Delta p)}{\eta\left(\frac{\alpha w V}{A} + R_m\right)} \tag{14.5}$$

A filter cycle may be carried out by maintaining a constant total pressure drop across the cake and medium. This is known as *constant pressure filtration*. As the cake builds up during the cycle, the rate of flow of filtrate decreases. Alternatively, the rate of flow of filtrate may be maintained constant throughout the cycle, in which case the pressure increases as the cake builds up. This is known as *constant rate filtration*. A combination of constant rate and constant pressure

filtration may also be employed by building up the pressure in the early stages of the cycle and maintaining it constant throughout the remainder of the cycle. Equation (14.5) may be applied to both constant pressure and constant rate filtration. In the case of a compressible cake, a relationship such as Eq. (14.2) needs to be used to account for the change in α with increase in pressure during constant rate filtration [2–10].

14.2.2 Filter Media

The main functions of the filter medium are to promote the formation of the filter cake and to support the cake once it is formed. Once the filter cake is formed, it becomes the primary filter medium. The medium must be strong enough to support the cake under the pressure and temperature conditions that prevail during the filtering cycle. It must be nontoxic and chemically inert with respect to the material being filtered. Filter media may be flexible or rigid. The most common type of flexible medium is a woven cloth, which may be made of cotton, wool, silk or synthetic material. The synthetic materials used include Nylon, polyester, polyacrylonitrile, polyvinylchloride, polyvinylidenechloride, polyethylene and polytetrafluoroethylene. Such woven materials are available with different mesh counts, mesh openings, thread sizes and weaves. Woven glass fibre and flexible metal meshes are also used as filter media. Nonwoven, flexible media are fabricated in the form of belts, sheets or pads of various shapes. These tend to be used for filtering liquids with relatively low solids content. Most of the solids remain enmeshed within the depth of the media rather than forming a cake on the surface. Rigid media may be fixed or loose. Fixed rigid media are made in the forms of disks, pads and cartridges. They consist of rigid particles set in permanent contact with one another. They include ceramic and diatomaceous materials and foamed plastics made from polyvinylchloride, polyethylene, polypropylene and other polymer materials. Perforated metal plates and rigid wire meshes are used for filtering relatively large particles. Loose rigid media consist of rigid particles that are merely in contact with each other but remain in bulk, loose form. They include sand, gravel, charcoal and diatomaceous material arranged in the form of beds. All types of media are available with different pore sizes to suit particular filtration duties. Practical trials are the most reliable methods for selecting media for particular tasks [7–11].

14.2.3 Filter Aids

Filter aids are employed to improve the filtration characteristics of highly compressible filter cakes or when small amounts of finely divided solids are being filtered. They consist of hard, strong, inert incompressible particles of irregular shape. They form a porous, permeable rigid lattice structure which allows liquid to pass through but retains solid particles. They are usually applied in small

amounts in the range 0.01–4.00% of the weight of the suspension. They may be applied in one of two ways. The filter medium may be precoated with a layer of filter aid prior to introducing the suspension to be filtered. This precoat, which is usually 1.5–3.0 mm thick, prevents the suspension particles from becoming enmeshed in the filter medium and reducing the flow of liquid. It may also facilitate the removal of the cake when filtration and washing are complete. Alternatively, the filter aid may be added to the suspension before it is introduced into the filter unit. It increases the porosity of the cake and reduces its compressibility. Sometimes a combination of precoating and premixing is used. The materials most commonly used as filter aids include: diatomaceous material (which is made from the siliceous remains of tiny marine plants known as diatoms, known as diatomite and kieselguhr), expanded perlite (made from volcanic rock), charcoal, cellulose fibres and paper pulp. These materials are available in a range of grades. Experimental methods are used to select the correct grade, amount and method of application for a particular duty [7–10].

14.2.4 Filtration Equipment

Gravity filtration is not widely applied to food slurries, but is used in the treatment of water and waste disposal. These applications are covered in Chapter 13.

14.2.4.1 Pressure Filters

In pressure filters the feed is pumped through the cake and medium and the filtrate exits at atmospheric pressure. The following are examples of pressure filters used in processing of foods.

Plate-and-Frame Filter Press In this type of press grooved plates, covered on both sides with filter medium, alternate with hollow frames in a rack (see Fig. 14.1). The assembly of plates and frames is squeezed tightly together to form a liquid-tight unit. The feed is pumped into the hollow frames through openings in one corner of the frames (see Fig. 14.2). The cake builds up in the frames and the filtrate passes through the filter medium onto the grooved surface of the plates, from where it exits via an outlet channel in each plate. When filtering is complete, wash liquid may be pumped through the press following the same path as the filtrate. Some presses are equipped with special wash plates (see Fig. 14.2). Every second plate in the frame is a wash plate. During filtration, these act as filter plates. During washing, the outlets from the wash plates are closed and the wash liquid is pumped onto their surfaces via an inlet channel (see Fig. 14.2). The wash liquid then passes through the full thickness of the cake and two layers of filter medium before exiting from the filter plates. This is said to achieve more effective washing than that attainable without the wash plates. After washing, the press is opened, the cake is removed from the frames, the filter medium is cleaned and the press is reassembled ready for the

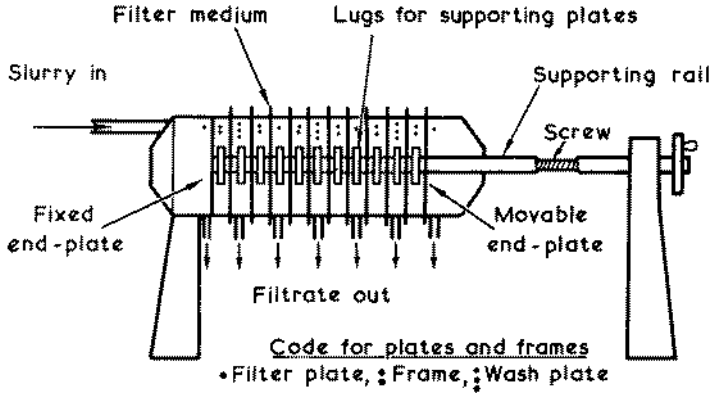


Fig. 14.1 Schematic drawing of assembled plate-and-frame filter press; from [2] with permission of the authors.

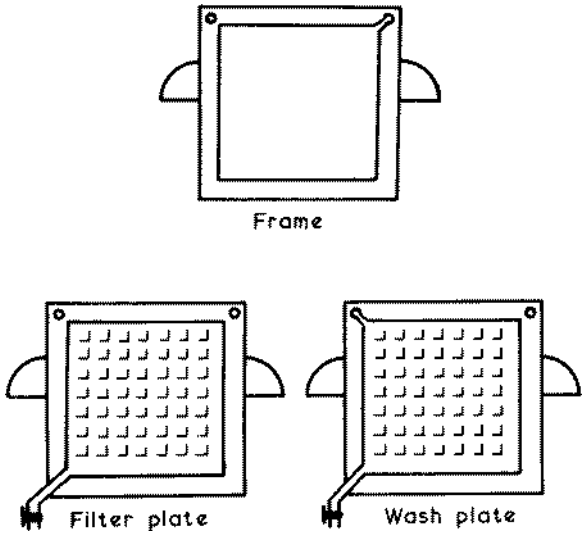


Fig. 14.2 Schematic drawings of plates and frames; from [2] with permission of the authors.

next run. This and other types of vertical plate filters are compact, flexible and have a relatively low capital cost. However, labour costs and filter cloth consumption can be high.

Horizontal Plate Filter In this type of filter, the medium is supported on top of horizontal drainage plates which are stacked inside a pressure vessel. The feed is pumped in through a central duct, entering above the filter medium. The filtrate passes down through the medium onto the drainage plates and exits from them through an annular outlet. The cake builds up on top of the filter medi-

um. After filtration, the feed is replaced by wash liquid which is pumped through the filter. After washing, the assembly of plates is lifted out of the pressure vessel and the cake removed manually. This type of filter is compact. The units are readily cleaned and can be sterilised if required. Labour costs can be high. They are used mainly for removing small quantities of solids and are known as polishing filters.

Shell-and-Leaf Filters A filter leaf consists of a wire mesh screen or grooved plate over which the filter medium is stretched. Leaves may be rectangular or circular in shape. They are located inside a pressure vessel or shell. They are either supported from the bottom or centre or suspended from the top, inside the shell. The supporting member is usually hollow and acts as a takeaway for the filtrate. In horizontal shell-and-leaf filters, the leaves are mounted vertically inside horizontal pressure vessels (see Fig. 14.3).

As the feed slurry is pumped through the vessel, the cake builds up on the filter medium covering the leaves while the filtrate passes through the medium into the hollow leaf and then out through the leaf supports. Leaves may be stationary or they may rotate about a horizontal axis. When filtering is stopped, washing is carried out by pumping wash liquid through the cake and leaves. The cake may be removed by withdrawing the leaf assembly from the shell and cleaning the leaves manually. In some designs, the bottom half of the shell may be opened and the cake sluiced down with water jets. In vertical shell-and-leaf filters, rectangular leaves are mounted vertically inside a vertical pressure vessel. Shell-and-leaf filters are generally not as labour intensive as plate-and-frame presses but have higher capital costs. They are mainly used for relatively long filtration runs with slurries of low or moderate solids content.

Edge Filters In this type of filter a number of stacks of rings or discs, known as filter piles or packs, are fixed to a header plate inside a vertical pressure ves-

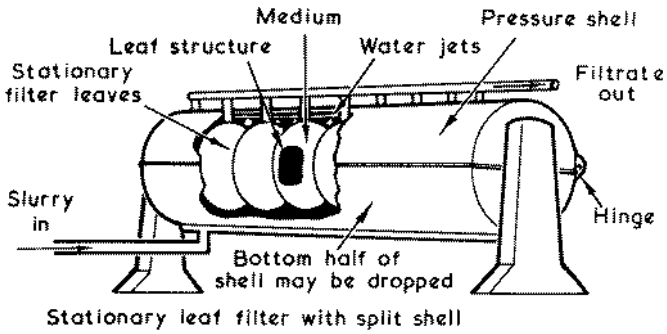


Fig. 14.3 Schematic drawing of a shell-and-leaf filter; adapted from [2] with permission of the authors.

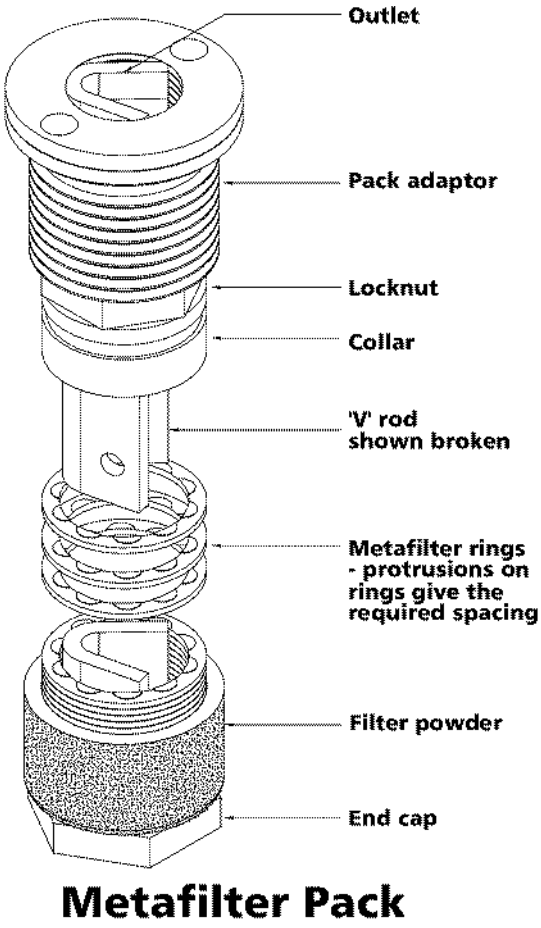


Fig. 14.4 Filter pile; by courtesy of Stella-Meta Ltd.

sel. Each pile consists of a number of discs mounted one above the other on a fluted vertical rod and held together between a boss and nut (see Fig. 14.4).

The clearance between the discs is in the range 25–250 μm. Before filtration commences, a precoat of filter aid is applied to the edges of the discs. When the feed slurry is pumped into the pressure vessel, the cake builds up on top of the precoat of filter aid, while the filtrate passes between the discs and exits via the grooves on the supporting rod. Additional filter aid may be mixed with the feed. When filtering and washing are complete, the cake is removed by back flushing with liquid through the filtrate outlet and removing the cake in the form of a sludge through an outlet in the bottom of the pressure vessel. The discs may be made of metal or plastic. Edge filters have a relatively low labour

requirement and use no filter cloth. They are used mainly for removing small quantities of fine solids from liquids.

14.2.4.2 **Vacuum Filters**

In vacuum filters a partial vacuum is created downstream of the medium and atmospheric pressure is maintained upstream. Most vacuum filters are operated continuously, as it is relatively easy to arrange continuous cake discharge under atmospheric pressure.

Rotary Drum Vacuum Filters There are a number of different designs of this type of filter, one of which is depicted in Fig. 14.5.

A cylindrical drum rotates about a horizontal axis partially immersed in a tank of the feed slurry. The surface of the drum is divided into a number of shallow compartments by means of wooden or metal strips running the length of the drum. Filter medium is stretched over the drum surface, supported on perforated plates or wire mesh. A pipeline runs from each compartment to a rotary valve located centrally at one end of the drum. Consider one of the compartments on the surface of the drum (shown shaded in Fig. 14.5). As the drum rotates, this compartment becomes submerged in the slurry. A vacuum is applied to the compartment through the rotary valve. Filtrate is drawn through the medium and flows through the pipe to the rotary valve, from where it is directed to a filtrate receiver. The solids form a layer of cake on the outer surface of the medium. The cake increases in thickness as long as the compartment remains submerged in the slurry. As it emerges from the slurry, residual filtrate is sucked from the cake. Next the compartment passes beneath sprays of wash

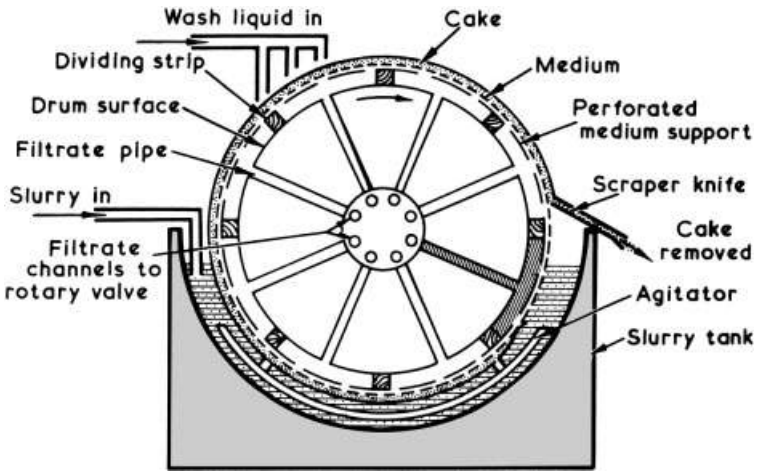


Fig. 14.5 Principle of operation of a rotary drum vacuum filter; from [2] with permission of the authors.

liquid. The washings are directed to a different receiver by means of the rotary valve. As the compartment passes from beneath the sprays, residual wash liquid is sucked from the cake. Next, by means of the rotary valve, the compartment is disconnected from the vacuum source and compressed air introduced beneath the medium for a short period of time. This loosens the cake from the surface of the medium and facilitates its removal by means of a scraper knife.

Many other designs of rotary drum filters are available featuring different methods of feeding the slurry onto the drum surface removing the cake from the medium.

Rotary drum vacuum filters incur relatively low labour costs and have large capacities for the space occupied. However, capital costs are high and they can only handle relatively free-draining solids. In common with all vacuum filters, they are not used to process hot and/or volatile liquids.

For removing small quantities of fine solids from a liquid, a relatively thick layer (up to 7.5 cm) of filter aid may be precoated onto the medium. A thin layer of this precoat is removed together with the cake by the scraper knife.

Rotary Vacuum Disc Filters In a disc filter, instead of a drum, a number of circular filter leaves, mounted on a horizontal shaft, rotate partially submerged in a tank of slurry. Each disc is divided into sections. Each section is covered with filter medium and is connected to a rotary valve, which controls the application of vacuum and compressed air to the section. Scraper knives remove the cake from each disc. Such disc filters have a larger filtering surface per unit floor area, compared to drum filters. However, cake removal can be difficult and damage to filter cloth excessive.

Other designs of continuous vacuum filters are available featuring moving belts, rotating tables and other supports for the filter medium. These are used mainly for waste treatment rather than in direct food applications [2, 5–7, 9, 10].

14.2.4.3 Centrifugal Filters (Filtering Centrifugals, Basket Centrifuges)

In this type of filter, the flow of filtrate through the cake and medium is induced by centrifugal force. The slurry is fed into a rotating cylindrical bowl with a perforated wall. The bowl wall is lined on the inside with a suitable filter medium. Under the action of centrifugal force, the solids are thrown to the bowl wall where they form a filter cake on the medium. The filtrate passes through the cake and medium and leaves the bowl through the perforations in the wall.

Batch Centrifugal Filters The principle of this type of filter is shown in Fig. 14.6. The cylindrical metal bowl in suspended from the end of a vertical shaft within a stationary casing. With the bowl rotating at moderate speed, slurry is fed into the bowl. A cake forms on the medium lining the inside of the perforated bowl wall and the filtrate passes through the perforations into the casing and out through a liquid outlet. The speed of the bowl is increased to recover most of the filtrate. Wash liquid may be sprayed onto the cake and spun off at high speed. The bowl

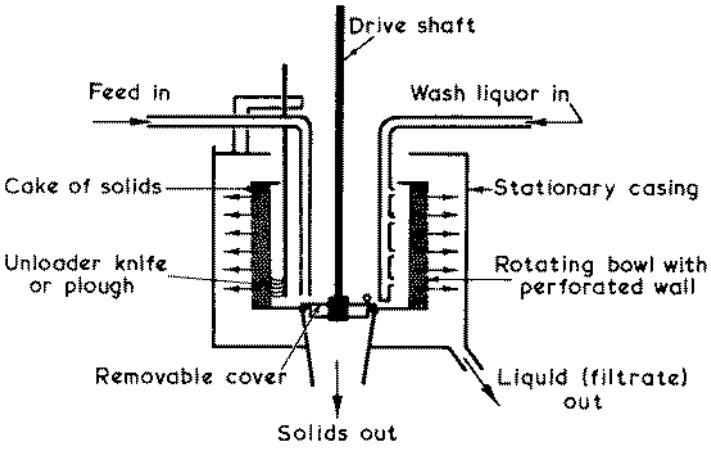


Fig. 14.6 Batch centrifugal filter; from [2] with permission of the authors.

is then slowed down, the cake cut out with an unloader knife or plough and removed through an opening in the bottom of the bowl. Cycle times vary over 3–30 min.

Fully automated versions of these batch filters operate at a constant speed, about horizontal axes, throughout a shorter cycle of 0.5–1.5 min. The feed and wash liquid are introduced automatically and the cake is cut out by a hydraulically operated knife.

Continuous Centrifugal Filters The principle of one type of continuous centrifugal filter is shown in Fig. 14.7.

A conical perforated bowl (basket) rotates about a vertical axis inside a stationary casing. The incline of the bowl causes the separation force to be split be-

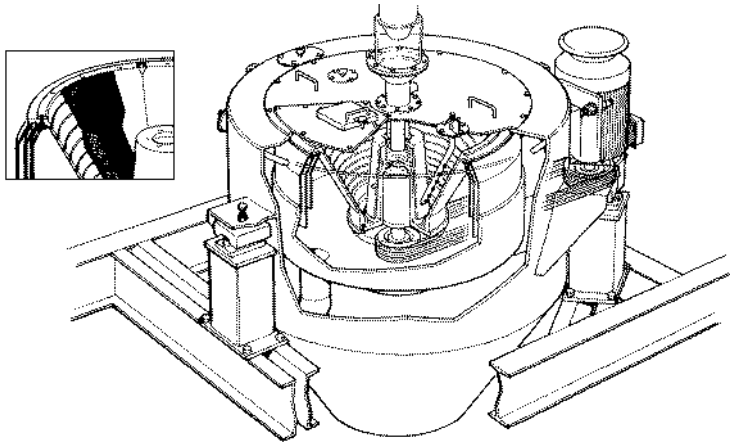


Fig. 14.7 A continuous centrifugal filter; by courtesy of Broadbent Customer Services Ltd.

tween vertical and horizontal elements resulting in the product moving upwards. The vertical force pushes the product up over the basket lip into the casing from where it is discharged. The horizontal element ensures that purging of the liquid phase takes place. This type of centrifuge is used for separating sugar crystals from syrup. Sliding of the product upwards and its discharge form the lip of the bowl, usually at high speed, is a relatively violent process and may damage the product, i.e. fracture of crystals. Washing the solid phase while it is moving may limit its effectiveness.

Other types of continuous centrifugal filters feature reciprocating pushing devices, screw conveyors or vibrating mechanisms to facilitate removal of the cake [2, 5, 6, 11].

14.2.5 Applications of Filtration in Food Processing

14.2.5.1 Edible Oil Refining

Filtration is applied at a number of stages in refining of edible oils. After extraction or expression, crude oil may be filtered to remove insoluble impurities such as fragments of seeds, nuts, cell tissue, etc. For large-scale applications rotary filters are used. Plate-and-frame filters are used for smaller operations. Bleaching earths used in decolourising oils are filtered off using rotary or plate filters. The catalysts used in hydrogenating fats and oils are recovered by filtration. Since hydrogenated fats have relatively high melting points, heated plate filters may be used. During winterisation and fractionation of fats, after cooling, the higher melting point fractions are filtered off using plate-and-frame or belt filters [12–15].

14.2.5.2 Sugar Refining

The juice produced by extraction from sugar cane or sugar beet contains insoluble impurities. The juice is treated with lime to form a flocculent precipitate which settles to the bottom of the vessel. The supernatant liquid is filtered to produce a clear juice for further processing. Plate-and-frame presses, shell-and-leaf and rotary drum vacuum filters are used. The settled 'mud' is also filtered to recover more juice. Plate-and-frame presses or rotary drum vacuum filters are used for this duty. Filtration is also used at a later stage in the refining process to further clarify sugar juice. In the production of granulated sugar, purified sugar juice is concentrated up to 50–60% solids content by vacuum evaporation and seeded with finely ground sugar crystals to initiate crystallisation. When the crystals have grown to the appropriate size, they are separated from the juice in batch or continuous centrifugal filters (see Section 3.1.4.2) [16, 17].

14.2.5.3 **Beer Production**

During maturation of beer, a deposit of yeast and trub forms on the bottom of the maturation tank. Beer may be recovered from this by filtration using plate-and-frame presses, shell-and-leaf or rotary drum vacuum filters. The beer is clarified by treatment with isinglass finings, centrifugation or filtration. If filtration is used, the beer is first chilled and then filtered through plate-and-frame, horizontal plate or edge filters. In the case of plate filters, the filter medium consists of sheets of cellulose, aluminium oxide or zirconium oxide fibres, with added kieselguhr. Insoluble polyvinyl pyrrolidone may also be incorporated into the medium to absorb phenolic materials associated with beer haze. Edge filters are precoated with filter aid and more filter aid is usually added to the beer prior to filtration. Yeasts and bacteria may also be removed from beer by filtration. Although the pore sizes in the media are much larger than the microorganisms, the fibres hold the negatively charged microorganisms electrostatically. The pressure drop across these filters needs to be limited to avoid the microorganisms being forced off the media fibres. When a sterile product is desired, the sealed filter must be presterilised before use [18, 19].

14.2.5.4 **Wine Making**

Wine is filtered at different stages of production: after racking, after decolourising and finally just before bottling. Plate-and-frame presses, shell-and-leaf filters, edge filters and precoated rotary drum vacuum filters have been used. Filter media are mainly sheets made of cellulose incorporating filter aid material (mainly diatomaceous earth) which is bound into the cellulose sheets with bitumen. With edge and precoated drum filters, loose filter aid material is used. Sterile wine may be produced by filtration in presterilised equipment [20–22].

There are many other applications for filtration in the food industry, including the filtration of starch and gluten suspensions and the clarification of brines, sugar syrups, fruit juices, yeast and meat extracts.

14.3 Centrifugation

James G. Brennan

14.3.1 General Principles

Centrifugation involves the application of centrifugal force to bring about the separation of materials. It may be applied to the separation of immiscible liquids and the separation of insoluble solids from liquids.

14.3.1.1 Separation of Immiscible Liquids

If two immiscible liquids, A and B, with different densities, are introduced into a cylindrical bowl rotating about a vertical axis, under the influence of centrifugal force, the more dense liquid A moves towards the wall of the bowl where it forms an annular ring (see Fig. 14.8). The less dense liquid B is displaced towards the centre of the bowl where it forms an inner annular ring.

If the feed is introduced continuously into the bottom of the bowl through a vertical feed pipe, the liquids may be removed separately from each layer by a weir system, as shown in Fig. 14.9. The more dense liquid A flows out over a circular weir of radius R_A and the less dense liquid B over a weir of radius R_B.

The interface between the two layers is known as the neutral zone. The position of this interface can influence the performance of the centrifuge. In the outer zone (A), light liquid is effectively stripped from a mass of dense liquid while, in the inner zone (B), dense liquid is more effectively stripped from a mass of light liquid. Thus, if the centrifuge is being used to strip a mass of dense liquid free of light liquid so that the dense phase leaves in as pure a state

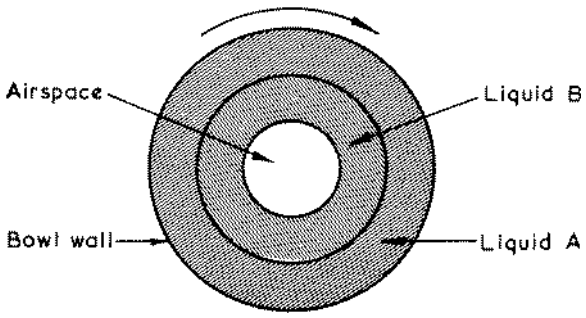


Fig. 14.8 Separation of immiscible liquids in a cylindrical bowl (plan view); from [2] with permission of the authors.

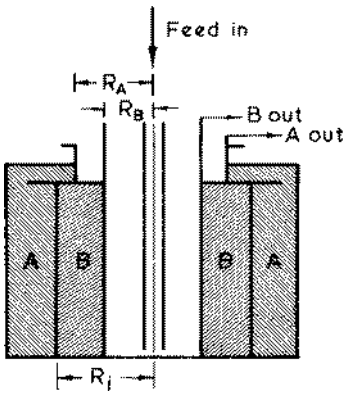


Fig. 14.9 Separation of immiscible liquids in a cylindrical bowl with submerged weir (sectional view); from [2] with permission of the authors.

as possible, then the dwell time in zone A should be greater than that in zone B. For such a duty, the interface is best moved towards the centre of rotation so that the volume of zone A exceeds that of zone B. In this situation, the light component is exposed to a relatively small centrifugal force for a short time, while the heavy component is exposed to a large force for a longer time. An example of such a duty is the separation of cream from milk, where the objective is to produce skim milk with as little fat in it as possible. In contrast, if the duty is to strip a mass of light liquid free of dense liquid, i.e. to produce a pure light phase, the interface is best moved out towards the bowl wall so that the volume occupied by zone B exceeds that of zone A. An example of such a duty would be the removal of small amounts of water from an oil. The actual change in position of the interface is quite small, in the order of 25–50 μm. However, it does affect the performance of the separator. The position of the interface can be changed by altering the radii of the liquid outlets. For example, if the radius of the light liquid outlet R_B is fixed, decreasing the radius of the dense liquid outlet R_A will move the interface towards the centre of rotation. In practice, the radius of either liquid outlet and hence the position of the interface, is determined by fitting a ring with an appropriate internal diameter to the outlet. Such rings are known as *ring dams* or *gravity discs*. It has also been established that the best separation is achieved by introducing the feed to the bowl at a point near the interface. The density difference between the liquids needs to be 3% or more for successful separation. Other factors which influence the performance of liquid-liquid centrifugal separators are bowl speed and the rate of flow of the liquids through them. In general, the higher the speed of the bowl, the better the separation. However, at very high speeds the viscosity of the oil phase may impede its flow through the centrifuge. The higher the rate of flow of the liquids through the bowl, the shorter the dwell time in the action zone; and so the less effective the separation is likely to be. For each duty a compromise needs to be struck between throughput and efficiency of separation.

14.3.1.2 Separation of Insoluble Solids from Liquids

If a liquid containing insoluble solid particles is fed into the bottom of a cylindrical bowl rotating about a vertical axis, under the influence of centrifugal force, the solid particles move towards to the bowl wall. If a particular solid particle reaches the bowl wall before being swept out by the liquid leaving through a central outlet in the top of the bowl (see Fig. 14.10), it remains in the bowl and thus is separated from the liquid. If it does not reach the bowl wall, it is carried out by the liquid. The fraction of the solid particles remaining in the bowl and the fraction passing out in the liquid depend on the rate of feed, i.e. the dwell time in the bowl.

The following expression relates the throughput of liquid through a cylindrical bowl centrifuge to the characteristics of the feed and the dimensions and speed of the bowl:

$$q = 2\left[\frac{g(\rho_s - \rho_l)D_p^2}{18\eta}\right]\left[\frac{\omega^2 V}{2g\ln\left(\frac{R_2}{[(R_1^2+R_2^2)/2]^{1/2}}\right)}\right] \tag{14.6}$$

where q is the volumetric flow rate of liquid through the bowl, g is acceleration due to gravity, ρ_s is the density of the solid, ρ_l is the density of the liquid, D_p is the minimum diameter of a particle that will be removed from the liquid, η is the viscosity of the liquid, ω is the angular velocity of the bowl, V is the volume of liquid held in the bowl at any time, R_1 is the radius of the liquid outlet and R_2 is the inner radius of the bowl. Note the quantities contained within the first set of square brackets relate to the feed material, while those within the second set refer to the centrifuge. This expression can be used to calculate the throughput of a specified feed material through a cylindrical bowl centrifuge of known dimensions and speed. It can also be used for scaling-up calculations. Alternative expressions for different types of bowl (see Section 14.3.2) can be found in the literature [2, 5, 6, 23].

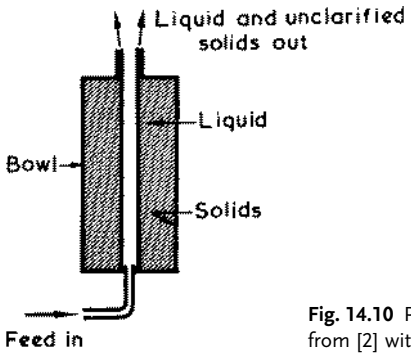


Fig. 14.10 Principle of simple cylindrical centrifugal clarifier; from [2] with permission of the authors.

14.3.2
Centrifugal Equipment

14.3.2.1 Liquid-Liquid Centrifugal Separators

Tubular Bowl Centrifuge This type of centrifuge consists of a tall, narrow bowl rotating about a vertical axis inside a stationary casing. Bowl diameters range from 10 cm to 15 cm with length:diameter ratios of 4–8. The feed enters into the bottom of the bowl through a stationary pipe and is accelerated to bowl speed by vanes or baffles. The light and dense phases leave via a weir system at the top of the bowl and flow into stationary discharge covers. Depending on the duty it has to perform, a gravity disc of appropriate size is fitted to the dense phase outlet, as explained in Section 14.3.1.1. Bowl speeds range from 15 000 rpm (large) to 50 000 rpm (small).

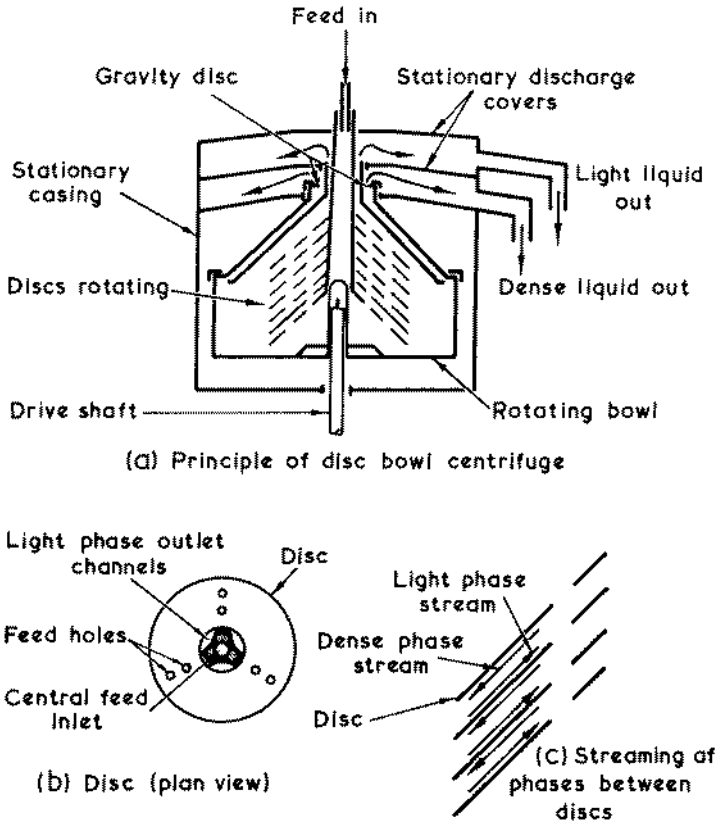


Fig. 14.11 Principle of disc bowl centrifuge; from [2] with permission of the authors.

Disc Bowl Centrifuge In this type of centrifuge a relatively shallow, wide bowl rotates within a stationary casing. The bowl usually has a cylindrical body, with a diameter in the range 20–100 cm and a conical top (see Fig. 14.11). The bowl contains a stack of truncated metal cones, known as discs, which rotate with the bowl. The clearance between the discs is of the order of 50–130 μm. The discs have one or more sets of matching holes which form vertical channels in the stack. The feed is introduced to the bottom of the bowl, flows through these channels and enters the spaces between the discs. Under the influence of centrifugal force, the dense phase travels in a thin layer down the underside of the discs towards the bowl wall while the light phase, displaced towards the centre of rotation, flows over the top of the discs. Thus the space between each pair of discs is a minicentrifuge. The distance any drop of one liquid must travel to get into the appropriate stream is small compared to that in a tubular bowl machine or indeed an empty bowl of any design. In addition, in a disc machine there is considerable shearing at the interface between the two countercurrent streams of liquid which contributes to the breakdown of emulsions. The phases leave the bowl through a weir system fitted with an appropriate gravity disc and flow into stationary discharge covers.

14.3.2.2 **Solid-Liquid Centrifugal Separators**

Both tubular bowl and disc bowl centrifuges can be used for solid-liquid separation, within certain limitations. For this type of duty, the dense phase outlet is closed off and the clear liquid exits the bowl through the central, light phase outlet. The solid particles which are separated from the liquid remain in the bowl, building up as a deposit on the wall of the bowl. Consequently, the centrifuges are operated on a batch principle and have to be stopped and cleaned at intervals. The tubular bowl machines have a relatively small solids capacity and are only suitable for handling feeds with low solids content, less than 0.5%. However, because of the high speeds they operate at, they are particularly suited to removing very fine solids. Disc bowl machines have up to five times the capacity for solids, compared to tubular bowl centrifuges. However, to avoid frequent cleaning, they are also used mainly with feeds containing relatively low solids content, less than 1.0%.

Solid Bowl Centrifuge (Clarifier) For separating solid particles which settle relatively easily, a bowl similar in shape to that shown in Fig. 14.7 may be used. However, the bowl wall is not perforated and no filter medium is used. The solids build up on the inside of the bowl wall and the clear liquid spills out over the top rim of the bowl into the outer casing. At intervals, the feed is stopped and the solids removed by means of a knife or plough and discharged through an opening in the bottom of the bowl. This type of clarifier can handle feeds with up to 2.0% solids content.

Nozzle-discharge Centrifuge In this type of centrifuge there is provision for the continuous discharge of solids, in the form of a sludge, as well as the clear liquid. There are many different designs available. One design consists of a disc-bowl machine with two to twenty four nozzles spaced around the bowl. The size of the nozzles is in the range 0.75 to 2.00 mm, depending on the size of the solid particles in the feed. From 5 to 50% of the feed is continuously discharged in the form of a slurry through these nozzles. The slurry may contain up to 25% v/v solids. By recycling some of the slurry the solids content may be increased. Up to 75% of the slurry may be recycled, depending on its flowability, and the solids content increased up to 40%.

Self-opening Centrifuge In this type of centrifuge the ports discharging the slurry open at intervals and the solids are discharged under a pressure of up to 3500 kN m^{-2}. The opening of the ports may be controlled by timers. Self-triggering ports are also available. The build-up of solids in the bowl is monitored and a signal is generated which triggers the opening of the ports. An example of one such centrifuge, used in the brewing industry, is shown in Fig. 14.12. The slurry discharged from these self-opening centrifuges usually has a higher solids content compared to that continuously discharged through open nozzles.

Decanting Centrifuge Nozzle and valve discharge centrifuges can only handle feeds containing a few percent or less of solids. For feeds containing a higher percent of solids, decanting or conveyor bowl centrifuges may be used. The principle of operation of one such centrifuge is shown in Fig. 14.13. A solid

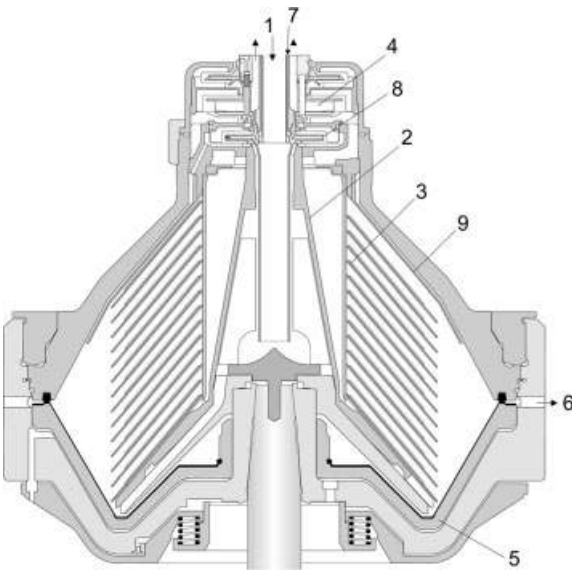


Fig. 14.12 A self-triggering solids-ejecting clarifier centrifuge; by courtesy of Alfa Laval Ltd.

bowl containing a screw conveyor rotates about a horizontal axis. The bowl and conveyor rotate in the same direction but at different speeds. The feed enters the bowl through the conveyor axis. The solids are thrown to the bowl wall and are conveyed to one end of the bowl, up a conical section, from where they are discharged. The clear liquid is discharged through an adjustable weir at the other end of the bowl. Such machines can handle feeds containing up to 90% (v/v) of relatively large solid particles. Particles 2 μm or less in diameter are normally not removed from the liquid. Where necessary, the liquid discharged from decanting centrifuges may be further clarified in tubular or disc bowl centrifuges [2, 5, 6, 10].

14.3.3 Applications for Centrifugation in Food Processing

14.3.3.1 Milk Products

Centrifugation is used in the separation of milk to produce cream and/or skim milk. Disc bowl centrifuges are generally used for this duty. They may be hermetically sealed and fitted with centripetal pumps. Milk is usually heated to between 40 °C and 50 °C prior to separation, to reduce its viscosity and optimise the density difference between the fat and aqueous phases. The fat content of the skim milk may be reduced to less than 0.05%. Although the process is continuous, insoluble solids present in the milk (dirt particles, casein micelles, microorganisms) build up as sludge in the centrifuge bowl. The bowl has to be cleaned out at intervals. Alternatively, nozzle or self-opening centrifuges may be used, but with outlets for the cream and skim milk as well as the sludge.

Fat may be recovered from whey and buttermilk by centrifugation [24].

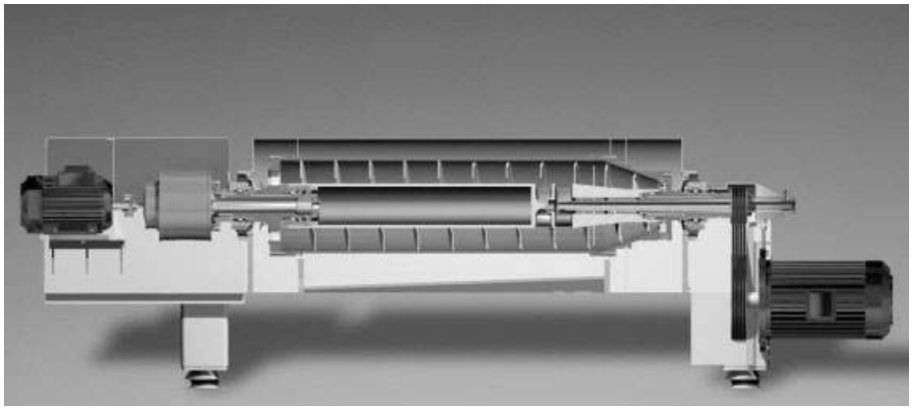


Fig. 14.13 Cut away view – Alfa Leval Decanter, by courtesy of Alfa Laval Ltd.

14.3.3.2 **Edible Oil Refining**

In the early stages of oil refining, the crude oil is treated with water, dilute acid or alkali to remove phosphatides and mucilaginous material. This process is known as degumming. Nozzle or self-opening centrifuges are used to remove the gums after these treatments. In the case of acid-degumming, the degummed oil may be washed with hot water and the washings removed by centrifugation. The next step in oil refining is neutralisation. The free fatty acids, phosphatides and some of the pigments are treated with caustic soda to form soapstock which is then separated from the oil by centrifugation, using nozzle or self-opening centrifuges. The oil is then washed with hot water and the washings removed by centrifugation [13].

14.3.3.3 **Beer Production**

Centrifugation may be used as an alternative to filtration at various stages in the production of beer. Nozzle discharge centrifuges may be used for clarifying rough beer from fermenting vessels and racking tanks. Self-opening centrifuges may be used for wort and beer clarification. Centrifuges used for the treatment of beer may be hermetically sealed to prevent the loss of carbon dioxide and the take-up of oxygen by the beer. Self-opening centrifuges may also be used for the recovery of beer from fermenters and tank bottoms. Decanting centrifuges may be used for clarifying worts and beers containing relatively high contents of yeast or trub. They may also be used as an alternative to self-opening machines to recover beer from fermenters and tank bottoms [18].

14.3.3.4 **Wine Making**

Centrifugation may be used instead of or in combination with filtration at various stages in the production of wine. Nozzle or self-opening centrifuges are generally used. Applications include: the clarification of must after pressing, provided that the solids content is relatively low, the clarification of wine during fermentation to stabilise it by gradual elimination of yeast, the clarification of new wines after fermentation and before filtration, the clarification of new red wines before filling into barrels and the facilitation of tartrate precipitation for the removal of tartrate crystals [20, 21, 22].

14.3.3.5 **Fruit Juice Processing**

Centrifugation may be used for a variety of tasks in fruit juice processing. Self-opening centrifuges are used to remove pulp and control the level of pulp remaining in pineapple and citrus juices. Centrifuged apple juice is cloudy but free from visible pulp particles. Tubular bowl centrifuges were originally used to clarify apple juice but more recently nozzle and self-opening machine are used. The use of hermetically sealed centrifuges prevents excessive aeration of the juice. In the production of oils from citrus fruits centrifugation is applied in

two stages. The product from the extractor contains an emulsion of 0.5–3.0% oil. This is concentrated up to 50–70% oil in a nozzle or self-opening centrifuge. The concentrated emulsion is then separated in a second centrifuge to produce the citrus oil [25, 26].

There are many other applications for centrifugation in food processing, e.g. tubular bowl machines for clarifying cider and sugar syrups and separating animal blood into plasma and haemoglobin, nozzle and self-opening machines for dewatering starches and decanting centrifuges for recovering animal and vegetable protein, separating fat from comminuted meat and separating coffee and tea slurries.

14.4 Solid-Liquid Extraction (Leaching)

James G. Brennan

14.4.1 General Principles

This is a separation operation in which the desired component, the *solute*, in a solid phase is separated by contacting the solid with a liquid, the *solvent*, in which the desired component is soluble. The desired component leaches from the solid into the solvent. Thus the compositions of both the solid and liquid phases change. The solid and liquid phases are subsequently separated and the desired component recovered from the liquid phase.

Solid-liquid extraction is carried out in single or multiple stages. A stage is an item of equipment in which the solid and liquid phases are brought into contact, maintained in contact for a period of time and then physically separated from each other. During the period of contact, mass transfer of components between the phases takes place and they approach a state of equilibrium. In an *equilibrium* or *theoretical* stage, complete thermodynamic equilibrium is attained between the phases before they are separated. In such a stage, the compositional changes in both phases are the maximum which are theoretically possible under the operating conditions. In practice, complete equilibrium is not reached and the compositional changes in a *real* stage is less than that attainable in an equilibrium stage. The *efficiency* of a real stage may be defined as the ratio of the compositional change attained in the real stage to that which would have been reached in an equilibrium stage under the same operating conditions. When estimating the number of stages required to carry out a particular task in a multistage system, the number of equilibrium stages is first estimated and the number of real stages calculated by dividing the number of equilibrium stages by the stage efficiency. Graphical and numerical methods are used to estimate the number of equilibrium stages required for a particular duty [2, 4–6].

After the period of contact, the solid-liquid mixture is separated into two streams: a 'clear' liquid stream or *overflow* consisting of a solution of the solute in the solvent and a 'residue' stream or *underflow* consisting of the insoluble solid component with some solution adhering to it. In an equilibrium stage, the composition of the overflow is the same as that of the solution leaving with the insoluble solid in the underflow. In a real stage, the concentration of solute in the overflow is less than that in the solution leaving with the insoluble solid in the underflow.

The extraction of the solute from a particle of solid takes place in three stages. The solute dissolves in the solvent. The solute in solution then diffuses to the surface of the particle. Finally, the solute transfers from the surface of the particle into the bulk of the solution. One or more of these steps can limit the rate of extraction. If the correct choice of solvent has been made, the solution of the solute in solvent is rapid and is unlikely to influence the overall rate of extraction. The rate of movement of the solute to the surface of the solid particle depends on the size, shape and internal structure of the particle and is difficult to quantify. The rate of transfer of the solute from the surface of the solid particle to the bulk of the solution may be represented by the expression:

$$\frac{dw}{dt} = KA(C_s - C) \tag{14.7}$$

Here, $\frac{dw}{dt}$ is the rate of mass transfer of the solute, A is the area of the solid-liquid interface, C_s and C are the concentration of the solute at the surface of the solid particle and in the bulk of the solution, respectively, and K is the mass transfer coefficient.

In a single stage extraction unit where V is the total volume of the solution and is constant, then:

$$\frac{dw}{dt} = VdC$$

and so:

$$\frac{dC}{dt} = \frac{KA(C_s - C)}{V} \tag{14.8}$$

The main factors which influence the rate of extraction include:

1. The solid-liquid interface area. The rate of mass transfer from the surface of the particle to the bulk of the solution increases with increase in this area. Reducing the size of the solid particles increases this area and so increases the rate of mass transfer. In addition, the smaller the particle the shorter the distance the solute has to travel to reach the surface. This is likely to further speed up the extraction. However, very small particles may impede the flow of solvent through the bed of solid in an extractor and some particles may

not come in contact with the solvent. In the case of cellular material, such as sugar beet (see Section 14.4.3.2), the cell wall acts as a semipermeable membrane releasing sugar but retaining larger nonsugar molecules. Therefore, the beet is sliced rather than comminuted to increase the surface area for extraction but to limit cell wall damage.

2. Concentration gradient. To ensure as complete extraction as possible, a gradient must be maintained between the concentration of solute at the surface of the solid particles and that in the bulk of the solution. In a single stage extractor, as the phases approach equilibrium, this gradient decreases and so does the rate of extraction until it ceases. When this occurs, the solid may still contain a significant amount of solute and the solution may be relatively dilute, depending on the equilibrium conditions. This solution could be drained off and replaced with fresh solvent resulting in further extraction of the solute. This could be repeated until the solute content of the solid reached a suitably low level. However, this would result in the production of a large volume of relatively dilute solution. The cost of recovering the solute from this solution increases as its solute content decreases. For example, the lower the concentration of sugar in the solution obtained after extraction of sugar beet, the more water has to be evaporated off before crystallisation occurs. Multistage countercurrent extraction systems enable a concentration gradient to be maintained even when the concentration of solute in the solid is low (see Fig. 14.14 b). This results in more complete extraction as compared with that attainable in single-stage or multistage concurrent systems (see Fig. 14.14 a).
3. Mass transfer coefficient. An increase in temperature increases the rate of solution of the solute in the solvent and also the rate of diffusion of solute through the solution. This is reflected in a higher value of K in Eq. (14.7) and Eq. (14.8). Thus, the solvent is usually heated prior to and/or during extraction. The upper limit in temperature depends on the nature of the solids. For example, in the extraction of sugar from beet, too high a temperature can result in peptisation of the beet cells and the release of nonsugar compounds into the solution (see Section 14.4.3.2). In the case of the extraction of solubles from ground roasted coffee beans, too high a temperature can result in the dried coffee powder having an undesirable flavour (see Section 14.4.3.3).

   Increasing the velocity and turbulence of the liquid as it flows over the solid particles can result in an increase in the value of K in Eq. (14.7) and Eq. (14.8) and hence an increase in the rate of extraction. In some industries, when fine particles are being extracted, they are mechanically stirred. However, in most food applications, this is not the case as agitation of the solid can result in undesirable breakdown of the particles. In most food applications, the solvent is made to flow through a static bed of solids under the influence of gravity or with the aid of a pump. Alternatively, the solids are conveyed slowly, usually countercurrent to the flow of solvent [2, 4–6, 27].

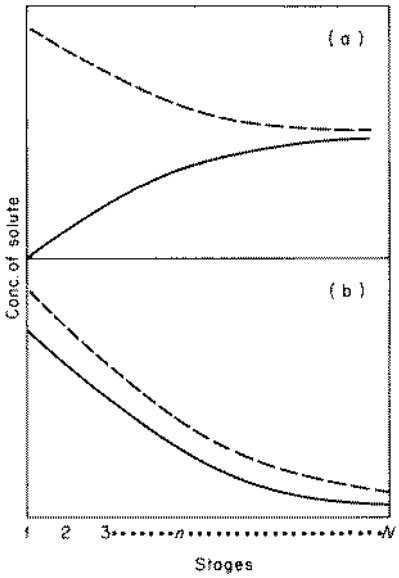


Fig. 14.14 Graphical representation of concurrent and countercurrent extraction systems. (a) Concurrent system, (b) countercurrent system. Solid lines indicates solution, dashed lines indicate solid matter; from [2] with permission of the authors.

14.4.2 Extraction Equipment

14.4.2.1 Single-Stage Extractors

A simple extraction cell consists of a tank fitted with a false bottom which supports a bed of the solids to be extracted. The tank may be open or closed. If extraction is to be carried under pressure, as in the case with extraction of ground roasted coffee (see Section 14.4.3.3), or if volatile solvents are used, as in the case of edible oil extraction (see Section 14.4.3.1), the tank is enclosed (see Fig. 14.15). The solvent is sprayed over the top surface of the bed of solids, percolates down through the bed and exits via an outlet beneath the false bottom. The tank may be jacketed and/or a heater incorporated into the solvent feed line to maintain the temperature of the solution at the optimum level. Usually a pump is provided for recirculating the solution. The spent solid is removed manually or dumped through an opening in the bottom of the tank. In large cells, additional supports may be provided for the bed of solids to prevent consolidation at the bottom of the cell.

Single extraction cells are used for laboratory trials and for small-scale industrial applications. As discussed in Section 14.4.1, the bulked solution from such units is relatively dilute. If a volatile solvent is used, the overflow from the cell may be heated to vapourise the solvent, which is then condensed and recycled through the cell. In this way, a more concentrated solution of the solute may be obtained.

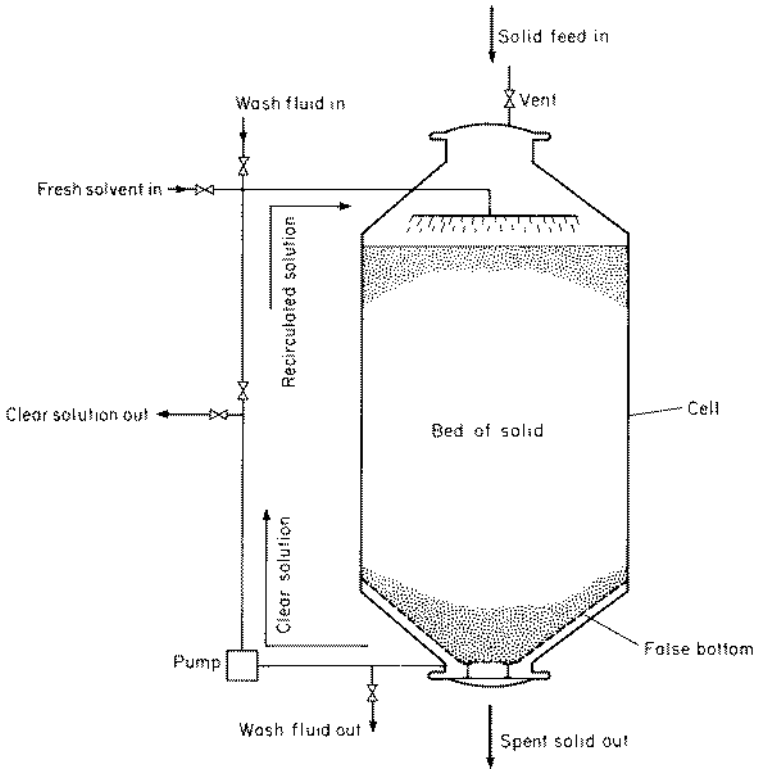


Fig. 14.15 Single-stage, enclosed extraction cell; from [2] with permission of the authors.

14.4.2.2 **Multistage Static Bed Extractors**

One method of applying multistage countercurrent extraction is to use a number of single cells arranged in a circuit. Each cell contains a charge of solids. The solution from the preceding cell is sprayed over the surface of the bed of solids and percolates down through the bed, becoming more concentrated as it does so. The solution leaving from the bottom of the cell is introduced into the top of the next cell. A typical battery, as used for the extraction of sugar beet, contains 14 cells, as shown in Fig. 14.16. At the time depicted in this figure, three of the cells are excluded from the circuit. Cells 10, 11 and 12 are being filled, washed and emptied, respectively. The fresh water enters cell 13 and the concentrated sugar solution, or overflow, leaves from cell 9. When the beet in cell 9 is fully extracted, this cell is taken out of the circuit and cell 10 brought in to take its place. Fresh water then enters cell 14 and the concentrated sugar solution leaves from cell 10. By isolating cells in turn around the circuit, the principle of countercurrent extraction may be achieved without physically moving the beet from one cell to the next. The number of cells in such a circuit may vary from three to 14.

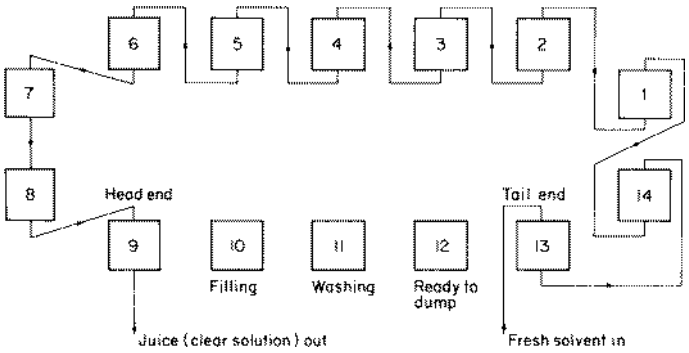


Fig. 14.16 Mulistage, countercurrent extraction battery showing flow of solution at one particular point in time; from [2] with permission of the authors.

14.4.2.3 **Multistage Moving Bed Extractors**

There are many different designs of moving bed extractors available. They usually involve moving the solid gently from one stage to the next, countercurrent to the flow of the solution. One type of continuous extractor consists of a trough set at a small angle to the horizontal containing two screw conveyors with intermeshing flights. The solvent is introduced at the elevated end of the trough. The solid is fed in at the other end and is carried up the slope by conveyors countercurrent to the flow of the solution. The trough is enclosed and capable of withstanding high pressure. Extractors of this type are used for sugar beet and ground roasted coffee. Another type, known as the *Bonotto* extractor is shown in Fig. 14.17. It consists of a vertical tower divided into sections by horizontal plates. Each plate has an opening through which the solid can pass downwards from plate to plate; and each plate is fitted with a wiper blade which moves the solid to the opening. The holes are positioned 180° from each other in successive plates. The solid is fed onto the top plate. The wiper blade moves it to the opening and it falls onto the plate below and so on down the tower from plate to plate. Fresh solvent is introduced at the bottom of the tower and is pumped upwards countercurrent to the solid. The rich solution leaves at the top of the tower and the spent solid is discharged from the bottom. This type of extractor is used for oil extraction from nuts and seeds.

Many other designs of continuous moving bed extractors are in use in industry. One design features moving perforated baskets which carry the solid through a stream of the solvent. In another design, the solid is conveyed by screw conveyors, with perforated blades, through vertical towers, countercurrent to the flow of solvent [2, 4–6, 27].

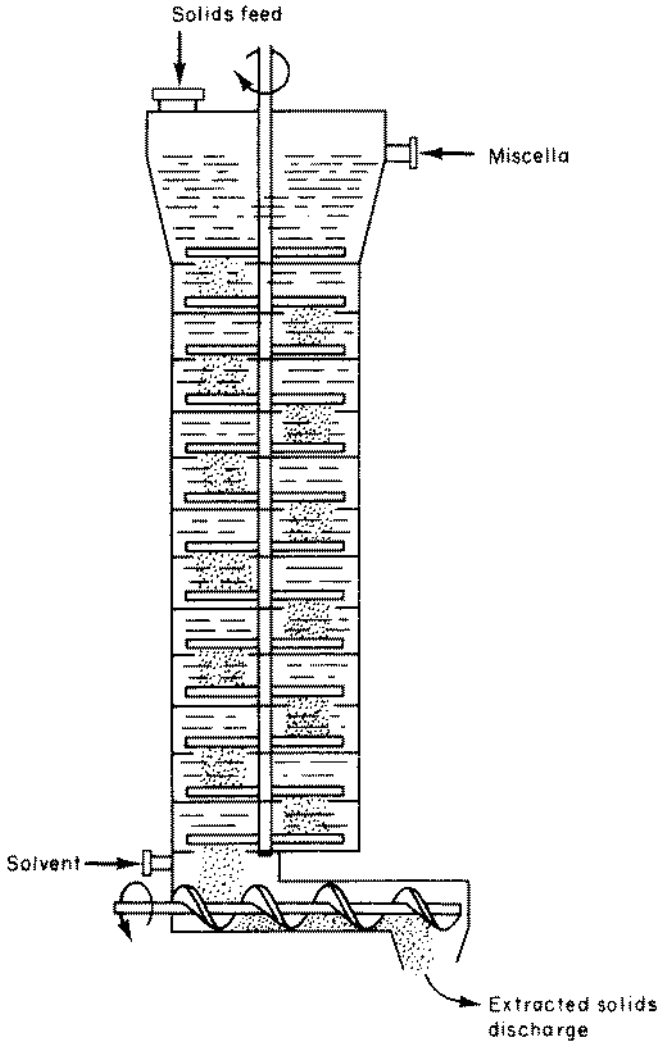


Fig. 14.17 Bonotto extractor.

14.4.3 Applications for Solid-Liquid Extraction in Food Processing

14.4.3.1 Edible Oil Extraction

Solvent extraction may be used as an alternative to or in combination with expression to obtain oil from nuts, seeds and beans. The most commonly used solvent is hexane. This is a clear hydrocarbon, derived from petroleum that boils at 68.9 °C. It is miscible with oil, immiscible with water and does not impart any objectionable odour or taste to the oil or spent solid. Hexane is highly flammable and so the plant must be vapour-tight and care must be taken to avoid the generation of sparks that might ignite the solvent. Other solvents have been investigated, including heptane and cyclohexane. Nonflammable solvents, such as trichloroethylene and carbon disulphide, have been studied but are toxic and difficult to handle. Various alcohols and supercritical carbon dioxide (see Section 14.4.5) have also been investigated. Various designs of moving bed extractors are used in large scale-oil extraction, including those described in Section 14.4.3. After extraction, the solution of oil in solvent is filtered, the solvent removed by vacuum evaporation followed by distillation and the solvent reused. Residual solvent may be removed from the spent solid by direct or indirect heating with steam and the resulting meal used for animal feed. Batch extractors featuring solvent recovery and reuse can be used for small-scale operations. Cottonseed, linseed, rapeseed, sesame, sunflower, peanuts, soybean and corn germ may be solvent-extracted [2, 28].

14.4.3.2 Extraction of Sugar from Sugar Beet

Sugar is extracted from sugar beet using heated water as solvent. The beets are washed and cut into slices, known as cossettes. This increases the surface area for extraction and limits cell wall damage (see Section 14.4.1). Water temperature ranges from 55 °C in the early stages of extraction to 85 °C towards the end. Higher temperatures can cause peptisation of the beet cells and release nonsugar compounds into the extract. Multistage static bed batteries, as depicted in Fig. 14.17, are widely used. So also are various designs of moving bed extractors, including those described in Section 14.4.2.3. The solution leaving the extractor contains about 15% of dissolved solids. This is clarified by settling and filtration, concentrated by vacuum evaporation, seeded and cooled to crystallise the sugar. The crystals are separated from the syrup by centrifugation, washed and air dried (see Section 3.1.5.2) [2, 29].

14.4.3.3 Manufacture of Instant Coffee

A blend of coffee beans is roasted to the required degree, ground to the appropriate particle size range and extracted with heated water. Extraction may be carried out in a multistage, countercurrent static bed system consisting of 5–8 cells. Each cell consists of a tall cylindrical pressure vessel as temperatures

above 100 °C are used. Heat exchangers are located between the cells. Water at about 100 °C is introduced into the cell containing the beans that are almost fully extracted and then passes through the other cells, until the rich solution exits from the cell containing the freshly ground beans. The temperature of the solution increases up to a maximum of 180 °C as it passes through the battery of cells. In the later stages of extraction, some hydrolysis of insoluble carbohydrate material occurs, resulting in an increase in the yield of soluble solids. Higher temperatures may impart an undesirable flavour to the product due to excessive hydrolysis. Continuous, countercurrent extractors featuring screw conveyors within pressurised chambers (see Section 14.4.2.3) may be used instead of the static bed system. The rich solution leaving the extractor usually contains 15–28% solids. This may be fed directly to a spray drier. Alternatively, the solution may be concentrated up to 60% solids by vacuum evaporation (see Section 3.1.5.2). The volatiles may be stripped from the extract before or during evaporation and added back to the concentrated extract prior to dehydration either by spray drying or freeze drying [2, 30, 31].

14.4.3.4 **Manufacture of Instant Tea**

Dried, blended tea leaves may be extracted with heated water in a static bed system consisting of 3–5 cells. Water temperature ranges from 70 °C in the early stages of extraction to 90 °C in the later stages. The cells may be evacuated after filling with the dry leaves and the pressure brought back to atmospheric level by introducing gaseous carbon dioxide. This facilitates the flow of the water through the cells. Continuous tower or other moving-bed extractors are also used to extract tea leaves. The rich solution coming from the extractor usually contains 2.5–5.0% solids. This is concentrated by vacuum evaporation to 25–50% solids. The volatile aroma compounds are stripped from the extract prior to or during evaporation and added back before dehydration by spray drying, vacuum drying or freeze drying.

14.4.3.5 **Fruit and Vegetable Juice Extraction**

In recent years there has been considerable interest in using extraction instead of expression for recovering juices from fruits and vegetables. Countercurrent screw extractors, some operated intermittently, have been used to extract juice with water. In some cases this results in higher yields of good quality compared to that obtained by expression [32].

14.4.4
The Use of Supercritical Carbon Dioxide as a Solvent

The critical pressure and temperature for carbon dioxide are 73.8 kPa and 31.06 °C, respectively. At pressures and temperatures above these values carbon dioxide exists in the form of a supercritical fluid (supercritical carbon dioxide;

SC-CO_2). In this state it has the characteristics of both a gas and a liquid. It has the density of a liquid and can be used as a liquid solvent, but it diffuses easily like a gas. It is highly volatile, has a low viscosity, a high diffusivity, is nontoxic and nonflammable. These properties make it a very useful solvent for extraction. However, the fact that SC-CO_2 has to be used at high pressure means that relatively expensive pressure resistant equipment is required and running costs are also high. The solvent power of SC-CO_2 increases with increase in temperature and pressure. For the extraction of highly soluble compounds or for deodorisation, pressures and temperatures close to the critical values may be used. When a single component is to be extracted from an insoluble matrix, so called *simple extraction*, the highest pressure and temperature possible for each application should be used. The upper limit on temperature will depend on the heat-sensitivity of the material. The limit on pressure will be determined by the cost of the operation. When all soluble matter is to be extracted, so called *total extraction*, high pressures and temperatures are again necessary.

The following are examples of the industrial application of SC-CO_2 extraction.

Hop Extract A good quality hop extract, for use in brewing, may be obtained by extraction with SC-CO_2. A multistage, countercurrent, static bed system, consisting of four extraction cells, is normally used. The SC-CO_2 percolates down through the hop pellets in each cell in turn. The solution of the extract in the SC-CO_2 leaving the battery is heated and the carbon dioxide evaporates, precipitating out the extract. The carbon dioxide is recompressed and cooled and condenses back to SC-CO_2 which is chilled to 7 °C and recycled through the extraction battery.

Decaffeination of Coffee Beans SC-CO_2 may be used as an alternative to water or methylene chloride for the extraction of caffeine from coffee beans. The beans are moistened before being loaded into the extractor. SC-CO_2 is circulated through the bed of beans extracting the caffeine. The caffeine-laden SC-CO_2 passes to a scrubbing vessel where the caffeine is washed out with water. Alternatively, the caffeine may be removed by passing the caffeine-laden SC-CO_2 through a bed of activated charcoal.

Removal of Cholesterol from Dairy Fats SC-CO_2 at 40 °C and 175 kPa has been used to remove cholesterol from butter oil in a packed column extractor. The addition of methanol as an entrainer increases the solubility of cholesterol in the fluid phase. The methanol is introduced with the oil into the column.

Many other potential applications for SC-CO_2 extraction have been investigated including: extraction of oils from nuts and seeds, extraction of essential oils from roots, flowers, herbs and leaves, extraction of flavour compounds from spices and concentration of flavour compounds in citrus oils [2, 28, 33–37].

14.5 Distillation

James G. Brennan

14.5.1 General Principles

Distillation is a method of separation which depends on there being a difference in composition between a liquid mixture and the vapour formed from it. This difference in composition develops if the different components of the mixture have different vapour pressures or *volatilities*. In *batch distillation*, a given volume of liquid is heated and the vapours formed are separated and condensed to form a product. In batch distillation, the compositions of the liquid remaining in the still and the vapour collected change with time. Batch distillation is still used in some whisky distilleries. However, continuous distillation columns are used in most industrial applications of distillation.

Consider a liquid mixture consisting of two components with different volatilities. If such a mixture is heated under constant pressure conditions, it does not boil at a single temperature. The more volatile component starts to vaporise first. The temperature at which this commences is known as the *bubble point*. If a vapour consisting of two components with different volatilities is cooled, the less volatile component starts to condense first. The temperature at which this commences is known as the *dew point*. A diagram of the temperature composition for liquid- vapour equilibrium of a two-component mixture is presented in Fig. 14.18.

The bottom 'L' line in the phase envelope represents liquid at its bubble point and the top 'V' line represents vapour at its dew point. The 0–1.0 composition axis refers to the more volatile component 'a', x_a and y_a are the mole fractions of 'a' in the liquid and vapour phases, respectively, and x_b and y_b are the mole fractions of component 'b', the less volatile component, in the liquid and vapour phases, respectively. The region below the bubble point curve represents subcooled liquid. The region above the dew point curve represents superheated vapour. Within the envelope, between the L and V lines, two phases exist. Saturated liquid and saturated vapour exist in equilibrium with each other.

If a liquid mixture at temperature θ_1 is heated until it reaches temperature θ_2, its bubble point, it will start to vaporise. The vapour produced at this temperature will contain mole fraction y_2 of component 'a'. Note that the vapour is richer in 'a' than the liquid. As a result of the evaporation the liquid becomes less rich in component 'a' and richer in 'b' so its temperature rises further. At temperature θ_3 the liquid phase contains mole fraction x_3 of 'a' and vapour phase y_3 of 'a'. Note that, at this temperature, the vapour is less rich in 'a' than it was at its bubble point. When temperature θ_4 is reached, all of the liquid is evaporated and the composition of the vapour is the same as the original liquid, $y_4 = x_1$. A similar sequence of events occurs if we start with a superheated va-

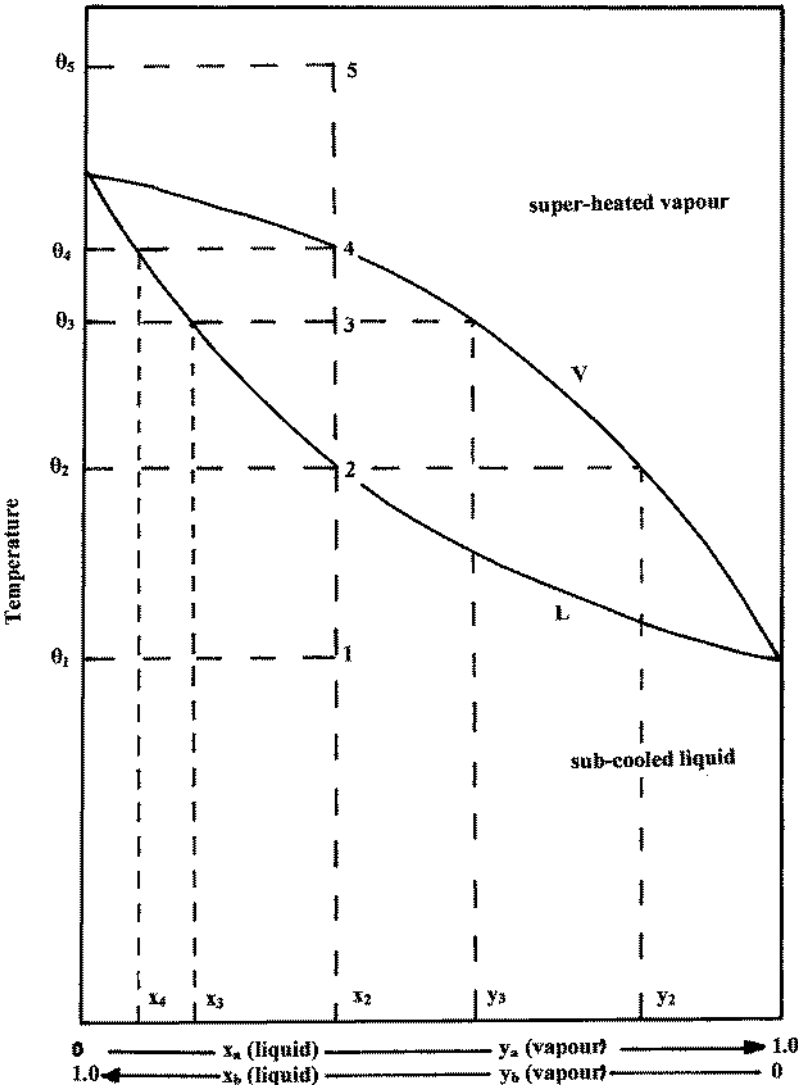


Fig. 14.18 Temperature-composition diagram for liquid-vapour equilibrium for a two-component mixture.

pour at temperature θ_5 and cool it. When it reaches its dew point θ_4, it begins to condense and the liquid contains mole fraction x_4 of 'a'. If cooled further to θ_3, the liquid and vapour contain mole fractions x_3 and y_3 of 'a', respectively. Thus both partial vaporisation and partial condensation bring about an increase of the more volatile component in the vapour phase. A distillation column consists of a series of stages, or *plates*, on which partial vaporisation and condensation takes place simultaneously.

The principle of a continuous distillation column, also known as a *fractionation* or *fractionating column*, is shown in Fig. 14.19.

The column contains a number of plates which are perforated to allow vapour rising from below to pass through them. Each plate is equipped with a weir over which the liquid flows and then through a *downtake* onto the plate below. The liquid contained in the *reboiler* at the bottom of the column is heated. When the liquid reaches its bubble point temperature, vapour is formed and this vapour bubbles through the liquid on the bottom plate. The vapour from the reboiler has a composition richer in the more volatile components than the liquid remaining in the reboiler. This vapour is at a higher temperature than the liquid on the bottom plate. Some of that vapour condenses and causes some of the liquid on the bottom plate to evaporate. This new vapour is richer in the more volatile components than the liquid on the bottom plate. This vapour in turn bubbles through the liquid on the plate above the bottom plate, causing some of it to evaporate and so on up the column. Thus, partial condensation and partial vaporisation takes place on each plate. The vapour rising up the column becomes increasingly rich in the more volatile components while the liquid flowing down from plate to plate becomes richer in the less volatile components. If all the vapour leaving the top of the column is condensed and removed, then the liquid in the column becomes progressively less rich in the volatile components as does the vapour being removed at the top of the column. This is the equivalent of batch distillation. However, if some of the condensed vapour is returned to the column and allowed to flow down from plate to plate, the concentration of the volatile components in the column is maintained at a higher level. The condensed vapour returned to the column is known as *reflux*. If feed material is introduced continuously into the column, then a product rich in volatile components can be withdrawn continuously from the top of the column and one rich in the less-volatile components from the reboiler at the bottom of the column. The feed is usually introduced onto a plate partway up the column.

Each plate represents a stage in the separation process. As is the case in solid-liquid extraction (see Section 14.4.1), the terms *equilibrium* or *theoretical* plate and *plate efficiency* may be applied to distillation. Graphical and numerical methods are used to estimate the number of equilibrium plates required to perform a particular duty and the number of real plates is calculated by dividing the number of equilibrium plates by the plate efficiency.

Steam distillation is applicable to mixtures which have relatively high boiling points and which are immiscible with water. If steam is bubbled through the liquid in the still, some of it will condense and heat the liquid to boiling point. Two liquid layers will form in the still. The vapour will consist of steam and the volatile vapour, each exerting its own vapour pressure. The mixture will boil when the sum of these pressures equals atmospheric pressure. Thus, the distillation temperature will always be lower than 100 °C at atmospheric pressure. By reducing the operating pressure, the distillation temperature will be reduced further and less steam will be used. Steam distillation may be used to separate

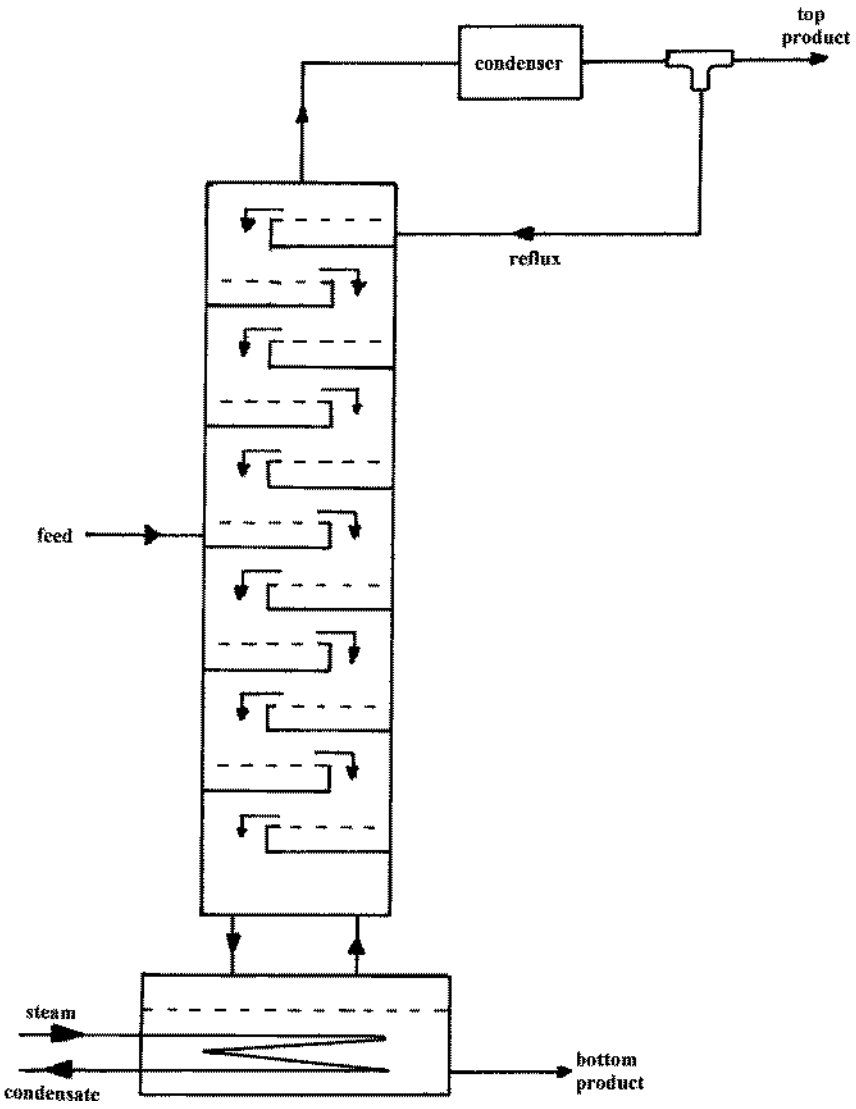


Fig. 14.19 Principle of a continuous distillation (fractionating) column.

temperature-sensitive, high boiling point materials from volatile impurities, or for removing volatile impurities with high boiling points from even less volatile compounds. The separation of essential oils from nonvolatile compounds dissolved or dispersed in water is an example of its application [5, 6, 38, 39].

14.5.2 Distillation Equipment

14.5.2.1 Pot Stills

Pot stills, used in the manufacture of good quality whiskey, are usually made from arsenic-free copper. Apparently the copper has an influence on the flavour of the product. The still consists of a pot which holds the liquor to be distilled and which is fitted with a swan neck. Because of their shape, pot stills are sometimes known as onion stills. A lyne arm, a continuation of the swan neck, tapers towards the condenser. The condenser is usually a shell and tube heat exchanger also made of copper. Heat is applied to the pot by means of steam passing through coils or a jacket. There is very limited use of direct heating by means of a solid fuel furnace beneath the pot. Such stills operate on a batch principle and two or three may operate in series (see Section 14.5.3.1).

14.5.2.2 Continuous Distillation (Fractionating) Columns

A distillation column consists of a tall cylindrical shell fitted with a number of plates or trays. The shell may be made of stainless steel, monel metal or titanium. As described in Section 14.5.1, the vapour passes upwards through the plates while the refluxed liquid flows across each plate, over a weir and onto the plate below via a downtake. There are many different designs of plate including the following examples.

Sieve plates consist of perforated plates with apertures of the order of 5 mm diameter, spaced at about 10 mm centres. The vapour moving up through the perforations prevents the liquid from draining through the holes. Each plate is fitted with a weir and downtake for the liquid.

Bubble cap plates are also perforated but each hole is fitted with a riser or 'chimney' through which the vapour from the plate below passes. Each riser is covered by a bell-shaped cap, which is fastened to the riser by means of a spider or other suitable mounting. There is sufficient space between the top of the riser and the cap to permit the passage of the vapour. The skirt of the cap may be slotted or the edge of the cap may be serrated. The vapour rises through the chimney, is diverted downwards by the cap and discharged as small bubbles through the slots or from the serrated edge of the cap beneath the liquid. The liquid level is maintained at some 5–6 cm above the top of the slots in the cap by means of the weir. The bubbles of vapour pass through the layer of liquid, heat and mass transfer occur and vapour, now richer in the more volatile components, leaves the surface of the liquid and passes to the plate above.

Valve plates are also perforated but the perforations are covered by liftable caps or valves. The caps are lifted as the vapour flows upwards through the perforations, but they fall and seal the holes when the vapour flow rate decreases. Liquid is prevented from falling down through the perforations when the vapour flow rate drops. The caps direct the vapour horizontally into the liquid thus promoting good mixing.

Packed columns may be used instead of plate columns. The cylindrical column is packed with an inert material. The liquid flows down the column in the form of a thin film over the surface of the packing material providing a large area of contact with the vapour rising up the column. The packing may consist of hollow cylindrical rings or half rings, which may be fitted with internal cross pieces or baffles. These rings may be made of metal, various plastics or ceramic materials. The packing is supported on perforated plates or grids. Alternatively, the column may be packed with metal mesh. The liquid flows through the packing in a zigzag pattern providing a large area of contact with the vapour [5, 38–40].

The spinning cone column consists of a vertical cylinder with a rotating shaft at its centre. A set of inverted cones are fixed to the shaft and rotate with it. Alternately between the rotating cones is a set of stationary cones fixed to the internal wall of the cylinder. The feed material, which may be in the form of a liquid, puree or slurry, is introduced into the top of the column. It flows by gravity down the upper surface of a fixed cone and drops onto the next rotating cone. Under the influence of centrifugal force, it is spun into a thin film which moves outwards to the rim of the spinning cone and onto the next stationary cone below. The liquid, puree or slurry moves from cone to cone to the bottom of the column. The stripping gas, usually nitrogen or steam, is introduced into the bottom of the column and flows upwards, countercurrent to the feed material. The thin film provides a large area of contact and the volatiles are stripped from the feed material by the gas or steam. Fins on the underside of the rotating cones create a high degree of turbulence in the rising gas or steam which improves mass transfer. They also provide a pumping action which reduces the pressure drop across the column. The gas or steam flows out of the top of the column and passes through a condensing system, where the volatile aroma compounds are condensed and collected in a concentrated form. This equipment is used to recover aroma compounds from fruits, vegetables and their by-products, tea, coffee, meat extracts and some dairy products [41].

14.5.3 Applications of Distillation in Food Processing

14.5.3.1 Manufacture of Whisky

Whisky is a spirit produced by the distillation of a mash of cereals, which may include barley, corn, rye and wheat, and is matured in wooden casks. There are three types of Scotch and Irish whisky: malt whisky produced from 100% malted (germinated) barley, grain whisky produced from unmalted cereal grains and blended whisky which contains 60–70% grain whisky and 30–40% malt whisky.

Malting of barley is carried out by steeping the grain in water for 2–3 days and allowing it to germinate. The purpose of malting is the production of amylases which later convert grain starch to sugar. Malting is stopped by drying the grain down to a moisture content of 5% in a kiln. In traditional Scotch whisky production, the grain is dried over a peat fire which contributes to the character-

istic flavour of the end product. Alternatively, the kiln may be heated indirectly by gas or oil or directly by natural gas. The dried grain is milled by means of corrugated roller mills, hammer mills or attrition mills (see Section 15.3.2), in order to break open the bran layer without creating much fines. The milled grain is mashed. In the case of malted barley, the grain is mixed with water at 63–68 °C for 0.5–1.5 h before filtering off the liquid, known as wort. In the production of grain whisky, the milled grain is cooked for 1.5 h at 120 °C to gelatinise the starch in the nonbarley cereals. It is cooled to 60–65 °C and 10–15% freshly malted barley is added to provide a source of enzymes for the conversion of the starch to the sugar maltose. The wort is filtered, transferred to a fermentation vessel, cooled to 20–25 °C, inoculated with one or more strains of the yeast *Saccharomyces cerevisiae* and allowed to ferment for 48–72 h. This produces a wash containing about 7% ethanol and many flavour compounds. The fermented wash is then distilled. In the batch process for the production of Scotch whisky, two pot stills are used. In the first, known as the *wash still*, the fermented mash is boiled for 5–6 h to produce a distillate, known as *low wines*, containing 20–25% (v/v) ethanol. This is condensed and transferred to a smaller pot still, known as the *low wines still*, and distilled to produce a spirit containing about 70% (v/v) ethanol. A crude fractionation is carried out in this second still. The distillate first produced, known as the *foreshots*, contains aldehydes, furfurols and many other compounds which are not used directly in the product. The foreshots are returned to the second still. The distillation continues and the distillate collected as product until a specified distillate strength is reached. Distillation continues beyond that point but the distillate, known as *feints*, is returned to the second still. A similar process, but incorporating three pot stills, is used in the production of Irish whiskey.

The continuous distillation of fermented mash to produce whisky is usually carried out using two distillation columns. The fermented wash is fed towards the top of the first column, known as the *beer column*. Alcohol-free stillage is withdrawn from the bottom of this column. The vapour from the top of the first column is introduced at the base of the second column, known as the *rectifier column*. The vapour from the top of this column is condensed and collected as product. The bottom product is returned as reflux to top of the first column. The rectifier column contains mainly sieve plates but with some bubble cap plates near the top. If the columns are fabricated from stainless steel, a flat disc of copper mesh may be fitted near the top of the rectifier column to improve the flavour of the product.

Whiskies produced by batch or continuous distillation are matured in wooden barrels, usually oak, for periods ranging from 1 year to more than 18 years, depending on the type and quality of the whisky. The type of barrel used has a pronounced effect on the flavour of the matured product. The matured products are usually blended before bottling.

The following are examples of other distilled beverage spirits. *Brandy* is a distillate from the fermented juice, mash or wine of fruit, *rum* is a distillate from the fermented juice of sugar cane, sugar cane syrup, sugar cane molasses or

other sugar cane products and *gin* is obtained by distillation from mash or by redistillation of distilled spirits, or by mixing neutral spirits, with or over juniper berries and other aromatics, or extracts from such materials. It derives its main characteristic flavour from juniper berries. *Tequila* is a distillate produced in Mexico from the fermented juice of the heads of *Agave tequilana* Weber, with or without other fermentable substances [42–45].

14.5.3.2 **Manufacture of Neutral Spirits**

A multicolumn distillation plant is used for producing neutral spirits from fermented mash. A typical system would be comprised of five columns: a whisky-separating column, an aldehyde column, a product-concentrating column, an aldehyde-concentrating column and a fusel oils concentrating column (see Fig. 14.20). The whisky-separating column is fitted with sieve plates, with some bubble cap plates near the top of the column. The other four columns are fitted with bubble cap plates. The fermented mash containing 7% (v/v) of alcohol is fed to near the top of the whisky-separating column. The overhead distillate from this column is fed to the aldehyde column. The bottom product from this column is pumped to the middle of the product-concentrating column. The end product, neutral spirit, is withdrawn from near the top of this column. The top product from the aldehyde column is rich in aldehydes and esters and is fed to the aldehyde-concentrating column. The top product from this column is rich in aldehydes and is removed while the bottom product is recycled to the aldehyde column. Fusel oils concentrate near the bottom of the aldehyde column and from there are fed to the fusel oil-concentrating column. The bottom product from this column is rich in fusel oils and is removed. The top product is recycled to the aldehyde column. The product from the very top of the product-concentrating column is condensed and returned as reflux to the aldehyde column [42, 45].

There are many other applications for distillation including the following examples.

Recovery of solvents from oil after extraction Most of the solvent can be recovered by evaporation using a film evaporator (see Section 3.1.2.3). However, when the solution becomes very concentrated, its temperature rises and the oil may be heat-damaged. The last traces of solvent in the oil may be removed by steam distillation or stripping with nitrogen.

Concentration of Aroma Compounds from Juices and Extracts By evaporating 10–30% of the juice in a vacuum evaporator, most of the volatile aroma compounds leave in the vapour. This vapour can be fed to a distillation column. The bottom product from the column is almost pure water and the aroma concentrate leaves from the top of the column. This is condensed and may be added back to the juice or extract prior to drying. Fruit juices and extract of coffee may be treated in this way (see Sections 3.1.5.2, 3.1.5.3). A spinning cone evaporator (see Section 14.5.2.2) may be used for this duty.

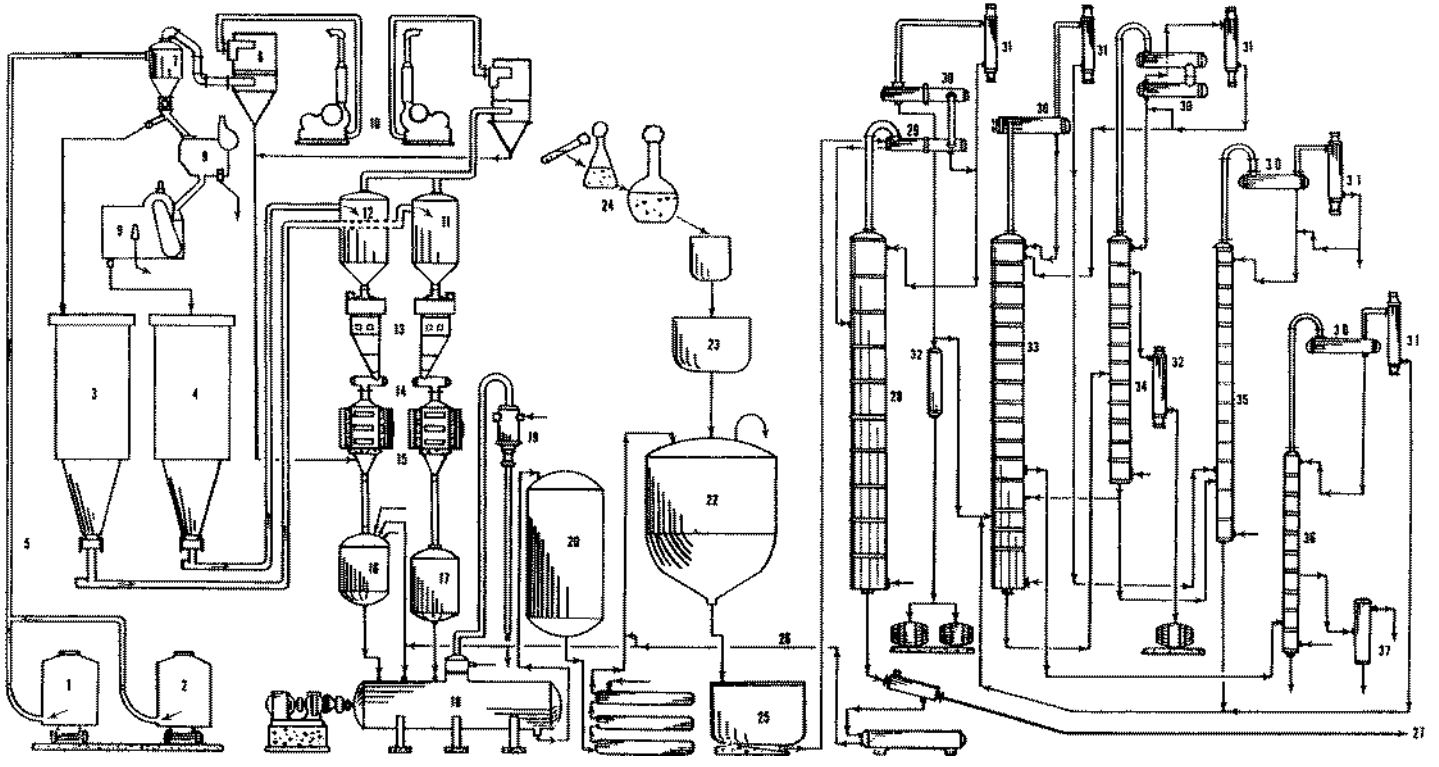


Fig. 14.20 Material process flow, modern beverage spirits plant; from [42] with permission. 1 cereal grains; 2 malt; 3 malt bin; 4 cereal grain bin; 5 unloading elevator; 6 dust filter; 7 collector; 8 scalperator; 9 millerator; 10 reclaiming exhauster; 11 malt receiver; 12 cereal grain receiver; 13 automatic scale; 14 mill feeder; 15 roller mills; 16 precooker; 17 malt infusion; 18 cooker; 19 barometric condenser; 20 converter; 21 mash coolers; 22 fermenter; 23 final yeast propagator; 24 yeast culture and intermediate yeast propagator; 25 fermented-mash holding vessel; 26 stillage return system; 27 stillage flow to recovery system; 28 whisky separating column; 29 heat exchanger; 30 dephlegamtor; 31 vent condenser; 32 product cooler; 33 selective distillation column; 34 product concentrating column; 35 aldehyde concentrating column; 36 fusel oil concentrating column; 37 fusel oil decanter.

Extraction of Essential Oils from Leaves, Seeds, etc. This may be achieved by steam distillation. The material in a suitable state of subdivision is placed on a grid or perforated plate above heated water. In some cases the material is in direct contact with the water or superheated steam may be used. If the oil is very heat sensitive distillation may be carried out under vacuum [6].

14.6 Crystallisation

Alistair S. Grandison

14.6.1 General Principles

Many foods and food ingredients consist of, or contain crystals. Crystallisation has two types of purpose in food processing: (a) the separation of solid material from a liquid in order to obtain either a pure solid, e.g. salt or sugar, or a purified liquid, e.g. winterised salad oil and (b) the production of crystals within a food such as in butter, chocolate or ice cream.

In either case, it is desirable to control the process such that the optimum yield of crystals of the required purity, size and shape is obtained. It is also important to understand crystallisation when considering frozen food (see Chapter 4) or where undesirable crystals are produced, e.g. lactose crystals in dairy products, or precipitated fat crystals in salad oils.

14.6.1.1 Crystal Structure

Crystals are solids with a three-dimensional periodic arrangement of units into a spatial lattice. They differ from amorphous solids in having highly organised structures of flat faces and corners. A limited number of elementary crystal cells are possible with accurately defined angles; and any crystalline material has one of 14 possible lattice structures. Some examples of these structures are shown in Fig. 14.21.

It is important to note that the final macroscopic shape of a crystal is usually not the same as its elementary lattice structure, as growth conditions can change the final 'habit'. The units involved in lattice structures may be metallic nuclei or atoms, but most food crystals are formed of molecular units bonded by van der Waals forces, or in a limited number of cases, ions bonded by ionic bonds. Detailed information on crystal structure and the crystallisation process may be found elsewhere [46–48].

14.6.1.2 The Crystallisation Process

Crystallisation is the conversion of one or more substances from an amorphous solid or the gaseous or liquid state to the crystalline state. In practice, we are

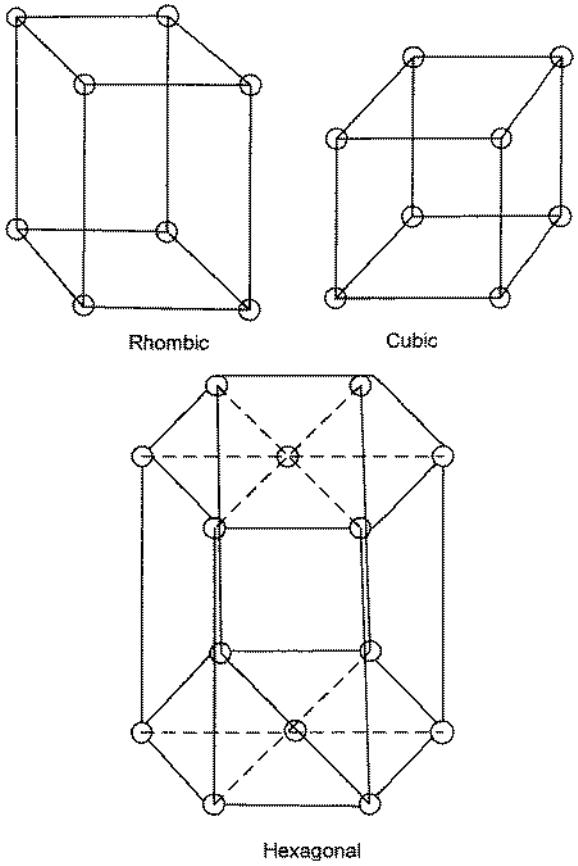


Fig. 14.21 Elementary cells of some crystal systems.

only concerned with conversion from the liquid state. The process involves three stages: supersaturation of the liquid, followed by nucleation (formation of new crystal structures) and crystal growth. A distinction that is commonly used is 'crystallisation from a solution', which is the case where a purified substance is produced from a less pure mixture, as opposed to 'melt crystallisation' in which both or all components of a mixture crystallise into a single solid phase.

Saturation of a solution is the equilibrium concentration which would be achieved by a solution in contact with solute after a long period of time. In most solute/solvent systems, the saturation concentration increases with temperature, although this is not always the case, e.g. with some calcium salts. Supersaturation occurs when the concentration of solute exceeds the saturation point ($S=1$). The saturation coefficient (S) at any temperature is defined as:

$S =$ (Concentration of solute in solution)/
(Concentration of solute in saturated solution)

Solutes differ in their ability to withstand supersaturation without crystallisation – for example sucrose can remain in solution when $S = 1.5–2.0$, whereas sodium chloride solutions crystallise with only a very small degree of supersaturation. Crystals cannot form or grow in a solution at or below its saturation concentration ($S \leq 1$) at any given temperature; and thus supersaturation must be achieved in two main ways: cooling or evaporation. Cooling moves the system along the solubility curve such that a saturated solution becomes supersaturated at the same solute concentration, while evaporation increases the concentration into the supersaturated zone. It is also possible to produce supersaturation by chemical reaction or by addition of a third substance which reduces solubility, e.g. addition of ethanol to an aqueous solution, but these are not commercially important in food processing.

Supersaturation does not necessarily result in spontaneous crystallisation because, although the crystalline state is more thermodynamically stable than the supersaturated solution and there is a net gain in free energy on crystallisation, the activation energy required to form a surface in a bulk solution may be quite high. In other words, the probability of aligning the units correctly to form a viable crystal nucleus is low and is dependent on a number of factors. Viscosity is one such factor; and crystallisation occurs less readily as viscosity increases. This can readily be seen in sugar confectionery which frequently consists of supercooled viscous liquids. Miers' theory (Fig. 14.22) defines three regions for a solute/solvent mixture. Below the saturation curve (in the undersaturated zone) there is no nucleation or crystal growth; and in fact crystals dissolve. In the metastable zone, crystal growth occurs, but nucleation does not occur spontaneously. In the labile zone, both nucleation and crystal growth occur and, the higher the degree of supersaturation, the more rapidly these occur. While the solubility curve is fixed, the supersolubility curve is not only a property of the

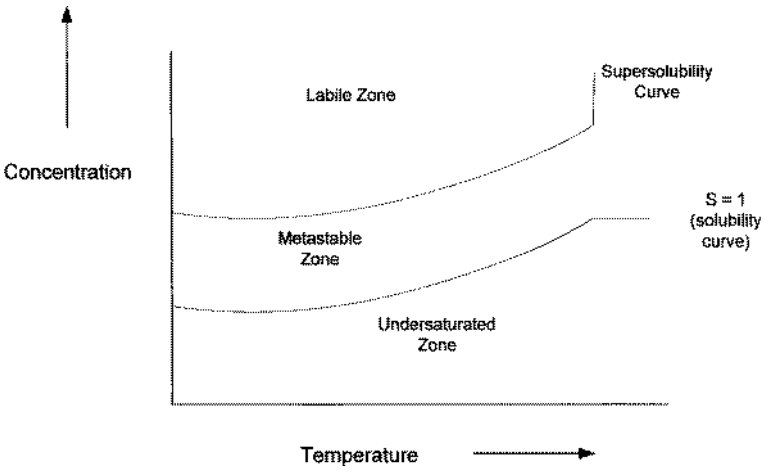


Fig. 14.22 Crystallisation equilibria.

system, but also depends on other factors such as presence of impurities, cooling rate or agitation of the system, in other words factors which affect the activation energy of the system as mentioned above.

In practice, crystals can be produced by several methods:

1. Homogeneous nucleation is the spontaneous production of crystals in the labile zone.
2. Heterogeneous nucleation occurs in the presence of other surfaces, such as foreign particles, gas bubbles, stirrers, which form sites for crystallisation in the metastable zone.
3. Secondary nucleation requires the presence of crystals of the crystallising species itself and also occurs in the upper regions of the metastable zone. The reason for this phenomenon is not clear but may be due to fragments breaking off existing crystals by agitation or viscous drag and forming new nuclei.
4. Nucleation is also stimulated by outside effects such as agitation or ultrasound.

Alternatively, crystalline materials can be produced by 'seeding' solutions in the metastable zone. In this case, very finely divided crystals are added to a supersaturated solution and allowed to grow to the finished size without further nucleation.

Control of crystal growth following nucleation or seeding is essential to obtain the correct size and shape of crystals. The rate of growth depends on the rate of transport of material to the surface and the mechanism of deposition. The rate of deposition is approximately proportional to S, while diffusion to the crystal surface can be accelerated by stirring. Impurities generally reduce the rate.

The final shapes or 'habits' of crystals are distinguished into classes such as platelike, prismatic, dendritic and acicular. Habits are determined by conditions of growth. Invariant crystals maintain the same shape during growth, as deposition in all directions is the same (see Fig. 14.23 a). Much more commonly, the shape changes and overlapping of smaller faces occurs (see Fig. 14.23 b).

Crystals grown rapidly from highly supersaturated solutions tend to develop extreme habits, such as needle-shaped or dendritic, with a high specific surface, due to the need to dissipate heat rapidly. The final shape is also affected by impurities which act as habit modifiers, interacting with growing crystals and causing selective growth of some surfaces, or dislocations in the structure.

Some substances can crystallise out into chemically identical, but structurally different forms. This is known as polymorphism; and perhaps the best recognised examples are diamond and graphite. Polymorphism is particularly important in fats, which can often crystallise out into different polymorphs with different melting points [48, 49]. In some cases, polymorphs can be converted to other, higher melting point crystal forms, which is the basis of tempering some fat-based foods.

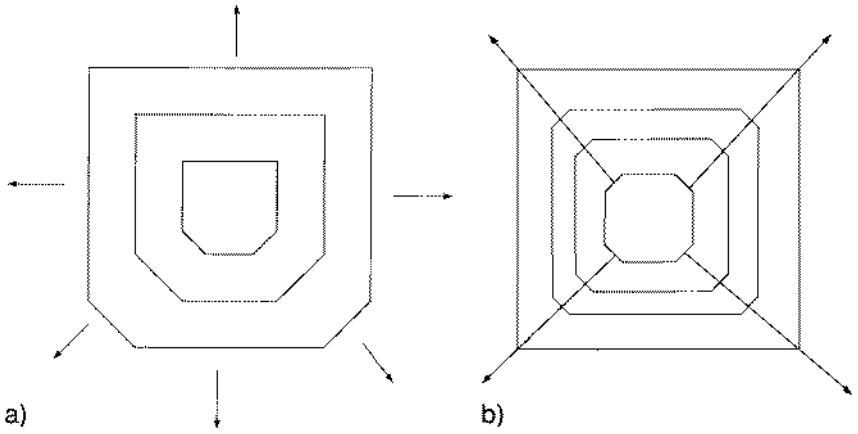


Fig. 14.23 Crystal growth: (a) invariant crystal growth, (b) overlapping crystal growth.

14.6.2
Equipment Used in Crystallisation Operations

Industrial crystallisers are classified according to the method of achieving supersaturation, i.e. by cooling, evaporation or mixed operations [50], as well as factors such as mode of operation (continuous or batch), desired crystal size distribution and purity. Detailed descriptions of design and operation are given by Mersmann and Rennie [51]. The crystallising suspension is often known as 'magma', while the liquid remaining after crystallisation is the 'mother liquor'. Fluidised beds are common with either cooling or evaporative crystallisation, in which the solution is desupersaturated as it flows through a bed of growing crystals (see Figs. 14.24, 14.25).

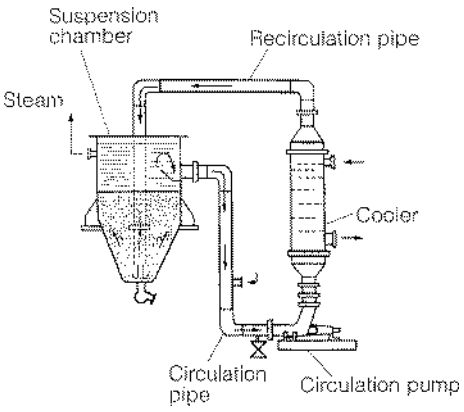


Fig. 14.24 Fluidised bed cooling crystalliser; from [51] with permission.

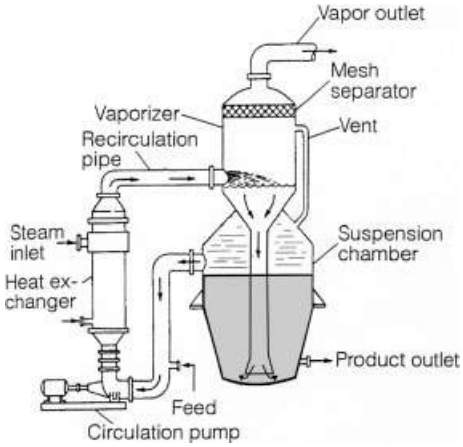


Fig. 14.25 Fluidised bed evaporative crystalliser; from [51] with permission.

Yield from a crystalliser (Y) can be calculated from:

$$Y = W[C_1 - C_2(1 - V)] \tag{14.9}$$

Where W is the initial mass of water, C_1 and C_2 are the concentrations of solute before and after crystallisation and V is the fraction of water evaporated.

Cooling crystallisers may incorporate continuous circulation through a cooling heat exchanger (e.g. Fig. 14.24) or for viscous materials, may incorporate a scraped surface heat exchanger (see Chapter 2).

Evaporative crystallisers are similar to forced circulation evaporators with a crystallisation vessel below the vapour/liquid separator (see Fig. 14.25). Simultaneous evaporation and cooling can be carried out without heat exchangers, the cooling effect being produced by vacuum evaporation of the saturated solution.

14.6.3 Food Industry Applications

14.6.3.1 Production of Sugar

Crystallisation is a major operation in sugar manufacture. Beet or cane sugar consist essentially of sucrose; and different grades of product require uniform crystals of different sizes. Supersaturation is effected by evaporation, but the temperature range is limited by the fact that sugar solutions are sensitive to caramelisation above 85 °C, while high viscosities limit the rate of crystallisation below 55 °C, so all operations are carried out within a fairly narrow temperature range. The supersaturated sugar solution is seeded with very fine sugar crystals and the 'massecuite', i.e. syrup/crystal mixture, is evaporated with further syrup addition. When the correct crystal size has been achieved, the crystals are removed and the syrup is passed to a second evaporator. Up to four evaporation stages may be used, with the syrup becoming less pure each time.

14.6.3.2 **Production of Salt**

Salt is much less of a problem then sugar, in that it is not temperature-sensitive and forms crystals more easily than sugar. Evaporation of seawater in lagoons is still carried out, but factory methods are more common. Continuous systems based on multiple effect evaporators (see Chapter 3) are widespread. Sodium chloride normally forms cubic crystals, but it is common to add potassium ferrocyanide as a habit-modifier, producing dendritic crystals which have better flow properties.

A number of other food materials are produced in pure form by crystallisation, including lactose, citric acid, monosodium glutamate and aspartame.

14.6.3.3 **Salad Dressings and Mayonnaise**

In some cases, crystallisation is carried out to remove unwanted components. Salad oils, such as cottonseed and soybean oil, are widely used in salad dressings and mayonnaise. They contain high melting point triglycerides which crystallise out on storage. This is not especially serious in pure oil, but would break an emulsion and hence lead to product deterioration. *Winterisation* is fractional crystallisation to remove higher melting point triglycerides. It is essential to remove this fraction while retaining the maximum yield of oil, which requires extremely slow cooling to produce a small number of large crystals, i.e. crystal growth with little nucleation. Crystallisation is carried out over 2–3 days with slow cooling to approximately 7 °C, followed by very gentle filtration. Agitation is avoided after the initial nucleation to prevent the formation of further nuclei. The winterised oil should then pass the standard test of remaining clear for 5.5 h at 0 °C.

14.6.3.4 **Margarine and Pastry Fats**

Fractional crystallisation of fats into high (stearin) and low (olein) melting point products is used to improve the quality of fats for specific purposes, e.g. margarine, pastry fats. Crystallisation may be accelerated by reducing the viscosity in the presence of solvents such as hexane. Adding detergents also improves the recovery of high melting point crystals from the olein phase.

14.6.3.5 **Freeze Concentration**

Ice crystallisation from liquid foods is a method of concentrating liquids such as fruit juices or vinegar without heating, or adjusting the alcohol content of beverages. Its use is limited as only a modest level of concentration is possible; and there is an inevitable loss of yield with the ice phase.

There are many applications of crystallisation in the manufacture of foods where a separation is not involved and will therefore not be dealt with here. These include ice cream, butter, margarine, chocolate and sugar confectionery.

14.7
Membrane Processes

Michael J. Lewis

14.7.1
Introduction

Over the last 50 years, a number of membrane processes have evolved which make use of a pressure driving force and a semipermeable membrane in order to effect a separation of components in a solution or colloidal dispersion. The separation is based mainly on molecular size, but to a lesser extent on shape and charge. The four main processes are reverse osmosis (hyperfiltration), nanofiltration, ultrafiltration and microfiltration. The dimensions of the components involved in these separations are typically in the range from <1 nm to >1000 nm. In fact, they can be considered to be a continuous spectrum of processes, with no clearcut boundaries between them. Most suppliers of membranes now offer a selection of membranes which cover this entire spectrum. Figure 14.26 illustrates these processes and how they also relate to traditional particle filtration.

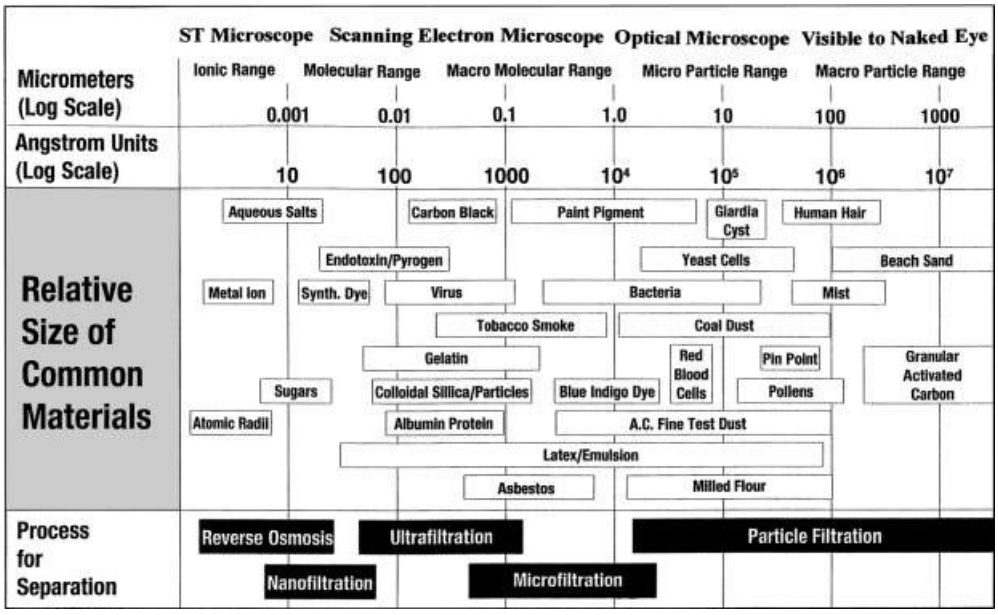


Fig. 14.26 Comparison of the different membrane processes with particle filtration; courtesy of GE Infrastructure – Water and Process Technologies.

14.7.2 Terminology

The feed material is applied to one side of a membrane and subjected to a pressure. In most cases, the feed flows in a direction parallel to the membrane surface and the term crossflow filtration is used to describe such applications. Dead-end systems are also used, but mainly for laboratory-scale separations. The stream which passes through the membrane under the influence of this pressure is termed the permeate (filtrate). The stream left after the required amount of permeate is removed is termed the concentrate or retentate.

If the membrane has a very small pore diameter (tight pores), the permeate will be predominantly water and the process is known as reverse osmosis (RO), similar in its effects to evaporation or freeze-concentration. In some cases, the permeate is the required material; for example in the production of 'potable' water from seawater or polluted waters or in the production of ultrapure water. In RO, the pressure applied needs to be in excess of the osmotic pressure of the solution. Osmotic pressures are highest for low molecular weight solutes, such as salt and sugar solutions; and large increases in their osmotic pressure occur during RO. The osmotic pressure, Π, of a dilute solution can be predicted from the Van t'Hoff equation:

$$\Pi = iRT\left(\frac{c}{M}\right) \tag{14.10}$$

where i is the degree of ionisation, R is the ideal gas constant, T is the absolute temperature, M is the molecular weight and c is the concentration (kg m^{-3}).

As the membrane pore size increases, the membrane becomes permeable to low molecular weight solutes in the feed. Lower pressure driving forces are required. However, larger molecular weight molecules, e.g. proteins, are still rejected by the membrane. It is this fractionation which makes ultrafiltration a more interesting process than RO. Membranes with even larger pore sizes allow smaller macromolecules to pass through, but retain particulate matter and fat globules; and this is termed microfiltration.

Concentration factor and rejection are two important processing parameters for all pressure activated processes. The concentration factor (f) is defined as follows:

$$f = \frac{V_F}{V_C} \tag{14.11}$$

where V_F is the feed volume and V_C is the final concentrate volume.

As soon as the concentration factor exceeds 2.0, the volume of permeate will exceed that of the concentrate. Concentration factors may be as low as 1.5 for some viscous materials and 5.0–50 for some dilute protein solutions. Generally higher concentration factors are used for ultrafiltration than for RO: over 50.0 can be achieved for UF treatment of cheese whey, compared to about to 5 for RO treatment of cheese whey.

The rejection or retention factor (R) of any component is defined as:

$$R = \frac{c_F - c_P}{c_F} \tag{14.12}$$

where c_F is the the concentration of component in the feed and c_p is the concentration in the permeate. It can easily be measured and is very important, as it influences the extent (quality) of the separation that can be achieved.

Rejection values normally range between 0 and 1.0; and sometimes they are expressed as percentages (0–100%). Occasionally negative rejections are found for some charged ions (Donnan effect).

1. When $c_p = 0$, $R = 1$, all the component is retained in the feed.
2. When $c_p = c_F$, $R = 0$, the component is freely permeating.

If the concentration factor and rejection value are known, the yield of any component, which is defined as the fraction of that component present in the feed, which is recovered in the concentrate, can be estimated. Obviously for reverse osmosis, the yield for an ideal membrane is 1.0.

The yield (Y) can be calculated from:

$$Y = f^{R-1} \tag{14.13}$$

The derivation of this equation is provided in Lewis [52]. Thus for a component where $R = 0.95$, at a concentration factor of 20, the yield is 0.86; i.e. 86% is retained in the concentrate and 14% is lost in the permeate.

14.7.3 Membrane Characteristics

The membrane itself is crucial to the process. The first commercial membranes were made of cellulose acetate and these are termed first generation membranes. However, temperatures had to be maintained below 30 °C and the pH range was 3–6. These constraints limited their use, as they could not be disinfected by heat or cleaned with acid or alkali detergents. These were followed in the mid-1970s by other polymeric membranes (second generation membranes), with polyamides (with a low tolerance to chlorine) and, in particular, polysulphones being widely used for foods. It is estimated that over 150 organic polymers have now been investigated for membrane applications. Inorganic membranes based on sintered and ceramic materials are also now available and these are much more resistant to heat and cleaning and disinfecting fluids.

The main terms used to describe membranes are microporous or asymmetric. Microporous membranes have a uniform porous structure throughout, although the pore size may not be uniform across the thickness of the membrane. They are usually characterised by a nominal pore size and no particle larger than this will pass through the membrane. In contrast to this, most membranes used for ultra-

filtration are of the asymmetric type, having a dense active layer or skin of 0.5–1.0 micron in thickness, with a further support layer which is much more porous and of greater thickness. The membrane also has a chemical nature; and many materials have been evaluated. It may be hydrophilic or hydrophobic in nature. The hydrophobic nature can be characterised by measuring its contact angle, θ. The higher the contact angle, the more hydrophobic is the surface. Polysulphones are generally much more hydrophobic than cellulosic membranes. The surface may also be charged. All these factors give rise to interactions between the membrane and the components in the feed and influence the components passing through the membrane, as well as the fouling of the membrane.

14.7.4
Flux Rate

Permeate flux and power consumption are two important operating characteristics.

The permeate flux is usually expressed in terms of $\mathrm{l\,m^{-2}\,h^{-1}}$. This permits a ready comparison of different membrane configurations of different surface areas. Flux values may be from $<5\,\mathrm{l\,m^{-2}\,h^{-1}}$ to $>500\,\mathrm{l\,m^{-2}\,h^{-1}}$. Factors affecting the flux rate are the applied pressure, the volumetric flow rate of feed across the membrane surface, its temperature and its viscosity. The flux is also influenced by concentration polarization and fouling, which in turn are influenced by the flow conditions across the membrane. Inducing turbulence increases the wall shear stress and promotes higher flux rates [52].

The main energy consumption for membrane techniques is the power utilisation of the pumps. The power used, W, is related to the pressure (head) developed and the mass flow rate as follows:

$$W = m'hg \tag{14.14}$$

where m' is the mass flow rate ($\mathrm{kg\,s^{-1}}$), h is the head developed by the pump (m) and g is the acceleration due to gravity ($9.81\,\mathrm{m\,s^{-2}}$).

This energy is largely dissipated within the fluid as heat and results in a temperature rise. Cooling may be necessary if a constant processing temperature is required.

14.7.5
Transport Phenomena and Concentration Polarisation

A very important consideration for pressure driven membrane processes is that the separation takes place not in the bulk of solution, but in a very small region close to the membrane, known as the boundary layer, as well as over the membrane itself. This gives rise to the phenomenon of concentration polarisation over the boundary layer. It is manifested by a quick and significant reduction (2- to 10-fold) in flux when water is replaced by the feed solution, for example in a dynamic start.

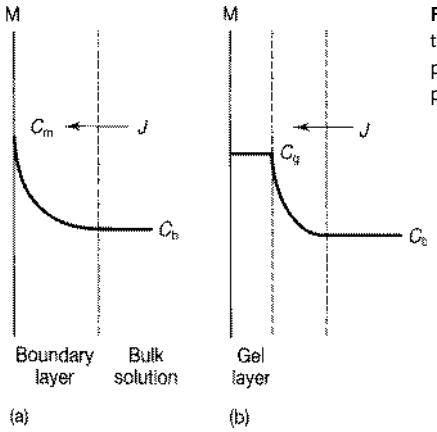


Fig. 14.27 (a) Concentration polarisation in the boundary layer, (b) concentration polarisation with a gel layer from [52] with permission.

Concentration polarisation occurs whenever a component is rejected by the membrane. As a result, there is an increase in the concentration of that component at the membrane surface, together with a concentration gradient over the boundary layer (see Fig. 14.27).

Eventually a dynamic equilibrium is established, where the convective flow of the component to the membrane surface equals the flow of material away from the surface, either in the permeate or back into the bulk of the solution by diffusion, due to the concentration gradient established. This increase in concentration, especially of large molecular weight components, offers a very significant additional resistance. It may also give rise to the formation of a gelled or fouling layer on the surface of the membrane. Whether this occurs will depend upon the initial concentration of the component and the physical properties of the solution. It could be very important, as it may affect the subsequent separation performance. Concentration polarisation itself is a reversible phenomenon, i.e. if the solution is then replaced by water, the original water flux should be restored. However, this rarely occurs in practice due to the occurrence of fouling, which is detected by a decline in flux rate at constant composition. Fouling is caused by the deposition of material on the surface of the membrane or within the pores of the membrane. Fouling is irreversible and the flux needs to be restored by cleaning. Therefore, during any membrane process, flux declines due to a combination of these two phenomena. More recently, it has been recognised that fouling can be minimised by operating at conditions at or below the critical flux. When operating below this value, fouling is minimised, but when operating above it, fouling deposits accumulate. This can be determined experimentally for different practical situations [53].

14.7.6
Membrane Equipment

Membrane suppliers now provide a range of membranes, each with different rejection characteristics. For ultrafiltration, different molecular weight cutoffs are available in the range 1000 Da to 500 000 Da. Tight ultrafiltration membranes have a molecular weight cutoff value of around 1000–5000 Da, whereas the more 'open' or 'loose' membranes will have a value in excess of 100 000 Da. However, because there are many other factors that affect rejection, molecular weight cutoff should only be regarded as giving a relative guide to its pore size and true rejection behaviour. Experimental determinations should always be made on the system to be validated, at the operating conditions to be used.
Other desirable features of membranes to ensure commercial viability are:

- reproducible pore size, offering uniformity both in terms of their permeate rate and their rejection characteristics
- high flux rates and sharp rejection characteristics
- compatible with processing, cleaning and sanitising fluids
- resistance to fouling
- an ability to withstand temperatures required for disinfecting and sterilising surfaces, which is an important part of the safety and hygiene considerations.

Extra demands placed upon membranes used for food processing include: the ability to withstand hot acid and alkali detergents (low and high pH), temperatures of 90 °C for disinfecting or 120 °C for sterilising and/or widely used chemical disinfectants, such as sodium hypochlorite, hydrogen peroxide or sodium metabisulphite. The membrane should be designed to allow cleaning both on the feed/concentrate side and the permeate side.

Membrane processing operations can range in their scale of operation, from laboratory benchtop units, with samples less than 10 ml through to large commercial-scale operations, processing at rates greater than 50 $m^3 h^{-1}$. Furthermore, the process can be performed at ambient temperatures, which allows concentration without any thermal damage to the feed components.

14.7.7
Membrane Configuration

The membranes themselves are thin and require a porous support against the high pressure. The membrane and its support, together are normally known as the module. This should provide a large surface area in a compact volume and must allow suitable conditions to be established, with respect to turbulence, high wall shear stresses, pressure losses, volumetric flow rates and energy requirements, thereby minimising concentration polarisation. Hygienic considerations are also important: there should be no dead spaces and the module should be capable of being cleaned in-place on both the concentrate and the permeate side. The membranes should be readily accessible, both for cleaning and re-

placement. It may also be an advantage to be able to collect permeate from individual membranes in the module to be able to assess the performance of each individually.

The three major designs are the tubular, flat plate and spiral wound configurations (see Figs. 14.28, 14.29).

Sintered or ceramic membranes can also be configured in the form of tubes. Tubular membranes come in range of diameters. In general tubes offer no dead spaces, do not block easily and are easy to clean. However, as the tube diameter increases, they occupy a larger space, have a higher hold-up volume and incur higher pumping costs. The two major types are the hollow fibre, with a fibre diameter of 0.001–1.2 mm and the wider tube with diameters up to 25 mm, although about 12 mm is a popular size.

For the hollow fibre system, the membrane wall thickness is about 250 μm and the tubes are self-supporting. The number of fibres in a module can be as few as 50 but sometimes >1000. The fibres are attached at each end to a tube sheet, to ensure that the feed is properly distributed to all the tubes. This may give rise to pore plugging at the tube entry point. Prefiltration is recommended to reduce this. They are widely used for desalination and in these RO applica-

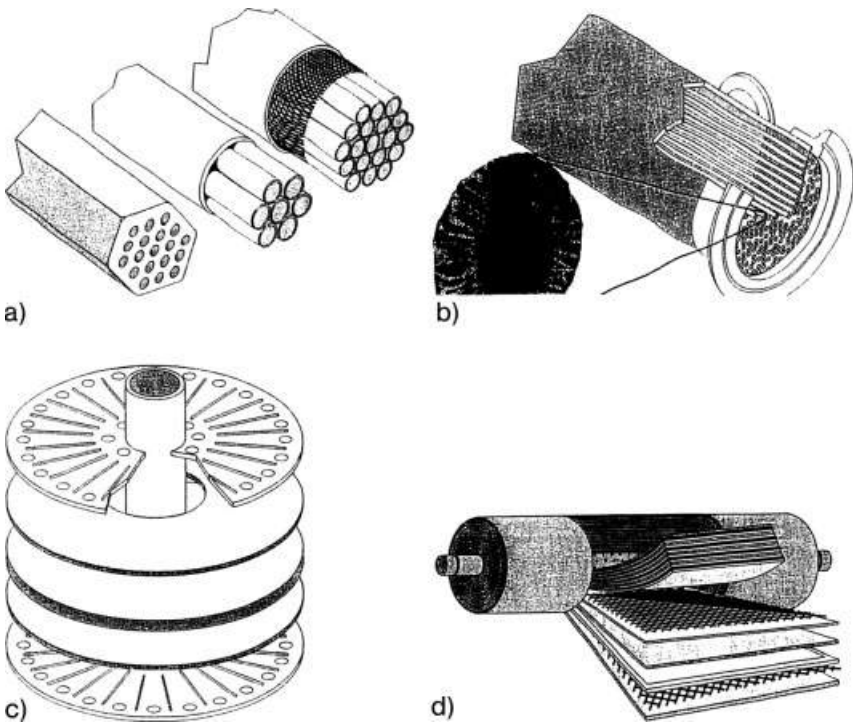


Fig. 14.28 This shows the tubular, hollow fibre, plate and frame and spiral wound configurations; courtesy of ITT Aquious.

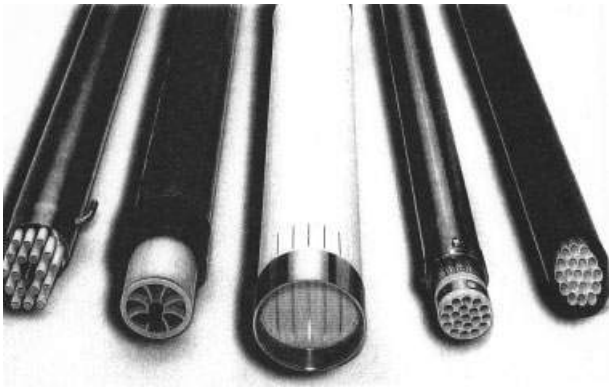


Fig. 14.29 Tubular, hollow fibre and spiral wound configurations; courtesy of ITT Aquious.

tions are capable of withstanding high pressures. It is the ratio of the external to internal diameter, rather than the membrane wall thickness which determines the pressure that can be tolerated. Hollow fibre systems usually operate in the streamline flow regime. However the wall shear rates are high. They tend to be expensive, because if one or several fibres burst, the whole cartridge needs to be replaced.

For wider tubes, the feed is normally pumped through the tube, which may be up to 25 mm in diameter, although a popular size is about 12 mm diameter. There may be up to 20 tubes in one module, tube lengths may be 1.2–3.8 m and tubes within the module may be connected in series or parallel. The membrane is cast or inserted into a porous tube which provides support against the applied pressure. Therefore they are capable of handling higher viscosity fluids and even materials with small suspended particles, up to one-tenth the tube diameter. They normally operate under turbulent flow conditions with flow velocities greater than 2 m s^{-1}. The corresponding flux rates are high, but pumping costs are also high, in order to generate the high volumetric flow rate required and the operating pressure.

The flat plate module can take the form of a plate-and-frame type geometry or a spirally wound geometry. The plate-and-frame system employs membranes stacked together, with appropriate spacers and collection plates for permeate removal, somewhat analogous to plate heat exchangers. The channel height can be 0.4–2.5 mm. Flow may be either streamline or turbulent and the feed may be directed over the plates in a parallel or series configuration. This design permits a large surface area to be incorporated into a compact unit. Membranes are easily replaced and it is easy to isolate any damaged membrane sandwich. Considerable attention has been devoted to the design of the plate to improve performance. This has been achieved by ensuring a more uniform distribution of fluid over the plate, by increasing the width of the longer channels and by reducing the ratio of the longest to the shortest channel length.

The spiral wound system is now widely used and costs for membranes are relatively low. In this case, a sandwich is made from two sheet membranes which enclose a permeate spacer mesh. This is attached at on end to a permeate removal tube and the other three sides of the sandwich are sealed. Next to this is placed a feed spacer mesh and the two together are rolled round the permeate collection tube in the form of a Swiss roll. The channel height is dictated by the thickness of the feed spacer. Wider channel heights will reduce the surface area to volume ratio, but reduce the pressure drop.

The typical dimensions of one spiral membrane unit would be about 12 cm in diameter and about 1 m in length. Up to three units may be placed in one housing, with appropriate spacers to prevent telescoping, which may occur in the direction of flow and could damage the sandwich. This configuration is becoming very popular and is relatively cheap. Again, the flow may be streamline or turbulent. Pressure drop/flow rate relationships suggest that flow conditions are usually turbulent.

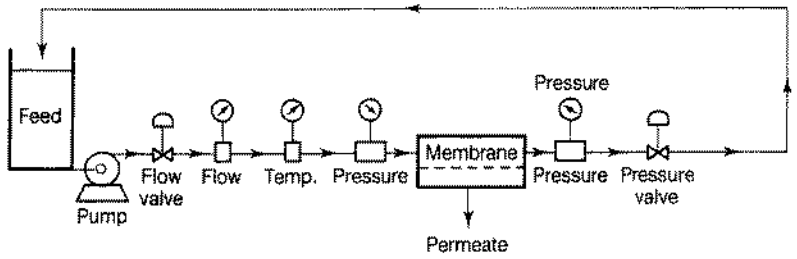
Each system does and will continue to have its devotees. An alternative, much used, unit for simple laboratory separations is the stirred cell with agitation facilities. In contrast to the systems described earlier, this is a dead-end rather than a flow-through system.

As well as the membrane module, there will be pumps, pipeline, valves and fittings, gauges, tanks, heat exchangers, instrumentation and control and perhaps in-place cleaning facilities. For small installations, the cost of the membrane modules may only be a relatively small component of the total cost of the finished plant, once these other items have been accounted for. This may also apply to some large installations such as water treatment plants, where other separation processes are numerous and the civil engineering costs may also be high.

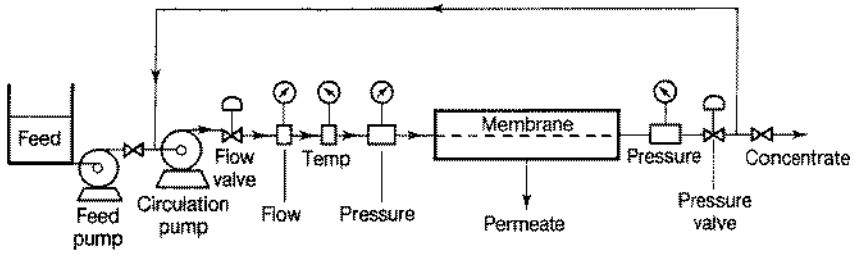
The simplest system is a batch process. The feed is usually recycled, as sufficient concentration is rarely achieved in one pass. Flux rates are initially high but decrease with time. Energy costs are high because the pressure is released after each pass. Residence times are long. Batch processes are usually restricted to small-scale operations. Batch processing with top-up is used in situations when the entire feed volume will not fit into the feed tank. Continuous processes may be single-stage (feed and bleed), or multistage processes, depending upon the processing capacity required. Figure 14.30 illustrates these different systems.

14.7.8
Safety and Hygiene Considerations

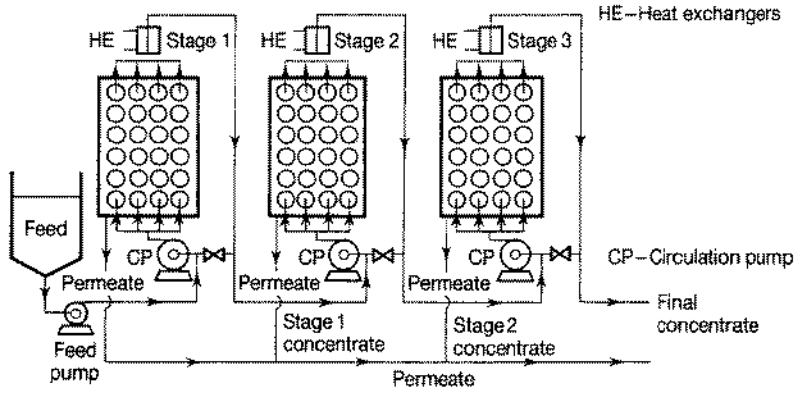
It is important that safety and hygiene are considered at any early stage when developing membrane processes. These revolve round cleaning and disinfecting procedures for the membranes and ancillary equipment, as well as the monitoring and controlling the microbial quality of the feed material. For many processes, thermisation or pasteurisation are recommended for feed pretreatment



a) UF plant – batch operation



b) UF plant – continuous, internal recycle or feed and bleed



c) UF plant , commercial scale

Fig. 14.30 Different plant layouts: (a) batch operation,
(b) continuous with internal recycle (feed and bleed),
(c) commercial scale with three stages; courtesy of ITT Aquious.

(see Chapter 2). Microfiltration may also be considered for heat-labile components. Relatively little has been reported about the microbiological hazards associated with membrane processing. All microorganisms will be rejected by the membrane and will therefore increase in number in the concentrate, by the

concentration factor. There may also be some microbial growth during the process, so the residence time and residence time distribution should be known, as well as the operating temperature. If residence times are long, it may be advisable to operate either below 5 °C or above 50 °C, to prevent further microbial growth.

14.7.9 Applications for Reverse Osmosis

The main applications of RO are for concentrating fluids, by removal of water. RO permits the use of relatively low temperatures, even lower than vacuum evaporation. It reduces volatile loss caused by the phase change in evaporation and is very competitive from an energy viewpoint. RO uses much higher pressures than other membrane processes, in the range 2–8 MPa, and incurs greater energy costs and requires special pumps. Products of RO may be subtly different to those produced by evaporation, particularly with respect to low molecular weight solutes, which might not be completely rejected, and to volatile components, which are not completely lost.

Thin-film composite membranes, based on combinations of polymers have now largely replaced cellulose acetate, allowing higher temperatures, up to 80 °C and greater extremes of pH (3–11) to be used, thereby facilitating cleaning and disinfection. Therefore, the main applications of RO are for concentrating liquids, recovering solids and treatment of water.

14.7.9.1 Milk Processing

RO can be used for concentrating full cream milk up to a factor of 2–3 times. Flux rates for skimmed milk are only marginally higher than those for full cream milk. The product concentration attainable is nowhere near as high as that for evaporation, due to increasing osmotic pressure and fouling, due mainly to the increase in calcium phosphate, which precipitates out in the pores of the membrane. Therefore, most of the commercial applications have been for increasing the capacity of evaporation plant. Other possible applications that have been investigated and discussed include: (a) the concentration of milk on the farm for reducing transportation costs, (b) for yoghurt production at a concentration factor of about 1.5, to avoid the addition of skimmed milk powder, (c) for ice cream making, also to reduce the use of expensive skimmed milk powder, (d) for cheesemaking to increase the capacity of the cheese vats and (e) for recovering rinse water. Cheese whey can also be concentrated, to reduce transportation costs or prior to drying. Flux values for sweet whey are higher than for acid whey, which in turn are higher than for milk, for all systems tested [54]. Reviews of the use of RO and UF in dairying applications include El-Gazzar and Marth [55] and Renner [56].

14.7.9.2 Other Foods

Reverse osmosis has found application in the processing of fruit and vegetable juices, sometimes in combination with ultrafiltration and microfiltration. The osmotic pressure of juices is considerably higher than that of milk. It is advantageous to minimise thermal reactions, such as browning, and to reduce loss of volatiles. From a practical viewpoint, the flux rate and rejection of volatiles is important. RO modules can cope with single strength clear or cloudy juices and also fruit pulp. RO can be used to produce a final product, as in the case of tomato paste and fruit purees, or to partially concentrate, prior to evaporation. RO is a well established process for concentrating tomato juice from about 4.5° Brix, to 8–12° Brix. Other fruit juices which have been successfully concentrated are apple, pear, peach and apricot. Where juices have been clarified, osmotic pressure limits the extent of concentration and up to 25° Brix can be achieved. Unclarified juices may be susceptible to fouling. With purees and pulps, the viscosity may be the limiting factor and these can be concentrated to a maximum of 1.5 times. It is possible to concentrate coffee extract from about 13–36% total solids at 70°C, with little loss of solids. Tea extracts can also be similarly concentrated.

Reverse osmosis is also used for waste recovery and more efficient use of processing water in corn wet-milling processes. Commercial plant is available for concentrating egg white to about 20% solids. In one particular application, egg white is concentrated and dried, after lysozyme has been extracted.

Dealcoholisation is an interesting application, using membranes which are permeable to alcohol and water. In a process akin to diafiltration, water is added back to the concentrated product, to replace the water and alcohol removed in the permeate. Such technology has been used for the production of low or reduced alcohol, beers, ciders and wine. Leeper [57] reported ethanol rejections for cellulose acetate ranged between 1.5% and 40.0%, for polyamides between 32.8% and 60.9% and, for other hybrid membranes, as high as 91.8%.

Reverse osmosis is used in many areas worldwide for water treatment, where there are shortages of fresh water, although it is still well exceeded by multistage fractional distillation. Potable water should contain less than 500 ppm of dissolved solids. Brackish water, e.g. bore-hole or river water, typically contains from 1000 ppm up to about 10 000 ppm of dissolved solids, whereas seawater contains upwards of 35 000 ppm of dissolved solids. If lower total solids are required, the permeate can be subjected to a second process, known as double reverse osmosis water.

14.7.10 Applications for Nanofiltration

Nanofiltration (NF) has been used for partially reducing calcium and other salts in milk and whey, with typical retention values of 95% for lactose and less than 50% for salts. Guu and Zall [58] have reported that permeate subject to NF gave improved lactose crystallisation. NF provides potential for improving the heat stability of the milk.

NF has also been investigated for removing pesticides and components responsible for the colour from ground water, as well as for purifying water for carbonation and soft drinks. For water production of high-grade purity, for analytical purposes, it may be double RO treated, as mentioned earlier.

NF is currently being investigated for fractionating oligosaccharides with prebiotic potential, produced by the enzymatic breakdown of different complex carbohydrates.

14.7.11 Applications for Ultrafiltration

14.7.11.1 Milk Products

Milk will be taken as an example to show the potentialities of ultrafiltration (UF). Milk is chemically complex, containing components of a wide range of molecular weights, such as protein, fat, lactose, minerals and vitamins. It also contains microorganisms, enzymes and perhaps antibiotics and other contaminants. Whole milk contains about 30–35% protein and about the same amount of fat (dry weight). Therefore, it is an ideal fluid for membrane separation processes, in order to manipulate its composition, thereby providing a variety of products or improving the stability of the colloidal system. The same principles apply to skimmed milk, standardised milk and some of its byproducts, such as cheese whey. Skimmed milk can be concentrated up to seven times and full cream milk up to about five times Kosikowski [59]. An IDF publication [60] gives a summary of the rejection values obtained during the ultrafiltration of sweet whey, acid whey, skimmed milk and whole milk, using a series of industrial membranes.

Bastian et al. [61] compared the rejection values during UF and diafiltration of whole milk. They found that the rejection of lactose, riboflavin, calcium, sodium and phosphorus was higher during diafiltration than UF. Diafiltration of acidified milk gave rise to lower rejections of calcium, phosphorus and sodium. Premaratne and Cousin [62] reported a detailed study on the rejection of vitamins and minerals during UF of skimmed milk. During a five-fold concentration, the following minerals were concentrated by the following factors: Zn (4.9), Fe (4.9), Cu (4.7), Ca (4.3), Mg (4.0) and Mn (3.0), indicating high rejection values. In contrast, most of the B vitamins examined were almost freely permeating.

Ultrafiltration has been used to concentrate cheese whey ($\sim$6.5% TS), which contains about 10–12% protein (dry weight), to produce concentrates which could then be dried to produce high protein powders (concentrates and isolates) which retain the functional properties of the proteins. Some typical concentration factors, f, used are as follows:

f=5: protein content (dry weight) about 35% (similar to skimmed milk)
f=20: protein content about 65%
f=20 plus diafiltration: protein content about 80%.

The product starts to become very viscous at a concentration factor of about 20, so diafiltration is required to further increase the protein in the final product.

The permeate from ultrafiltration of whey contains about 5% total solids, the predominant component being lactose. Since this is produced in substantial quantities, the economics of the process are dependent upon its utilisation. It can be concentrated by reverse osmosis and hydrolysed to glucose and galactose to produce sweeteners or fermented to produce alcohol or microbial protein. Skimmed milk has been investigated also but protein concentrates based on skimmed milk have not received the same amount of commercial interest as those based on whey proteins.

However, yoghurt and other fermented products have been made from skimmed milk and whole milk concentrated by ultrafiltration [55]. Whey protein concentrates have also been incorporated [63]. Production of labneh, which is a strained or concentrated yoghurt at about 21% total solids, has been described by Tamime et at. [64], by preconcentrating milk to 21% TS. Inorganic membranes have also been used for skimmed milk; and Daufin et al. [65] have investigated the cleanability of these membranes using different detergents and sequestering agents.

As well as exploiting the functional properties of whey proteins, full cream milk has been concentrated by UF prior to cheesemaking. The UF concentrate has been incorporated directly into the cheese vats. Some advantages of this process include: increased yield (particularly of whey protein), lower rennet and starter utilisation, smaller vats or even complete elimination of vats, little or no whey drainage and better control of cheese weights. Lawrence [66] suggests that concentration below a factor of 2.0 gives protein standardisation, reduced rennet and vat space, but no increased yield. Concentration factors greater than 2.0 result in an increased yield.

Some problems result from considerable differences in the way the cheese matures and hence its final texture and flavour. The types of cheese that can be made in this way include: Camembert type cheese, mozzarella, feta and many soft cheeses. Those which are difficult include the hard cheeses, such as Cheddar and also cottage cheese; and the problems are mainly concerned with poor texture. More discussion is given by Kosikowski [59]. Further reviews on the technological problems arising during the conversion of retentate into cheeses are discussed by Lelievre and Lawrence [67]. Quarg is also produced from ultrafiltered milk.

Ultrafiltration is an extremely valuable method of concentrating and recovering many the minor components, particularly enzymes from raw milk, many of which would be inactivated by pasteurisation. Such enzymes are discussed in more detail by Kosikowski [68]. Further reviews on membrane processing of milk are provided by Glover [53], El-Gazzar and Marth [54], Renner and El-Salam [55] and the International Dairy Federation [69].

14.7.11.2 Oilseed and Vegetable Proteins

There have been many laboratory investigations into the use of ultrafiltration for extracting proteins from oil seed residues, or for removing any toxic components. Lewis [70] and Cheryan [71] have reviewed the more important of these. The investigations include: for soya, the separation of low molecular weight peptides from soy hydrolysates (with the aim of improving quality), the dissociation of phytate from protein (followed by its removal by UF), the removal of oligosaccharides, the removal of trypsin inhibitor and performance of different membrane configurations. For cottonseed, the use of different extraction conditions has been evaluated, as have the functional properties of the isolates produced by UF. Investigations were performed with sunflower and alfalfa to remove the phenolic compounds responsible for the colour and bitter flavour and glucosinolates from rapeseed.

Many have been successful in terms of producing good quality concentrates and isolates, particularly with soyabean. However, few have come to commercial fruition, mainly because of the economics of the process, dictated by the relatively low value of products and the fact that acceptable food products can be obtained by more simple technology, such as isoelectric precipitation. A further problem arises from the fact that the starting residue is in the solid form, thereby imparting an additional extraction procedure. Extraction conditions may need to be optimised, with respect to time; temperature, pH and antinutritional factors. Another problem arises from the complexity of oil seed and vegetable proteins, compared to milk products, evidenced by electrophoretic measurement. It is likely that many of these proteins are near their solubility limits after extraction and further concentration will cause them to come out of solution and promote further fouling. Fouling and cleaning of membranes was found to be a serious problem during ultrafiltration of rapeseed meal extracts [72].

A further important area is the use of enzyme reactors. The earliest examples were to breakdown polysaccharides to simpler sugars in a continuous reactor and to use a membrane to continuously remove the breakdown products.

14.7.11.3 Animal Products

Slaughterhouse wastes contain substantial amounts of protein. Two important streams that could be concentrated by ultrafiltration are blood and waste water.

Blood contains about 17% protein. It can be easily separated by centrifugation into plasma (70%) and the heavier erythrocytes (red blood corpuscles or cells, ca. 30%). Plasma contains about 7% protein, whereas the blood corpuscles contain 28–38% protein. The proteins in plasma possess useful functional properties, particularly gelation, emulsification and foaming. They have been incorporated into meat products and have shown potential for bakery products, as replacers for egg white.

Whole blood, plasma and erythrocytes have all been subjected to UF processes [71, 73]. The process is concentration polarisation controlled and flux rates are low. High flow rate and low pressure regimes are best. Gel concentrations were ap-

proximately 45% for plasma protein and 35% for red blood cells. The fouling characteristics of different blood fractions have been investigated [74]. Whole blood was found to be the worst foulant, when compared to lysed blood and blood plasma.

Another important material is gelatin, which can be concentrated from very dilute solutions by UF. As well as concentration, ash is removed, which improves its gelling characteristics. This is one example where there have been some high negative rejections recorded for calcium, when ultrafiltered at low pH.

Eggs have also been processed by UF. Egg white contains 11–13% total solids (about 10% protein, 0.5% salts, 0.5% glucose). Large amounts of egg white are used in the baking industry. The glucose can cause problems during storage and causes excessive browning during baking. Whole egg contains about 25% solids and about 11% fat, whereas egg yolk contains about 50% solids. It is unusual to evaporate eggs prior to drying, because of the damage caused. Compared to RO, UF also results in the partial removal of glucose; and further removal can be achieved by diafiltration. Flux values during UF are much lower than for many other food materials, most probably due to the very high initial protein concentration; and rates are also highly velocity- and temperature-dependent [71].

Membrane-based bioreactors appear to be a very promising application for the production of ethanol, lactic acid, acetone, butanol, starch hydrolysates and protein hydrolysates.

14.7.12
Applications for Microfiltration

Microfiltration (MF) is generally used to separate particles suspended in liquid media and may frequently be considered as an alternative to conventional filtration or centrifugation. For industrial use, the aim is usually to obtain either a clear permeate or the concentrate. Therefore most applications are either clarification, or the recovery of suspended particles such as cells or colloids, or the concentration of slurries.

One application in the food industry has been in the treatment of juices and beverages. As MF is a purely physical process, it can have advantages over traditional methods, which may involve chemical additives, in terms of the quality of the product as well as the costs of processing.

Finnigan and Skudder [75] report that very good quality, clear permeate was found when MF processing cider and beer, with high flux rates and no rejection of essential components.

Clarification and biological stabilisation of wine musts and unprocessed wine have also been described for MF. This avoids the requirement for fining and, possibly, pasteurisation. Another section of the industry with several applications is dairy processing. Piot et al. [76] and Merin [77] have clarified sweet cheese whey using crossflow MF. This has the dual benefit of removing fat and

reducing the bacterial population and could eliminate the need for fat separation and heat treatment in the production of whey protein powders prior to UF. The former authors reported that a 5-log reduction of microorganisms could be obtained in the microfiltrate compared to the whey, although some loss of whey protein was observed. Hanemaaijer [78] described a scheme for whey treatment incorporating MF and UF to produce 'tailor-made' whey products with specific properties for specific applications. The products include whey protein concentrates which are rich in whey lipids, as well as highly purified protein.

Bacterial removal from whole milk by MF is a problem because the size range of the bacteria overlaps with the fat globules and, to a lesser extent, with the casein micelles. However, some success has been achieved with skim milk. The 'Bactocatch' system can remove 99.6% of the bacteria from skimmed milk using ceramic membranes on a commercial scale [79]. The retentate (approximately 10% of the feed) can then be sterilised by a UHT process, mixed with the permeate and the mixture pasteurised, to give a product with 50% longer shelf life but no deterioration in organoleptic properties compared to milk that has only been pasteurised. One such product on the market in the UK is Cravendale milk [80]. The combination of MF and heat reduces the bacterial numbers by 99.99%.

Alternatively, the permeate could be used for cheesemaking, or the production of low-heat milk powder [81]. Piot et al. [82] described the use of membranes of pore diameter 1.8 μm to produce skimmed milk of low bacterial content. Recovery of fat from buttermilk has also been described [83].

Membranes have been used to concentrate milk prior to the manufacture of many cheese types. This results in improved yields and other associated benefits such as reduced requirement for rennet and starter and the ability to produce much more cheese per vat [84]. However, the use of MF is an attractive alternative. Rios et al. [83] have carried out extensive trials on this application and concluded that the use of 0.2 μm pore diameter membranes gave a product with better texture and yield than with centrifugation. The choice of ceramic membranes allowed the curd to be contacted directly with the membrane.

Other food applications have been reported with meat and vegetable products including the following. Devereux and Hoare [85] described the use of MF to recover precipitated soya protein. This could have advantages over recovery of the dissolved protein using UF. Gelatin is a proteinaceous material derived by hydrolysis of collagen. This is purified by filtration incorporating diatomaceous earth. The latter process can be replaced by crossflow microfiltration (CMF), which effectively removes dirt, coagulated proteins, fats and other particulate materials from the feed. Again, CMF gives higher yields of high quality product on a continuous basis. Short [86] calculated that incorporating plants for gelatin would have a payback time of 3 years for a capacity of 30 t h^{-1}.

Overall, MF has made significant advances in new applications in the food and biotechnology industries. However, it has not yet realised its full potential, largely due to the severe problems of flux decline due to fouling. It is believed that further developments in membrane design and a greater knowledge of

fouling mechanisms will result in greater application in the future, especially in the field of downstream processing.

14.8
Ion Exchange

Alistair S. Grandison

14.8.1
General Principles

Ion exchange can be used for separations of many types of molecules, such as metal ions, proteins, amino acids or sugars. The technology is utilised in many sensitive analytical chromatography and laboratory separation procedures, frequently on a very small scale. However, industrial-scale production operations, such as demineralisation or protein recovery, are possible. More detailed information on the theory of ion exchange can be found elsewhere [87–89].

Ion exchange is the selective removal of a single, or group of, charged species from one liquid phase followed by transfer to a second liquid phase by means of a solid ion exchange material. This involves the process of adsorption – the transfer of specific solute(s) from a feed solution on to a solid ion exchanger. The mechanism of adsorption is electrostatic involving opposite charges on the solute(s) and the ion exchanger. After washing off the feed solution, the solute(s) is desorbed back into solution in a much purified form.

Ion exchange solids have fixed ions covalently attached to a solid matrix. There are two basic types of ion exchanger:

(a) *Cation exchangers* bear fixed negative charges (e.g. $-SO_3^-H^+$, $-PO_3^{2-}(H^+)_2$, -COOH) and therefore retain cations.
(b) *Anion exchangers* bear fixed positive charges (amines or imines, such as quaternary amine or diethylaminoethyl groups) and thus retain anions.

Ion exchangers can be used to retain simple ionised species such as metal ions, but may also be used in the separation of polyelectrolytes, such as proteins, which carry both positive and negative charges, as long as the overall charge on the polyelectrolyte is opposite to the fixed charges on the ion exchanger. This overall charge depends on the isoelectric point (IEP) of the polyelectrolyte and the pH of the solution. At pH values lower than the IEP, the net overall charge will be positive and vice versa. The main interaction is via electrostatic forces and, in the case of polyelectrolytes, the affinity is governed by the number of electrostatic bonds between the solute molecule and the ion exchanger. However, with large molecules such as proteins, size, shape and the degree of hydration of the ions may affect these interactions and hence the selectivity of the ion exchanger for different solutes. Figure 14.31 gives a generalised anion exchanger – i.e. bearing fixed positive charges.

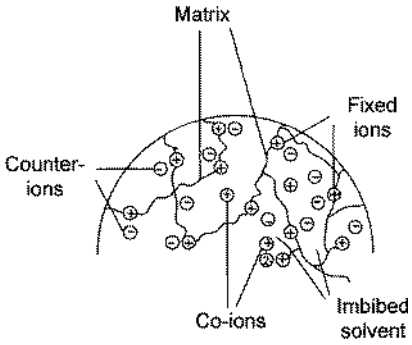


Fig. 14.31 Schematic diagram of a generalised anion exchanger.

To maintain electrical neutrality, these fixed ions must be balanced by an equal number of mobile ions of the opposite charge, i.e. anions, held by electrostatic forces. These mobile ions can move into and out of the porous molecular framework of the solid matrix and may be exchanged stoichiometrically with other dissolved ions of the same charge and are termed counterions. As the distribution of ions between the internal phase of the ion exchanger and the external phase is determined by the Donnan equilibrium, some co-ions (mobile ions having the same sign – positive in this example – as the fixed ions) will be present even in the internal phase. Therefore, if an anion exchanger, as in Fig. 14.31, is in equilibrium with a solution of NaCl, the internal phase contains some Na^+ ions, although the concentration is less than in the external phase because the internal concentration of Cl^- ions is much larger.

When an ion exchanger is contacted with an ionised solution, equilibration between the two phases rapidly occurs. Water moves into or out of the internal phase so that osmotic balance is achieved. Counter ions also move in and out between the phases on an equivalent basis. If two or more species of counter ion are present in the solution, they are distributed between the phases according to the proportions of the different ions present and the relative selectivity of the ion exchanger for the different ions. It is this differential distribution of different counter ions which forms the basis of separation by ion exchange. The relative selectivity for different ionised species results from a range of factors. The overall charge on the ion and the molecular or ionic mass are the primary determining factors, but selectivity is also related to degree of hydration, steric effects and environmental factors such as pH or salt content.

In the adsorption stage, a negatively charged solute molecule (e.g. a protein, P^-) is attracted to a charged site on the ion exchanger (R^+), displacing a counterion (X^-):

$$R^+X^- + P^- \rightarrow R^+P^- + X^-$$

This is shown schematically in Fig. 14.32 a.

In the desorption stage, the anion is displaced from the ion-exchanger by a competing salt ion (S^-) and hence is eluted:

$$R^+P^- + S^- \rightarrow R^+S^- + P^-$$

This is shown schematically in Fig. 14.32 b.

Alternatively, desorption can be achieved by the addition of H^+ or OH^- ions. Ion exchangers are further classified, in terms of how their charges vary with changes in pH, into weak and strong exchangers. Strong ion exchangers are ionised over a wide range of pH and have a constant capacity within the range, whereas weak exchangers are only ionised over a limited pH range, e.g. weak cation exchangers may lose their charge below pH 6 and weak anion exchangers above pH 9. Thus, weak exchangers may be preferable to strong ones in some situations, for example where desorption may be achieved by a relatively small change in pH of the buffer in the region of the pKa of the exchange group. Regeneration of weak ion exchange groups is easier than with strong groups and therefore has a lower requirement of costly chemicals.

14.8.2
Ion Exchange Equipment

All ion exchangers consist of a solid insoluble matrix (termed the resin, adsorbent, medium, or just ion exchanger) to which the active, charged groups are attached covalently. The solid support must have an open molecular framework which allows the mobile ions to move freely in and out and must be completely insoluble throughout the process. Most commercial ion exchangers are based on an organic polymer network, e.g. polystyrene and dextran, although inorganic materials such as porous silica may be used. The latter are much more rigid and incompressible. The support material does not directly determine the ionic distribution between the two phases, but it does influence the capacity, the flow rate through a column, the diffusion rate of counterions into and out of the matrix, the degree of swelling and the durability of the material.

As the adsorption is a surface effect, the available surface area is a key parameter. For industrial processing, the maximum surface area to volume should be used to minimise plant size and product dilution. It is possible for a 1-ml bed of ion exchanger to have a total surface area $>100\ m^2$. The ion exchange material is normally deployed in packed beds and involves a compromise between large particles (to minimise pressure drop) and small particles to maximise mass transfer rates. Porous particles are employed to increase surface area/volume.

The capacity of an ion exchanger is defined as the number of equivalents (eq) of exchangeable ions per kilogram of exchanger, but is frequently expressed as x meq g^{-1} (usually in the dry form). Most commercially available materials have capacities in the range 1–10 eq kg^{-1} of dry material, but this may decline with age due to blinding or fouling, i.e. nonspecific adsorption of unwanted materials, such as lipids, onto the surface, or within the pores.

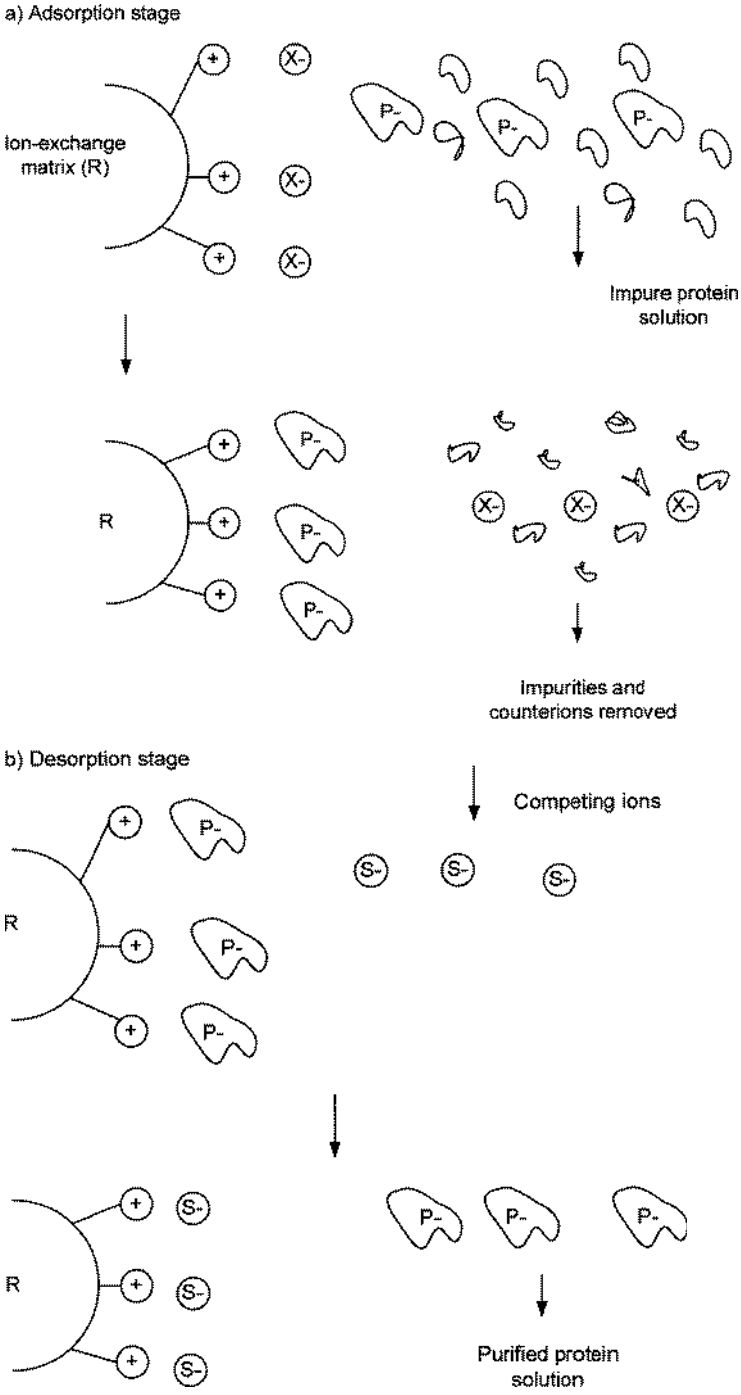


Fig. 14.32 Process of anion exchange: (a) adsorption stage, (b) desorption stage.

The choice of method of elution depends on the specific separation required. In some cases the process is used to remove impurities from a feedstock, while the required compound(s) remains unadsorbed. No specific elution method is required in such cases, although it is necessary to regenerate the ion exchanger with strong acid or alkali. In other cases the material of interest is adsorbed by the ion exchanger, while impurities are washed out of the bed. This is followed by elution and recovery of the desired solute(s). In the latter case, the method of elution is much more critical – for example, care must be taken to avoid denaturation of adsorbed proteins.

The adsorbed solute is eluted from the ion exchanger by changing the pH or the ionic strength of the buffer, followed by washing away the desorbed solute with a flow of buffer. Increasing the ionic strength of the buffer increases the competition for the charged sites on the ion exchanger. Small buffer ions with a high charge density displace polyelectrolytes, which can subsequently be eluted. Altering the buffer pH, so that the charge on an adsorbed polyelectrolyte is neutralised or made the same as the charges on the ion exchanger, results in desorption.

Fixed bed operations consisting of one or two columns connected in series (depending on the type of ions which are to be adsorbed) are used in most ion exchange separations. Liquids should penetrate the bed in plug flow, in either downward or upward direction. The major problems with columns arise from clogging of flow and the formation of channels within the bed. Problems may also arise from swelling of organic matrices when the pH changes. These problems may be minimised by the use of stirred tanks. However, these batch systems are less efficient and expose the ion exchangers to mechanical damage, as there is a need for mechanical agitation. The system involves mixing the feed solution with the ion exchanger and stirring until equilibration has been

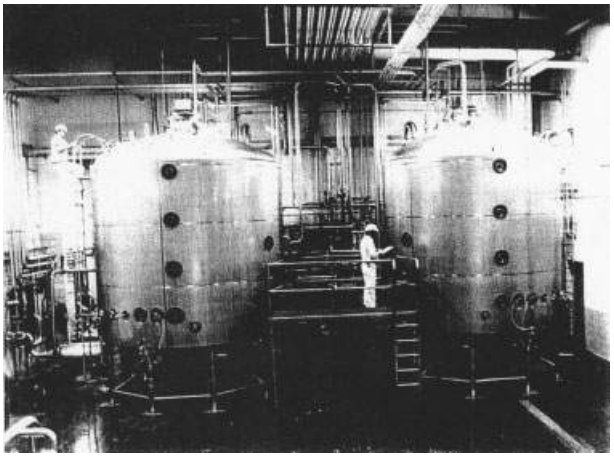


Fig. 14.33 Commercial stirred tank reactors; by courtesy of Bio-Isolates plc.

achieved (typically 30–90 min in the case of proteins). After draining and washing the ion exchanger, the eluant solution is then contacted with the bed for a similar equilibration time before draining and further processing. Commercial stirred tank reactors for recovering protein from whey are shown in Fig. 14.33.

Mixed bed systems, containing both anion and cation exchangers, may be used to avoid prolonged exposure of the solutions to both high and low pH environments, as are frequently encountered when using anion and cation exchange columns in series, e.g. during demineralisation of sugar cane juice to prevent hydrolysis of sucrose, as described below.

14.8.3 Applications of Ion Exchange in the Food Industry

The main areas of the food industry where the process is currently used or is being developed are sugar, dairy and water purification. Ion exchange is also widely employed in the recovery, separation and purification of biochemicals and enzymes.

The main functions of ion exchange are:

(a) removal of minor components, e.g. de-ashing or decolourising
(b) enrichment of fractions, e.g. recovery of proteins from whey or blood
(c) isolating valuable compounds, e.g. production of purified enzymes.

Applications can be classified as follows.

14.8.3.1 Softening and Demineralisation

Softening of water and other liquids involves the exchange of calcium and magnesium ions for sodium ions attached to a cation exchange resin, e.g.:

$$R-(Na^{+})_2 + Ca(HCO_3)_2 \rightarrow R-Ca^{++} + 2NaHCO_3$$

The sodium form of the cation exchanger is produced by regenerating with NaCl solution. Apart from the production of softened water for boiler feeds and cleaning of food and processing equipment, softening may be employed to remove calcium from sucrose solutions prior to evaporation (which reduces scaling of heat exchanger surfaces in sugar manufacture) and from wine (which improves stability).

Demineralisation using ion exchange is an established process for water treatment, but over the last 20 years it has been applied to other food streams. Typically the process employs a strong acid cation exchanger followed by a weak or strong base anion exchanger. The cations are exchanged with H^{+} ions, e.g.:

$$2R^{-}H^{+} + CaSO_4 \rightarrow (R^{-})_2Ca^{++} + H_2SO_4$$

$$R^{-}H^{+} + NaCl \rightarrow R^{-}Na^{+} + HCl$$

and the acids thus produced are fixed with an anion exchanger, e.g.:

$$R^+OH^- + HCl \rightarrow R^+Cl^- + H_2O$$

Demineralised cheese whey is desirable for use mainly in infant formulations, but also in many other products such as ice cream, bakery products, confectionery, animal feeds etc. The major ions removed from whey are Na^+, K^+, Ca^{++}, Mg^{++}, Cl^-, HPO_4^-, citrate and lactate. Ion exchange demineralisation of cheese whey generally employs a strong cation exchanger followed by a weak anion exchanger. This can produce more than 90% reduction in salt content, which is necessary for infant formulae.

Demineralisation by ion exchange resins is used at various stages during the manufacture of sugar from either beet or cane, as well as for sugar solutions produced by hydrolysis of starch. In the production of sugar from beet, the beet juice is purified by liming and carbonatation and then may be demineralised by ion exchange. The carbonated juice is then evaporated to a thick juice prior to sugar crystallisation. Demineralisation may, alternatively, be carried out on the thick juice which has the advantage that the quantities handled are much smaller. To produce high quality sugar the juice should have a purity of about 95%. Ash removal or complete demineralisation of cane sugar liquors is carried out on liquors that have already been clarified and decolourised, so the ash load is at minimum. The use of a mixed bed of weak cation and strong anion exchangers in the hydrogen and hydroxide forms, respectively, reduces the prolonged exposure of the sugar to strongly acid or alkali conditions which would be necessary if two separate columns were used. Destruction of sucrose is thus minimised.

The cation and anion resins are sometimes used in their own right for dealkalisation or deacidification, respectively. Weak cation exchangers may be used to reduce the alkalinity of water used in the manufacture of soft drinks and beer, while anion exchangers can be used for deacidification of fruit and vegetable juices. In addition to deacidification, anion exchangers may also be used to remove bitter flavour compounds (such as naringin or limonin) from citrus juices. Anion or cation exchange resins are used in some countries to control the pH or titratable acidity of wine although this process is not permitted by other traditional wine-producing countries. Acidification of milk to pH 2.2, using ion exchange during casein manufacture by the Bridel process, has also been described.

Ion exchange processes can be used to remove specific metals or anions from drinking water and food fluids, which has potential application for detoxification or radioactive decontamination. Procedures have been described for the retention of lead, barium, radium, aluminium, uranium, arsenic and nitrates from drinking water. Removal of a variety of radionuclides from milk has been demonstrated. Radiostrontium and radiocaesium can be removed using a strongly acidic cation exchanger, while iodine 131 can be adsorbed on to a variety of anion exchangers. The production of low-sodium milk, with potential dietetic application, has been demonstrated.

14.8.3.2 **Decolourisation**

Sugar liquors from either cane or beet contain colourants such as caramels, melanoidins, melanins or polyphenols combined with iron. Many of these are formed during the earlier refining stages and it is necessary to remove them in the production of a marketable white sugar. The use of ion exchangers just before the crystallisation stage results in a significant improvement in product quality. It is necessary to use materials with an open, porous structure to allow the large colourant molecules access to the adsorption sites. A new approach to the use of ion exchange for decolourisation of sugar solutions is the application of powdered resin technology. Finely powdered resins (0.005–0.2 mm diameter) have a very high capacity for sugar colourants due to the ready availability of adsorption sites. The use of such materials on a disposable basis eliminates the need for chemical regenerants, but is quite expensive.

Colour reduction of fermentation products such as wine uses a strongly basic anion exchanger to remove colouring matter, followed by a strong cation exchanger to restore the pH. It is claimed that colour reduction can be achieved without substantially deleteriously affecting the other wine qualities.

14.8.3.3 **Protein Purification**

High purity protein isolates can be produced in a single step from dilute solutions containing other contaminating materials by ion exchange. The amphoteric nature of protein molecules permits the use of either anion or cation exchangers, depending on the pH of the environment. Elution takes place either by altering the pH or increasing the ionic strength. The eluate can be a single bulk, or a series of fractions produced by stepwise or linear gradients, although fractionation may be too complex for large-scale industrial production. Separation of a single protein may take place on the basis that it has a higher affinity to the charged sites on the ion exchanger compared to other contaminating species, including other proteins present in the feed. In such cases, if excess quantities of the feed are used, the protein of interest can be adsorbed exclusively, despite initial adsorption of all the proteins in the feed. Alternatively, it may be possible to purify a protein on the basis that it has a much lower affinity for the ion exchanger than other proteins present in the feed; and thus the other proteins are removed leaving the desired protein in solution. One limitation of the process for protein treatment is that extreme conditions of pH, ionic strength and temperature must be avoided to prevent denaturation of the protein.

An area of great potential is the recovery of proteins from whey, which is a byproduct of the manufacture of cheese and related products such as casein. Typically whey contains 0.6–0.8% protein which is both highly nutritious and displays excellent physical properties, yet the vast majority of this is wasted or under-utilised. Anion exchange materials can produce high purity functional protein from cheese whey, using a stirred tank reactor into which the whey is introduced at low pH. Following rinsing of nonadsorbed material, the protein fraction is eluted at high pH and further purified by ultrafiltration, so that the

final protein content is approximately 97% (dry weight). It is further possible to fractionate the whey proteins into their separate components or groups of components. This approach has the potential of producing protein fractions with a range of functional properties which could be extremely valuable for use in the food industry. Lactoperoxidase and lactoferrin are valuable proteins with potential pharmaceutical applications which are present in small quantities in cheese whey. They may be purified from whey on the basis that these proteins are positively charged at neutral pH, whereas the major whey proteins are negatively charged. Another application of adsorption of whey protein by ion exchangers could be to improve the heat stability of milk. The use of ion exchange to recover or separate the caseins in milk is not carried out commercially, although it has been shown to be feasible.

This system has also been demonstrated for recovery of food proteins from waste streams resulting from the processing of soya, fish, vegetables and gelatine production, plus abattoir waste streams. Such protein fractions could be used as functional proteins in the food industry or for animal feeds. A variety of other food proteins have been purified or fractionated by ion-exchangers, including pea globulins, gliadin from wheat flour, egg, groundnut and soya protein.

Purification of proteins from fermentation broths usually involves a series of separation steps and frequently includes ion exchange. Large-scale purification of a variety of enzymes with applications in the food industry has been described, e.g. α-amylase, β-galactosidase.

14.8.3.4 **Other Separations**

Ion exchange has been used for various other separations in the food industry which do not fit into the above categories.

Fructose is sweeter than sucrose and glucose and can be used as a natural sweetener at reduced caloric intake. Although present in many natural sources, it is produced commercially from corn starch by hydrolysis to dextrose, which is then partially converted to fructose using the enzyme isomerase. The resulting high fructose corn syrup may be deionised by ion exchange and then a pure fructose fraction can be recovered with a sulphonic cation exchanger. Another application is the production of lactose-free milk. A process using sulphonated cation exchangers has been used to reduce the lactose level of skim milk to $<10\%$ of that in the feed, while retaining $>90\%$ of protein, minerals and citrate.

The purification of phenylalanine, which may be used in aspartame sweetener production, from fermentation broths using cationic zeolite material has been demonstrated. Ion exchange may also be used to purify enzymic reaction products such as flavour constituents from the enzymic degradation of fruit wastes.

14.8.4
Conclusion

There are many potential applications for ion exchange in the food industry, but few have been fully exploited in commercial practice. This is because of the complexity of the process and problems of scale-up. New applications are most likely to be developed in the food related aspects of biotechnology and in the production of high value protein fractions.

14.9
Electrodialysis

Alistair S. Grandison

14.9.1
General Principles and Equipment

Electrodialysis (ED) is a separations process in which membranes are used to separate ionic species from nonionic species. More detailed information on the theory and applications can be found elsewhere [88, 90, 91]. The process permits the separation of electrolytes from nonelectrolytes, concentration or depletion of electrolytes in solutions and the exchange of ions between solutions. Separation depends on ion-selective membranes, which are essentially ion exchange resins cast in sheet form, and electromigration of ions through ion-selective membranes depends on the electrical charge on the molecules, combined with their relative permeability through membranes. The membranes are composed of polymer chains which are crosslinked and intertwined into a network and bear either fixed positive or fixed negative charges. These may be heterogeneous membranes which consist of ion exchange resins dispersed in a polymer film or, more commonly, homogeneous membranes in which the ionic groups ($-NH_3^+$ or $-SO_3^-$) are attached directly to the polymer. Counter ions (see Section 14.8) are freely exchanged by the fixed charges on the membranes and thus carry the electric current through the membranes, while co-ions are repelled by the fixed charges and cannot pass through the membrane. Therefore cation membranes (with $-SO_3^-$ groups) allow the passage of positively charged ions, while anion membranes (with $-NH_3^+$ groups) allow the passage of negatively charged ions.

In practice, the cation and anion membranes are usually arranged alternately with plastic spacers to form thin solution compartments, as shown in Fig. 14.34.

In commercial practice 100–200 membranes may be assembled to form a membrane stack (Fig. 14.35) and an ED system may be composed of one or more stacks. Commercial ED membranes may be as large as 1–2 m^2.

The basic unit of a membrane stack is called a cell pair and comprises a pair of membranes and spacers, as illustrated in Figs. 14.34, 14.36.

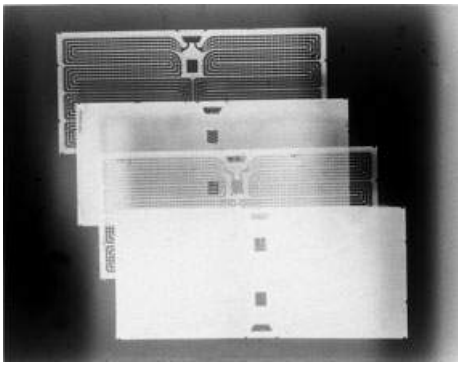


Fig. 14.34 Electrodialysis membranes and spacers; with permission of Ionics Inc.

Fig. 14.35 Electrodialysis membrane stacks; with permission of Ionics Inc.

A positive electrode at one end and a negative electrode at the other permit the passage of a DC current. The electrical potential causes the anions to move towards the anode and the cations to move towards the cathode. However, the ion-selective membranes act as barriers to either anions or cations. Hence, anions migrating towards the anode will pass through anion membranes, but will be rejected by cation membranes, and vice versa. The membranes, therefore, form alternating compartments of ion-diluting (even-numbered compartments in Fig. 14.36) and ion-concentrating (odd-numbered) cells. If a feed stream containing dissolved salts, e.g. cheese whey, is circulated through the ion-diluting cells and a brine solution through the ion-concentrating cells, free mineral ions will leave the feed and be concentrated in the brine solution. Demineralisation of the feed is therefore achieved. Note that any charged macromolecules in the feed, such as proteins, will attempt to migrate in the electrical field, but will not pass through either anion or cation membranes, due to their molecular size. The efficiency of electrolyte transfer is determined by the current density and the residence time of the solutions within the membrane cells; and in practice efficiency this is limited to about 90% removal of minerals. The membranes are subject to concentration polarisation and fouling, as described in Section 14.7.

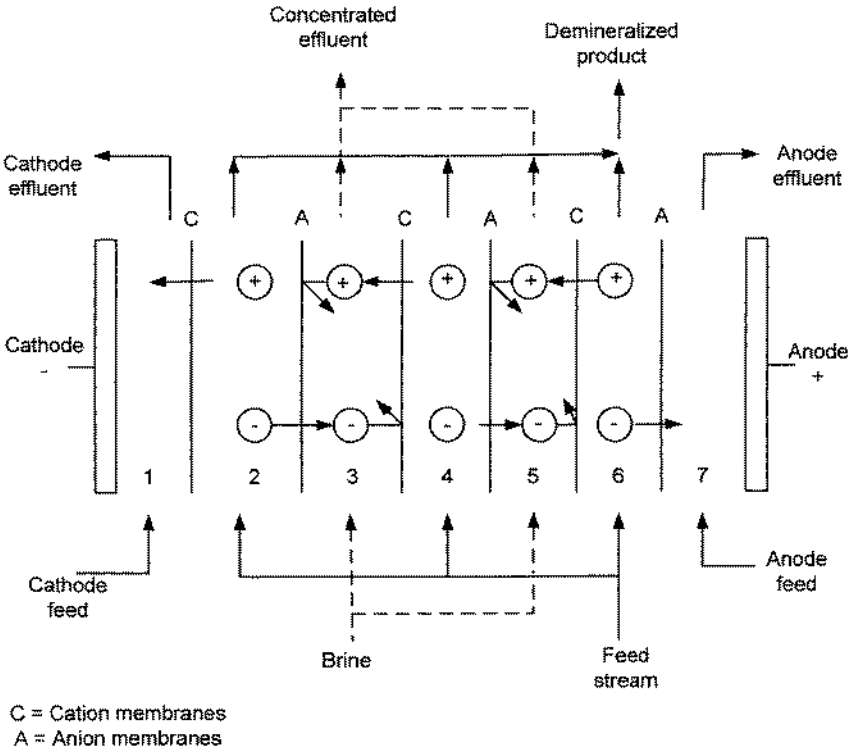


Fig. 14.36 Schematic diagram of electrodialysis process.

Alternative membrane configurations are possible, such as the use of cation membranes only for ion replacement. In Fig. 14.37, X^+ ions are replaced with Y^+ ions.

14.9.2 Applications for Electrodialysis

The largest application of ED has been in the desalination of brackish water to produce potable water. In Japan, all the table salt consumed is produced by ED of sea water. The major application of ED in the food industry is probably for desalting of cheese whey. Following ED, the demineralised whey is usually concentrated further and spray dried. ED could potentially be employed in the refining of sugar from either cane or beet but, in fact, commercial applications in these industries are limited by severe membrane fouling problems.

Other potential applications of ED in food processing include:

- demineralisation of ultrafiltration permeate to improve lactose crystallisation
- separation of lactic acid from whey or soybean stock
- removal of Ca from milk, either to improve protein stability during freezing, or to simulate human milk

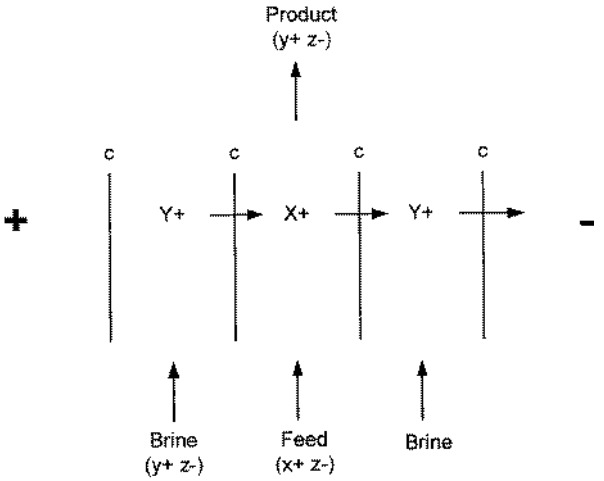


Fig. 14.37 Ion replacement using cation membranes.

- removal of radioactive metal ions from milk
- demineralisation of fermented milk products to improve flavour and textural quality
- extraction of salts from grape musts and wine to improve their stability
- controlling the sugar/acid ratio in wine either by deacidification of the grape musts by ion substitution ED using anionic membranes, or acidification using cationic membranes
- deacidification of fruit juices, either to reduce the sourness of the natural juices, or for the health food market
- desalination of spent pickling brine.

In addition, the process can be integrated into continuous fermentation or reactor designs.

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