# 1

# General Introduction

## 1.1 Overview of Distillation Processes

The term "distillation" refers to any process that facilitates the separation of solution components using their different volatilities. Distillation processes are categorized according to the number and nature of the components being separated as shown in Figure 1.1. At a primary level, distillation processes can be categorized as simple distillation or fractional distillation. Simple distillation utilizes a still to effect the separation of two miscible liquids or a single liquid and its nonvolatile solutes in a single vaporization–condensation process. Fractional distillation refers to the separation of two or more liquids using repeated vaporization–condensation steps in a single column.

Simple distillation of a mixture of two liquids facilitates enrichment of the distillate (vaporized fraction) with the most volatile component with a corresponding enrichment of the residue with the second component. The distillate is the desired component in typical industrial applications. The degree of enrichment depends on the relative volatilities of the liquids. In some applications, the distillate is subjected to a second simple distillation step in a separate still to obtain the required separation. In simple distillation involving a liquid and its nonvolatile solutes, a high degree of separation can be achieved by prolonged boiling of the liquid. Here, the distillate is free of solutes other than trace amounts transferred by the entrainment of liquid droplets in the vapor. In many cases, distillation is carried out progressively through a series of simple distillation steps in a continuous process. Removal of the liquid from its nonvolatile solutes defines this process as a stripping operation. Furthermore, the still or series of stills in which stripping occurs is referred to as an evaporator. Fractional distillation results in a high degree of

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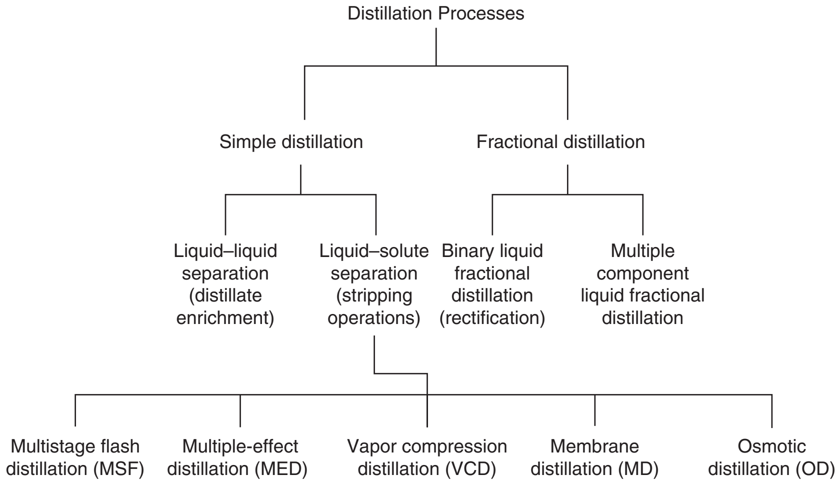


**Figure 1.1** Overview of distillation processes.

liquid–liquid separation due to repetitive distillation steps. This process is referred to as rectification when used for the separation of just two liquids. Examples highlighting the importance and widespread use of simple distillation and fractional distillation processes in society are discussed below.

The production of whisky and brandy are examples of simple distillation involving two liquids, water with a boiling point of 100 °C and ethanol with a boiling point of 78 °C. Whisky is distilled from grain mash that has been fermented to an ethanol concentration of 5–7% v/v, while brandy is distilled from wine having an ethanol concentration of 8–12% v/v. These low-alcohol solutions are boiled in a pot still to produce a distillate with an ethanol concentration of 20–35% v/v. The distillate is then subjected to simple distillation in a second pot still to produce a spirit with an ethanol concentration of about 70% v/v. The volatile organic aroma components of the base material are transferred and condensed with the vapor in both steps of the process. Finally, the spirit is subjected to maturation in accordance with product identification requirements.

Simple distillation involving a single liquid and its nonvolatile solutes is a widely used form of industrial distillation. An important example in which the distillate is the desired product is the desalination of seawater or brackish water. Water is evaporated from the salty solution for subsequent condensation and consumption. This stripping process is generally carried out using multistage flash distillation (MSF), multiple-effect distillation (MED), or vapor compression distillation (VCD). These simple distillation processes owe their success to internal energy recovery mechanisms as discussed in Section 1.5. With an estimated one billion people currently without access to safe drinking water [Blanco et al. (2009)] and a rapidly expanding global population, the role of desalination processes will continue to expand.

There are numerous examples of stripping operations in the food industry where the residue is the desired product. Water is stripped from materials such as fruit juices and dairy products to produce concentrates for cost-effective transport, storage, preservation, or spray drying. MED and VCD are typically used for such purposes with MSF confined to desalination applications. In other food industry applications, water stripping is undertaken to effect solute crystallization. Indeed, one of the largest operations of this type is the concentration of sugarcane juice for subsequent sugar recovery. In this case, MED is used to concentrate the juice to near saturation before entering a separate (pan) stage where crystallization is induced. An example of rectification is the production of industrial alcohol with an ethanol concentration in excess of 90% v/v for use in formulations such as biofuels, antiseptics, and solvents. Sugars from several different sources may be fermented to produce dilute aqueous ethanol solutions for this purpose. An upper limit of 96% v/v ethanol is dictated by the formation of an ethanol–water azeotrope from which no further separation can be achieved using conventional distillation processes. Rum and vodka are also produced by rectification using feedstocks produced by the fermentation of molasses and potatoes, respectively.

A basic requirement for rectification is a column filled with high-surface area packing material. A dilute aqueous ethanol solution for example is boiled at the base of the column to produce a vapor enriched in ethanol. The vapor cools as it rises to the point where condensation occurs on the surface of the packing material. The condensate then trickles toward the base of the column. Rising hot vapor from the increasingly higher boiling residue boils some of the returning liquid to produce a vapor that is further enriched in ethanol. The new vapor rises further up the column due to its higher volatility. This process is repeated many times as vapor ascends the column to produce the required ethanol concentration for external condensation. The vapor is removed from the top of the column while the water-enriched residue remains at the base. This process may be carried out in batch or continuous steady-state mode.

A modified fractional distillation column is used when several liquid fractions require separation. A well-known example of this is the refining of crude oil using a column containing horizontal condensation plates at different heights. The feedstock is boiled at the base of the column at a temperature at which all but the heaviest components vaporize. Controlled temperature reduction with increasing column height facilitates the condensation of different boiling point fractions on plates at different heights. In this way, the crude oil is separated into fuel oil, lubricating oil, diesel, kerosene, naptha, and gasoline in ascending order for removal through ports at the side of the column. Heavy residuals such as tar, asphalt, and waxes are collected from the base of the column while light hydrocarbon gases ($C_1$–$C_4$) are collected from the top of the column for external condensation. This process is operated as a continuous process.

Membrane distillation (MD) and osmotic distillation (OD) separate water from its nonvolatile solutes through vaporization and condensation and can therefore be classified as stripping distillation processes. Accordingly, desalination applications involve recovery of the distillate whereas concentrate production applications involve recovery of the residue.

In accordance with normal practice, the terminology applicable to conventional distillation processes has been changed in favor of membrane process terminology when discussing MD and OD. That is, the residue is referred to as retentate, while the distillate is referred to as permeate. In concentrate production applications, the fully concentrated retentate is referred to as concentrate.

MD and OD differ from MSF, MED, and VCD by effecting distillation through a porous, air-filled (usually) hydrophobic membrane using opposing membrane faces as evaporation and condensation surfaces. Membrane hydrophobicity excludes liquid water and its nonvolatile solutes from entering the porous structure and mixing with the permeating vapor. Furthermore, the small vapor gap afforded by the membrane reduces the resistance to vapor transfer to the point of condensation. Despite the success of MSF, MED, VCD, and other nondistillation stripping processes including freeze concentration (FC), reverse osmosis (RO), and electrodialysis (ED), MD and OD have attracted considerable attention as potential alternatives to these processes in some applications. This has been due to their special characteristics with respect to product quality, simplicity of operation, and potential energy savings.

This chapter traces the development of MD and OD from laboratory novelties to their present status as advanced stripping processes entering commercialization. Qualitative descriptions of the fundamental principles and characteristics of each process are provided and compared with those of established processes. Here, a heavy emphasis is placed on the factors that affect product quality. Before proceeding, however, it is beneficial to consider the meaning of the term "°Brix" frequently encountered in this and subsequent chapters. Strictly, the term refers to the percent by weight of pure sucrose in water at 20 °C. More generally, it has been used as a measure of the approximate sugars concentration in multisolute solutions in several industries. Indeed, °Brix has been adopted as the standard unit of concentration in the fruit juice [Bates et al. (2001)] and sugar industries [ICUMSA (2015)]. Simple and rapid measurement as refractometer or hydrometer Brix is convenient for use in process control.

## 1.2 Membrane Distillation (MD)

### 1.2.1 Historical Perspective

While MD is currently regarded as an emerging process, it is not new. The concept of MD was introduced during the 1960s and 1970s when several patents on MD equipment appeared [Hassler (1964), Weyl (1967), Miller (1968), Bodell (1968), Rogers (1968, 1969, 1970, 1971, 1972a,b, 1975)]. These included one general process patent [Rogers (1971)], while the others focused on desalination. The first journal articles on MD, which also focused on desalination, were published during that same period [Findley (1967), Findley et al. (1969), Henderyckx (1967), Van Haute and Henderyckx (1967)]. However, a major obstacle faced by workers in the field at that time was the unavailability of membranes with sufficient water vapor permeability and natural hydrophobicity for use in MD. Rather, primitive membranes fabricated from materials such as silicone rubber, paper, glass fibers, cellophane, nylon, and diatomaceous earth were used. Most of these required treatment with water-repelling materials to provide some degree of hydrophobicity.

Without suitable membranes, interest in MD waned in favor of RO, which was itself a relatively new process at that time. The timely fabrication of the first high-flux RO membranes [Loeb and Sourirjan (1963)] assured the future of this process in desalination applications. Indeed, the rate of production of potable water using RO was several-fold greater than that of MD at that time. In addition, the cost of energy required to generate the high feed pressures required by RO (30–80 bar) was less significant than in the years that followed. As an indicator, the world price of crude oil in the 1960s and early 1970s adjusted for inflation to 2015 prices was about US $20 per barrel compared with US $90–100 in 2015. The interest in desalination applications alone and the lack of concern over energy costs meant that the advantages of MD with respect to product quality and energy savings went largely unrecognized.

However, there was a resurgence of interest in MD in the early 1980s when new types of microfiltration (MF) membranes were found to be suitable for use as MD membranes based on their permeability and hydrophobicity. The best performing membranes were found to be those fabricated from polypropylene (PP), polytetafluoroethylene (PTFE), and polyvinylidinefluoride (PVDF) with nominal pore diameters in the 0.1–0.45 μm range. These membranes remain in common use in MD systems today. Membranes with pores in this size range have variously been referred to as microporous or macroporous membranes by different workers in the field. The International Union of Pure and Applied Chemistry (IUPAC) convention defines materials with pore diameters of greater than 0.05 μm as being macroporous [Rouquerol et al. (1994)] and hence this terminology has been adopted here.

The renewed interest in MD fostered the first attempts to produce modules to house and support these membranes. These included the Gore-Tex MD spiral wound PTFE membrane module in 1982 [Gore (1982)], the Swedish Development Co. plate-and-frame PTFE membrane module in 1983 [Carlsson (1983), Andersson et al. (1985)] and the Enka AG Trans MD tubular PP membrane module in 1984 [Enka AG catalogue (1984)], all of which were intended for desalination applications. The Goretex and Sweedish Development Co. modules were designed for air gap membrane distillation (AGMD), while the ENKA module was designed for direct contact membrane distillation (DCMD), the simplest and most commonly used form of the process. The different forms of MD are discussed below. Problems associated with these modules highlighted the need for future research and development in module construction. Major research programs operated by groups at the University of Calabria (Italy) and the University of New South Wales (Australia) were initiated during that same period and remain in place today. Similar programs are now commonplace worldwide as reflected by the increasing number of journal articles and conference papers on this topic. The major application studies reported to date are discussed in Chapter 5.

### 1.2.2 MD Process

The DCMD process is shown in Figure 1.2. Central to the operation of this process is a hydrophobic macroporous membrane that allows water vapor to enter the porous structure while excluding aqueous liquids and their nonvolatile solutes. The aqueous solution from which water is being extracted (feed stream) is passed over one face of the membrane (upstream side), while pure water (strip stream) is passed over the opposite face (downstream side), usually in counter-current flow. Both streams are in direct contact with the membrane. The driving force for mass transfer from the feed to the strip side is a water vapor pressure gradient generated by maintaining the bulk feed stream at a higher temperature than that of the bulk strip stream. Water evaporates at the feed–membrane interface, diffuses through the air-filled (usually)

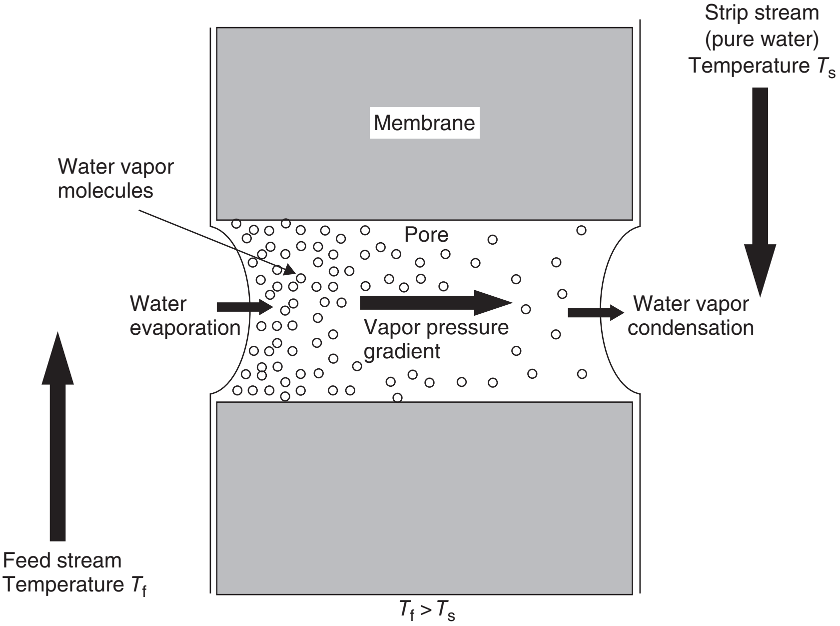


**Figure 1.2** Direct contact membrane distillation (DCMD) process.

membrane pores, and condenses at the membrane–strip interface. Depending on the heat sensitivity of the feed material, feed temperatures in the 35–90 °C range are generally used [Bui and Nguyen (2006)]. The strip stream is typically maintained at ambient temperature.

There are three lesser used forms of MD distinguishable from DCMD and each other by the way permeate recovery is achieved. These are AGMD, sweeping gas membrane distillation (SGMD), and vacuum membrane distillation (VMD). The feed and strip flow arrangement for each of the four forms of MD is shown in Figure 1.3. AGMD utilizes a stagnant air gap between the downstream side of the membrane and a cold plate located a few millimeters away inside the membrane module. Permeate diffuses through the air gap to the cold plate where it is condensed and drained from the module. The temperature of the plate is maintained by a stream of cooling water in contact with the opposite surface of the plate. In this case, the driving force is maintained by the applied temperature difference between the bulk feed stream and cooling water stream. This form of the process was designed to minimize conductive heat loss through the membrane. As their names suggest, SGMD and VMD use an inert sweeping gas (air) and a partial vacuum, respectively, to remove water vapor permeate from the downstream side of the membrane. In both cases, permeate condensation takes place externally to the module. Here, the driving force is generated by a combination of an elevated bulk feed temperature (usually) and permeate removal.

DCMD is the form of MD that has attracted most attention from researchers with about 60% of all MD publications focusing on this configuration [El-Bourawi et al. (2006)]. This is despite ranking third behind VMD and then SGMD in achievable water fluxes. A major reason for this has been the simplicity and ease of use of the process. Product can be drawn directly from the strip tank at the rate of permeate production. A schematic layout of a basic DCMD plant is shown in Figure 1.4. The preference for DCMD can also be attributed to some unattractive operational features of the other forms of the process. AGMD, for example, has a relatively low flux due to the high mass transfer resistance provided by the air gap. This is despite a marked reduction in conductive heat loss through the membrane with better maintenance of the driving force. On the other hand, industrial-scale membrane modules developed for desalination in recent years have

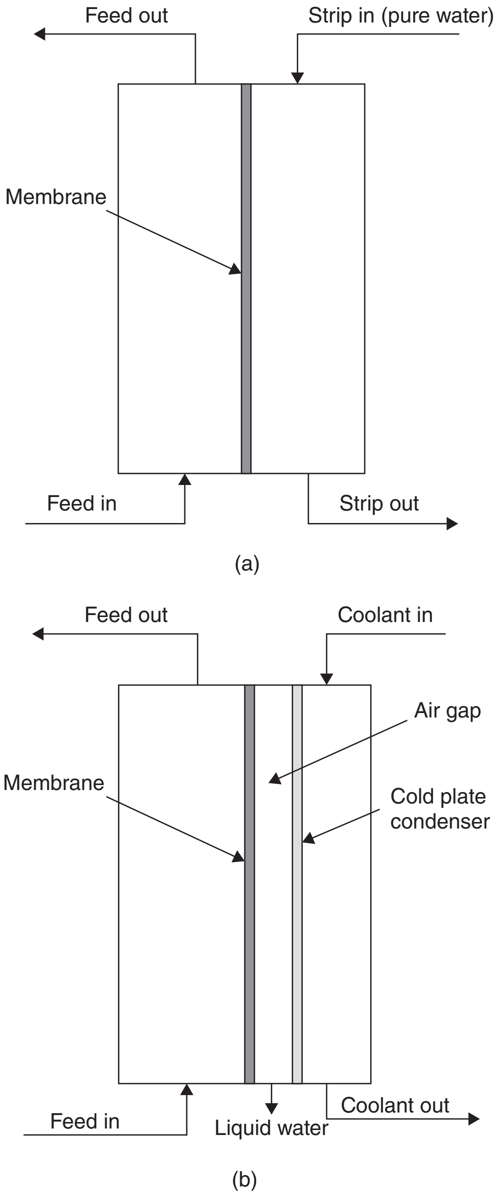


**Figure 1.3** The four different forms of membrane distillation. (a) Direct contact membrane distillation (DCMD). (b) Air gap membrane distillation (AGMD). (c) Sweeping gas membrane distillation (SGMD). (d) Vacuum membrane distillation (VMD).

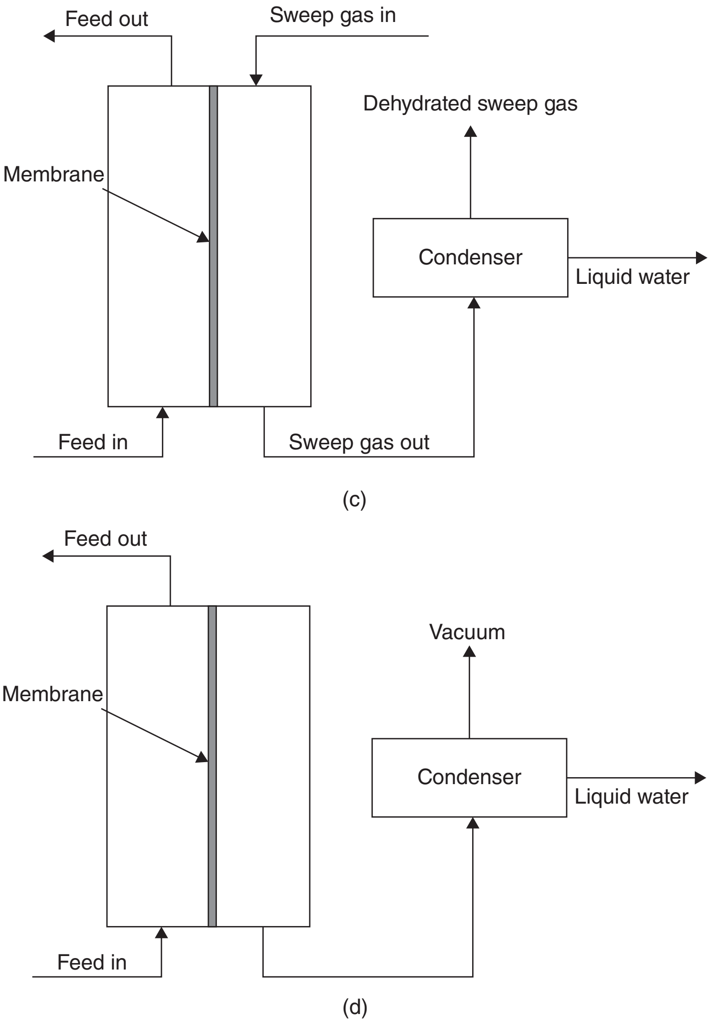


**Figure 1.3** (*Continued*)

utilized AGMD as this design is readily amenable to energy recovery strategies. SGMD requires large air flows with often prohibitive air transportation costs. In addition, external condensation is a relatively expensive process because of the low thermal conductivity of air. VMD on the other hand carries a high risk of liquid entering the membrane pores. The strip side vacuum must be regulated to prevent the transmembrane pressure drop from exceeding that at which liquid

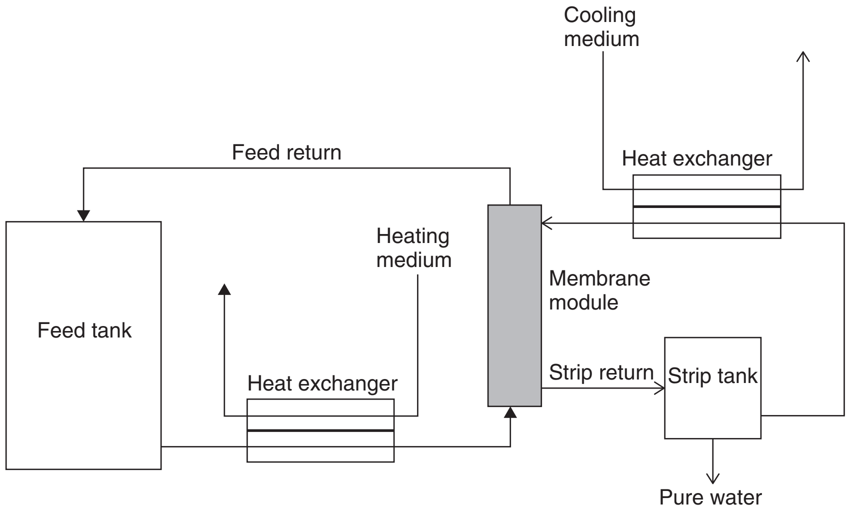


**Figure 1.4** Layout of a DCMD plant.

entry occurs. SGMD and VMD are more often used for the removal of organic volatiles and dissolved gases from aqueous solutions than for water recovery [Lawson and Lloyd (1997)].

## 1.3 Osmotic Distillation (OD)

### 1.3.1 Historical Perspective

The term “osmotic distillation” was proposed in 1986 to describe an isothermal membrane-based concentration process considered by many to be a variant of MD [Lefebvre (1986)]. Syrinx Research Institute Pty Ltd (Australia) recognized the potential of OD as a producer of high-quality concentrates and undertook process development for a range of applications [Lefebvre et al. (1987), Lefebvre (1988), Johnson et al. (1989), Thompson (1991)]. A commercial facility operated by the Wingara Wine Group (Australia) was subsequently used for the concentration of varietal grape juices for use in the production of high-quality vintage wines [Hogan et al. (1998)]. Apple, carrot, and various tropical fruit juice concentrates were also produced. This plant utilized commercially available 3M (formerly Membrana) Liqui-Cel$^{TM}$ Membrane Contactors housing X-50 hollow-fiber PP membranes. These modules were designed for use as gas–liquid or vacuum–liquid contactors, requiring small pores (X-50 pore diameter 0.04 μm) to prevent liquid entry under vacuum [Liqui-Cel (2017)]. Notwithstanding flux limitations imposed by membrane morphological features, this plant demonstrated the successful production of high-quality OD fruit and vegetable juice concentrates [Wingara Wine Group, Personal communication].

Subsequent developments have resulted in marked increases in OD flux. These can be attributed to better selection of the most appropriate MF membranes for use in OD [Johnson and Bailey (1994)] and the development of new osmotic agent formulations [Michaels and Johnson (1996), Shin and Johnson (2007)]. As for MD, the best performing membranes were found to be those fabricated from PP, PTFE, or PVDF with nominal pore diameters in the 0.1–0.45 μm range. Despite some differences in ideal MD and OD membrane requirements, the morphological features possessed by these membranes offer suitable compromises with respect to process performance. Like MD, there has been a marked increase in the number of journal articles and conference papers on OD in recent years. These have been heavily weighted in favor of fruit juice concentrate production as discussed in Chapter 6. It should be noted that the literature contains many examples of OD being referred to by other names including isothermal MD [Johnson and Bailey (1994)], osmotic evaporation [Brodard et al. (2003)], and osmotic MD [Babu et al. (2006)].

### 1.3.2 OD Process

The OD process is shown in Figure 1.5. The principle of operation is similar to that for MD, differing only in the way in which the water vapor pressure gradient across the membrane is generated. In MD, the water vapor pressure of the feed stream is increased relative to that of the strip medium by heating the feed stream. In OD, the water vapor pressure of the strip stream is lowered relative to that of the feed stream by incorporating a concentrated osmotic agent in the strip stream. The osmotic agent typically consists of a solution of a single salt with well-defined properties and is often referred to as the “brine” [Michaels and Johnson (1996), Hogan et al. (1998), Shin and Johnson (2007)]. Additional vapor pressure lowering may in some cases be obtained by blending the salt with its corresponding acid [Shin and Johnson (2007)]. As in the case of DCMD, the water vapor condenses at the membrane–strip interface. The use of an osmotic agent rather than a temperature gradient allows

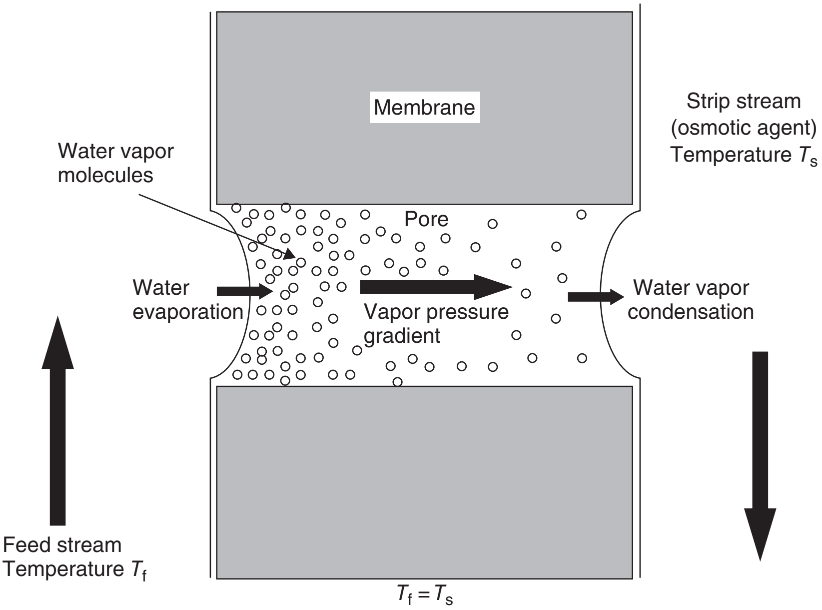


**Figure 1.5** Osmotic distillation (OD) process.

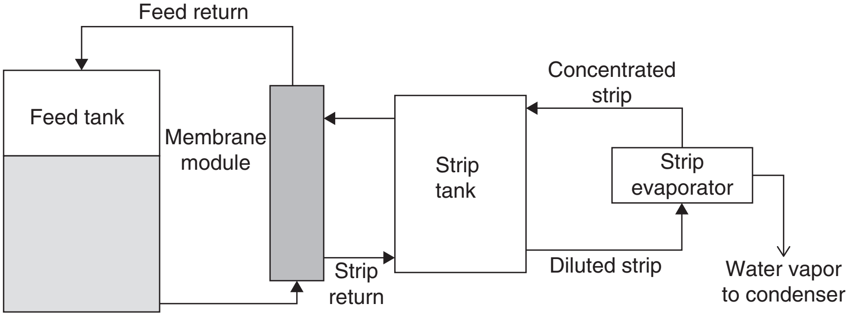


**Figure 1.6** Layout of an OD plant.

OD to be operated at or below ambient temperature. This has obvious advantages when producing concentrates that are heat sensitive or subject to volatiles loss. A schematic layout of an OD plant is shown in Figure 1.6.

Just as DCMD, AGMD, SGMD, and VMD are considered to be different forms of the MD process, varying only in the method by which permeate is collected, it can be argued that OD is another form of MD. However, there is a fundamental technical difference between MD and OD that is reflected in the type of membrane best suited to their operation. Theoretically, MD membranes should be fabricated from material of low thermal conductivity in order to reduce conductive heat loss to the strip side and thereby minimize the energy needed to maintain the required temperature gradient across the membrane. OD on the other hand does not have an applied temperature gradient to be maintained. Furthermore, latent heat deposited at the membrane–strip interface in OD produces a temperature gradient in opposition to the osmotically induced vapor pressure gradient. This effect is relatively more significant in OD than in MD due to the lower driving force of the former process. Water vapor pressure is less sensitive to osmotic agent concentration than to temperature. Accordingly, OD should ideally use a membrane of high thermal conductivity to assist the return of latent heat to the feed side. While this technical difference between MD and OD supports their separate identities, there is little to be gained by exploiting these requirements when operating with air-filled pores. The membranes used in MD and OD are highly porous (0.75–0.90) and hence the thermal conductivity of the membrane as a whole is largely determined by that of air, which is relatively poorly conducting. Nevertheless, MD and OD are treated separately here for convenience as the choice between processes is in most cases dictated by the susceptibility of the feed material to heat degradation and organic volatiles loss.

## 1.4 MD and OD as Alternatives to Established Stripping Processes

MD research has been undertaken in three major areas of application namely desalination, wastewater treatment, and concentrate production. Desalination refers specifically to the extraction of potable water from seawater or brackish water. Wastewater treatment may involve either water recovery or the isolation of a toxic or reusable substance. Concentrate production refers principally to the concentration of liquid foods such as fruit juices, vegetable juices, and dairy products. Examples of other types of applications are included in Chapter 5. OD research on the other hand has been confined to concentrate production because of the presence of an osmotic agent in the strip stream.

The increasing interest in MD and OD as potential alternatives to conventional processes has been driven by product quality and operational characteristics that collectively set them apart from these processes. These include a theoretical 100% retention of nonvolatile solutes, minimal heat damage to delicate feed components, high organic volatiles retention, concentration to high levels, and the ability to utilize waste heat or heat from natural sources. Conventional processes generally possess some but not all of these characteristics. The significance of each is discussed below. This is followed by a discussion of the operating principles and characteristics of conventional processes. A comparison of MD, OD, and conventional stripping operation characteristics is shown in Table 1.1.

### 1.4.1 Nonvolatile Solutes Retention

The hydrophobicity of MD and OD membranes prevents aqueous liquids and their nonvolatile solutes from entering their porous structure under normal operating pressures. That is, there is a theoretical 100% retention of nonvolatile solutes in the feed stream. Membrane terminology refers to this condition as 100% rejection by the membrane. Solute leakage due to membrane imperfections is often observed but is generally negligible. Accordingly, the US Environmental Protection Agency (EPA) recommendation of a maximum total dissolved solids (TDS) concentration of 500 ppm for potable water [Greenlee et al. (2009)] is readily achievable using MD. Indeed, water produced by MD as a long-term drinking water supply requires the addition of electrolytes to maintain a normal physiological balance. On the other hand, total solutes rejection is required for water use in dialysis, pharmaceuticals manufacture, laboratories, and the electronics industry. Importantly, MD is the most suitable technology for the concentration and subsequent disposal of low-level radioactive waste solutions. All processes currently used for this purpose (chemical precipitation, conventional distillation, ion exchange, reverse osmosis, ultrafiltration (UF), and sedimentation) lose some radioactive material to the environment [Zakizewska-Trznadel (2001), Khayet et al. (2006)].

### 1.4.2 Minimization of Heat Damage to Feed Components

MD feeds with complex chemical profiles such as liquid foods are concentrated using feed temperatures at the lower end (35–50 °C) of the MD operating range depending on their susceptibility to heat damage.

**Table 1.1** General comparison of MD, OD, and conventional stripping operation characteristics.

| Process | Major applications | Achievable TDS level in desalination | Damage to heat-sensitive feeds | Organic volatiles loss | Achievable solutes concentration in concentrate production |
|---|---|---|---|---|---|
| MSF | Seawater desalination | <100 ppm | Not applicable | Not applicable | Not applicable |
| MED | Seawater desalination<br>Concentrate production | <100 ppm | Moderate | High | 60–70 °Brix |
| VCD | Seawater desalination<br>Concentrate production<br>Clean water from highly concentrated solutions | <100 ppm | Moderate | High | 60–70 °Brix |
| FC | Seawater desalination<br>Brackish water desalination<br>Concentrate production | <100 ppm | Negligible | Negligible | 40–55 °Brix |
| RO | Seawater desalination<br>Brackish water desalination<br>Concentrate production<br>Wastewater treatment | <500 ppm | Negligible | Low | 30–35 °Brix |
| ED | Seawater desalination<br>Brackish water desalination<br>High purity water production<br>Salt production<br>Liquid food desalting | <300 ppm | Negligible | Low | Not applicable |
| MD | Seawater desalination<br>Brackish water desalination<br>Wastewater treatment<br>Concentrate production | Negligible | Low | Low | 60–70 °Brix |
| OD | Concentrate production | Not applicable | Negligible | Very low | 60–70 °Brix |

As previously indicated, the strip solution is normally maintained at ambient temperature. Heat damage detectable by a change in color or the development of off-flavors [Onsekizoglu (2012)] is maintained at reasonably low levels under these operating conditions. Heat damage may be reduced further by maintaining a temperature gradient across the membrane at lower feed and strip temperatures. However, lower average temperatures result in a lower driving force and hence flux. Heat damage in MD desalination and water treatment applications is inconsequential, allowing higher feed temperatures to be used.

OD on the other hand operates at ambient temperature with negligible heat damage to the feed material. Indeed, fruit juice concentrates produced by OD and reconstituted to single strength are generally indistinguishable from the fresh product. This has been confirmed by several studies as discussed in Chapter 6. This characteristic is unique among processes capable of achieving high concentration levels where deterioration occurs over extended processing times. An important consequence of avoiding heat damage to liquid foods is the maintenance of nutritional value. This is becoming increasingly recognized by dietitians, particularly those advocating the consumption of fruit juices high in antioxidants [Petrotis and Lazarides (2001), Koroknai et al. (2008)]. In addition to the production of high-quality liquid food concentrates, OD is suitable for the concentration of pharmaceutical and biological products whose activities are compromised by excessive heat [Hogan et al. (1998)].

In some applications, an OD feed temperature that is moderately elevated relative to that of the strip stream is accommodated within the normal ambient temperature range. MD fluxes are typically an order of magnitude greater than those of OD and hence a feed temperature of just a few degrees above that of the strip stream may provide a more attractive flux without significantly compromising product quality [Koroknai et al. (2006)]. Furthermore, this combined OD–MD process facilitates reduced processing time, which restricts heat damage. The advantages of using OD may in some cases be compromised by heat damage suffered during preliminary feed clarification. However, this damage may be eliminated or appreciably reduced by replacement of the conventional clarification process with an integrated MF or UF system.

### 1.4.3 Organic Volatiles Retention

A major problem encountered during the production of liquid food concentrates by conventional thermal evaporation is a substantial loss of the volatile organic species whose aromas contribute to the characteristic flavor of the food. This is particularly relevant to fruit juices with their complex volatiles profiles of alcohols, aldehydes, ketones, terpenes, hydrocarbons, amines, mercaptans, ethers, phenols, lactones, esters, and carboxylic acids [Pereira et al. (2006)]. The propensity for volatiles loss during the concentration of several fruit juice types by conventional thermal evaporation is illustrated in Table 1.2. The table shows the amount of water evaporation corresponding to the loss of 90% of the aroma content. Given that concentration to standard concentrate levels of 60–70 °Brix generally requires in excess of 80% water removal, it is clear that thermally produced concentrates of the juices listed are almost devoid of organic volatiles [Ramteke et al. (1993)].

This loss of volatiles can be alleviated to some extent during conventional thermal processing using a volatiles recovery process [Kumar et al. (2013)]. Typically, the juice is boiled under reduced pressure and the mixed vapor collected until the volume of the juice is reduced by 10–25% depending on the ease of volatiles removal. Table 1.2 clearly shows that fruit juices vary widely in their susceptibilities to volatiles loss. The mixed vapor is then subjected to rectification to recover

**Table 1.2** Percent water removal corresponding to 90% aroma loss in conventional thermal evaporation.

| Fruit juice type | % Evaporation |
|---|---|
| Apple | 10 |
| Plum | 32 |
| Grape | 73 |
| Strawberry | 82 |
| Banana | 20 |
| Mango | 67 |
| Guava | 68 |
| Pineapple | 85 |

*Source*: After Ramteke et al. (1993).

and condense the volatiles while the residual juice is concentrated in the normal way. The condensed volatiles are then added to the concentrated juice to partly restore flavor. However, this process has the disadvantages of heat damage to the volatiles during rectification and increased processing costs.

In MD and OD, the loss of volatiles is driven by their individual partial pressure gradients across the membrane. The partial pressure of a given volatile at the membrane pore entrance is higher for MD than OD because of the elevated MD feed temperature. However, both are considerably lower than that in a boiling liquid. Consequently, MD volatiles losses are generally maintained at low levels, while OD losses are generally very low. Volatiles removal occurs most rapidly in SGMD and VMD where a downstream sweep gas and vacuum, respectively, maintain a steep partial pressure gradient across the membrane. In the case of OD, the driving force for volatiles transfer is further reduced by their lower solubility in the high ionic strength strip stream [Hogan et al. (1998)].

An additional factor allowing volatiles loss to be minimized in MD and OD is the selection of an appropriate membrane pore diameter. The greater intrusion of the stagnant feed meniscus afforded by larger pores significantly increases the distance over which the volatiles must diffuse from the bulk feed solution to replace those entering the air-filled pores. Water is present in much higher concentration at the meniscus–air interface and is relatively unaffected by the extent of meniscus intrusion. A similar process occurs on the strip side with permeated volatiles having to diffuse further to enter the bulk strip stream. That is, larger pore diameters provide lower volatiles loss to water removal ratios [Barbe et al. (1998)].

### 1.4.4 Production of Highly Concentrated Solutions

MD and OD have the capability of achieving higher levels of concentration than conventional processes in many applications due to fewer process restrictions. The vapor pressure driving force in MD and OD exists at all concentrations despite a progressive loss of water activity as concentration proceeds. Furthermore, the temperature conditions under which MD and OD operate make it is unnecessary to limit the extent of concentration to restrict heat damage to the concentrate. In conventional thermal evaporation, for example, highly viscous fruit juice concentrates deposit a layer of burnt organic material on hot heat transfer surfaces resulting in concentrate damage and a loss in evaporator efficiency [Ramteke et al. (1993)]. Other restrictions to the achievable level of concentration by conventional processes are discussed below. Highly concentrated solutions offer better microbiological stability and reduced handling, storage, and transport costs.

### 1.4.5 Utilization of Waste Heat or Heat from Natural Sources

Water evaporation is a highly energy-intensive process with a power requirement of 628 kW h $m^{-3}$ of pure water produced [Wang and Chung (2015)]. However, the moderate operating temperature of MD allows the required heat to be drawn from waste factory or natural sources (solar, geothermal). For example, VMD has been used to desalinate seawater heated by warm cooling water (65 °C) from the diesel engines of a seagoing vessel [Xu et al. 2006]. In addition, solar-driven AGMD pilot plants have been applied to the desalination of seawater [US Department of the Interior (2004), Banat et al. (2007), Gullen-Burrieza et al. (2011), Camacho et al. (2013)], brackish water [Rommel et al. (2007)], and groundwater [Wang et al. (2009)]. These processes are examined in more detail in Chapter 5. Waste or natural heat can also be used to reconcentrate the diluted osmotic agent in OD operations. For example, the Wingara Wine Group OD plant referred to above utilized a 70 °C factory wastewater stream to concentrate $CaCl_2$ strip solution using a single-stage vacuum evaporator in a closed loop with the strip tank [Wingara Wine Group, Private communication].

## 1.5 Established Stripping Processes

### 1.5.1 Multistage Flash Distillation (MSF)

MSF is the major desalination process in use worldwide with respect to the volume of drinking water produced. This is despite there being more RO plants than MSF plants dedicated to this application. MSF plants are energy intensive and are typically coupled to power plants to take advantage of the plentiful waste heat supply. Cost savings of at least one-half are achieved by this means. Coupled with the economy of scale associated with thermal distillation processes, these cost savings have resulted in MSF plants being used exclusively for large-scale seawater desalination. Seawater with a typical TDS content of 35 000 ppm can be treated by MSF to produce a distillate with a purity of less than 100 ppm [Porteous (1975), Linstrum (1983), Halel and Odeh (2004)].

A schematic representation of an MSF plant is shown in Figure 1.7. MSF involves distillation through several (usually 15–25) stages or flash chambers. Seawater is heated in a brine heater under elevated pressure, $P_{\max}$, to just below its boiling point, $T_{\max}$, at that pressure. An initial brine temperature of about 110 °C is used. The heated seawater is fed into the first flash chamber held at a lower pressure than $P_{\max}$. The pressure reduction causes the seawater to boil rapidly with resulting flashing of a portion of the water into steam. This process is repeated as the seawater is passed through each successive flash chamber under successively lower pressures. The vapor is condensed onto heat recovery tubes that run through the entire set of chambers commencing at the final stage. These tubes carry the incoming seawater for preheating prior to entering the brine heater. Preheating of the incoming seawater is also effected by heat exchange with the reject seawater. That is, energy is recycled in the plant with little loss in the outflow. Generally, only a small fraction of the seawater is vaporized and condensed in each stage. In some MSF plants, the feed water is passed through the system once before being disposed of, while in others, it is returned to the system to be mixed with incoming raw water. A typical MSF plant has a potable water production rate of about 3 Ml $h^{-1}$. The success

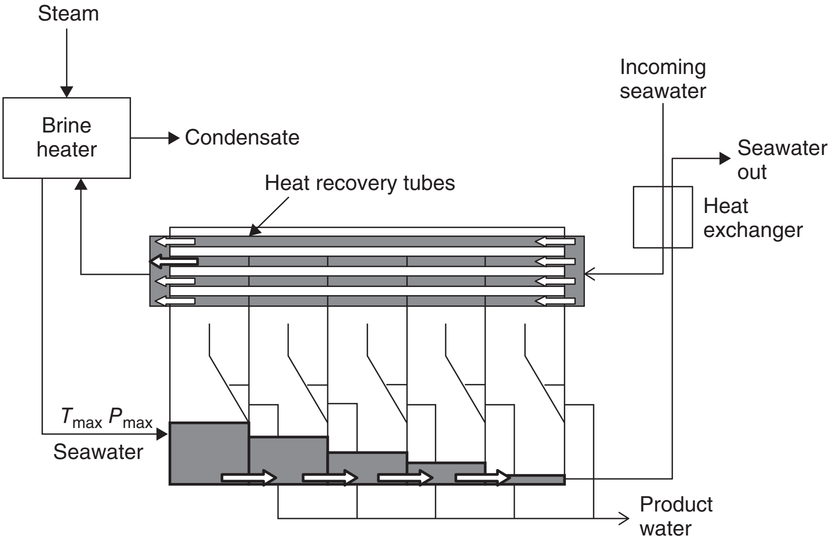


**Figure 1.7** Multistage flash distillation (MSF) plant.

of MSF in utilizing waste heat from a power plant for large-scale seawater desalination is unlikely to be surpassed by any other existing technology.

### 1.5.2 Multiple-Effect Distillation (MED)

MED plants consist of several single evaporator stages (effects) in series through which progressively more concentrated feed material passes [Al-Shammiri and Safar (1999)]. They are widely used for both desalination and concentrate production. Indeed, MED plants are the largest producers of liquid food concentrates worldwide. The success of MED has been due to cost savings achieved through utilization of the vapor produced by evaporation in the first effect to evaporate more of the liquid in the second effect and so on for each successive effect. That is, nominally 1.0 kg of heating steam fed to the first effect produces 1.0 kg of vapor in that effect plus 1.0 kg of vapor in each successive effect. This is achieved by operating each effect under lower pressure than the previous one, thereby reducing the boiling point and allowing progressively cooler vapor to be used. The number of effects is limited by the available temperature range as determined principally by the initial heat input. A maximum of four effects are used in the absence of a cheap supply of energy. Furthermore, additional effects increase the residence time, which is an important consideration when concentrating heat-sensitive materials such as liquid foods.

A major advantage of MED is that it allows continuous, once-through processing with a high throughput. The concentration of sugarcane juice to the point where raw sugar crystallization can be induced is a relevant example. Raw sugar factories vary considerably in capacity but a single-strength juice throughput of 400 tonnes $h^{-1}$ (500 tonnes cane) is typical [Australian Cane Farmers Association (2016)]. This corresponds to a water evaporation requirement of 300 tonnes $h^{-1}$. Furthermore, this is an example of an application in which more than four effects, usually five or six, are economical. Raw sugar factories generate a large quantity of cane fiber (bagasse) that serves as cost-free boiler fuel for steam generation.

Several different evaporator designs have been developed to cater for the different physicochemical properties of a wide range of feed materials [Ramteke et al. (1993)]. Fruit juices, for example, are produced as pulpy, cloudy, or clear juices with different suspended solids content, thermal properties, and rheological properties. The majority of MED plants use tubular heating surfaces although plate evaporators are preferred in some applications. Tubular evaporators consist of rising (climbing) film or falling-film types. While different evaporator designs are better suited to different feeds, most MED operations involving heat-sensitive feeds result in moderate heat damage. In addition, MED plants are conducive to high volatiles loss due to their elevated temperature, reduced pressure operation. These effects can be understood by considering the operation of each evaporator type.

In a tubular rising film evaporator, the material being concentrated passes upward through vertically mounted tubes while heating steam contacts the outside of the tubes. The feed boils as it rises to form a thin film of concentrated solution on the surface surrounding a core of water vapor. This system delivers a high rate of heat transfer due to the use of a relatively large temperature difference between the heating steam and the liquid. While this minimizes residence time, the combination of a large film surface area to volume ratio and operation under reduced pressure is conducive to heat degradation and volatiles loss. In addition, this process is limited to the production of relatively low viscosity concentrates (0.1 Pa s) in order to maintain the dynamics of the rising film.

The operation of the tubular falling-film evaporator is similar to that of the rising film evaporator. In this case, however, the material being concentrated flows downward through the tubes. The residence time is shorter and the maximum tolerable viscosity (0.2 Pa s) is greater than that of the rising film evaporator due to the assistance of gravity in facilitating downward flow. While the shorter residence time reduces heat damage to some extent, the volatiles loss remains high under the reduced pressure conditions. Concentration to 60–70 °Brix is usually achievable and consequently this type of evaporator is used in the majority of MED applications. A schematic representation of a tubular falling-film evaporator is shown in Figure 1.8.

A major advantage of plate evaporators is the ability to process more viscous liquids (0.3–0.4 Pa s) than tubular types due to flexibility in the distance between plates. These include feeds such as cloudy fruit juices where high viscosities are imparted by suspended cellulose, hemicellulose, and pectic substances. Plate evaporators provide higher rates of heat transfer than tubular forms allowing higher feed velocities to be employed. The lower residence time reduces damage to heat-sensitive feeds. Other characteristics resulting from this design include gentle boiling and lower fouling of the heat transfer surfaces. Plate evaporators

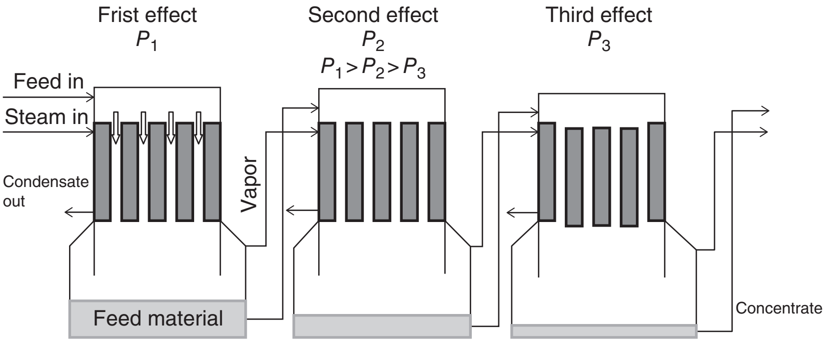


**Figure 1.8** Falling-film multiple-effect distillation (MED) plant. $P_1$ = Heating steam pressure. $P_2$, $P_3$ = Water vapor pressures.

are normally designed for single-pass operation in order to minimize thermal stress on the product.

MED is well suited to desalination on an appreciable scale due to energy savings inherent to multiple-effect operation and the high throughput associated with continuous operation. However, the production of complex liquid food concentrates presents a different case. While 60–70 °Brix MED concentrates have long been accepted as standard beverages, the use of MD and in particular OD in concentrate production is rapidly changing quality expectations. Indeed, numerous publications on the production of fruit and vegetable juice concentrates by MD and OD have appeared in recent years. In addition to volatiles loss and direct heat damage, MED can in some cases result in a loss of important solutes through thermally induced chemical reactions. In sugarcane juice, for example, sucrose is lost by inversion to glucose and fructose as the result of pH lowering by organic acids formed from invert sugars at elevated temperatures. While this typically accounts for a sucrose loss of less than 1%, the loss of revenue to a raw sugar factory over a crushing season can be substantial [Wong et al. (1996)]. Furthermore, increased glucose and fructose levels in the juice decrease sugar factory efficiency and sugar quality [Eggleston et al. (2004)]. The low-to-moderate operating temperatures of MD and OD would be expected to minimize inversion losses. A smaller loss of sucrose occurs by the entrainment of liquid droplets in the MED vapor. Droplets cannot enter the pores of hydrophobic membranes.

### 1.5.3 Vapor Compression Distillation (VCD)

The general layout of a VCD plant is shown in Figure 1.9. VCD is characterized by compression of part or all of the steam produced in an evaporator for use as an additional heat source. Compression increases the steam temperature to above that of the boiling chamber. The compressed steam is passed through a heat exchanger located inside the boiling (evaporation) chamber where it condenses, giving up its latent heat to the feed material. The heat retained by the condensed vapor is used to preheat incoming feed material in an external heat exchanger. VCD can be used alone but is normally applied to the first effect of a MED plant. In the latter case, the additional evaporation provided can be equivalent to that gained by having an additional effect.

Two methods of vapor recompression are in common use, thermal recompression and mechanical recompression [Aly and El-Fiqi (2003)]. In thermal recompression, the high pressure energy of steam from an external source (motive steam) is firstly converted to kinetic energy by

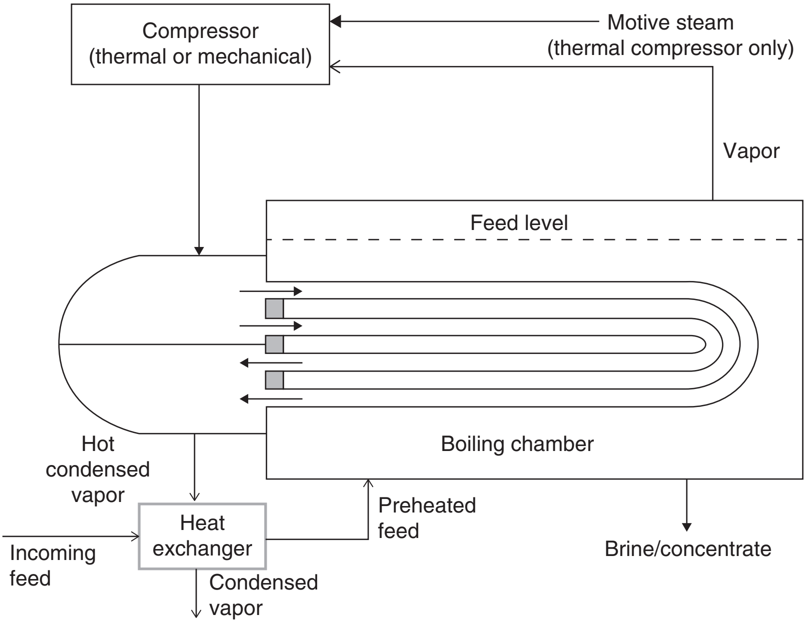


**Figure 1.9** Single-effect vapor compression distillation (VCD) plant.

passage through a converging nozzle in a thermal ejector. This creates a low-pressure region, which causes entrainment of a portion of the steam from the boiling chamber. The kinetic energy of the mixed vapor is then converted to pressure energy by expansion as it enters the internal heat exchanger through the throat of the ejector. In the case of mechanical vapor recompression, all vapor from the evaporator is recompressed. The power for the mechanical compressor is supplied by a combustion engine, an electric motor, or a steam turbine.

VCD has been used in large-scale desalination processes for many years, providing considerable capital and operating cost savings when compared with MED alone. The process is capable of producing potable water with less than 100 ppm TDS from any water source. Indeed, VCD has the advantage that it can treat water with TDS levels far in excess of normal seawater levels as it is able to heat the water to its elevated boiling point. VCD is also used widely for the production of liquid food concentrates. As in the case of MED operating alone, concentrate production results in moderate heat damage and high volatiles loss.

### 1.5.4 Freeze Concentration (FC)

FC facilitates desalination or concentrate production by the formation and removal of ice crystals. The layout of a FC plant is shown in Figure 1.10. The plant has four main components, a crystallizer (freezer) with an associated feed precooler, a refrigeration unit, an ice–liquid separator, and an ice melter. In an indirect contact crystallizer, the solution to be concentrated is passed through a scraped-surface heat exchanger for cooling by the refrigerant. Crystals are formed at the cold surface and then removed and mixed with the liquid by a rotating shaft. In a direct contact crystallizer, the feed material is brought into direct contact with the refrigerant. Latent heat is withdrawn by vacuum evaporation of the refrigerant and part of the water. Low-level organic volatiles loss may occur at this stage depending on the nature of the feed material. However, this process eliminates the need for an expensive scraped-surface heat exchanger. Direct contact crystallization is used mainly in nonfood applications in which feed contamination by the refrigerant is tolerable. Following crystallization by either method, the crystals are subject to ripening whereby most of the smaller crystals dissolve while the larger crystals grow larger [Ramteke et al (1993)].

Ice–liquid separation is achieved using a filter press, a filtering centrifuge, a wash column, or a combination of these. The effectiveness

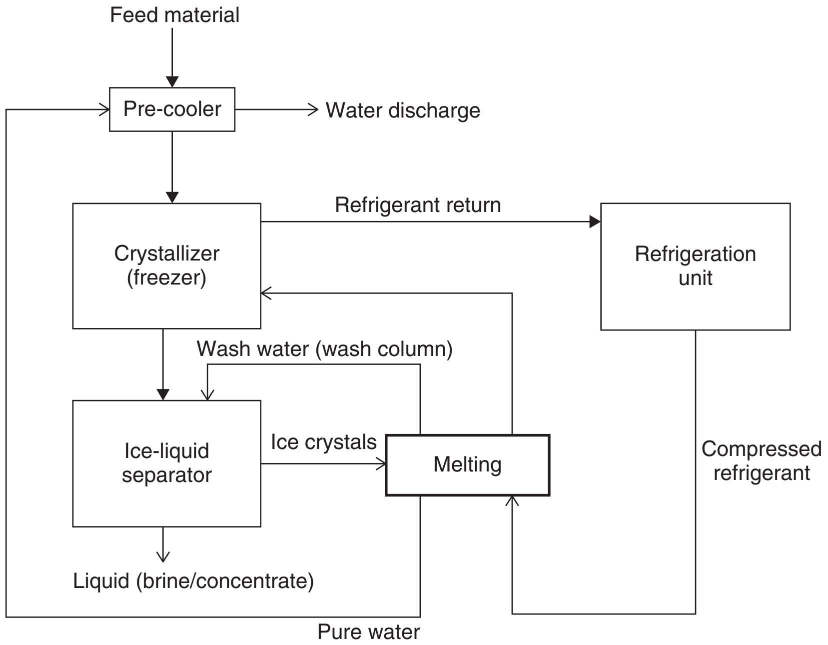


**Figure 1.10** Freeze concentration (FC) plant.

of each process with respect to product yield and organic volatiles retention is different. Filter presses cause some loss of dissolved solids through liquid entrapment in the compressed ice. Centrifuges separate the ice crystals from the concentrate using their density differences in which case the effectiveness of separation depends on the viscosity of the concentrate. Highly viscous solutions more readily adhere to the surface of the ice crystals than those of lower viscosity. In addition, centrifuges operate with a headspace that accelerates organic volatiles loss. Wash columns on the other hand offer more effective separation of ice crystals and concentrate than either of these processes. Furthermore, wash columns operate without a headspace with insignificant volatiles loss. Typically, the ice-concentrate slurry enters the bottom of the column and the crystals are then compressed by the upward motion of a filter to form a packed bed containing residual mother liquor. The crystals are then melted utilizing heat released by the refrigerant during compression. A small portion of this water is used to wash the packed bed entering from the top of the column. The remainder is used to precool the incoming feed material prior to discharge.

FC may be used in desalination applications to give a potable product containing less than 100 ppm TDS. However, its low-temperature operation makes it particularly amenable to the production of liquid food concentrates due to negligible heat damage and, in the case of indirect contact crystallization, negligible volatiles loss. Both of these characteristics are shared by OD. However, a major disadvantage of FC in concentrate production is difficulty in achieving the required separation of ice crystals and concentrate in a single step due to the high viscosity of the concentrate at low temperatures. This can be overcome to some extent using multistage FC, which also has the advantage of lower energy consumption. Nevertheless, the final product concentration is restricted to 40–55 °Brix. As previously indicated, MD and OD are capable of producing concentrates of 60–70 °Brix.

### 1.5.5 Reverse Osmosis (RO)

RO plants are widely used for the production of potable water from brackish water and seawater [Kucera (2010)]. Brackish water contains less than 5000 ppm TDS, while seawater typically contains about 35 000 ppm. Indeed, greater than 30% of the world's potable water production by technology-based processes is by RO. However, there are many other applications of RO in which the concentrate rather than the permeate is the desired product. Many of these are found in the food industry where RO is used as a preliminary dewatering step in preparation for spray drying or further concentration. The main attributes of RO are good solutes rejection by the membrane (usually >99%), attractive fluxes at low solute concentrations, the absence of an energy-intensive phase change, negligible heat damage to the feed material, simplicity of plant design, and the ease of scale-up of modular membrane plants generally. Disadvantages include high feed-pressure operation and relatively low concentration factors.

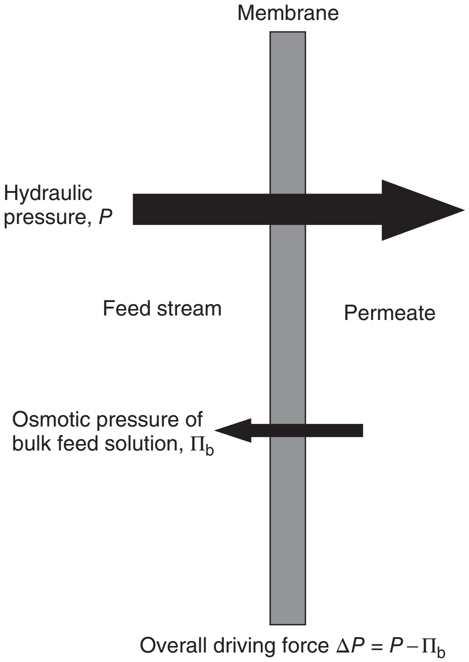
In RO, the feed solution is pumped under elevated pressure (30–70 bar) across one face of a hydrophilic (liquid water-loving) membrane. The membrane allows water permeation through its structure while salts and most other solutes are rejected. Modern RO membranes are asymmetric in structure whereby a thin dense (nonporous) skin (thickness 0.1–1.0 μm) that provides the required selectivity is supported by a much thicker uniform layer of the same or different (composite membrane) polymer. RO membranes are typically manufactured from polyamide (PA) while polysulfone (PS) or polyethersulfone constitute the support layer. The overall driving force for water transport through the membrane is the difference between the applied feed pressure and the opposing concentration-dependent osmotic pressure of the bulk feed solution.

$$\Delta P = P - \Pi_b \tag{1.1}$$

where $\Delta P$ is the overall driving force (Pa), $P$ the applied feed (hydraulic) pressure (Pa), and $\Pi_b$ the osmotic pressure of the bulk solution (Pa). This relationship is illustrated diagrammatically in Figure 1.11.

The transport of water through the membrane and the rejection of solutes at the feed–membrane interface are usually accounted for in terms of the solution-diffusion model. Accordingly, water dissolves in the hydrophilic membrane matrix and diffuses across the membrane under the influence of the net pressure gradient. Solutes on the other hand have poor solubilities and low diffusivities in the membrane and accumulate at the feed–membrane interface. This phenomenon and the solutes concentration profile associated with this accumulation are depicted in Figure 1.12. The region of higher solutes concentration is known as the concentration polarization boundary layer. This layer offers a hydraulic resistance to water transport to the membrane surface.

**Figure 1.11** Principle of reverse osmosis (RO).



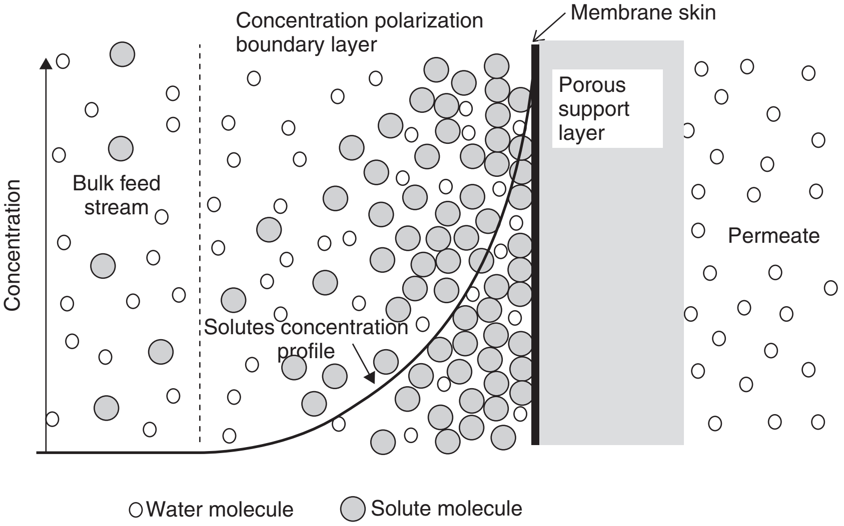


Figure 1.12 Concentration polarization in RO.

RO flux is determined by the overall driving force and the magnitude of the overall mass transfer coefficient.

$$J = K\Delta P \tag{1.2}$$

where $J$ is the water flux ($\mathrm{kg\,m^{-2}\,s^{-1}}$) and $K$ the overall mass transfer coefficient ($\mathrm{kg\,m^{-2}\,s^{-1}\,Pa^{-1}}$). Here, $K$ is inversely proportional to the combined resistances of the boundary layer and the membrane. Equations 1.1 and 1.2 show that water flux decreases as concentration proceeds due to a progressive increase in $\Pi_b$. This effect becomes appreciable in desalination applications due to the high osmotic activity (high solubility–low equivalent weight) of inorganic salts generally. Indeed, water recovery from seawater is limited to 35–40%. That is, seawater is discharged with a salt content of less than 6 wt%.

The osmotic pressure limitation to flux is less important in concentrate production applications where higher equivalent weight solutes such as simple sugars, polysaccharides, and proteins predominate. Indeed, liquid food concentrates have an upper concentration limit of 30–35 °Brix. This corresponds to 60–70% water removal based on an initial feed solutes concentration of 10 °Brix. The practical limit may, however, be somewhat lower than this due to uneconomical fluxes. Nevertheless, there are potential advantages to using RO in a preliminary concentration role for subsequent MD or OD concentration to higher levels. The results of studies conducted on fruit juice concentration using integrated RO–OD processes are discussed in Chapter 6.

### 1.5.6 Electrodialysis (ED)

ED is a membrane-based process used primarily for the production of potable water from brackish water and to a lesser extent seawater. Other applications include the production of salt from seawater, high purity water production, and the desalting of liquid foods [McRae (1983)]. ED differs from other desalination processes in that salts are removed from the feed stream rather than water being the component that is removed.

ED systems consist of a set of ion-selective membranes placed side by side and separated by spacing material to allow liquid flow between them. Cation-exchange membranes that allow the penetration of cations ($M^+$) alternate with anion-exchange membranes that allow the penetration of anions ($X^-$) as shown in Figure 1.13. Electrodes placed at each end of the membrane stack provide an electric potential across the system whereby cations move toward the negative electrode (cathode) and anions move toward the positive electrode (anode). That is, a direct electric current flows between the electrodes. Cations may move across the adjacent cation-exchange membrane but then become trapped in that cell by an anion-exchange membrane. Similarly, anions moving in the opposite direction may move across the adjacent anion-exchange membrane and then become trapped in that cell by a cation-exchange membrane. In this arrangement, salt is removed from

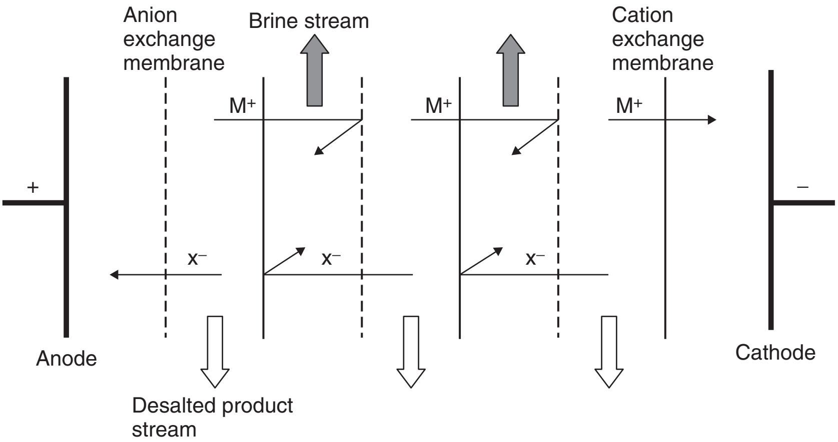


**Figure 1.13** Electrodialysis (ED) operation.

the feed stream in every second compartment and concentrated in every other compartment.

The membranes employed in ED are essentially thin sheets of ion-exchange resins blended with other types of polymers to improve mechanical strength and flexibility. Cation-exchange membranes have negatively charged groups such as sulfonate groups ($—SO_3^-$) bonded to the resin to electrostatically repel anions that approach the membrane. Likewise, anion-exchange membranes contain positively charged groups such as quaternary ammonium groups ($—N—R_3^+$ where R is usually $CH_3$) to repel cations. The counter ions associated with the charged sites are freely exchangeable and occupy the water-filled spaces in the swollen membrane.

ED is capable of reducing TDS levels in water to less than 300 ppm for drinking purposes. Very low levels can be achieved by extended treatment but this is hampered by the increased electrical resistance of water at low ionic concentrations. High purity water is more readily produced using a modified form of ED known as electrodeionization (EDI). In this process, mixed ion-exchange resins are contained between the membranes enclosing the feed channels to provide a pathway for the ions contained in low conductivity feeds such as RO permeate to their respective electrodes. Automatic regeneration of the resins occurs through the electrolytic production of hydronium and hydroxide ions on the resin surface. This method of high purity water production has been fully commercialized by Millipore [Ganzi et al. (1987)]. MD on the other hand is capable of producing high purity water from solutions of any solute concentration provided that the feed water is free of other volatile species.

## 1.6 Other Membrane Processes

MF, UF, and nanofiltration (NF) are briefly reviewed here in preparation for discussions on their proposed feed pretreatment roles in MD and OD applications. These processes differ from RO in that selected groups of components rather than all components are concentrated in the retentate. That is, MF, UF, and NF are more aptly described as fractionation rather than concentration processes [Karakulski et al. (2006)]. Water pretreatment using these processes for subsequent MD desalination or wastewater recovery has attracted some attention but the overwhelming majority of research into process integration has involved the production of OD fruit juice concentrates. Several examples are discussed in Chapter 6. Gentle clarification is of particular importance to OD operations where the exceptional product quality that characterizes this process may otherwise be jeopardized.

The selectivity of membranes used in MF, UF, and NF is based on size exclusion. That is, components too large to pass through the membrane pores are rejected and remain in the retentate. Each process utilizes a well-defined range of pore diameters that decrease in the order MF > UF > NF. Furthermore, these processes utilize different membrane structural types to cater for individual fractionation requirements. Both pore size and structural type must be considered when selecting a membrane for a given application. However, industrial feeds are often complex solutions with respect to component types and physical properties making membrane selection less effective in the regulation of process performance. For example, membranes with different pore sizes may display similar fluxes in cases where a gel (hydrocolloid) layer forms on the membrane surface.

### 1.6.1 Microfiltration (MF)

MF facilitates the separation of suspended solids and large colloidal particles from aqueous streams using a membrane with a nominal pore diameter in the 0.1–1.0 μm range. Colloids vary in size from 0.001 to 1.0 μm such that smaller particles may be lost to the permeate. Solutes of all sizes are able to pass through the membrane. Membranes manufactured from several different organic polymers are available to suit a range of requirements with respect to chemical and heat stability, pH tolerance, mechanical properties, and hydrophobicity. These polymers include cellulose acetate (CA), mixed cellulose esters (MCE), PS, polyacrylonitrile (PAN), polyether ketone (PEK), PA, and, as previously indicated, PP, PTFE, and PVDF. The relatively large pores of MF membranes allow operation under low feed pressures (0.5–2 bar). In some cases, this may require increasing membrane hydrophilicity to facilitate pore flow by treatment with a low-surface tension agent such as ethanol. Ceramic membranes composed of oxides, nitrides, or carbides of aluminum, zirconium, or titanium are also available. The latter membranes offer greater mechanical strength and better pH, oxidant (chlorine), and heat tolerance than organic polymers albeit at higher cost.

MF membranes are referred to as being symmetric by virtue of their similar structure of tortuous, nonuniform pores throughout as opposed

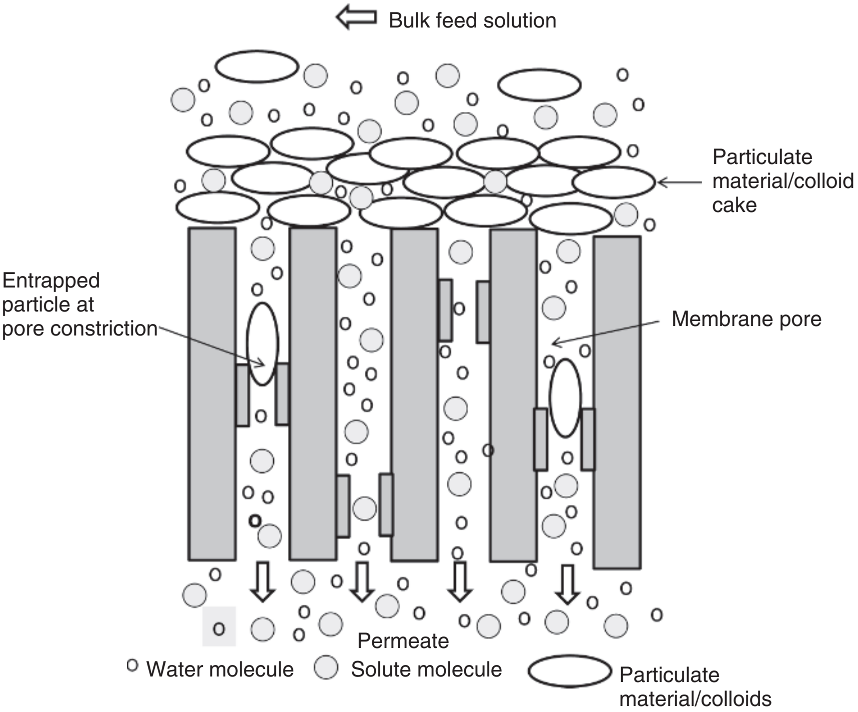


Figure 1.14 Schematic representation of microfiltration (MF) process.

to a thin selective layer on top of a porous support as in the case of RO membranes. Pore constrictions facilitate the entrapment of particles that may enter the MF membrane through a surface imperfection or a pore with an anomalously large entrance. This membrane structural type is of particular importance in water pretreatment for MD desalination. Particle entrapment ensures that the permeate is free of harmful pathogens that may subsequently enter the drinking water stream by leakage through a damaged MD membrane. Concentration polarization in MF results in the formation of a "cake" of solid particles, a gel layer, or a mixture of both on the membrane surface. A schematic representation of the MF process is shown in Figure 1.14.

### 1.6.2 Ultrafiltration (UF)

UF systems utilize membranes with pore diameters in the 0.01–0.1 μm range to remove suspended solids, colloidal particles, and macromolecules from solution. That is, the MF function discussed above is extended to facilitate sieving at the molecular level. These membranes have a molecular weight cutoff rating that defines the size of the largest molecules able to pass through the pores. These ratings are generally in the $1 \times 10^3$–$1 \times 10^6$ Da range. Like modern RO membranes, UF membranes are asymmetric with a thin skin (thickness 0.1–1.0 µm) that effects separation on top of a spongy support layer. Organic polymers used in membrane manufacture include PS, PP, CA, PAN, and PVDF. In this case, however, the void space of the support layer increases with increasing distance from the skin layer to minimize permeate flow resistance. UF operations utilize feed pressures in the 0.5–10 bar range. UF plants effecting macromolecule separations operate under the feed pressure corresponding to the onset of gel layer formation on the membrane surface. Higher pressures result in an increase in gel layer thickness with no flux advantage. In food industry applications, gels are formed by concentrated polysaccharides, proteins, and colloids. A schematic representation of the UF process is shown in Figure 1.15.

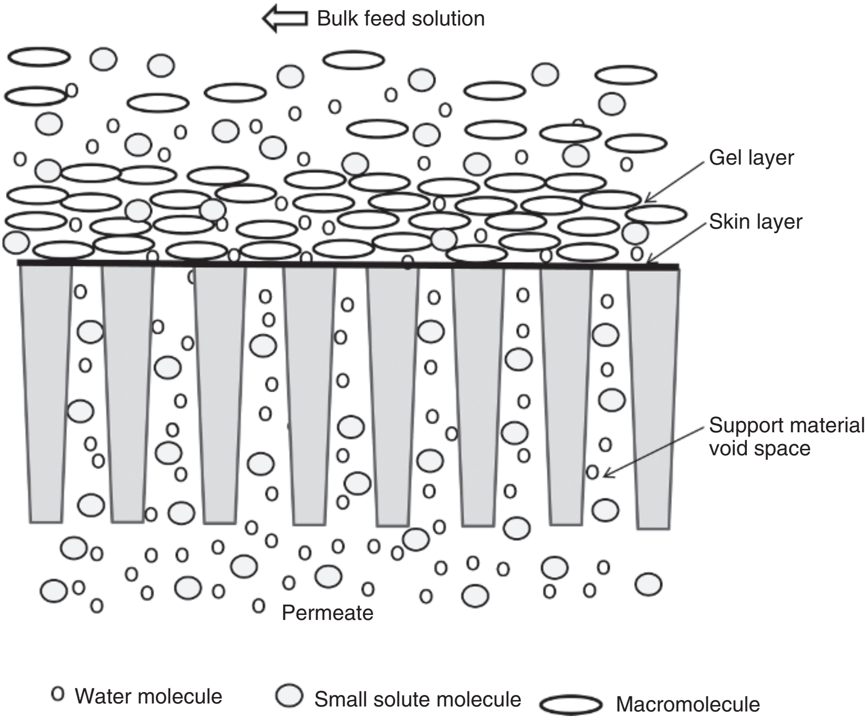


**Figure 1.15** Schematic representation of ultrafiltration (UF) process.

### 1.6.3 Nanofiltration (NF)

NF utilizes finely porous membranes to remove suspended solids, colloidal particles, macromolecules, and small solutes from solution. The minimum size of solutes rejected by different NF membranes lies in the 0.0005–0.01 μm range (100–300 Da). That is, NF can be considered to fill the gap between UF and RO. Accordingly, NF pumping pressures (10–40 bar) are generally lower than those of RO. NF membranes are usually composite in structure with a thin skin of PA or CA on top of a macroporous supporting material such as PS. In separations involving polar and charged species, size-exclusion selectivity is assisted by electrostatic repulsions. Dissociable groups on the polymeric chains produce surface charges that are normally negative at neutral pH. The influence of these charges on selectivity is relatively more important in NF than other pressure-driven processes because of the close proximity of the pore walls to permeating solutes. Greater than 90% rejection of multivalent ions such as $CO_3^{2-}$, $SO_4^{2-}$, and $PO_4^{3-}$ can be achieved with a lower albeit significant rejection of monovalent ions such as $Cl^-$. Cations are distributed between the retentate and permeate in accordance with the electrostatic force requirement for electrical neutrality [Xu et al. (2011)].

Historically, the main application of NF has been water treatment and in particular water softening through the rejection of scale-forming divalent ions. Accordingly, NF has the potential to prevent scale formation on MD membranes in desalination operations. Another potential NF application is the recovery of caustic cleaning solutions used to remove organic foulants from MD and OD membranes during regular cleaning cycles. The excess sodium hydroxide may be recovered as NF permeate for reuse in the plant, while suspended solids and moderate-to-large organic species are rejected by the membrane. NF has fewer potential feed pretreatment roles than MF and UF in the food industry because of the loss of essential low-molecular-weight organic solutes. However, NF has the potential to participate in secondary separation roles such as the enrichment of beneficial polar species in MF or UF permeate prior to MD or OD concentration. A schematic representation of the NF process is shown in Figure 1.16. A comparison of the separation capabilities of MF, UF, NF, and RO is shown in Figure 1.17.

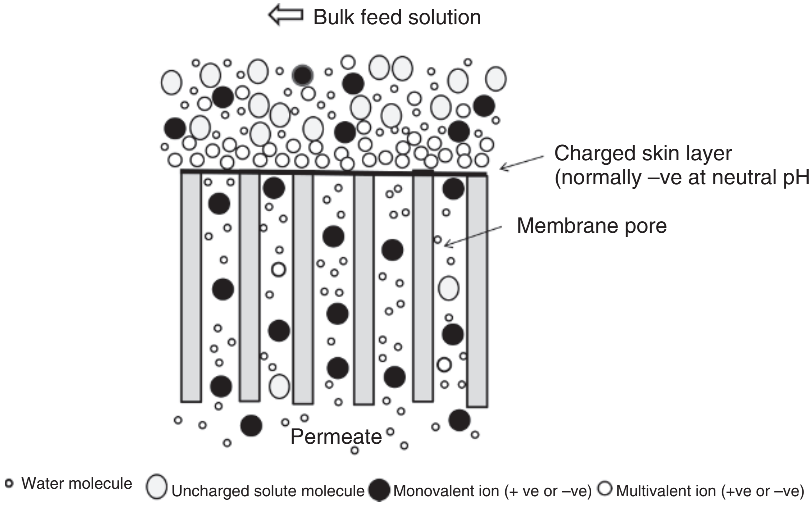


**Figure 1.16** Schematic representation of nanofiltration (NF) process.

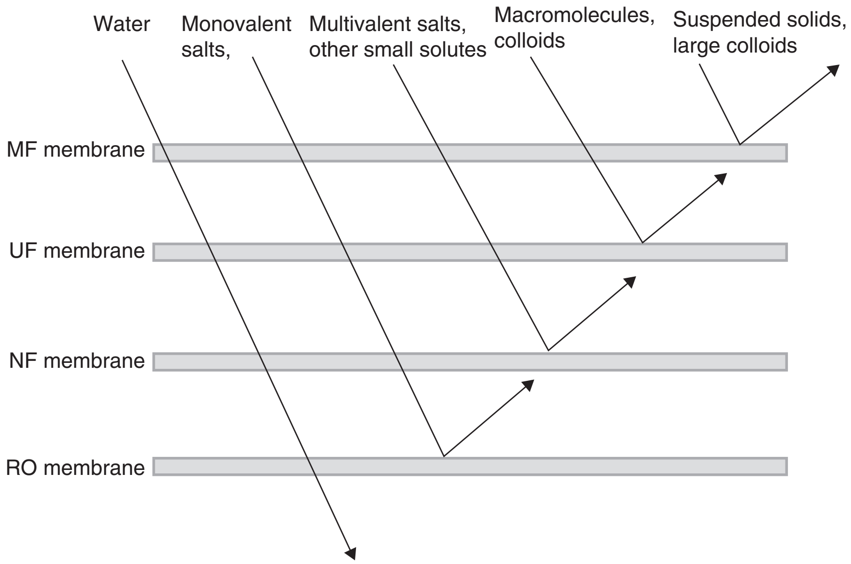


**Figure 1.17** Relative separation capabilities of MF, UF, NF, and RO.

## 1.7 Concluding Remarks

MD and OD are examples of the mergence of classical distillation and modern membrane separation technologies. Central to both MD and OD is a hydrophobic membrane whereby the upstream surface constitutes the required evaporation surface while the downstream surface constitutes or provides access to the required condensation surface. The close proximity of these surfaces maximizes the water vapor pressure gradient across the membrane in partial compensation for the low driving force resulting from a low-to-moderate feed temperature. Mild operating temperatures and the hydrophobic nature of the membrane provide the special characteristics of MD and OD. These include a theoretical 100% retention of nonvolatile solutes, low-to-negligible heat damage, low-to-very-low organic volatiles loss, concentration to high levels, and the ability to utilize waste heat or heat from natural sources. This set of characteristics is not shared in its entirety by any conventional distillation or nondistillation process.