

## 8

# Membrane Contactors in Integrated Processes for Fruit-Juice Processing

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### 8.1

#### Introduction

The overall market for fruit juices has grown substantially in recent years probably due to public perception of juices as a healthy natural source of nutrients and increased public interest in health issues. Indeed, epidemiological studies have established a positive association between the intake of fruit and vegetables and a reduced rate of heart diseases mortality, common cancers and other degenerative diseases [1].

This protective role may be related to phytochemicals acting as antioxidants, free-radical scavengers and saviors of the cell. These biologically active compounds may act independently or in combination as anticancer compounds by different mechanisms and are better absorbed from juices than from plant tissues. However, it is well known that naturally occurring antioxidants could be significantly lost as a consequence of processing and storage. Processing operations, such as peeling, cutting and slicing and thermal treatments induce rapid depletion in natural antioxidants in food [2]. Therefore, in order to preserve the quality of fruit juices the food industry has focused on the development of new processing techniques for minimally processed fruit and vegetable products.

Traditional membrane processes such as enzyme membrane reactors (EMRs), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are today key processes in the food industry for concentration, fractionation and purification of liquid foods. Their intrinsic properties (low operating temperature, no special chemicals required, no phase changes involved, easy scale-up and modularity, uncomplicated operation and possibility of automation) make them a valid alternative to traditional methods of liquid foods treatment. Additionally, potential energy savings derived by membrane processes application in the food and drink industry can be estimated as 50%, as reported by Eichhammer [3].

The introduction of these technologies in fruit-juice processing represents one of the technological answers to the problem of the production of juices with high quality, natural fresh taste and additive free. Juice clarification, stabilization, depectinization, fractionation and concentration are typical steps successfully realized by using

EMRs, MF, UF, NF and RO. In particular, UF and MF represent a valid alternative to the use of traditional fining agents (gelatin, bentonite and silica sol) and filter aids in fruit-juice clarification, color removal and stabilization [4, 5]. Basically the juice is treated after enzymatic pulping. EMRs are new approaches in which, by choosing an effective membrane configuration, pulping and clarification can be realized in one step [6].

Fruit juices are usually concentrated in order to reduce storage, package and shipping costs [7]. In addition, concentrated fruit juices, because of their low water activity, have a higher stability than single-strength juices. The concentration of fruit juices is usually obtained by multistage vacuum evaporation; however, this process results in a loss of fresh juice flavors, color degradation and a “cooked” taste, recognized as off-flavors, due to thermal effects. Alternative techniques, such as freeze concentration systems (cryoconcentration), in which water is removed as ice rather than as vapor, allow preservation of the aroma compounds but they are characterized by high energy consumptions [8]. Besides, the achievable concentration (about 50 °Brix) is lower than the values obtained in thermal evaporation (60–65 °Brix).

The concentration of fruit juices by RO has been of interest in the fruit-processing industry for about 30 years. The advantages of RO over conventional concentration techniques are in terms of low thermal damage of the product, reduction of energy consumption and lower capital investments [9] as the process is carried out at low temperatures and it does not involve phase change for water removal.

Most studies concerning the concentration of fruit juices (including apple, pear, grapefruit, kiwi, pineapple, passion fruit, tomato juice, etc.) by RO have mainly focused on the effect of membrane type and operating conditions on the retention of juice components and permeate fluxes [10–19]. However, the osmotic pressure of the juice increases rapidly with the increasing of the sugar concentration (100 and 200 bar for concentrations of 42 and 60 °Brix, respectively). The concentration also determines an increasing viscosity. Both factors influence the RO process, so the final concentration cannot be higher than 20%: otherwise the process is not convenient from an economical point of view. For these limitations, RO can be considered an advantageous technique as a preconcentration step [20].

The separation and concentration of polyphenolic compounds from apple juice by using 1- and 0.25-kDa molecular weight cut-off spiral-wound NF membranes has been reported by Saleh *et al.* [21]. The concentration of apple and pear juices by NF at low pressures (between 8 and 12 bar) has also been investigated [22].

Other membrane processes such as pervaporation (PV) and electrodialysis (ED) and gas separation (GS) have been studied in the fruit and vegetable sector. ED is a promising method for juice deacidification able to preserve the organoleptic properties of the juice and to produce valuable by-products such as citric acid [23]. PV constitutes a promising alternative to traditional techniques, such as distillation and partial condensation, for aroma recovery from fruit juices [24].

Membrane contactors (MCs) represent innovative membrane-based operations that, due their potential advantages, are considered as new interesting perspectives for industrial and scientific applications. In the field of fruit-juice processing the integration of MCs with conventional membrane operations emerges as

an interesting opportunity due to the synergistic effects that can be achieved. As a matter of fact this integration makes MCs very competitive against conventional energy-intensive techniques (i.e., distillation and evaporation) in terms of energy consumption, product recovery and improvement of quality. Moreover, industrial cycles can be redesigned according to a process-intensification strategy that aims at minimizing environmental impact, increasing safety, improving remote control and automation, and reducing production costs and equipment size [25, 26].

In this chapter the main properties of MCs of interest in fruit-juice processing are described. Their potentialities within integrated membrane systems as well as their main drawbacks related to their further implementation at the industrial level will be also discussed.

## 8.2

### Membrane Contactors: Fundamentals

Membrane contactors are systems in which the membrane acts as a barrier between two phases (gas/liquid or liquid/liquid) permitting mass transfer of the components without dispersion of one phase within another. Unlike traditional pressure-driven membrane processes, membrane contactors are not selective towards particular components and the separation is based on the principles of phase equilibrium. Basically, the two phases are kept in contact through a microporous membrane in correspondence of the pore mouths, where the interface is established, and the species are transferred from one phase to the other by simple diffusion through the membrane pores [27].

Membranes used in MCs can be both hydrophobic and hydrophilic. Polypropylene (PP), polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene (PE) and perfluoropolymers (e.g., hyflon) are typical hydrophobic polymers used for these applications. They can be wetted by nonpolar solutions, while the polar phase cannot enter into the membrane pores; in order to avoid dispersion phenomena, the pressure of the polar phase has to be equal to or higher than the pressure of the wetting phase. Moreover, in order to prevent the penetration of the polar phase into the pores, and consequently, a loss of membrane hydrophobicity, the critical penetration pressure should not be exceeded. For a specific material the critical penetration pressure ( $\Delta P$ ) depends on the liquid surface tension, the pore radius and the contact angle, as reported in the Laplace's equation:

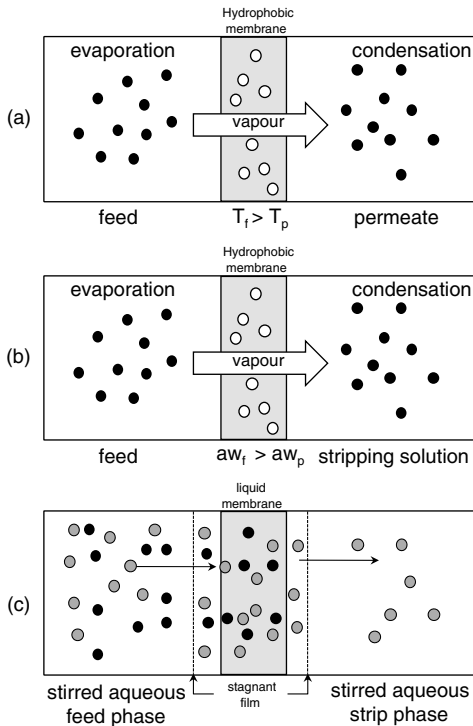
$$\Delta P = 2\gamma \frac{\cos \theta}{r} \quad (8.1)$$

where  $\gamma$  is the surface tension of the liquid,  $\theta$  the contact angle between the liquid and the membrane,  $r$  the radius of the pore. According to this equation, membranes with large pore sizes guarantee lower values of the critical penetration pressure and, consequently, a maintenance of their hydrophobic character, which is very important for a good performance of the system, especially in long-term applications.

When the membrane is hydrophilic, the nonpolar phase remains blocked at the pore mouth, while the polar phase wets the membrane pores. In this case the pressure of the nonpolar phase must be equal to or higher than the polar phase pressure to avoid dispersion between the phases. The interface is formed at the pore mouth of the nonpolar phase side and it is maintained if the critical penetration pressure is not exceeded [28].

Typical advantages of MCs over conventional technologies (such as strippers, scrubbers, distillation columns, evaporators, etc.) are in terms of high and constant specific interfacial area, use of plastic equipments, high modularity and compatibility, easy scale-up and control, independence of the fluid phases in contact, possibility to operate at room temperature, no flooding, loading and foaming. On the contrary, drawbacks are mainly related to the presence of an additional resistance offered by the membrane, membrane fouling, operative pressures depending on critical penetration ones, limited lifetime of the membranes, high replacement costs and channeling of fluids [25, 29].

Figure 8.1 shows basic configurations of MCs that can be employed in fruit-juice processing; they include membrane distillation, osmotic distillation and liquid supported membranes. These processes can be integrated in the production lines



**Figure 8.1** Schematic representation of membrane contactors: (a) membrane distillation; (b) osmotic distillation; (c) supported-liquid membrane.

together with conventional membrane operations in order to achieve advanced molecular separations overcoming existing limits of the traditional membrane processes (i.e., osmotic pressure limits in RO).

Membrane distillation (MD) and osmotic distillation (OD) are typical processes for fruit-juice concentration. In these processes, the driving force for mass transfer is induced by a vapor-pressure difference across the membrane [30].

Supported-liquid membranes (SLMs) have been proposed for the extraction of organic acids from fruit juices. In SLMs the two sides of a microporous support are in contact with two aqueous phases: a feed phase and a strip phase, respectively. A carrier transports a specific substance through the micropores from the feed to the strip side.

### 8.3

#### Osmotic Distillation

##### 8.3.1

##### Process Fundamentals

Osmotic distillation is a membrane-contactor technique also known as osmotic evaporation, membrane evaporation, isothermal membrane distillation or gas membrane extraction. Its main advantage lies in its ability to achieve high concentrations, working at low temperature and pressure, thus avoiding mechanical damage and thermal degradation of the solutes [31].

The OD process is based on the use of a macroporous hydrophobic membrane separating two circulating aqueous solutions of different solute concentration: a dilute solution on one side and a hypertonic salt solution on the other side. The hydrophobic nature of the membrane prevents penetration of the pores by aqueous solutions, creating a vapor/liquid interface at each entrance of the pores. The difference in solute concentration, and consequently in water activity between the two solutions, induces a vapor-pressure gradient at the vapor/liquid interfaces that constitutes the driving force of the water transport from the high vapor pressure phase to the low one [32].

The water transport through the membrane can be summarized in three steps: (1) evaporation of water at the dilute vapor/liquid interface; (2) diffusional or convective vapor transport through the membrane pore; (3) condensation of water vapor at the membrane/brine interface [33–36].

The water vapor pressures at the pore mouths are related to the temperature and activities prevailing in the liquids facing the membrane by:

$$P_{w1} = P_w^* a_{w1} \quad (8.2)$$

$$P_{w2} = P_w^* a_{w2} \quad (8.3)$$

in which  $P_w^*$  represents the vapor pressure of pure water and  $a_w$  the water activity in the solutions. The driving force ( $\Delta P_w = P_{w1} - P_{w2}$ ) for water transport is sustained by the activity difference  $\Delta a_w = a_{w1} - a_{w2}$ .

The stripping solution, after its dilution, can be reconcentrated by evaporation and reused in the OD operation. Therefore, it should be thermally stable and also preferably nontoxic, noncorrosive and of low cost. Consequently, salts showing large increases in solubility with temperatures and low equivalent weights are preferred since they can be evaporated at high concentrations without risk of crystallization in the evaporator. A number of salts such as  $\text{MgSO}_4$ ,  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$  is suitable.  $\text{NaCl}$  is characterized by a relatively low water solubility and a rather low temperature coefficient of solubility, while  $\text{CaCl}_2$  is sensitive to precipitation in the presence of  $\text{CO}_2$ ; further, they are quite corrosive to ferrous alloys at elevated temperatures. Potassium salts of ortho- and pyrophosphoric acid offer several advantages, including low equivalent weight, high water solubility, steep positive temperature coefficients of solubility and safe use in foods and pharmaceuticals.

The equivalent weight of salts and their water solubilities as well increase in the order  $\text{NaCl} > \text{CaCl}_2 > \text{K}_2\text{HPO}_4$ . Since the osmotic activity of a salt is considered as the ratio between its water solubility and its equivalent weight,  $\text{K}_2\text{HPO}_4$  and  $\text{CaCl}_2$  can be considered as better osmotic agents than  $\text{NaCl}$  [34].

It is known that fruit and vegetable juices contain small concentrations of volatile aroma compounds, which are generally lost by thermal evaporation reducing remarkably their quality. In the OD process the concentration is performed at low temperatures and the vapor pressure of these volatile compounds is depressed, reducing the driving force for their transport across the membrane. Furthermore, the solubilities of these solutes in pure water are much higher than in concentrated saline solutions and, consequently, the vapor pressures of these solutes are much higher than those encountered over water at the same concentration. Therefore, the driving force for the vapor transfer of these solutes from the juice to the stripping solution is lower when compared with the driving force of the thermal evaporation. Finally, the diffusive permeabilities of these solutes through the membrane are lower than the water due to their higher molecular weights [34]. As a result, the loss of volatile compounds in OD can be markedly limited in comparison with the traditional evaporation and the organoleptic characteristics of the original juice are very well preserved.

### 8.3.2

#### **OD Membranes and Modules**

Membranes used in OD are typically hydrophobic in nature and realized with apolar polymers with low surface free energy such as PE, PTFE, PP and PVDF. However, OD membranes can also be realized by grafting on the surface of hydrophilic ceramic membranes molecules containing hydrophobic fluorocarbon chains like fluoroalkyl-silanes or by coating the surface of alumina membranes with a thin lipid film [37, 38].

The risk of wetting of the hydrophobic membrane, with a consequent reduction of the evaporation flux and separation performance, is the main drawback of the OD process. Consequently, the membrane surface should be sufficiently hydrophobic in

order to prevent penetration of both feed and strip solutions into the pores by capillary forces (the contact angle between the liquid and solid phase should be greater than  $90^\circ$ ). Furthermore, the surface tension of the liquids should be high enough so that the capillary penetration pressure into the membrane pores is higher than the maximum operating transmembrane pressure difference in order to avoid a mixing of feed and strip solutions. For most concentrated salt solutions the surface tension is higher than that of pure water imploring the intrusion of such solutions into membrane pores at pressures normally used in the OD process. However, some fruit juices, especially citrus juices, contain peel oils and other highly lipophilic components that reduce their surface tension and promote wetting of hydrophobic surfaces. In this case, membrane materials with contact angles much higher than the water are needed. Furthermore, surface-active agents contained in cleaning solutions can also promote membrane wet-out and liquid penetration in OD membranes. Hydrophilic polymers, including cross-linked gelatin, agar, cross-linked polyacrylamide, esters of cellulose, cross-linked polyvinylalcohol, can be used to produce laminate membranes preventing liquid intrusion without impeding vapor transport [39]. The hydrogel-film-side of the laminate should be in contact with the feed liquid or solution to be concentrated. Cellophane membranes and sodium alginate hydrogel coating on PTFE membranes has been also proposed to prevent membrane wet-out [40, 41].

Hydrophobic membranes resistant to oily feeds (e.g., limonene solution) have been developed by Mansouri and Fane [39] by coating the feed side of commercial flat-sheet membranes, including Celgard 2500 (PP/PE, Hoechst Celanese), Durapore GVPS (PVDF, Millipore) and the UPVP (ultrahigh molecular weight PE, Millipore), with a thin layer of polyvinylalcohol (PVA). The laminate membranes were stable in oil emulsions for concentrations up to 1 wt.% for periods up to 24 h; on the contrary, membranes without the hydrogel coating were wetted out very rapidly by the oily feed.

Membranes for OD applications should be highly porous (60–80%) and as thin as possible (0.1–1  $\mu\text{m}$ ) since the flux is directly proportional to the porosity and inversely proportional to the membrane thickness. Basically, the overall thickness for OD membranes can vary from 80 to 250  $\mu\text{m}$ , depending on the absence or presence of support.

The thermal conductance of an OD membrane should be sufficiently high so that the energy of vaporization can be supplied by conduction across the membrane at a low temperature gradient. Consequently, the temperature difference between the two sides of the membrane is quite small (generally not exceeding  $2^\circ\text{C}$ ), making the process isothermal.

Barbe *et al.* [20] found higher organic volatile retentions per unit water removal in membranes characterized by large pore size at the surface when compared with membranes with small surface opening. These membranes offered a greater intrusion of the feed and the stripping solution, resulting in an increase in the resistance of the boundary layer to the diffusion of volatile components. Mengual *et al.* [31] found also that membranes with a small pore size (0.05–0.5  $\mu\text{m}$ ) did not show a significant change in the transmembrane flux. A similar behavior was also observed by Brodard *et al.* [42] in ceramic membranes with pore sizes in the range 0.2–0.8  $\mu\text{m}$ .

Stirred membrane cell, plate and frame, tubular, spiral-wound and hollow fiber are typical membrane modules used for OD operations. Flat-sheet membranes are preferred for pilot-scale studies for their versatility when compared with tubular and hollow-fiber membrane modules. However, many studies on the pilot scale have been performed by also using tubular, hollow fiber and spiral-wound membranes.

Plate-and-frame modules with a net-shaped spacer on the extract side and a smooth juice-side path have also been developed for the concentration of unclarified juice with a high pulp content [43]. Helically wound hollow-fiber modules offer an improvement in the hydrodynamic conditions on the shell-side if compared with axial flow modules; consequently, higher concentration of solutes and higher evaporation fluxes can be obtained when viscous feeds are processed [44].

The most well-known module designed for OD is the Liqui-Cel<sup>®</sup> Extra-Flow membrane contactor (Membrana-Charlotte, North Carolina, USA). It is constituted by microporous polypropylene hollow-fiber membranes approximately 300 mm in external diameter with a mean pore diameter of about 30 nm and a porosity of about 40%. The fibers are potted into a polyethylene tubesheet and the shell casing is polypropylene, PVDF or 316L stainless steel [27, 34, 45]. The smallest modules are 2.5 inches in diameter with a membrane surface area of 1.4 m<sup>2</sup>, while the largest are 10 inches in diameter and offer a contact area of 130 m<sup>2</sup>.

Commercial asymmetric OD membranes characterized by a thin PTFE layer supported by PP net have been manufactured by Pall-Gelman (East Hills, NY, USA). The top layer offers a resistance to the gas transfer, while the membrane support offers an additional resistance to water transfer in the liquid form. The mass-transfer resistance in the vapor phase is about 40–70% of the total resistance. The resistance of diluted brine entrapped in the PP support can cover up to 30% of the total resistance and the diluted brine boundary layer up to 60%, indicating the sensitivity of the OD system to concentration polarization phenomena [33].

### 8.3.3

#### Effect of Operating Conditions on the OD Flux

The water-vapor flux in OD is affected by different operating conditions. First, the OD flux is significantly affected by the solute content of the stripping solution. In particular, an increase of the transmembrane flux by increasing the concentration of the stripping solution was observed both in real systems [46, 47] and in model systems in which water was used as feed [48–50]. These results may be explained assuming the strong dependence of the water activity of the stripping solution on salt content.

The OD flux is also differently affected by the type of stripping solution. Nagaraj *et al.* [46] studied the concentration of pineapple juice by OD by using calcium chloride and sodium chloride as stripping solutions. Calcium chloride produced higher fluxes due to its higher osmotic activity, which resulted in a higher vapor pressure gradient across the membrane. Celere and Gostoli [51] compared the evaporation fluxes in OD by using aqueous solutions of propylene glycol, glycerol



and glycerol–salt mixtures as an alternative to calcium chloride in order to overcome the problem of corrosion and scaling associated with the use of brines. Propylene glycol and glycerol solutions (70–75 wt.%) resulted less effective than highly concentrated  $\text{CaCl}_2$  and exhibited a similar extractive power. Ternary mixtures water–glycerol– $\text{NaCl}$  were characterized by lower viscosities in comparison with the glycerol alone and offered similar fluxes.

The OD flux is also affected by the feed concentration. Ravindra Babu *et al.* [47] reported a decreasing of the evaporation flux in the concentration of sweet-lime juice and phycocyanin solution by OD when the feed concentration is raised. A similar behavior was observed by Sheng *et al.* [52] during the concentration of apple, orange and grape juice through a PTFE membrane and by Courel *et al.* [49] when sugar solutions of increasing sucrose content were dehydrated by using stripping solutions of 45.5 w/w% initial  $\text{CaCl}_2$  content. This phenomenon can be attributed to the exponential increase of the viscosity and a decrease of the diffusion coefficient when the solute content is raised. The increasing viscosity results in an increase of the concentration polarization effect, which reduces the driving force and, consequently, the evaporation flux [53].

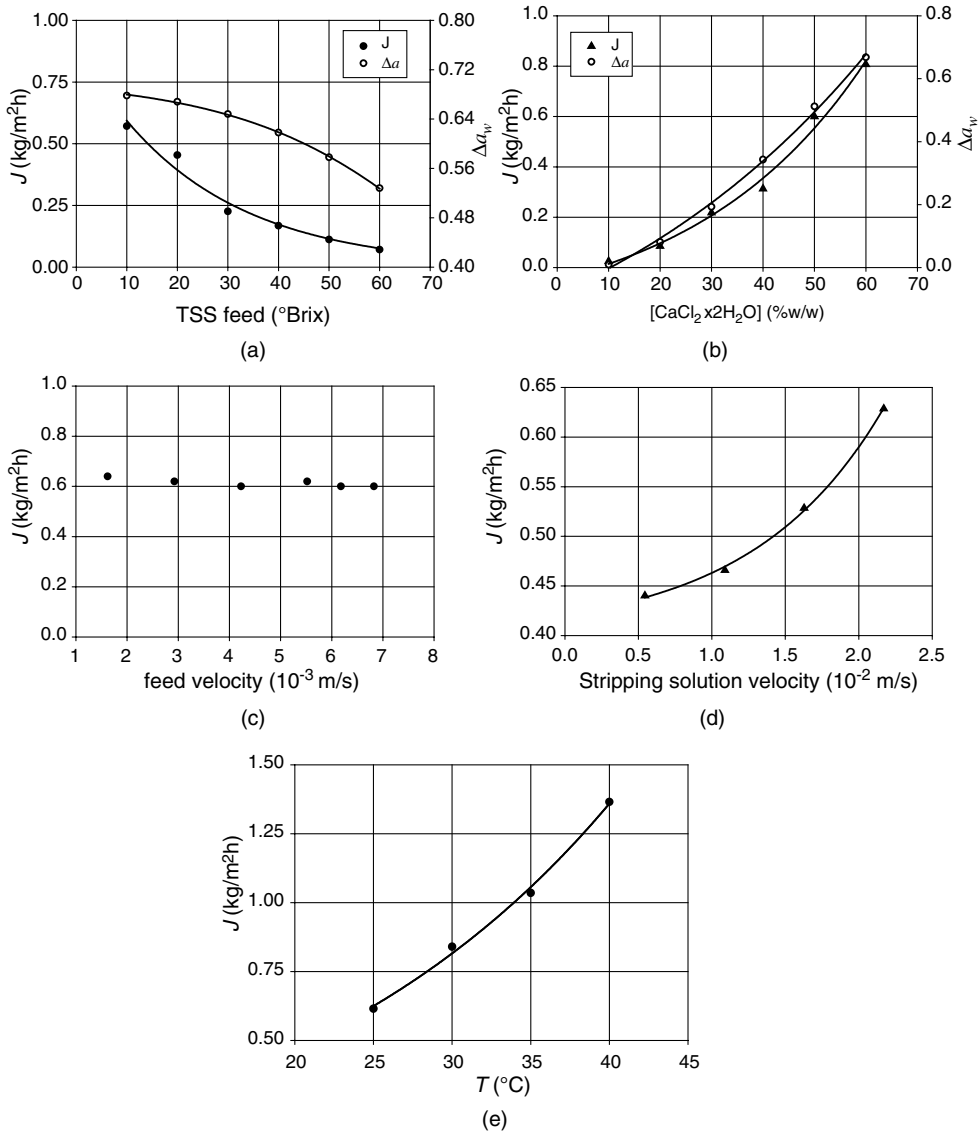
The transmembrane flux increases by increasing the flow rate of the osmotic agent due to the reduction of the concentration polarization layer along the condensation side of the membrane. This phenomenon was observed in the OD of pure water [33], sucrose solutions [49] and sweet-lime juice [46, 47].

Ravindra Babu *et al.* [54] observed also an increase in transmembrane flux when the flow rate of pineapple juice was increased from 25 ml/min to 100 ml/min; the increase in transmembrane flux can be explained assuming a reduction in concentration polarization effect on the feed side. The increase in flux, however, was more prominent (about 20%) by increasing the osmotic agent velocity. This phenomenon can be attributed to a lower concentration polarization on the feed side if compared to that on the brine side.

Finally, the OD flux is strongly affected by the feed temperature. Courel *et al.* [49] reported an increase of the evaporation fluxes of 120% in the range 20–35 °C for a 35 w/w% sucrose solution. Similarly, Bui and Nguyen [55] reported a 200% increase in the evaporation flux for a feed temperature increasing of 20 °C in the concentration of 40 and 50 w/w% aqueous glucose solutions by means of PVDF hollow fibers. The increase in the OD flux when the temperature is raised can be explained assuming an exponential type relation between the vapor pressure difference across the membrane and the temperature according to Clapeyron's law. Moreover, an increasing temperature determines a decrease in the feed and brine viscosities and an increasing of the solute diffusion coefficient.

In Figure 8.2 the general trend showing the effect of process parameters (concentration and flow rate of feed and osmotic agent, operating temperature) on OD evaporation fluxes is reported. Experimental curves are referred to the concentration of clarified grape must by using a hollow-fiber polypropylene OD membrane module and calcium chloride dehydrate as stripping solution [56].

Vaillant *et al.* [57] evaluated the potential of OD for concentrating clarified passion fruit juice on an industrial scale at 30 °C, up to a total soluble solids (TSS) higher



**Figure 8.2** Concentration of clarified grape must by OD. Evaporation flux ( $J$ ) as a function of: (a) grape must concentration; (b) stripping solution concentration; (c) flow rate of grape must at a TSS content of 19.2 °Brix; (d) flow rate of stripping solution (calcium chloride dehydrate); (e) operating temperature. Reprinted from [56] with permission of Chiriotti Ed.

than 60 °Brix, by using a pilot plant containing a 10 m<sup>2</sup> hollow-fiber module. Average evaporation fluxes of 0.65 kg m<sup>-2</sup> h<sup>-1</sup> and of 0.50 kg m<sup>-2</sup> h<sup>-1</sup> were obtained at 40 and 60 °Brix, respectively. These values were 10 times lower than those obtained in RO. The flux decay during OD was attributable more to the dilution of

the stripping solution at a low TSS of the juice, while it mainly depended on the juice viscosity when juice concentration reached a value higher than 40 °Brix. Cassano *et al.* [58–60] confirmed these observations in the concentration of clarified kiwifruit, orange and cactus-pear juice, by using a Liqui-Cel membrane module containing PP hollow fibers.

#### 8.3.4

#### OD Applications

Most OD applications in fruit-juice processing are related to the concentration of fruit juices up to concentrations of total soluble solids higher than 60 °Brix, values significantly higher than those achievable by RO.

OD has the ability to remove selectively water from low molecular weight compounds, both volatiles and nonvolatiles, producing concentrated juices having superior quality. However, it is characterized by low fluxes and it is inherently more costly when compared to thermal evaporation and RO [34]. In order to overcome these drawbacks and to improve the economics, many researchers have developed integrated membrane operations involving the clarification of the initial raw juice (eventually after a depectinization process), an optional pre-concentration of the clarified juice and a final concentration of the clarified or pre-concentrated juice by OD.

Table 8.1 summarizes OD applications concerning the concentration of fruit and vegetable juices including membrane type, stripping solution and type of treated juice. Few studies refer to the treatment of unclarified juices.

In particular, unclarified noni juice was concentrated from 8 up to 32 °Brix using a  $\text{CaCl}_2$  solution with an initial concentration of  $6 \text{ mol kg}^{-1}$  as extraction brine. At isothermal conditions (30 °C) transmembrane water-vapor fluxes ranged between 0.09 and  $0.413 \text{ kg m}^{-2} \text{ h}^{-1}$ . Phenolic compounds were well preserved during the concentration step [61].

Ravindra Babu *et al.* [47] studied the influence of the osmotic agent concentration, flow rate of feed and osmotic agent and membrane pore size on transmembrane flux in the OD concentration of unclarified sweet-lime juice. The juice was concentrated from 5 to 55 °Brix at ambient temperature and atmospheric pressure. The mass-transfer mechanism was in the transition region between Knudsen and molecular diffusion. The contribution of Knudsen diffusion was higher when the membrane pore size was 0.05  $\mu\text{m}$ , while for a pore size of 0.20  $\mu\text{m}$  molecular diffusion was the prevailing mechanism.

The retention of volatile organic flavor/fragrance components in the concentration of both unclarified Gordo grape juice and Valencia orange juice was evaluated by using two flat-sheet OD membranes (Celgard 2500 and Goretex L31189) of different materials (polypropylene and PTFE) and pore diameters at the surface (0.27 and 1.08  $\mu\text{m}$ ) by using 45%  $\text{CaCl}_2$  as a stripper [20]. As in the case of model solutions the degree of organic volatiles retention was the greatest for the membrane with the largest pore diameter at the surface (Goretex L31189).

The clarification step performed by MF or UF allows removal of suspended solids and colloids minimizing possible fouling of either RO or OD units. UF of single-

**Table 8.1** OD applications in fruit-juice concentration.

Fruit juice	Membrane type	Stripping solution	Reference
Noni	Liquicel, hollow fiber, polypropylene	Calcium chloride, 2, 4 and 6 M	[61]
Pineapple and sweet lime (clarified by pectinase)	Accurel Enka, flat-sheet, polypropylene	Calcium chloride dehydrate, 2–14 M Sodium chloride, 2–6 M	[46]
Pineapple (clarified by bentonite)	Accurel Enka, flat-sheet, polypropylene	Calcium chloride dehydrate, 2, 4, 6, 8 and 10 m	[54]
Sweet-lime	Accurel Enka, flat-sheet, polypropylene	Calcium chloride dehydrate, 2, 4, 6, 8, 10 m Sodium chloride, 2, 3, 4, 5 and 6 m	[47]
Grape (clarified by UF)	Liquicel, hollow fiber, polypropylene	Calcium chloride dehydrate, 10–60% w/w	[56]
Blackcurrant, redcurrant, sour cherry, raspberry (clarified by UF)	Microdyn, tubular, polypropylene	Calcium chloride dehydrate, 6 M	[62]
Orange and passionfruit (clarified by MF)	Hollow fiber, polypropylene	Calcium chloride, 4.6 M	[63]
Pineapple (clarified by MF)	Hollow fiber, polypropylene	Calcium chloride, 4.6 M	[64]
Kiwi (clarified by UF)	Liquicel, hollow fiber, polypropylene	Calcium chloride dehydrate, 60% w/w	[59, 65, 66]
Orange and grape	Celgard 2500, flat-sheet, polypropylene Goretex L31189, flat-sheet, PTFE	Calcium chloride, 45% w/w	[20]
Raspberry, sour cherry, redcurrant, blackcurrant	Microdyn, tubular, polypropylene	Calcium chloride, 6 M	[67]
Camu-camu (clarified by MF)	Pall-Gelman TF200, flat-sheet, PTFE	Calcium chloride, 4.0–5.2 M	[68]
Chokeberry, redcurrant, cherry (clarified by UF)	Microdyn, tubular, polypropylene	Calcium chloride dehydrate, 6 M	[69]
Cactus pear (clarified by UF)	Liquicel, hollow fiber, polypropylene	Calcium chloride dehydrate, 60% w/w	[60]
Citrus and carrot (clarified by UF and pre-concentrated by RO)	Liquicel, hollow fiber, polypropylene	Calcium chloride dehydrate, 4.1–4.5 M	[58]
Red orange (clarified by UF and pre-concentrated by RO)	Liquicel, hollow fiber, polypropylene	Calcium chloride dehydrate, 60% w/w	[70]
Apple	Microdyn, tubular, polypropylene	Calcium chloride, 3.5 and 6 M	[62, 67]
Grape (clarified by UF)	Liquicel, hollow fiber, polypropylene	Calcium chloride, 40% w/w	[71]
Anthocyanin extract from red radishes (clarified by UF and pre-concentrated by RO)	Flat-sheet, polypropylene	Calcium chloride dehydrate, potassium phosphate	[72]

Table 8.1 (Continued)

Fruit juice	Membrane type	Stripping solution	Reference
Passionfruit (clarified by MF)	Hollow fiber, polypropylene	Calcium chloride, 45%w/w	[57]
Orange juice (diluted from commercial concentrate)	Accurel, follow fiber, polypropylene	Calcium chloride dehydrate, 4.9 M	[73]
Pineapple (unclarified and clarified by MF)	Pall-Gelman TF200, flat-sheet, PTFE	Calcium chloride, 5.5–6.0 M	[74]
Orange (clarified by MF)	Hollow fiber, polypropylene	Calcium chloride, 5.5 M	[75]
Melon (clarified by MF)	Hollow fiber, polypropylene	Calcium chloride, 5.3–5.6 M	[76]
Blackcurrant (clarified by MF and preconcentrated by RO)	Microdyn, hollow fiber, polypropylene	Calcium chloride dehydrate, 65 °Brix	[77]

strength Gordo grape juice using membranes with nominal pore diameters of 0.1 mm or less resulted in appreciable osmotic distillation flux increases over that observed for juice not subjected to the UF [71]. Similarly, evaporation fluxes between 7 and 10 kg m<sup>-2</sup> h<sup>-1</sup> were obtained by Hongvaleerat *et al.* [74] in the concentration of clarified pineapple juice. These values were higher than those obtained with the single-strength juice due to the complete removal of suspended solids in the clarification step. This phenomenon can be attributed to a reduction in the viscosity of the concentrated juice-membrane boundary layer where the solute concentration is highest and the effect of protein removal is expected to be more pronounced. UF pretreatment results also in a small increase in juice surface tension with a consequent reduction in the tendency for membrane wet-out to occur.

Rodrigues *et al.* [68] evaluated the performance of the OD and RO processes in the concentration of camu-camu juice previously clarified by MF. RO permitted to reach higher fluxes (50 kg m<sup>-2</sup> h<sup>-1</sup>) than OD, but a lower concentration of soluble solids (25 °Brix). OD allowed to concentrate the juice up to 63 °Brix with evaporation flux values of 10 kg m<sup>-2</sup> h<sup>-1</sup>.

Several studies demonstrated the efficiency of the OD process in maintaining the nutritional, sensorial and organoleptic characteristics of the original juice. An integrated MF/OD membrane process was implemented on a semi-industrial scale by Cisse *et al.* [75] to produce concentrated orange juices. The clarified juice was concentrated through a two-stage OD process producing concentrated juices at 45 and 62 °Brix, respectively. Most aroma compounds and ascorbic acid were recovered in the clarified juice, while apolar compounds, such as terpenic hydrocarbons and carotenoids, were retained by the MF membrane. Significant losses of Vitamin C (from 6 to 15%) were mainly observed at the beginning of the concentration. This phenomenon was attributed to the Vitamin C oxidation by the residual oxygen

entrapped within the pores of the membrane. As the residual oxygen contained in the circuit was consumed, vitamin C losses decreased during processing. The low temperatures employed (lower than 28 °C) in the concentration steps preserved the color of the juice (L-values, hue angle and color purity of both concentrates were similar to those of the clarified juice). Also, the sugar and acid contents were not modified during the juice concentration. Losses of aroma compounds were higher in the first OD stage (about 31%) than in the final one (about 22%). However, sensorial analyses revealed no significant differences between the clarified juice and the final concentrate juice at 62 °Brix. Further, the quality of the pulpy juice obtained by mixing the MF retentate, previously pasteurized, with the OD concentrate was high and much closer to that of the initial single-strength juice than to the commercial thermal concentrate.

An excellent preservation (>97%) of the total antioxidant activity (TAA) of red fruit juices (chokeberry, redcurrant and cherry juices) was also observed in an UF-OD sequence investigated by Koroknai *et al.* [69].

Integrated membrane processes were also studied and proposed by Cassano *et al.* [58–60, 65] to produce high quality concentrated fruit juices (such as kiwifruit, orange, lemon and cactus pear) with final TSS concentration of 63–65 °Brix. Fresh juices were previously depectinized, clarified by UF and then optionally preconcentrated by RO before the final OD concentration step. OD was performed by using a Liqui-Cel Extra-Flow 2.5 × 8 inch membrane contactor equipped with polypropylene hollow fibers and a calcium chloride dehydrate solution at 60%w/w as the stripping solution. During the concentration process of red orange juice, a slight decrease of the total antioxidant activity (TAA) was observed (about 15%) due to the partial degradation of ascorbic acid (about 15%) and anthocyanins (about 20%). Nevertheless, this degradation was lower than that observed in the thermally concentrated juice where anthocyanins and hydroxycinnamates (particularly ferulic and p-coumaric acid) underwent a reduction of 36% and 55%, respectively; for the ascorbic acid and flavonones removals were in the order of 30 and 23%, respectively [70].

Table 8.2 shows the physical characterization of the Chilean kiwifruit juice (Hayward variety) and of clarified and concentrated fractions obtained in an integrated UF/OD process. The UF process determines a complete removal of suspended solids and turbidity in the depectinized raw juice. Most sugars are recovered in the clarified juice; the low reduction of TSS content in the clarified juice can be attributed to the removal of suspended solids that, together with the soluble pectin, can interfere with the measurements of the refractive index.

In Table 8.3 measurements of total antioxidant activity (TAA) and ascorbic acid in clarified and concentrated fractions are reported. In particular, the clarified juice showed a reduction of vitamin C and TAA of 16 and 8%, respectively, in comparison with the fresh juice. During the OD process the vitamin C content was constant independent of the achieved TSS level. TAA of samples concentrated at 20 and 30 °Brix was similar to that of the clarified juice while a little reduction was observed at higher concentrations. On the contrary, the juice concentrated by thermal evaporation at 65 °Brix showed an 87% reduction of the ascorbic acid when compared to the

**Table 8.2** Physical characterization of Chilean kiwifruit juice clarified and concentrated by integrated UF/OD process.

Parameter	Feed	Permeate UF	Retentate OD
Total soluble solids (°Brix)	12.6	12.1	61.4
Turbidity (NTU)	299.5	0	—
Viscosity at 25 °C (MPa s)	1.455	1.427	44.5
pH	3.58	3.60	3.40
Suspended solids (% w/w)	17.0	0	—

clarified juice. The TAA was reduced by about 50% independent of the TSS content achieved [66].

A pervaporation (PV) step was also investigated to recover aroma compounds from kiwifruit juice and introduced in an integrated UF-OD process in order to evaluate the best configuration giving the minimal loss of aroma compounds. For the majority of the aroma compounds detected, the enrichment factor in the permeate of the fresh juice was higher than the clarified and concentrated juice suggesting the use of PV for the removal and enrichment of aroma compounds directly from the fresh juice, before any concentration process [65].

Shaw *et al.* [63] evaluated the retention of flavors in concentrated orange and passionfruit juices (previously clarified by MF) obtained by using a pilot-scale osmotic evaporator containing 10.3 m<sup>2</sup> of PP hollow fibers. Both juices were concentrated threefold to 33.5 and 43.5 °Brix, respectively. Quantitative headspace gas chromatographic analyses showed a loss of volatile compounds of about 32% and 39% in orange and passionfruit juice, respectively.

A multistep membrane process on laboratory and large scale was implemented by Kozák *et al.* [77] for the production of blackcurrant concentrated juices. The raw juice (15–18 °Brix as TSS content) was clarified by MF and then preconcentrated by RO. The final concentration step was performed by using OD in which the TSS

**Table 8.3** Analyses of TAA and ascorbic acid in Chilean kiwifruit juice clarified and concentrated by integrated UF/OD process.

Sample	TSS (°Brix)	Ascorbic acid (g l <sup>-1</sup> )	TAA (mM Trolox)
UF-F	12.6	0.90	17.6
UF-P	11.2	0.75	16.2
UF-R	12.4	0.72	16.9
OD-R1	20.0	0.81	16.2
OD-R2	35.0	0.84	16.2
OD-R3	44.0	0.81	15.5
OD-R4	53.8	0.81	15.4
OD-R5	61.2	0.82	15.1

Legend: F: feed; P: permeate; R: retentate.

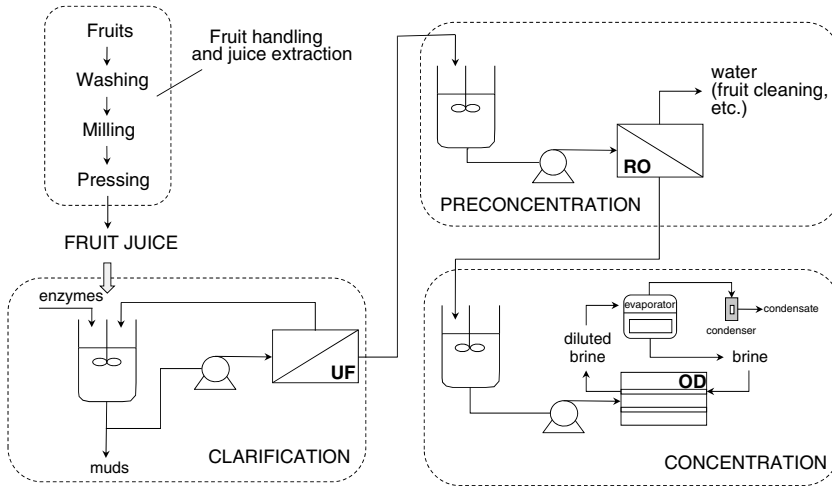
content of the juice was increased up to 63–72 °Brix. Results of sensory profile analyses revealed that the color intensity, the transparent ability and the acidic flavor intensity of the concentrated juice were similar to those of the raw juice. The anthocyanin content of the concentrated juice was more than three times higher than that of the raw juice.

The effect of an integrated MF/OD process on the physicochemical, nutritional and microbiological qualities of melon juice was investigated by Vaillant *et al.* [76]. The raw juice was macerated with an enzymatic solution containing hemicellulase and cellulose activities before the MF step performed by using a ceramic multi-channel membrane. Average permeation fluxes of about  $80 \text{ l m}^{-2} \text{ h}^{-1}$  were obtained with the continuous extraction of retentate at a volumetric reduction ratio of 3. OD was performed by using a module containing polypropylene hollow-fiber membranes circulating the cold clarified juice (6 °C) in the lumen of the fibers, and calcium chloride brine 5.3–5.6 M in the shell side. The clarified juice was concentrated from 7 to 55 °Brix of TSS. Evaporation fluxes decreased from 0.7 to  $0.57 \text{ kg m}^{-2} \text{ h}^{-1}$  when juice TSS reached the final value. Insoluble solids of the raw juice were removed in the MF step; the MF membrane also rejected  $\beta$ -carotene probably due to its association with membrane and wall structures of the cell fragments. Thus, the authors proposed to use the pulpy juice (retentate MF) as raw material to extract  $\beta$ -carotene or directly in functional drinks. MF also ensured the microbiological stability of the juice in a single operation. In the OD concentrate the acidity, the color and the sugar content of the clarified were well preserved. No significant loss of vitamin C was observed in comparison with the clarified juice, while a loss in polyphenol compounds of about 30% was attributed to the presence of polyphenol oxidases in the clarified juice still acting during juice concentration.

Most OD studies in fruit-juice concentration refer to applications on laboratory scale. A successful application on pilot scale was conducted in pilot-plant facilities located in Mildura and Melbourne, Australia. The Melbourne facility, designed by Zenon Environmental (Burlington, Ont.), was a hybrid plant consisting of UF and RO pretreatment stages, an OD section containing two  $19.2\text{-m}^2$  Liqui-Cel membrane modules and a single-stage brine evaporator. Fresh fruit juices were concentrated up to 65–70 °Brix at an average throughput of  $50 \text{ l h}^{-1}$ . The system was used to develop operational parameters and economic data for the design of full-scale plants and for the production of concentrated samples for their testing and evaluation [34]. The Mildura plant, designed by Vineland Concentrates and Celgard LLC, contained 22 Liqui-Cel membrane modules ( $4 \times 28$  inches) for a total interfacial area of  $425 \text{ m}^2$ . It was used for the concentration of grape juices to make wine from reconstituted concentrate. The installation, having a feed rate of approximately  $80\text{--}100 \text{ l h}^{-1}$  was able to produce approximately  $20\text{--}25 \text{ l h}^{-1}$  of 68 °Brix concentrate [78].

In Figure 8.3 a general scheme for the production of fruit-juice concentrate by integrated membrane operations is reported. Concentrated juices of good quality, not exceeding TSS concentrations of 30 °Brix, can be obtained by RO. In this case, the loss of volatile and nonvolatile flavors can be minimized, limiting the fraction of water removed. The further concentration of the RO retentate by OD permits a concentrated product, similar to that achieved by using OD alone, to be obtained





**Figure 8.3** Process scheme of integrated membrane operations for the production of concentrated fruit juices.

reducing significantly the processing costs. The stripping solution used in the OD step can be reconcentrated by thermal evaporation, cooled and recycled to the OD system.

It has been suggested that the RO pre-concentration of a fruit juice with a TSS content of 18 °Brix to about half its original volume could reduce the amount of water needed to concentrate the juice by OD up to 68 °Brix of about 56% maintaining unchanged its quality. Furthermore, a reduction of the evaporator capacity requirement and of the OD membrane area can be achieved, leading to a decrease in capital and operating costs [34].

The management of the diluted brine step is one of the drawbacks associated with the commercial application of the OD in fruit-juice processing. Although the regeneration of exhausted brines can be realized by thermal evaporation, this operation is expensive due to corrosion and scaling phenomena. Solar ponding, RO and pervaporation have been proposed as alternatives to reconcentrate the diluted brine solutions [78]. Electrodialysis has been also suggested for the regeneration of NaCl brines [79].

## 8.4

### Membrane Distillation

#### 8.4.1

##### Process Fundamentals

Membrane distillation (MD) is a thermally driven process in which two aqueous solutions, at different temperatures, are separated by a microporous hydrophobic membrane to support a vapor/liquid interface. The hydrophobic nature of the membrane prevents liquid solutions from entering its pores due to the surface-tension forces. In these conditions, a water-vapor transfer from the warm

side to the cold one occurs. The driving force of the process, as in the OD operation, is a vapor-pressure difference between the two solutions separated by the membrane; however, unlike the OD process it is generated by a temperature gradient rather than a concentration gradient.

The process takes place at a temperature that may be much lower than the boiling point of the solutions (feed temperatures in MD typically range from 60 to 90 °C, although temperatures as low as 30 °C have been used). Operating pressures are generally of few hundred kPa, relatively low if compared to pressure-driven processes such as RO. Consequently, equipment costs and mechanical demands on the membrane are greatly reduced. These features make MD ideal for the treatment of food and pharmaceutical solutions.

Unlike pressure-driven processes, MD membranes operate as a support for a vapor/liquid interface and not as sieving devices. Therefore, they can be realized with chemically resistant polymers such as PTFE, PP and PVDF. Furthermore, fouling phenomena are greatly reduced since the pores are relatively large if compared to the pores or to the diffusional pathway in RO or UF and are not easily clogged. Finally, MD membranes operate on the principles of vapor-liquid equilibrium so that nonvolatile compounds (such as ions, colloids, macromolecules, cells, etc.) are totally rejected [80].

Basically, a vapor-pressure difference across a MD membrane can be realized through four different methods. In the direct contact membrane distillation (DCMD) the permeate side of the membrane consists of a condensing fluid in direct contact with the membrane (cold distillate) separated by the hot feed. In this case, the vapor-pressure gradient that results from the transmembrane temperature difference is the driving force of the mass transport across the membrane. DCMD is the most suitable technique for applications in which the volatile component is water. The water transport through the membrane can be summarized in three steps: (1) evaporation of water at the dilute vapor/liquid interface; (2) diffusion or convective vapor transport through the membrane pores; (3) condensation of water vapor.

In the air-gap membrane distillation (AGMD) the permeate side of the membrane is a condensing surface separated from the membrane by an air gap. Volatile molecules cross both the membrane pores and the air gap and finally condense over a cold surface inside the membrane module.

In the sweeping gas membrane distillation (SGMD) a cold inert gas sweeps the permeate side of the membrane carrying the volatile molecules. In this case, condensation occurs outside the membrane module [81, 82]. Finally, in the vacuum membrane distillation (VMD) vacuum is applied on the permeate side of the MD membrane by means of a vacuum pump and, similarly to SGMD, condensation takes place outside the membrane module [83, 84].

#### 8.4.2

#### **MD Membranes and Modules**

Microporous membranes for MD are typically realized in flat-sheet or tubular form with hydrophobic polymers such as polytetrafluoroethylene (PTFE), polypropylene

(PP), polyethylene (PE) and polyvinylidene difluoride (PVDF). They can be prepared by phase inversion, stretching of dense film and thermally induced phase separation. Hydrophilic membranes can be also used for MD applications after treatments aiming to make their surfaces hydrophobic [85–87]. The transmembrane flux through a MD membrane is related to the membrane pore size and other characteristic parameters by the following equation:

$$N \propto \frac{r^\alpha \varepsilon}{\delta_m \tau} \quad (8.4)$$

where  $N$  is the molar flux,  $r$  the mean pore size of the membrane pores,  $\alpha$  a factor whose value is 1 for Knudsen diffusion and 2 for viscous fluxes, respectively,  $\delta_m$  the membrane thickness,  $\varepsilon$  the membrane porosity and  $\tau$  the membrane tortuosity [80, 88]. According to Equation 8.4 the thinner the membrane and the greater the porosity of the membrane, the greater the flux rate. On the contrary to achieve better heat efficiency the membrane should be as thick as possible in order to limit heat loss by conduction through the membrane matrix [89].

Typical pore sizes of MD membranes are in the range 0.2–1.0  $\mu\text{m}$ . Membrane pores should be large enough to facilitate the required flux; however, in order to prevent membrane pore wettability, the pore size should be as small as possible. Schneider *et al.* [90] recommended a maximum pore radius of 0.5–0.6  $\mu\text{m}$  in order to avoid membrane wetting due to fluctuations in process pressure and temperature. MD membranes should also be characterized by low thermal conductivity to prevent heat loss through the membrane matrix, good thermal stability and chemical resistance towards different feed solutions.

In general, the porosity of MD membranes ranges between 30 and 85% of the volume and the overall thickness from 80 to 250  $\mu\text{m}$ , depending on the absence or presence of support.

Typical MD membranes show a pore-size distribution rather than a uniform pore size. Consequently, different mechanisms can occur simultaneously depending on the pore size and on the MD operating conditions.

The design of MD modules should provide high feed and permeate flow rates with high turbulence and low pressure drop along the membrane module. Good heat recovery function, thermal stability and high packing density should be also guaranteed.

Flat-sheet membranes assembled in plate and frame or spiral-wound modules and capillary membranes in tubular modules have been used in MD operations.

Most membrane modules for MD applications on the laboratory scale are assembled with flat-sheet membranes since they offer a higher versatility than tubular or hollow fiber configuration. Flat-sheet membranes can be easily removed from their modules for cleaning and examination; furthermore, the same membrane module can be used to evaluate the performance of different MD membranes. On the other hand, tubular membranes offer a much higher membrane surface area to module volume ratio and they are preferred for industrial applications. Additionally, they do not require a support, reducing the boundary-layer resistance in comparison with flat-sheet modules.

One of the first commercially available membrane module for MD operations was realized by Enka AG (Akzo) in a shell-and-tube configuration. On the industrial scale flat-sheet modules have been produced by Gore and Associates (in a spiral-wound configuration) and by the Swedish Development Co. (in a plate and frame configuration).

At the moment the availability of industrial membrane modules for MD applications is one of the main limitations for MD implementation. In most cases, the performance of the MD process is affected by the heat and mass transfer in the boundary layers. Furthermore, mass-transfer rates within boundary layers should be able to prevent excessive concentration polarization phenomena with consequent risks of wetting and scaling.

#### 8.4.3

##### **Effect of Operating Parameters on MD Fluxes**

Permeate fluxes in MD are affected by different operating conditions such as: feed concentration, operating temperature, feed circulation velocity, temperature difference, permeate inlet temperature, permeate flow velocity and vapor-pressure difference.

Permeate fluxes decrease by increasing the feed concentration. This phenomenon can be attributed to the reduction of the driving force due to the decrease of the vapor pressure of the feed solution and to an exponential increase in the viscosity of the feed solution. The increase in the feed concentration also contributes to the formation of a boundary layer on the feed membrane surface (concentration polarization). However, this contribution is very small if compared to that of the temperature polarization [91]. At high concentration, ratio fluxes observed in MD are higher than those observed in pressure-driven membrane processes [92, 93].

In all MD configurations the MD flux increases exponentially with the increase of the feed temperature. This is due to the increase of the vapor pressure of the feed solution with temperature with a consequent increase of the transmembrane vapor pressure. However, when the treated aqueous solutions contain volatile compounds, such as fruit juices, the exponential increase of the permeate flux with the feed temperature can be impeded by the drop in selectivity. This phenomenon can be attributed to the increased effect of both temperature and concentration polarization when the feed temperature is raised.

The increase in feed circulation velocity and feed stirring rate determines an increase of the MD permeate flux. This is due to the increase of the heat-transfer coefficient in the feed side of the membrane module and to the reduction of the temperature and concentration polarization effects. The shear forces generated at high flow rate cause a lower accumulation of particulates on the active membrane surface, thus reducing membrane fouling. Lower crossflow velocities cause a lower Reynolds number, thus preventing the heat transfer from the bulk of the solution to and from the membrane surface with an increase of the temperature polarization [94]. Consequently, higher performances in terms of productivity can be obtained by operating under a turbulent flow regime. In some MD applications, an increase in

flux with the feed circulation velocity up to an asymptotic value at higher flow rates is observed [95]; other studies report a linear increase of the MD fluxes with the feed circulation velocity [96].

The temperature difference is another parameter affecting MD fluxes. When the mean temperature is kept constant, a linear increase of the permeate flux is observed by increasing the temperature difference [89]. On the other hand, the permeate flux increases exponentially with the mean temperature when the temperature difference is maintained fixed [31].

In DCMD applications, the general effect of increasing the permeate temperature is to reduce the permeate flux: this can be attributed to the decrease of the transmembrane vapor pressure as long as the feed temperature is maintained constant [97].

The increase of the permeate velocity increases the heat transfer in the permeate side with a consequent reduction of temperature and concentration polarization effects. When the heat-transfer coefficient in the permeate side is increased, the temperature at the membrane surface approaches the temperature in the bulk permeate side. This results in an increase in the driving force of the process and, consequently, of the permeate fluxes.

Finally, in all MD configurations a linear increase of the permeate flux is obtained by increasing the transmembrane vapor-pressure difference between the two sides of the membrane.

#### 8.4.4

#### MD Applications

Table 8.4 shows some selected MD applications in fruit-juice processing: they refer to the concentration of clarified (or clarified and pre-concentrated) juices and to the recovery of aroma compounds by using DCMD and VMD configurations.

The potentiality of MD in orange juice concentration by integrated membrane systems was analyzed by Drioli *et al.* [92] and Calabrò *et al.* [101] considering the effect of the viscosity and the necessity of juice pretreating. In these studies commercial plate PVDF membranes made by Millipore Corp., with a nominal pore radius of  $0.11\ \mu\text{m}$  and a porosity of 75%, were used for the concentration of single-strength orange juice with a TSS content of  $10.8\ ^\circ\text{Brix}$ . The permeate flux decreased from  $5.31\ \text{m}^{-2}\ \text{h}^{-1}$  to about  $2.51\ \text{m}^{-2}\ \text{h}^{-1}$  when the juice was concentrated up to  $31\ ^\circ\text{Brix}$  at a transmembrane temperature gradient of  $20\ ^\circ\text{C}$  (feed temperature =  $40\ ^\circ\text{C}$ ; cooling water =  $20\ ^\circ\text{C}$ ). Results on juice composition showed a very good retention of soluble solids, sugars and organic acids with rejection of sugars and organic acids equal to 100%. The observed reduction of vitamin C of about 42% was associated to high temperature and oxidation. The color and flavor of the concentrated juice were satisfactory. The pretreatment of the juice by UF permitted removal of pulp and pectin and a clarified juice with a lower viscosity compared with the single-strength juice to be obtained. An increase of the permeate flux in MD was observed when the clarified juice was concentrated from 10 to  $40\ ^\circ\text{Brix}$  without flux decay.

**Table 8.4** MD applications in fruit-juice processing.

Fruit juice	Membrane type	MD configuration	Reference
Apple (diluted from commercial concentrate)	Enka Microdyn, hollow fiber, polypropylene	DCMD	[97]
Apple (clarified by UF)	MFK3, flat sheet, PVDF	DCMD	[98]
Blackcurrant (clarified by UF)	K150, flat sheet, PTFE	VMD	[99]
Blackcurrant (clarified by UF and preconcentrated by RO)	Hollow fiber, polypropylene	DCMD	[100]
Orange juice (diluted from commercial concentrate)	Millipore, flat sheet, PVDF; Gelman, G0712, flat sheet; Enka, hollow fiber, polypropylene	DCMD	[91, 101]
Pear (model solution)	Enka-Mycrodin, MD020 TP 2N, hollow fiber, polypropylene	VMD	[102]
Must (model solution)	Akzo-Nobel, Accurel V8/2, tubular	VMD	[103]
Apple (diluted from commercial concentrate)	Enka Microdyn, hollow fiber, polypropylene	DCMD	[104]

Legend: DCMD: direct contact membrane distillation; VMD: vacuum membrane distillation.

Kozák *et al.* [100] evaluated the applicability of MD to produce concentrated blackcurrant juice starting from the clarification of the raw juice by MF followed by a preconcentration step performed by RO. The preconcentrated juice, with a TSS content of 22 °Brix, was concentrated up to 58.2 °Brix by using a laboratory-size hollow-fiber polypropylene membrane module. The juice side and the water side temperature were maintained at 26 °C and 11 °C, respectively ( $\Delta T = 15$  °C). In these conditions a steady-state flux of  $0.45 \text{ kg m}^{-2} \text{ h}^{-1}$  was reached after the stabilization of the temperature. An increase of few degrees centigrade in the driving force ( $\Delta T = 19$  °C) increased the steady-state flux to  $0.8 \text{ kg m}^{-2} \text{ h}^{-1}$ , markedly reducing the operation time required to concentrate the same amount of the juice. All the analyzed parameters (density, total acidity and anthocyanin content) were directly proportional to the increase of the TSS in the juice.

Gunko *et al.* [98] applied the DCMD to the concentration of apple juice. The raw juice was depectinized and then submitted to an UF clarification step. The concentration of the clarified juice was carried out by using PVDF microfiltration membranes of MFFK3 type (NPO Polymersintez, Russian Federation) with a nominal pore size of 0.45 mm and a porosity of 80–85%. A TSS content of 50 °Brix was obtained when the permeate flux reached about  $91 \text{ m}^{-2} \text{ h}^{-1}$ . Further concentration to 60–65 °Brix resulted in reduced productivity (up to  $31 \text{ m}^{-2} \text{ h}^{-1}$ ). The permeate flux increased on decreasing the cooling water temperature, maintaining constant the juice temperature in the hot cell.

Highly concentrated apple juices up to 64 °Brix were also produced by using polypropylene hollow-fiber DCMD modules (Enka MD-020-2N-CP) with tube and shell configuration [97, 104]. Transmembrane fluxes of about  $1 \text{ kg m}^{-2} \text{ h}^{-1}$  were obtained. Flux rates were dependent essentially upon temperature polarization phenomena located mainly on the feed side, rather than concentration polarization. Osmotic effects on the permeate side, obtained by using cold solutions of  $\text{CaCl}_2$ , improved transmembrane fluxes up to 20%. Model simulations describing the fluid dynamics and the membrane behavior within the DCMS system were in good agreement with experimental results. In particular, a nonsymmetrical distribution gave results better than those obtained with a Gaussian distribution. An optimal membrane thickness value, ranging between 30 and 60 mm, was obtained from the model.

The technical feasibility of must concentration through vacuum membrane distillation (VMD) was evaluated by Bandini and Sarti [103] with the object of increasing the alcoholic potential of musts, while preserving quality and quantity of the original aroma compounds. Experimental tests were performed on bench-scale plant by using model aqueous mixtures containing glucose and typical must aromas (1-hexanol, linalool, geraniol). A tubular membrane module containing Accurel V8/2 membranes (1.5 mm thickness, 5.5 mm internal diameter,  $0.2 \mu\text{m}$  average pore size), manufactured by Akzo-Nobel and arranged in tube and shell configuration was used. The aqueous mixture containing aromas was continuously recirculated in the tube side while the permeate vapors were removed from the shell side using a vacuum pump and condensed in cold traps refrigerated by liquid nitrogen.

Experimental curves representing the transmembrane flux against the concentration of the aqueous mixture at different values of feed temperatures and vacuum-side pressures showed the typical trend encountered also in other VMD applications involving volatile organic compounds [105]. In particular, water flux decreased by increasing the downstream pressure and the feed concentration, whereas an increasing of the liquid phase temperature determined an increase in the transmembrane flux. On the basis of experimental results, a model to design a must concentration system was presented. The proposed system was an RO/VMD integrated process considering the relevant amount of water to be removed. The must is previously concentrated from 20 to 30 °Brix in the RO unit and then submitted to a VMD step designed for the residual concentration up to 50 °Brix at 60 °C and 30 mbar. The proposed process allows production of juice concentrates containing at least 43% of the aroma originally contained in the fresh juice.

Bagger-Jørgensen *et al.* [99] evaluated the potential of VMD in the recovery of aroma compounds from blackcurrant juice. Before the concentration step the raw juice was depectinized, clarified with gelatin-silica sol, centrifuged and finally ultrafiltered. VMD was performed at low temperatures (10–45 °C) and at different feed flow rates ( $100\text{--}500 \text{ l h}^{-1}$ ) by using a flat PTFE (K150) membrane with a pore size of  $0.1 \mu\text{m}$  manufactured by Osmonics.

The highest concentration factors for the blackcurrant aroma compounds (from 21 to 31) were obtained at high feed flow rate ( $400 \text{ l h}^{-1}$ ) and low temperatures (10 °C). At 5 vol.% feed volume reduction the recovery of highly volatile compounds ranged

between 68 and 83 vol.% and between 32 and 38 vol.% for the poorly volatile compounds.

The recovery of aroma compounds by VMD from a mixture containing water/ethanol/ethyl 2,4-decadienoate simulating the pear aroma compounds was also investigated by Diban *et al.* [102]. VMD experiments were performed by using a polypropylene hollow-fiber membrane module supplied by Enka-Mycrodin (unit MD 020 TP 2N) (pore diameter 0.2  $\mu\text{m}$ , porosity 75%, inner diameter of hollow fibers 5.5 mm). The highest values of enrichment factor (up to 15) for pear aroma compounds were obtained working at lower temperatures and higher downstream pressures.

#### 8.4.5

#### **Coupled Operation of Osmotic Distillation and Membrane Distillation**

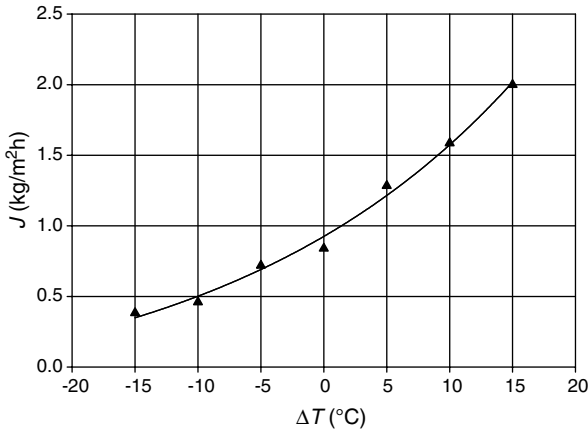
As previously described, both MD and OD processes are based on the use of similar membrane materials and module configurations and in both processes the driving force is a water-vapor pressure difference applied between the two sides of a hydrophobic membrane.

The water transport through the membrane can be summarized in three steps including vaporization and condensation on the boundary layers and diffusion or convective vapor transport through the membrane pores. The simultaneous vaporization/condensation phenomenon at the liquid/membrane interface determines a temperature variation on both sides of the membrane: the stripping solution is heated by the latent heat of the condensation while the feed solution is cooled by the vaporization. This thermal effect, reducing the driving force of the water transport across the membrane, can be exploited to obtain a coupled process where the stripper and the feed solution are thermostated separately at different temperatures: the osmotic solution on the cold side and the solution to be concentrated on the warm side [62]. This coupled operation of MD and OD, referred to as membrane osmotic distillation (MOD), permits enhancement of the water flux across the membrane [106].

The water transport through a porous hydrophobic membrane under a coupled transmembrane temperature/concentration difference was investigated by Godino *et al.* [107] in different experimental conditions (solute concentration, stirring rate, mean temperature and bulk temperature difference) by using pure water and sodium chloride solutions at different concentrations.

A coupled MD/OD process for the concentration of fruit juices (apple, redcurrant and blackcurrant, sour cherry and raspberry) was studied by Koroknai *et al.* [67] by using a membrane contactor containing 34 polypropylene tubular membranes (Microdyn) with a nominal pore size of 0.2  $\mu\text{m}$ , 70% porosity and thickness of 0.2 mm. The enzyme-treated raw fruit juice was pumped through the shell side, while the osmotic solution ( $\text{CaCl}_2$  6 M) was circulated in the lumen of fibers in a counter-current mode. Concentrated juices at 60 °Brix were obtained in an operation time of 15–20 h maintaining a temperature difference on both sides of the membrane of 15 °C. Enhanced water fluxes were obtained since the total driving force of the process was higher than the sum of the driving forces of single processes. During the process the water flux decay through the membrane as well as fouling phenomena





**Figure 8.4** Concentration of clarified grape must by OD. Effect of a transmembrane temperature gradient on the evaporation flux ( $J$ ) along with a concentration gradient (stripping solution = calcium chloride dehydrate 60%, w/w). Reprinted from [56] with permission of Chiriotti Ed.

were not significant. Furthermore, the organoleptic evaluation of the concentrated juices confirmed their high quality when compared with commercial juices prepared from concentrates.

Similarly, Bélafi-Bakó and Koroknai [108] found that the coupled process is more effective than MD or OD alone. The use of short membrane modules in cascade series, with heat exchangers placed between them, was suggested in order to minimize heat losses.

Figure 8.4 shows the effect of the coupled transmembrane temperature/concentration gradient on the OD evaporation flux obtained in the concentration of clarified grape must by using a polypropylene hollow-fiber membrane module and calcium chloride dehydrate (60% w/w) as stripping solution. The temperature difference applied between the feed and the extracting solution varied from  $-15\text{ }^{\circ}\text{C}$  to  $+15\text{ }^{\circ}\text{C}$ , while the average temperature of the system was kept at  $30\text{ }^{\circ}\text{C}$ . The increasing in OD flux with a temperature gradient of  $+5\text{ }^{\circ}\text{C}$ ,  $+10\text{ }^{\circ}\text{C}$  and  $+15\text{ }^{\circ}\text{C}$ , in comparison with the isothermal conditions, was of 53, 89 and 138%, respectively [56].

## 8.5 Supported-Liquid Membranes

### 8.5.1

#### Process Fundamentals

A supported-liquid membrane is a three-phase system in which a microporous support containing a carrier and a solvent is in contact with two aqueous solutions: the feed phase and the strip phase, respectively. The carrier binds the analyte of

interest on the feed side, transfers it selectively through the micropores and releases it on the strip side. The microporous support is used to stabilize the carrier–solvent mixture that is held in the pores of the membrane due to capillary and surface forces [109]. If the membrane used is hydrophobic, an organic solution containing a carrier selective for one of the species in the feed solution is immobilized in the micropores. Hydrophilic membranes can also be used for SLM systems: in this case the carrier-containing solution is in aqueous phase.

The selective transport is guaranteed if the affinity between the compound of interest and the carrier is higher than that between the carrier and other compounds in the feed solution.

The membrane pore size has to be large in comparison with the solute dimension in order to permit unhindered diffusion. Further, if the volumes of stagnant strip solutions are much smaller than the feed solution volumes, high preconcentration factors are achieved [110, 111].

The performance of the process is affected by the properties of the solution immobilized into micropores, such as viscosity and volatility, the carrier concentration and selectivity, the membrane characteristics and the fluid dynamics of the aqueous phases.

Basic aspects related to the stability of SLMs were reviewed by Kemperman *et al.* [112]. A rigorous model for mass transport through SLMs was proposed by Alhousseini and Ajbar [113].

### 8.5.2

#### SLMs Applications

The main applications of SLMs include the separation of metals from hydrometallurgical wastewaters [114], fructose extraction from mixtures of sugars contained in fermentation broths [115], olefin and paraffin hydrocarbon mixtures separation [116].

In the agro-food sector SLMs offer interesting perspectives in terms of extraction of valuable products from natural sources. Organic acids, for instance, are produced in large volumes for their use in biochemical and pharmaceutical industries. They are obtained as by-products of fermentation processes and have to be separated from excess reagents and impurities. Traditional methods, such as extractive fermentation and selective precipitation, suffer from some drawbacks due to solvent toxicity, incompatibility in fermentation media and overall recovery costs. On the contrary, the use of SLMs offers many advantages in terms of lower energy consumption, higher selectivity, faster separation rate, less-toxic solvent and minimum backmixing effects [117].

The extraction of organic acids from kiwifruit juice by using a SLM process was investigated by Schäfer and Hossain [118] as an alternative to the use of ion-exchange resins, electrodialysis and biological methods. The SLM consisted of an organic solution composed of a carrier (Aliquat 336/Alamine 336) and oleyl alcohol loaded on microporous polypropylene supports (Celgard 2500 and 2400). NaCl added to phosphate buffer solution to obtain a 1 M NaCl strip solution was used as the strip solution. Centrifuged and microfiltered kiwifruit juice was used as feed solution. The permeability of the SLM system was evaluated in a batch cell, while the effect of

various process parameters, such as flow rate of feed and strip solutions, carrier concentration and recycling mode of operation on the recovery of organic acids (quinic, citric, L-malic, L-ascorbic and fumaric) was analyzed in a continuous spiral-wound membrane module.

The results indicated that the flux rates of organic acids decreased with the flow rate of feed and strip solution and increased with the carrier concentration. Recycling of feed and strip solutions also resulted in a significant improvement of the extraction efficiency. Citric, malic and quinic acids were extracted from kiwifruit juice at a rate of 5% in a single-pass process.

One of the problems of the citrus industry is the formation of bitterness in citrus juice within hours after the extraction of the juice from the fruit due to the formation of bittering agents; limonoids and flavonoids. Different methods including preharvest treatment with auxin plant-growth regulators, able to inhibit the biosynthesis of limonoids, extraction of limonoids and flavonoids with cross-linked resin monomers and adsorption of bittering agent and acids with lignin-type adsorbents, have been developed to reduce or extract bittering agents from citrus juices. However, these methods present disadvantages that markedly limit their use. For instance, auxin plant-growth regulators are expensive and the adsorption of acid compounds along with bittering agents negatively affects flavor.

An extraction method of bittering agents in citrus juice, based on the use of membrane contactors, was proposed by van Eikeren and Brose [119]. In particular, the proposed approach was based on the use of two systems (A and B) of cellulose hollow-fiber membranes permeable to bittering agents and impermeable to flavor and nutritional compounds. The citrus juice and an organic extractant were circulated in the shell side and in the lumen side of the system A, respectively. Bittering agents diffused across the membrane and dissolved into the organic extractant. The organic solvent enriched in bittering agents was transported and circulated into the lumen of the system B while a strip solution was circulated on the shell side of the same membranes. The bittering agents diffused across the membrane, and, being ionized by the basic strip solution, were trapped on the shell side. In these conditions a strip solution enriched in bitter agents and an organic solvent depleted in bitter agents (recycled to the lumens of hollow fibers of the system A) were produced. The proposed system reduced the limonin concentration below the 6-ppm value, while the concentration of vitamin C remained unchanged. In another approach a supported-liquid membrane comprising a mixture of aliphatic solvents supported in the pores of a flat-sheet polypropylene membrane was used. The membrane was clamped between the feed solution and the strip compartment filled with a 0.01 M sodium hydroxide solution. The proposed system reduced the limonin content in the feed of 80%.

## 8.6 Conclusions

Table 8.5 summarizes main advantages and drawbacks of fruit-juice-concentration technique.

**Table 8.5** Advantages and drawbacks of fruit-juice-concentration techniques.

Process	Advantages	Disadvantages
Thermal evaporation	high evaporation fluxes; high TSS content achievable; broad industrial scale application; possibility to use the same plant for different types of juice; the capital investment/evaporation capacity decreases by increasing the capacity	high energy consumption; loss of organoleptic and nutritional properties; loss of aroma compounds; complex operation
Cryoconcentration	aroma retention; no chemical alteration of juice components; organoleptic and nutritional preservation	limit of concentration (30–50 °Brix); necessity of an inactivation enzyme pretreatment; high investment costs; high energy consumption
Reverse osmosis	broad industrial-scale application; low temperatures; modularity; easy scale-up; combination with vacuum evaporation; already commercially available; energetically and economically convenient if compared with thermal evaporation	fouling phenomena; high pressures; necessity of an inactivation enzyme pretreatment; juice concentration limited at 22–23 °Brix; loss of aroma compounds during the process; difficulty to concentrate solutions with high suspended solids content; high cost of membrane replacement
Direct osmosis	low temperatures; low pressures; no fouling problems; constant permeate flux in time; high TSS content achievable; modularity; easy scale-up; possibility to treat solutions with high suspended solids content; possibility to use the same unit to concentrate different products; low energy consumption; low cost of membrane replacement	new technology requiring an evaluation at industrial level; relatively low permeation ( $1.8\text{--}2.5\text{ l m}^{-2}\text{ h}^{-1}$ ); high investment costs; possibility to use the same unit to concentrate different products
Membrane distillation	lower operating temperature with respect to thermal evaporation; reduced influence of concentration polarization in comparison to pressure-driven processes; theoretical 100% rejection to nonvolatile solutes; low energy consumption; high product quality	temperature polarization phenomena; heat losses by conduction through the polymeric membrane; lower transmembrane fluxes in comparison with thermal evaporation
Osmotic distillation	lower operating temperature with respect to thermal evaporation; reduced influence of concentration polarization in comparison to pressure-driven processes; theoretical 100% rejection to nonvolatile solutes; low energy consumption; high product quality	lower transmembrane fluxes in comparison with thermal evaporation; brine disposal

The potential advantages of OD and MD over conventional evaporation and other techniques have been successfully demonstrated at the lab scale and pilot scale, including improved product quality, lower energy consumption, and easy scale-up.

With the enlargement of the world's fruit-juice market and the request of product quality, commercial applications of membrane operations in fruit-juice processing, will expand in the near future.

Within membrane operations membrane contactors can be considered applications in a breakthrough status with enhanced effectiveness. Their integration with standard membrane operations is a valid approach for a sustainable industrial growth within the process intensification strategy. However, in order to gain a foothold in fruit-juice processing, development of suitable membranes with improved diffusional characteristics, selectivity, pore geometry and stability needs to be undertaken at reasonable costs.

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