Potential of membrane distillation for production of high quality fruit juice concentrate- A comprehensive review

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Potential of membrane distillation for production of high quality fruit juice concentrate- A comprehensive review

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ABSTRACT

Fruit juices are generally concentrated in order to improve the stability during storage and to reduce handling, packaging and transportation costs. Thermal evaporation is the most widely used technique in industrial fruit juice concentrate production. In addition to high energy consumption, a large part of the characteristics determining the quality of the fresh juice including aroma, colour, vitamins and antioxidants undergoes remarkable alterations through the use of high operation temperatures. Increasing consumer demand for minimally or naturally processed stable products able to retain as much possible the uniqueness of the fresh fruit has engendered a growing interest for development of non-thermal approaches for fruit juice concentration. Among them, membrane distillation (MD) and its variants have attracted much attention for allowing very high concentrations to be reached under atmospheric pressure and temperatures near ambient temperature. This review will provide an overview of the current status and recent developments in the use of MD for concentration of fruit juices. In addition to the most basic concepts of MD variants, crucial suggestions for membrane selection and operating parameters will be presented. Challenges and future trends for industrial adaptation taking into account the possibility of integrating MD with other existing processes will be discussed.

1. Introduction

Concentration process is one of the major unit operations in industrial fuit juice processing, where the soluble solid content (SSC) of the juice is increased from 10-18 °Brix to 65-75 °Brix by removal of water through evaporation. The consequent reduction of liquid volume lowers transport, storage and packaging costs. Concentrates present higher resistance to microbial and chemical deterioration than the original juice as a result of water activity reduction. Therefore, concentration also promotes economical year-round utilisation of the seasonal fruits.

The industrial concentration of fruit juices is usually performed by multi-stage falling film evapourators, in which much more drastic temperature&time regimes than in the pasteurization process can be used (Bagger-Jorgensen et al., 2011).Thus, the removal and subsequent concentration of aroma compounds by distillation prior to concentration is a common practice in traditional fruit juice concentrate production. The volatiles are recovered in the condensate of the first evaporation stage and then concentrated to an aroma-enriched solution by distillation. Aroma concentrate is then added back to the dearomatized juice concentrate during reconstitution step to restore the original aroma profile. However, it is well known that there is an undesirable alteration of the original aroma profile of the juice due to high operation temperatures. Thus, in addition to high energy consumption, multi-stage evaporation process coupled with aroma recovery has many heat induced drawbacks including alteration of sensory attributes (i.e. color and aroma), reduction of nutritional value (i.e. vitamins and antioxidants) and formation of unfavorable compounds (i.e. hydroxymethyl furfural and furan) (Ibarz et al., 2011; Kadakal et al., 2002; Simsek et al., 2007; Toribio and Lozano 1986; Varming et al., 2004).

Increasing consumer demand for gently-processed fresh-like fruit juices with high sensory and nutritional qualities has led to a growing interest for non-thermal processing techniques (Raso and Barbosa-Canovas 2003; Rastogi 2011). In this respect, membrane technology has become more promising to meet consumer's expectations.

Membrane processes can be easily scaled up due to their compact and modular design; they are able to transfer specific components selectively; they are energy efficient systems operating under moderate temperature conditions ensuring gentle product treatment. Reverse osmosis (RO) have already gained wide acceptance for nonthermal concentration of fruit juices. However it is generally used as a preconcentration technique allowing concentration values of about 25–30 °Brix due to high osmotic pressure limitations (Echavarria et al., 2011).

Recently, technological advances related to the development of new membrane processes including membrane distillation (MD) and osmotic distillation (OD) have been proved to overcome this limitation (Bagger-Jorgensen et al., 2011; Cassano and Drioli 2007; Hongvaleerat et al., 2008; Kozak et al., 2009; Onsekizoglu et al., 2010b; Valdes et al., 2009). They have been proposed as attractive membrane processes allowing very high concentrations (above 65°Brix) to be reached under atmospheric pressure and temperatures near ambient temperature.

This review will cover the theoretical aspects, water transport mechanisms, effects of operating parameters on transmembrane flux, applications and challenges in MD applications. In this respect, the most promising recent developments for industrial implementation and long term performance avaluation of MD systems will be discussed. The suggestions for membrane selection taking into account the membrane material and module configuration together with contact angle and membrane wettability will also be presented in detail.

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2. Process fundamentals

2.1. Membrane distillation

The term MD comes from the similarity between conventional distillation process and its membrane variant as both technologies are based on the vapour-liquid equilibrium for separation and both of them require the latent heat of evaporation for the phase change from liquid to vapour which is achieved by heating the feed solution.

MD is a non-isotermal membrane process, in which fruit juice (feed side) is separated from a receiving phase (permeate side) by a hydrophobic microporous membrane. The hydrophobic nature of the membrane prevents penetration of the pores by aqueous solutions due to surface tensions, unless a transmembrane pressure higher than the membrane liquid entry pressure (LEP) is applied. Therefore, liquid-vapour interfaces are formed at the entrances of each pore. The driving force for MD process is given by the vapour pressure gradient across the membrane. Depending on the way in which the transmembrane vapour pressure gradient is created and the water vapour is condensed in the permeate side, various configurations have been proposed (El-Bourawi et al., 2006; Khayet 2011; Lawson and Lloyd 1997; Susanto 2011; Zhigang et al., 2005). Figure 1 illustrates the four commonly used configurations of MD, which are described as follows:

[1] In direct contact membrane distillation (DCMD), water having lower temperature than fruit juice in the feed side is used as condensing fluid in permeate side. In this configuration, the aqueous solutions in both sides of the membrane are in direct contact with the hydrophobic microporous membrane. The water transport through the membrane

can be summarized in three steps: (1) formation of a vapour gap at the hot feed solution–membrane interface; (2) transport of the vapour phase through the microporous system; (3) condensation of the vapour at the cold side membrane–permeate solution interface (Jiao et al., 2004; Peinemann et al., 2010). DCMD is the most commonly used configuration due to its convenience to set up in laboratory. However, direct contact of the membrane with the cooling side and poor conductivity of the polymeric material results heat losses throughout the membrane.

[2] In air gap membrane distillation (AGMD), a stagnant air gap is introduced between membrane and condensation surface to reduce heat losses. Therefore, water vapour is condensed on a cold surface that has been separated from the membrane via an air gap.

[3] In sweeping gas membrane distillation (SGMD), a cold inert gas is used in permeate side for sweeping and carrying the vapour molecules to outside the membrane module where the condensation takes place. Despite the advantages of a relatively low conductive heat loss with a reduced mass transfer resistance, due to the operational costs of the external condensation system, SGMD is the least used configuration.

[4] In vacuum membrane distillation (VMD), the driving force is maintained by applying vacuum at the permeate side. The applied vacuum pressure is lower than the equilibrium vapour pressure. Therefore, condensation takes place outside of the membrane module.

2.2. Osmotic distillation

Osmotic distillation (OD) is an isothermal MD variant, in which the driving force, transmembrane vapour pressure gradient, is obtained by using a hypertonic salt solution on

permeate side. Under these conditions, a net water flux from the high vapour pressure side to the low one occurs resulting in the concentration of feed and dilution of hypertonic salt solution. The water transport through the membrane can be summarized in three steps: (1) Evaporation of water at the dilute vapour–liquid interface; (2) diffusional or convective vapour transport through the membrane pore; (3) condensation of water vapour at the membrane-brine interface (Jiao et al., 2004; Peinemann et al., 2010). In the literature the OD technique is also termed as isothermal membrane distillation, osmotic membrane distillation, osmotic evaporation and gas membrane extraction (Gryta 2005b).

The OD process can be operated at atmospheric pressure and ambient temperature. The osmotic agent to be used in OD process should have high osmotic activity in order to maintain a lower vapour pressure and to maximize the driving force, should be non-volatile and thermally stable to allow reconcentration of diluted stripping solution by evaporation. Other factors that should be taken into consideration are solubility, toxicity, corrosivity and cost. Although NaCl or $CaCl_2$ have preferred in most of the reported studies, both of these salts have the disadvantage of being corrosive (Celere and Gostoli 2004; Shin and Johnson 2007). $MgCl_2$, $MgSO_4$, K_2HPO_4, and KH_2PO_4 are some other commonly used osmotic agents in OD. Potassium salts of ortho- and pyrophosphoric acid have been proposed to offer several advantages, including low-equivalent weight, high water solubility, steep positive temperature coefficients of solubility and safety in foods and pharmaceuticals (Jiao et al., 2004; Nagaraj et al., 2006a; Shin and Johnson 2007).

3. Characteristics of membranes

The selection of the membrane is the most crucial factor in separation performance of MD operations. As stated earlier, the membrane used for both MD and OD processes must be

solvents including dimethylformamide and triethylphosphate. PVDF membranes are generally prepared by phase inversion technique. PP exhibits excellent solvent resistant properties and high crystallinity. They are generally manufactured by stretching and thermal phase inversion (Curcio and Drioli, 2005).

The relationship between the transmembrane flux and membrane characteristic related parameters is given by (Lawson and Lloyd 1997):

$$N \ \alpha \ \frac{<r^{\alpha}> \varepsilon}{\tau \delta} \ [1]$$

where N is the molar flux, $<r^{\alpha}>$ is the mean pore size of the membrane pores (α equals 1 for Knudsen diffusion and equals 2 for viscous flux), ε is the membrane porosity, τ is the membrane tortousity and δ is the membrane thickness. Criteria for selection of the appropriate membrane should therefore include some additional characterictics such as pore size, tortuosity, porosity, membrane thickness and thermal conductivity.

3.1.1. Membrane pore size

Membranes with pore sizes ranging from 10 nm to l µm can be used in MD (Pabby et al., 2009). The permeate flux increases with the increase in pore size as determined by Knudsen model. However, in order to avoid wettability, small pore size should be preferred (El-Bourawi et al., 2006; Khayet 2011). Thus, an optimum value for pore size has to be determined for each MD application depending on the type of the feed solution.

3.1.2. Membrane porosity

Porosity is the ratio of the volume of the pores to the total volume of the membrane. Evaporation surface area increases with the increase in porosity level of the membrane, resulting in higher permeate fluxes (Huo et al., 2011; Susanto 2011). Membrane porosity also affects the amount of heat loss by conduction (Khayet and Matsuura 2011; Lawson and Lloyd 1996b):

$$Q_m = h_m \Delta T_m \quad [2]$$

$$h_m = \varepsilon h_{mg} + (1 - \varepsilon) h_{ms} \quad [3]$$

where ε is the membrane porosity, h_{mg} is the conductive heat transfer coefficient of the gases entrapped in the membrane pores; h_{ms} is the conductive heat transfer coefficient of the hydrophobic membrane material.

Conductive heat loss can be reduced by increasing porosity of the membrane, since h_{mg} is generally an order of magnitude smaller than h_{ms}. In general, the porosity of the membranes used in MD operations lines in the range of 65%-85%.

3.1.3. Pore tortuosity

Tortuosity is determined as the average length of the pores compared to membrane thickness. The membrane pores do not go straight across the membrane and the diffusing molecules must move along tortuous paths, leading a decrease in transmembrane flux. Therefore, permeate flux increases with the decrease in tortuosity. It must be pointed out here that this value is frequently used as a correction factor for prediction of transmembrane flux due to the difficulties in measuring its real value for the membranes used in MD applications. In general a value of 2 is

frequently assumed for tortuosity factor. (El-Bourawi et al., 2006; Khayet et al., 2004a; Phattaranawik et al., 2003a)

3.1.4. Membrane thickness

Permeate flux is inversely proportional to the membrane thickness in MD. Therefore, membrane must be as thin as possible to achieve high permeate flux. On the other hand, thickness also plays an important role in the amount of conductive heat loss though the membrane. In order to reduce heat resistances, it should be as thick as possible leading to a conflict with the requirement of higher permeate flux for MD operations. Hence membrane thickness should be optimized in order to obtain optimum permeate flux and heat efficiency. The optimum thickness for MD has been estimated within the range of 30–60 µm (Lagana et al., 2000).

In the case of OD, as the water evapourates on feed side and condenses on permeate side of the membrane, the feed cools down and the brine solution warms up. The resultant temperature gradient across the membrane reduces the effective driving force for mass transfer. Therefore, membrane should be thin so that the heat can readily be transferred from brine side to the feed side, making the process essentially isothermal. Nevertheless, the thickness is somewhat limited by the mechanical strenght.

3.1.5. Thermal conductivity

Thermal conductivity of the membrane should be small in order to reduce the heat loss through the membrane from feed to the permeate side. Conductive heat loss is inversely proportional to the membrane thickness. However selection of a thicker membrane decreases both the flux and permeability. One promising approach may be selection of a membrane with higher porosity

since thermal conductivity of polymer membrane is significantly higher than thermal conductivity of water vapour in the membrane pores (Khayet et al., 2006). The thermal conductivities of polymers used in MD generally varies in the range of 0.15–0.45 W $m^{-1}K^{-1}$, depending upon temperature and the degree of crystallinity (Alklaibi and Lior 2005). It should be noted that membrane with high thermal conductivity should be preferred so as to reduce the thermal effects associated to the mass transfer in OD applications.

3.1.6. Contact angle

The contact angle is a common measurement of the hydrophobic or hydrophilic behaviour of a material. It provides information about relative wettability of membranes. The contact angle is determined as the angle between the surface of the wetted solid and a line tangent to the curved surface of the drop at the point of three-phase contact (Figure 2). The value of contact angle is greater than 90° when there is low affinity between liquid and solid; in case of water, the material is considered hydrophobic. It is less than 90° in the case of high affinity in which the material is considered hydrophilic. Table 2 lists the contact angle values for few different materials in water at ambient temperature. Wetting occurs at 0°, when the liquid spreads onto the surface (Curcio et al., 2010; Curcio and Drioli 2005; Pabby et al., 2009). The wettability of a solid surface by a liquid decreases as the contact angle increases (Curcio et al., 2010; Hwang et al., 2011; Tomaszewska 2000). It must be pointed out here that the contact angle measuments should be taken at different locations of the membrane and the corresponding corrections due to membrane pore size and roughness must be taken into account.

3.1.7. Liquid entry pressure and wetting phenomena

One of the essential features of MD is that the membrane must not be wetted by the aqueous solutions in contact with and only water vapour or noncondensable gases should be present within the membrane pores (Khayet and Matsuura 2011). However, pore wetting may occur resulting in a reduction of both the permeate flux and separation performance if the applied transmembrane hydrostatic pressure exceeds the liquid entry pressure (LEP). LEP is the minimum transmembrane hydrostatic pressure that must be applied before liquid solutions penetrate into the membrane pores. LEP can be calculated using the Laplace-Young equation (Burgoyne and Vahdati 2000; Lawson and Lloyd 1997).

$$\Delta P = P_F - P_D = \frac{2\beta\gamma_L Cos\theta}{r_m} \quad [4]$$

where P_F and P_F are the hydraulic pressure of the feed and distillate side, β is the geometric pore coefficient (equals 1 for cylindrical pores), γ_L is the surface tension of the liquid, θ is the contact angle and r_m is the maximum pore size.

LEP depends on membrane characteristics and prevents wetting of the membrane pores during MD experiments. LEP increases with a decrease in maximum pore size at the surface and an increase at the hydrophobicity (i.e., large water contact angle) of the membrane material. The presence of strong surfactants or organic solvents can greatly reduce the liquid surface tension therefore causing membrane wetting. Therefore, care must be taken to prevent contamination of process solutions with detergents or other surfacting agents.

3.2 Membrane modules

Choice and arrangement of the membrane module in a MD application is based on economic considerations with the correct engineering parameters being employed. Plate and frame, spiral-wound, tubular, capillary and hollow fiber membrane modules have been used by MD researchers.

In plate and frame modules, the membranes which are usually prepared as discs or flat sheets are placed between two plates. The feed solution flows through flat, rectangular channels. Packing densities for flat sheet membranes may be in the range of 100–400 m^2/m^3 (Pabby et al., 2009). Polymeric flat sheet membranes are easy to prepare, handle, and mount. The same module can be used to test many different types of MD membranes. The membrane can be supported to enhance mechanical strength. Babu et al. (2008) used a plate and frame membrane module having a membrane area of 0.01 m^2 for the concentration of pineapple and sweet lime juice. The module consists of a polyester mesh (0.25 mm) and a hydrophobic microporous polypropylene membrane (pore size 0.20 μm and thickness 175 μm) supported in between a viton gasket (3.0 mm) and two stainless steel frames.

In spiral-wound membranes, the membrane, feed and permeate channel spacers and the porous membrane support form an envelope which is rolled around a perforated central collection tube and is inserted into an outer tubular pressure shell. The feed solution passes in axial direction through the feed channel across the membrane surface. The filtrate moves along the permeate channel and is collected in a perforated central collection tube. Spiral-wound modules have packing densities of about 300–1000 m^2/m^3 depending on the channel height, which is greater than that of the plate and frame module (Pabby et al., 2009). The major disadvantage of spiral-wound module is being quite sensitive to fouling.

Tubular, capillary or hollow fiber membrane modules are shell and tube type modules. The support is not needed in these modules. The membranes are usually a fixed integral part of the module and can not be easily replaced. Tubular membrane modules provide much higher membrane surface area to module volume ratio than plate and frame modules (Khayet 2011). The diameter of membranes in tubular module varies within the range of 10-25 mm. The packing density is around 300 m^2/m^3 (Pabby et al., 2009). These modules offer higher cross-flow velocities and large pressure drops and generally used for MD of high viscous liquids. The diameters of membranes in capillary modules typically vary between 0.2-3 mm with packing densities of about 600-1200 m^2/m^3 (Li et al., 2008) . The production costs are very low and membrane fouling can effectively be controlled by the proper feed flow and back-flushing of permeate in certain time intervals. The main disadvantage of the capillary membrane module is the requirement of low operating pressure (up to 4 bars). The inner diameter of hollow fiber membranes is around 50-500 µm with very high packing densities of about 3000 m^2/m^3. Hollow fiber module has the highest packing density of all module types. Its production is very cost effective and hollow fiber membrane modules can be operated at pressures in excess of 100 bars (El-Bourawi et al., 2006). The main disadvantage of the hollow fiber membrane module is the difficult control of membrane fouling. Therefore, a proper pretreatment should be applied for separation of macromolecules. For example, in the case of fruit juice concentration by MD using a hollow fiber module, clarification is a crucial pretreatment step to enhance MD flux (Cassano and Drioli 2007; Onsekizoglu et al., 2010b).

In the concentration of fruit juices, to achieve chemical and microbiological stability, nearly 80% of water has to be removed, resulting a concentrate with final SSC value of about 65-75 °Brix.

Such an operation can be held through a membrane with a relatively large area; in consequence, a great extent of holding volume is required. In order to reduce the holding volume, hollow fibers can be used; however they can not be used for concentration above 40-45 $^{\circ}$Brix owing to the drawbacks related to high viscosity and pressure drop. Therefore, it is possible to use different types of membrane modules throughout concentration of juices, especially when a preclarification step is not desired. For example, a hollow fiber module can be used up to 40 $^{\circ}$Brix and a module with larger capillaries or even tubular ones can be used for further concentration.

Table 3 summarizes the commercial membranes commonly used by the various researchers up to date together with their principal characteristics. In fact, there is a lack of commercially available MD units and most of the MD researches use modules actually designed for other membrane operations (i.e. microfiltration) rather than MD. Design of novel membranes fabricated especially for MD purposes have been recommended by MD investigators since commercially available membranes do not meet all the requirements listed above. Novel hydrophobic membranes for MD applications can be manufactured either by hydrophobic polymers or by surface modification of hydrophilic membranes. Various surface modification applications including coating, grafting and plasma polymerization have been attempted until now (Brodard et al., 2003; Bryjak et al., 2000; Chanachai et al., 2010; Huo et al., 2010; Kong et al., 1992; Krajewski et al., 2006; Lai et al., 2011; Li and Sirkar 2004; Vargas-Garcia et al., 2011; Wu et al., 1992; Yang et al., 2011b). However, there is very limited number of studies on the design of MD membranes (Khayet 2011; Khayet et al., 2010; Phattaranawik et al., 2009; Wang et al., 2009; Yang et al., 2011a). Therefore, further efforts need to be devoted for development of new

generation of membranes promising required features in MD applications, especially in fruit juice concentration field.

4. Transport mechanisms and polarization phenomena

4.1 Theory of heat transfer

Heat transfer in the MD includes three main steps:

i. Heat transfer through the feed side boundary layer

ii. Heat transfer through the membrane

iii. Heat transfer through the permeate side boundary layer

Heat transfer through boundary layers

Heat transfer from the feed solution to the membrane surface across the boundary layer in the feed side of the membrane module imposes a resistance to mass transfer since a large quantity of heat must be supplied to the surface of the membrane to vapourize the liquid. The temperature at the membrane surface is lower than the corresponding value at the bulk phase. This affects negatively the driving force for mass transfer. This phenomenon is called temperature polarization (El-Bourawi et al., 2006; Pabby et al., 2009; Qtaishat et al., 2008). Temperature polarization becomes more significant at higher feed temperatures (Burgoyne and Vahdati 2000; Lagana et al., 2000; Phattaranawik et al., 2003b).

The temperature polarization coefficient (TPC) is determined as the ratio of the transmembrane temperature difference to the bulk temperature difference:

$$TPC = \frac{T_{fm} - T_{pm}}{T_{fb} - T_{pb}} \quad [5]$$

where T_{fm}, T_{pm}, T_{fb} and T_{pb} are membrane surface temperatures and fluid bulk temperatures at the feed and permeate sides, respectively. A schematic diagram of the temperature polarization in MD is shown in Figure 3.

Heat transfer through the feed side boundary layer can be calculated using

$$Q_f = h_f \left(T_{fb} - T_{fm} \right) \quad [6]$$

where h_f is the heat transfer coefficient of the feed side boundary layer.

Heat transfer from membrane surface to the bulk permeate side across the boundary layer is also related with temperature polarization phenomenon. The temperature of membrane surface at the permeate side is higher than that of bulk permeate due to the temperature polarization effect.

Heat transfer through the permeate side boundary layer is given as:

$$Q_p = h_p \left(T_{pm} - T_{pb} \right) \quad [7]$$

where h_p is the heat transfer coefficient of the permeate side boundary layer.

Both feed and permeate side boundary layers are functions of fluid properties and operating conditions, as well as the hydrodynamic conditions. There are some convenient approaches in the literature to reduce the temperature polarization effects such as mixing thoroughly, working at high flow rates or using turbulence promoters (Cath et al., 2004; Chernyshov et al., 2005; El-Bourawi et al., 2006; Lawson and Lloyd 1996a; Martinez and Rodriguez-Maroto 2006).

Heat transfer through the membrane

Heat transfer through the membrane appears as a combination of latent heat of vapourization (Q_V) and conductive heat transfer across both the membrane matrix and the gas filled membrane pores (Q_C). The corresponding values can be estimated by following equations:

$$Q_V = J\Delta H_V \ [8]$$

$$Q_C = \left(\frac{k_m}{\delta}\right)\left(T_{fm} - T_{pm}\right) \ [9]$$

Therefore, the heat flux can be estimated by the following expression (El-Bourawi et al., 2006; Khayet and Matsuura 2011; Lawson and Lloyd 1997; Phattaranawik and Jiraratananon 2001):

$$Q_m = Q_V + Q_C \ [10]$$

$$Q_m = \frac{k_m}{\delta}\left(T_{fm} - T_{pm}\right) + J\Delta H_V \ [11]$$

where k_m is the thermal conductivity of the membrane, δ is the membrane thickness, J is the permeate water vapour flux and ΔH_V is the latent heat of vapourization.

Various models have been proposed for estimation of k_m in Equation [11]. Two of the most frequently used ones are given below;

$$k_m = \varepsilon k_g + \left(1-\varepsilon\right)k_s \ [12]$$

$$k_m = \left[\frac{\varepsilon}{k_g} + \frac{\left(1-\varepsilon\right)}{k_s}\right]^{-1} \ [13]$$

4.2 Theory of mass transfer

As previously mentioned, mass transfer in MD is driven by the vapour pressure gradient imposed between two sides of the membrane. In MD process, the gradient is generated by the temperature difference between two sides of the membrane, whereas in the case of OD, the difference in water activity between the juice and a hypertonic salt solution (concentrated brine stripper) induces the gradient at room temperature.

Mass transfer in membrane distillation consists of three consecutive steps:

i.   Evaporation of water at the liquid/gas interface on the membrane surface of the feed side

ii. Water vapour transfer through the membrane pores

iii. Condensation of water vapour at the gas-liquid interface on the membrane surface of the permeate side

The mass flux (J) can be expressed as (Close and Sorensen 2010; Zhang et al., 2010):

$$J = K \Delta P \ [14]$$

where K is the overall mass transfer coefficient which is the reciprocal of an overall mass transfer resistance. This overall resistance is the sum of three individual resistances:

$$K = \left[\frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_p} \right]^{-1} \ [15]$$

where K_f, K_m and K_p are the mass transfer coefficients of feed layer, membrane and permeate layer, respectively.

Mass transfer through boundary layers

In membrane distillation, only water vapour transport is allowed due to the hydrophobic character of the membrane. Therefore the concentration of solute(s) in feed solution becomes higher at the liquid/gas interface than that at the bulk feed as mass transfer proceeds. This phenomenon is called concentration polarization and results in reduction of the transmembrane flux by depressing the driving force for water transport. Concentration polarization coefficient (CPC) is determined as the ratio of the solute concentration at the membrane surface (C_{fm}) to that at the bulk feed solution (C_{fb}):

$$CPC = \frac{C_{fm}}{C_{fb}} \quad [16]$$

The concentration gradient between the interface and the bulk feed/permeate results a diffusive transfer of solutes from the surface of the membrane to the bulk solution. At steady state, the rate of convective solute transfer to the membrane surface is balanced by diffusion of solute to the bulk feed/permeate. The molar flux is expressed as follows (El-Bourawi et al., 2006; Khayet and Matsuura 2011):

$$J = k_s \ln\left(\frac{C_{fm}}{C_{fb}}\right) [17]$$

where k_s is the diffusive mass transfer coefficient through the boundary layer.

Several empirical correlation of dimensionless numbers, namely, Sherwood (Sh), Reynolds (Re), Schmidt (Sc), Nusselt (Nu) and Prandtl (Pr) numbers can be used to estimate the value of k_s depending on the hydrodynamics of the system:

$$Sh = \frac{kL}{D} \quad \text{Re} = \frac{Lu\rho}{\mu} \quad \text{Sc} = \frac{\mu}{\rho D} \quad \text{Nu} = \frac{hL}{k} \quad \text{Pr} = \frac{\mu C_P}{k} \text{ [18]}$$

where L: characteristic length, D: diffusion coefficient, ρ: density, μ: viscosity, u: feed velocity, k: thermal conductivity, C_P: specific heat, h: boundary layer heat transfer coefficient (Babu et al., 2008).

The concentration polarization in MD process is usually considered in the feed side, with the distillate being pure liquid, as in typical desalination applications (Gryta 2005b). Therefore it has an insignificant effect compared to temperature polarization in MD. However, in the case of OD, this effect becomes more important since polarization exists at each side of the membrane (Figure 4). During OD, as mass transfer proceeds, solute concentration increases at the membrane surface due to evaporation of water vapour at the feed side. On the other hand, the solute concentration decreases due to the condensation of water vapour on the permeate side, giving rise to the difference in brine concentrations (Babu et al., 2006; Babu et al., 2008; Nagaraj et al., 2006b).

Mass transfer through the membrane pores

The main mass transfer mechanisms through the membrane in MD are Knudsen diffusion and molecular diffusion (Figure 5). Knudsen diffusion model is responsible for mass transfer through the membrane pores if the mean free path of the water molecules is much greater than the pore size of the membrane and hence,the molecules tend to collide more frequently with the pore wall (Li et al., 2008; Nagaraj et al., 2006b; Pabby et al., 2009; Srisurichan et al., 2006).

In this case, the membrane diffusion coefficient is calculated using equation:

$$K_m = 1.064 \frac{r\varepsilon}{\tau\delta}\left(\frac{M}{RT}\right)^{0.5} \text{ [19]}$$

where ε is the fractional void volume, δ is the membrane thickness, τ is the tortuosity, M is the molecular weight of water, R is the gas constant and T is the absolute temperature.

On the other hand, when the pore size is relatively large, the molecule–molecule collisions are more frequent and molecular diffusion is responsible for mass transfer through the membrane pores (Khayet and Matsuura 2011).

$$K_m = \frac{1}{Y_{ln}}\frac{D\varepsilon}{\tau\delta}\frac{M}{RT} \text{ [20]}$$

where Y_{ln} is the log mean of mole fraction of air and D is the diffusion coefficient.

Both models were successfully applied for predicting the mass transfer through the membrane in MD applications (Babu et al., 2006; Bandini and Sarti 1999; Chen et al., 2009; Lawson and Lloyd 1996b; Nagaraj et al., 2006b; Srisurichan et al., 2006).

5. Operating parameters

5.1 Feed concentration

Permeate flux decreases with an increase in feed concentration. This phenomenon can be attributed to the reduction of the driving force due to decrease of the vapour pressure of the feed solution and exponential increase of viscosity of the feed with increasing concentration. The contribution of concentration polarization effects is also known, nevertheless, this is very small in comparison with temperature polarization effects in the case of MD (Lagana et al., 2000; Pabby et al., 2009).

In concentration process of fruit juices, the SSC is typically increased up to 65–75% to achieve chemical and microbiological stability. As it is well known, MD and OD can handle feed solutions at high concentrations without suffering the large drop in permeability observed in other pressure-driven membrane processes (i.e. reverse osmosis); therefore can be preferentially employed whenever elevated permeate recovery factors or high retentate concentrations are requested (Curcio and Drioli 2005; Li and Sirkar 2005; Schofield et al., 1990).

5.2. Feed temperature

Numerous investigations have been carried out on the effect of the feed temperature on permeate flux in MD. In general, an exponential increase of the MD flux has been proposed with the increase of the feed temperature (Bui and Nguyen 2006; Ding et al., 2008; Nagaraj et al., 2006b; Onsekizoglu et al., 2010a). As the driving force for membrane distillation is the difference in vapour pressure across the membrane, the increase in temperature increases the vapour pressure of the feed solution, thus results an increase in the transmembrane vapour pressure difference.

Several MD researches have proposed working under high feed temperatures in order to improve internal evaporation efficiency (the ratio of the heat that contributes to evaporation) and the total heat exchanged from the feed to the permeate side. Nevertheless, in the case of fruit juice concentration, quality losses and formation of unfavorable compounds (i.e. hydroxymethyl furfural and furan) due to high operation temperatures, restricts the temperature levels (Ciesarova and Vranova 2009; Crews and Castle 2007; Onsekizoglu et al., 2010b). In addition, as feed temperature increases, temperature polarization effect becomes more significant. (Moon et al., 2011).

5.3. Feed flow rate & stirring

In MD, the increase in flow and/or stirring rate of feed increases the permeate flux. The shearing forces generated at high flow rate and/or stirring reduces the hydrodynamic boundary layer thickness and thus reduce polarization effects. Therefore, the temperature and concentration at the liquid–vapour interface becomes closer to the corresponding values at the bulk feed solution (Winter et al., 2011). Onsekizoglu et al. (2010a) studied the effects of various operating parameters on permeate flux and soluble solid content of apple juice during concentration through OD and MD processes. They revealed that the effect of feed flow rate on transmembrane flux was only about half of the influence of temperature difference across the membrane. The effect of flow rate on MD flux becomes more noticeable at higher temperatures especially associated with higher temperature drop across the membrane (Walton et al., 2004). Consequently, higher productivity can be achieved by operating under a turbulent flow regime. On the other hand, the liquid entry pressure of feed solution (LEP) must be taken into account in order to avoid membrane pore wetting when optimizing feed flow rate (Hwang et al., 2011; Khayet et al., 2006).

5.4. Permeate temperature

The increase in permeate temperature results in lower MD flux due to the decrease of the transmembrane vapour pressure difference as soon as the feed temperature kept constant. It is generally agreed upon that the temperature of cold water on the permeate side has smaller effect on the flux than that of the feed solution for the same temperature difference. This is because the vapour pressure increases exponentially with feed temperature (Alklaibi and Lior 2005; El-Bourawi et al., 2006).

5.5. Permeate flow rate

The increase in permeate flow and/or stirring rate reduces the temperature polarization effect. Consequently, the temperature at the gas/liquid interface approaches to the bulk temperature at the permeate side. This will tend to increase driving force across the membrane; resulting an increase in MD flux (Courel et al., 2000; Hongvaleerat et al., 2008). It is important to note that as the permeate used in MD is distilled water and is the hypertonic salt solution in OD; the extent of the effect of flow rate is more prominent in the latter configuration. This is because of the contribution of concentration polarization effects on permeate side in OD.

6. Challenges & recent developments

MD and OD have been proposed as very challenging technologies for concentration of fruit juice allowing to overcome the drawbacks of conventional thermal evaporation encountered by application of high temperatures (Ali et al., 2003; Bui and Nguyen 2005; Cisse et al., 2005; Pabby et al., 2009; Shaw et al., 2002; Vaillant et al., 2001). However besides the lack of commercially available MD modules, low transmembrane flux in comparison with RO appears to be the major limitations for industrial use. Numerous studies have been performed to reduce polarization effects and to enhance transmembrane flux including cooperation of MD with other membrane processes as well as novel MD module design approaches. An overview of the current applications for fruit juice concentration and some of mentioned attempts to improve MD performance will be discussed in this section.

The preliminary study of effective concentration of orange juice by MD was presented by Calabro et al. (1994) using a microporous PVDF membrane. Barbe et al. (1998) investigated

nine types of hydrophobic microporous membranes for their retention of various volatile components in concentration of liquid foods (model aqueous solutions, Gordo grape juice and Valencia orange juice) by OD. It was observed that membranes having relatively large surface pore sizes allowed higher retention of organic volatiles due to the increase in the thickness and hence resistance of the boundary layer at the pore entrance. Alves and Coelhoso (2006) compared MD and OD in terms of water flux and aroma retention in model orange juice. A higher retention per amount of water removal was observed with OD together with higher flux values. Very recently, Bagger-Jorgensen et al. (2011) evaluated the potential of SGMD and VMD configurations for recovery of black currant and cherry juice aroma compounds. The influence of the sweeping gas flow rate (SGMD only), feed temperature and feed flow rate on the permeate flux and the concentrations factors of 12 selected aroma compounds were examined on an aroma model solution and on black currant juice in a laboratory scale set-up. At 45 °C the most volatile and hydrophobic aroma compounds was obtained with the highest concentration factors: 12.1–9.3 (black currant juice) and 17.2–12.8 (model solution). A volume reduction of 13.7% (vol.%) at 45 °C, 400 L/h, resulted in an aroma recovery of 73–84 vol.% for the most volatile compounds in black currant juice.

It has been well-established that the combination of MD with other membrane technologies offers important benefits over stand alone use of MD in the concentration of various types of juices including grape juice (Rektor et al., 2007), pineapple juice (Hongvaleerat et al., 2008), kiwi fruit juice (Cassano and Drioli 2007), camu-camu juice (Rodrigues et al., 2004), sugar-cane juice (Nene et al., 2004) and cactus pear (Cassano et al., 2007) juice. The integration of MD with other membrane operations such as MF, UF, RO and OD permits advantage of achieving high

quality fruit juice concentrates with higher economic feasibility through improved transmembrane flux and recovery factors. Each process is unique and contributes particular advantages to the integrated system design.

UF is a powerful method for removing natural polymers (polysaccharides, proteins) that could increase the viscosity of the feed stream through the MD process. For example, pretreatment of grape juice by UF has been shown to result in an increased flux during subsequent concentration of permeate by OD. The flux increase has been attributed to a reduction in the viscosity of the concentrated juice membrane boundary layer due to protein removal (Bailey et al., 2000). Lukanin et al. (2003) have evaluated the use of an enzymatic pretreatment step prior to UF of apple juices. The protein level which tend to deposit on the hydrophobic surface during subsequent OD process, have been shown to decrease significantly. Such a deposition improves membrane wetting and can eventually result in a convective flow of liquid through the membrane, which is not allowable in the MD process. Onsekizoglu et al. (2010b) have proposed the use of membrane processes for the production of clarified apple juice concentrate. The efficiency of UF was improved by an additional enzymatic pretreatment and flocculation step using fining agents such as gelatine and bentonite. The permeate coming from the UF with initial TSS contents of ca. 12 °Brix were subsequently concentrated up to TSS contents of 65 °Brix by MD, OD and coupled operation of MD & OD processes. The effect of clarification and concentration processes on formation of 5-hydroxymethylfurfural (HMF), retention of bioactive compounds (phenolic compounds, organic acids, glucose, fructose and sucrose) and their efficiency in preserving natural color and aroma (trans-2-hexenal, the most relevant compound in apple juice aroma) were evaluated in order to maintain a high quality product. The new

membrane based concentration techniques have been reported to be very efficient since the concentrated juice presented nutritional and sensorial quality very similar to that of the original juice especially regarding the retention of bright natural color and pleasant aroma, which were considerably lost during thermal evaporation. Further analysis have shown that the subsequent concentration treatments by MD, OD and coupled operation of MD & OD processes did not induce any significant changes in phenolic compounds, organic acids and sugars independently on the final concentration achieved.

RO or Forward osmosis (FO) processes, however have been proposed as a pre-concentration step before OD or MD to reduce processing costs. High quality fruit juice concentrates can be produced economically in this manner. (Martinetti et al., 2009; Nayak and Rastogi 2010; Wang et al., 2011). The combination of RO and OD processes for clarification and concentration of citrus (orange and lemon) and carrot juices have been proposed by Cassano et al. (2003). A limpid phase has been produced by ultrafiltration pilot unit. The clarified permeate coming from UF has been concentrated up to 15-20 °Brix by RO with a laboratory scale unit. Finally, OD step was applied to yield 60-63°Brix concentrate with a transmembrane flux of $1kg/m^2h$. A slight decrease in the total antioxidant activity has been reported during RO treatment, whereas no significant change was observed during OD treatment. Kozak et. al (2009) investigated an integrated approach for black currant juice concentration. The juice samples were prefiltered by MF and preconcentrated to 22°Brix by RO. A further concentration of the retentate coming from RO was obtained by MD and black currant concentrate with 58.2 °Brix was produced. The combined use of RO and OD processes was also evaluated by Vaillant at al. (2005) for concentration of melon juice, by Galaverna et al. (2008) for concentration of blood orange juice,

by Cabral et al. (2011) for concentration of Acerola juice. It is worth mentioning that in all the previously mentioned studies, a clarification pretreatment step mainly (i.e. ultrafiltration of microfiltration) is involved in order to improve both RO and OD flux.

The coupled operation of MD and OD processes is another promising approach to improve transmembrane flux and thus achieving high quality fruit juice concentrate. In this case, osmotic solution is cooled and the feed solution is slightly heated in order to provide additional driving force. Belafi-Bako & Koroknai (2006) compared MD, OD and coupled operation of OD and MD in terms of flux and final soluble solid concentration in sucrose model solutions and apple juice. Higher water flux and SSC values were achieved with coupled operation confirming an increase in driving force. More recently, Onsekizoglu (2011) proposed the use of a coupled membrane process capable of concentrating pomegranate juice under very mild conditions. The pomegranate juice was clarified by ultrafiltration in a cross-flow membrane filtration unit (MWCO: 100 kDa). The clarified juice then concentrated by coupled operation of OD and MD, in which the feed solution is gently heated ($30.0\pm2.0°C$) and the osmotic solution ($CaCl_2.H_2O$) is slightly cooled ($10.0\pm1.0°C$). The final step yielded a concentration of the clarified juice with an initial SSC of 17°Brix up to 60-62°Brix. The experiments have proven that the driving forces were added in coupled operation, which resulted in enhanced water flux during the operation, thus the coupled process was determined to be more effective.

One of the limitations of MD applications for concentration of fruit juices, especially for the those containing oily constituents (such as limonene in orange juice), is the possibility of membrane wetting due to high affinity of hydrophobic membrane material with such compounds. Coating of membrane with hydrophilic polymers such as polyvinyl alcohol

(Mansouri and Fane 1999) and alginate (Xu et al., 2004) has been proposed to overcome this problem. Recently, Chanachai et al. (2010) studied the coating of hydrophobic membrane PVDF with chitosan, a highly hydrophilic polymer, for protection against wetting by oils from fruit juice. The results indicated that the coated membrane well protected the membrane against wetting-out and could maintain stable flux. Coated membranes used to concentrate the oil solution (limonene 2%, v/v) for 5 h were not wetted out during flux measurement and no visual damage was observed indicating the stability on the base membrane.

7. Long-term performance

Membrane fouling & cleaning procedures

Membrane fouling refers to the loss of membrane performance due to deposition of suspended or dissolved substances on the membrane surface and/or within its pores. There are several types of fouling in the membrane systems including inorganic fouling or scaling, particulate/colloidal fouling, organic fouling and biological fouling (biofouling) (Gryta 2008). Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates, such as calcium salts ($CaCO_3$, $CaSO_4$), and magnesium carbonates on membrane surface or within pore structure. Precipitates are formed when the concentration of these sparingly soluble salts exceeds their saturation concentrations. Particulate/colloidal fouling is mainly associated with accumulation of biologically inert particles and colloids on the membrane surface. Organic fouling is related with the deposition or adsorption of organic matters on the pores of the membrane surface. Microbial fouling however is formed due to the formation of biofilms on membrane surfaces. Such films (bacterial, algal, or fungal) grow and release biopolymers (polysaccharides, proteins, and amino sugars) as a result of microbial activity (Pabby et al., 2009).

Even though the general agreement is that the fouling phenomena is significantly lower than those encountered in other pressure-driven membrane separation processes, it is one of the major drawbacks in membrane distillation (Gryta 2005b). The extensive research on membrane fouling has revealed that the efficiency of MD installation can be reduced by more than 50 percent after 50–100 h of process operation due to the presence of fouling effects. In fact, all of the known types of fouling have been determined to occur practically in MD operations (Gryta 2008).

Kullab & Martin (2011) pointed out that fouling and scaling may result pore clogging in MD membranes, leading to a decrease in effective membrane area, and therefore the permeate flux. Moreover, the flow channel area may be reduced resulting higher temperature polarization due to the pressure drop across the membrane. The increased deposition of the foulant species at the membrane surface would eventually lead to an increase in the pressure drop to levels that the hydrostatic pressure may exceed the LEP of the feed or permeate solution into the membrane pores. Therefore the hydrophobic surface of membrane can be partially wetted due to very small nature of the flow channels in MD modules (especially in hollow fiber membrane modules) (El-Bourawi et al., 2006).

Gryta (2005a) presented the results of the over 3 years' time research on the direct contact membrane distillation applied for production of the demineralised water using commercial capillary PP membranes. It was found that the membrane was thermally stable, maintaining its morphology and its good separation characteristics throughout the 3 years of DCMD operation. When using permeate of the RO system as DCMD feed solution, membrane pore wetting was not observed; and the DCMD flux was found to be similar to the initial permeate flux. However, precipitation of $CaCO_3$ on the membrane surface was observed when tap water was used directly

as a feed. A partial wetting of the membrane was found in this case resulting in a decrease of the permeate flux from 700 to 550 L/m^{2}day. However, the formed deposit was removed every 40–80 h by rinsing the module with a 2–5 wt% HCl solution, permitting the recovery of the initial process efficiency. On the other hand, authors reported that a multiple repetition of this operation resulted in a gradual decline of the maximum flux of permeate.

Ding et al. (2008) investigated the fouling resistance in concentrating traditional Chinese medicine (TCM) extract by DCMD. The observed permeate flux decline was attributed to membrane fouling introducing additional thermal resistance in the boundary layer. No considerable membrane wetting due to TCM deposition on the membrane surface was detected.

The membranes used in MD require regular periodic membrane cleaning to remove membrane fouling and keep the permeability loss within a given range. Durham & Nguyen (1994) evaluated the effectiveness of several cleaning agents for OD membranes fouled by tomato paste. The microporous PTFE and cross-linked acrylic-fluoroethane copolymer membranes were used in the study. The cleaning regime was determined by the membrane surface tension. The most effective cleaner for membranes with a surface tension greater than 23 mN/m was determined as 1% NaOH; however, hydrophobic integrity of these membranes was destroyed during repeated fouling/cleaning trials. On the other hand, P3 Ultrasil 56 was the most effective one for membranes with a surface tension less than 23 mN/m. Water vapour flux was maintained and no salt leakage during repeated fouling/cleaning trials were determined.

Bubbling seems to be an obvious strategy to induce flow and improve shear stress at the membrane surface to control polarization and fouling. Ding et al. (2011) successfully employed the intermittent gas bubbling method to reduce fouling layer formed in concentrating TCM

extract through DCMD. To limit membrane fouling or flux decline during concentrating process, intermittent gas bubbling was introduced to the feed side of membrane module. It was confirmed by experimental results that membrane fouling was effectively controlled in the way of removing deposited foulants from membrane surface by created two phase flow.

As can be concluded from the expressed results, most of the performed fouling studies so far examined fouling and scaling in seawater desalination or wastewater treatment applications. There is a lack of data and understanding of fouling phenomena in MD for fruit juice concentrate processing. However, the risk of fouling and wetting of membrane pores compromises the durability of the membranes limiting their applications in this field. The long term MD performance needs to be extensively studied so as to make the MD process more challenging in fruit juice industry.

9. Concluding remarks and future prospects

As a promising alternative to replace conventional thermal evaporation process, MD and its variants have gained much interest for achieving superior quality fruit juice concentrate with lower energy requirement. Although MD applications have been known for more than 40 years, a number of problems exist when they are considered for industrial implementation. Most of the conducted MD studies are still in the laboratory scale. In recent years, some pilot plant studies have been proposed for desalination (Blanco et al., 2011; Farmani et al., 2008; Song et al., 2008; Xu et al., 2006), however long term evaluations of pilot plant applications for the concentration and recovery of aqueous solutions containing volatile solutes especially in the food industry are still scarce. Therefore, achievement of high concentration levels in certain fruit juice samples taking into account the effects on mass and heat transfer mechanisms, membrane characteristics

and the quality parameters together with a detailed economical analysis should be examined on a large scale.

On the other hand, there is a lack of commercially available MD units; practically all membrane modules are designed for other membrane operations (i.e. microfiltration) rather than MD. Novel membranes specifically designed for MD applications should be fabricated in an economically feasible way. Research on transmembrane flux enhancement (i.e. acoustic field) for large scale applications is required. More attention should be paid to the possibility of integrating MD to other separation techniques in order to improve the efficiency of the overall system and to make the process economically viable for industrial applications. For fruit juice concentration, coupled operation of MD and OD seems promising to overcome high temperature related problems (i.e. aroma and colour loss) encountered in MD.

The ability to effectively operate at low temperatures makes MD possible to utilize low-grade waste and/or alternative energy sources. In recent years, coupling MD with solar, geothermal and waste energy systems has been proposed to decrease energy consumption in desalination systems. Such approach may be crucial for food processing systems. For example, in the case of fruit juice concentration, much lower temperatures should be applied in order to obtain stable products able to retain as much possible the uniqueness of the fresh fruit, its original color, aroma, nutritional value and structural characteristics. Thus, the possibility of operating under very mild conditions enables MD to utilize various alternative energy sources, making it more promising for industrial application. Further efforts need to be concentrated in this field, especially in utilization of waste energy and/or other renewable energy sources in the view of industrial implementation.

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Table 1. Critical surface tension values of some polymers (Krevelen and Nijenhuis 2009; Oliver 2004; Pabby et al., 2009)

Polymer	Surface tension (Dynes/cm)
Polytetrafluoroethylene (PTFE)	19
Polyvinylidenefluoride (PVDF)	25
Polypropylene (PP)	29
Polyethylene (PE)	31
Polyvinyl alcohol (PVA)	37
Polysulfone (PS)	41
Polycarbonate (PC)	45
Polyurethane (PU)	45

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Table 2. Contact angle values of some materials in water at ambient temperature (Khayet and

Matsuura 2011; Sigurdsson and Shishoo 1997)

Material	Contact Angle, °
Ordinary glass	20
Polycarbonate	70
Polyamide	69
Polyethersulphone	54
Polyethylene	96
Polypropylene	100
PTFE	123
PVDF	111
Teflon	112

Table 3. List of commercial membranes commonly used by various researchers

Membrane module	Manufacturer	Trade name	Polymer	Membrane thickness (μm)	Nominal pore size (μm)	Porosity (%)	References
Flat sheet							
	3M Corporation	3MA	PP	91	0.29	66	(Kim and Lloyd 1991; Lawson et al., 1995; Lawson and Lloyd 1996a)
		3MB	PP	81	0.40	76	
		3MC	PP	76	0.51	79	
		3MD	PP	86	0.58	80	
		3ME	PP	79	0.73	85	
	Gelman	TF1000	PTFE/PP	60	0.1	80	(Khayet et al., 2004b; Martinez et al., 2002; Rodrigues et al., 2004)
		TF450	PTFE/PP	60	0.45	80	
		TF200	PTFE/PP	60	0.20	80	
		TF 200	PTFE/PP	178	0.20	80	
		TF 200	PTFE/PP	165	0.20	60	
	Milipore	Durapore	PVDF	110	0.45	75	(Banat and Simandl 1999; Ding et al., 2003; Khayet et al., 2004b; Phattaranawik et al., 2003b)
		Durapore	PVDF	100	0.20	70	
		GVHP	PVDF	125	0.20	80	
		GVHP	PVDF	125	0.22	75	
		HVHP	PVDF	116	0.45	66	
	Sartorious		PTFE	70	0.20	70	(Phattaranawik et al., 2003b; Warczok et al., 2007)
	Gore		PTFE	64	0.20	90	(Garcia-Payo et al., 2000; Izquierdo-Gil et al., 1999; Phattaranawik et al., 2003b)
			PTFE	77	0.45	89	

Table 3. List of commercial membranes commonly used by various researchers (continued)

Membrane module	Manufacturer	Trade name	Polymer	Membrane thickness (µm)	Nominal pore size (µm)	Porosity (%)	References
Flat sheet							
	Osmonics		PP	150	0.22	70	(Cath et al., 2004)
			PTFE	175	0.22	70	
			PTFE	175	0.45	70	
			PTFE	175	1.0	70	
	Hoechst Celanese	Celgard 2400	PP	28	0.05	45	(Barbe et al., 2000; Mengual et al., 1993)
		Celgard 2500	PP	25	0.02	38	
	Enka	Accurel 1E-PP	PP		0.25	25	(Mengual et al., 1993; Narayan et al., 2002)
		Accurel 2E-PP	PP		0.48	90	
Capillary	Membrana	Accurel S6/2	PP	450	0.20	73	(Celere and Gostoli 2004; Gryta 2007)
		Accurel Q3/2	PP	400	0.20	70	
	Self-designed		PP	800	0.40	73	(Gryta et al., 2000)
	Memcor	PV 375	PVDF	125	0.20	75	(Bui et al., 2004)
		PV 660	PVDF	170	0.20	64	
Hollow fiber							
	Hoechst-Celanese	Liqui-Cel® Extra-Flow 2.5×8 in	PP	180		40	(Bailey et al., 2000)
			PP	53	0.074	50	
			PP	50	0.044	65	
			PP	47	0.056	42	

FIGURE CAPTIONS

Figure 1. Schematic representation of MD configurations

ACCEPTED MANUSCRIPT
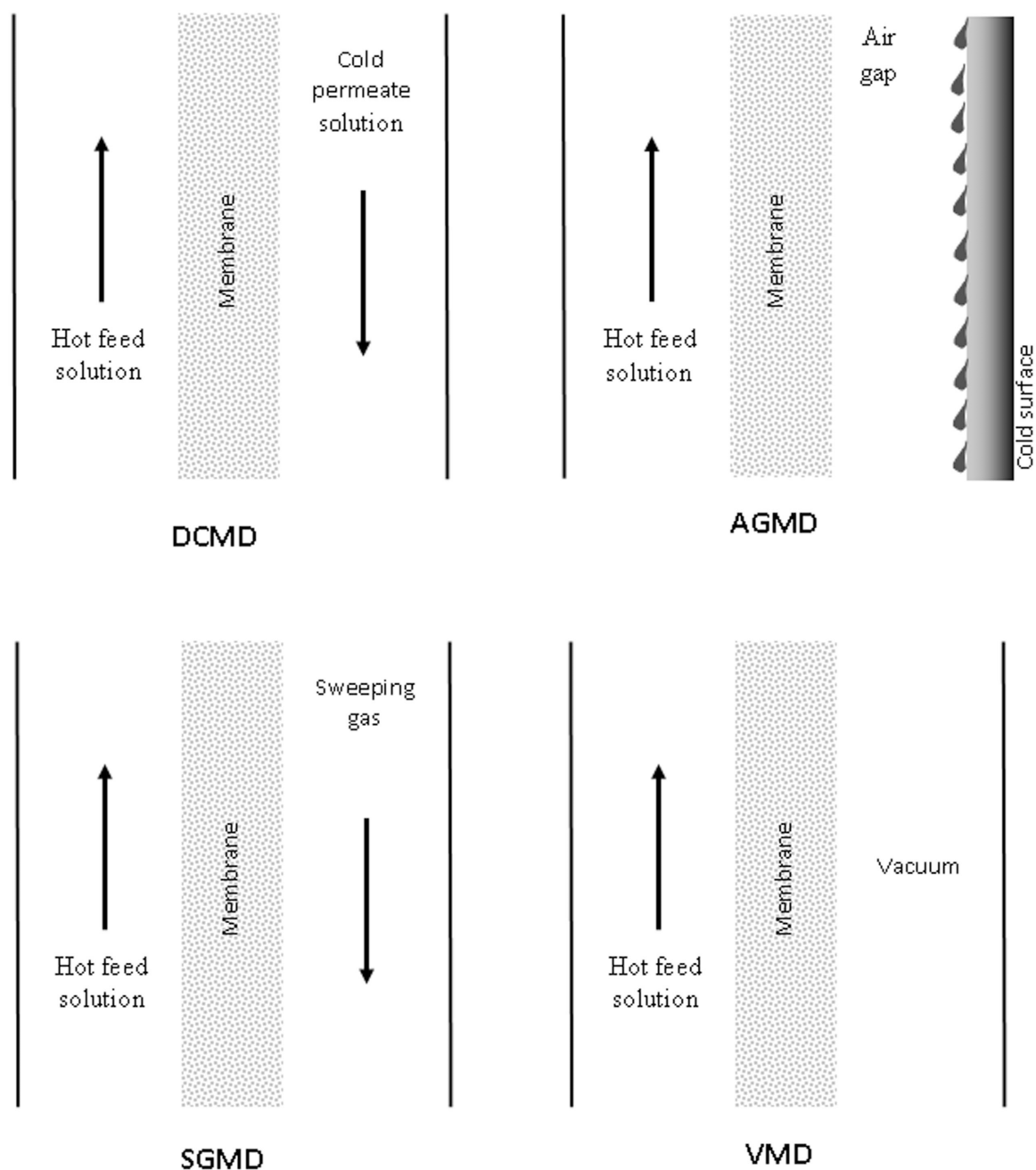
Figure 2. Schematic representation of contact angle

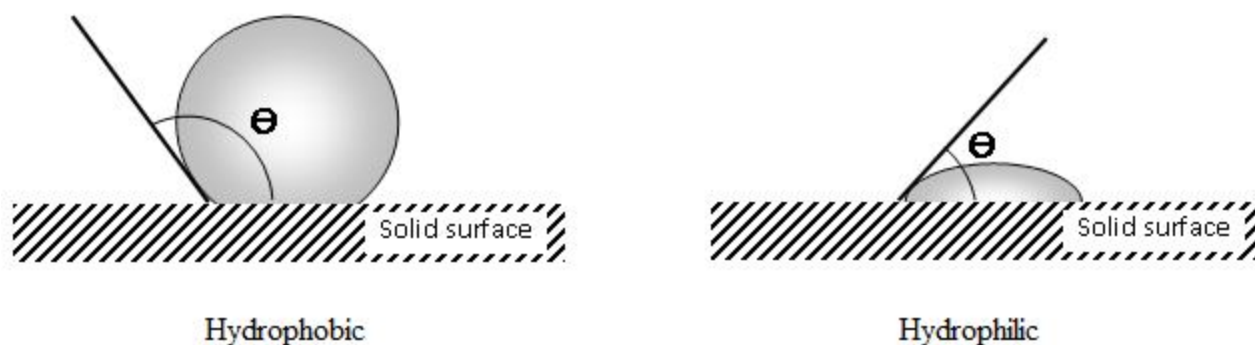
Hydrophobic   Hydrophilic

Figure 3. Schematic diagram of temperature polarization in MD. T_{fm}, T_{pm}, T_{fb} and T_{pb} are membrane surface temperatures and fluid bulk temperatures at the feed and permeate sides, respectively.
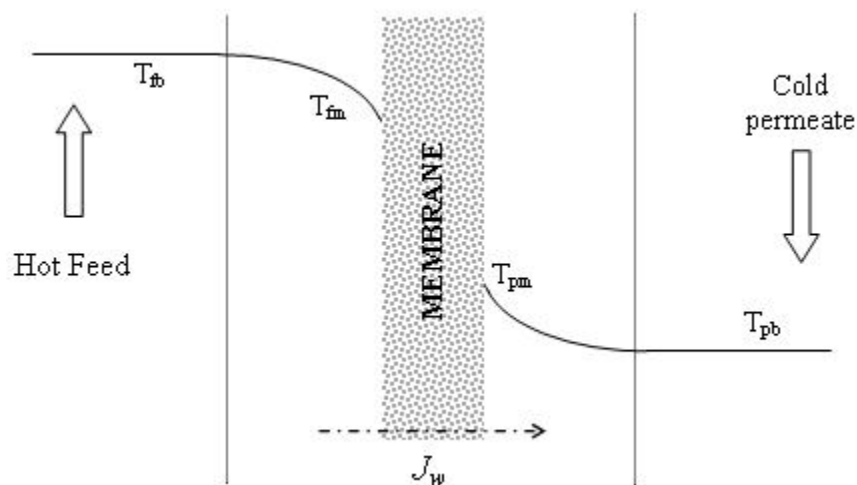
Figure 4. Schematic diagram of concentration polarization in OD. C_{fm}, C_{pm}, C_{fb} and C_{pb} are membrane surface and bulk solute concentrations at the feed and permeate sides, respectively.
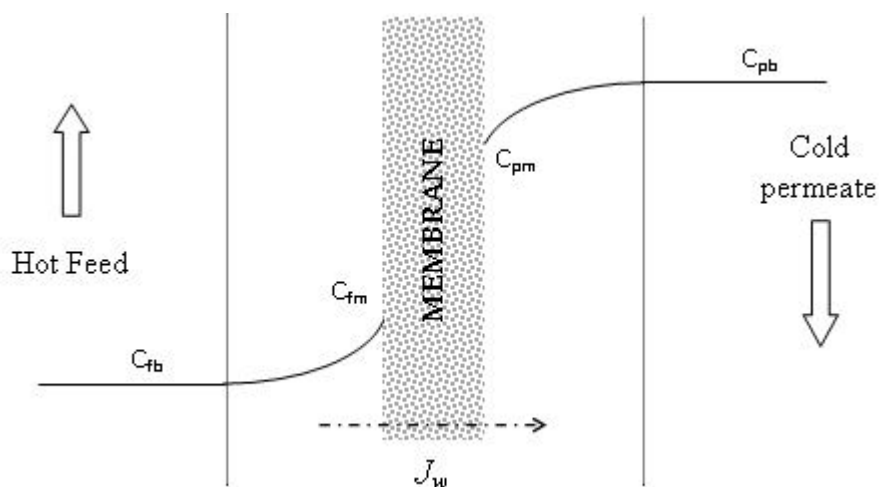

Figure 5. Mass transfer mechanism involved in water vapour transport through pores of MD module: [a] Knudsen diffusion; [b] molecular diffusion .

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