Chapter

Membrane Distillation: Basics, Advances, and Applications

Mohammad Reza Shirzad Kebria and Ahmad Rahimpour

Abstract

Membrane technology as an emerging separation process has become competitive with other separation techniques in recent decades. Among pressure-driven and isothermal membrane processes, membrane distillation (MD) as a thermally driven process has come out to put an end to hardships of such processes like distillation. MD process can be used in a wide variety of applications such as desalination and wastewater treatment. Generally, MD is a process which water is a main component of the feed solution and only water vapor can pass through a hydrophobic membrane pores. With four main configurations different from each other by their condensation procedure, the performance of MD process is limited due to the lack of appropriate module, membrane, and energy consumption rate. In recent years, many experiments have been carried out to find well-suited membrane type and module. Also, applying solar or waste heat as heat source and the capability of coupling with other processes like forward osmosis and osmotic distillation distinguish MD process from other membrane processes. This chapter addresses membrane characteristics, MD applications, transport mechanisms, and process challenges.

Keywords: separation process, membrane distillation, desalination, hydrophobic membrane

1. Introduction to history and fundamentals of membrane distillation (MD)

1.1 Brief introduction to history

When the term membrane distillation (MD) is the subject of discussion, traditional thermal distillation process comes to mind, unconsciously. In fact, MD and thermal distillation are temperature-dependent processes in which work is based on vapor-liquid equilibrium (VLE) and needs heat source to be supplied to attain the requisite latent heat of vaporization of the feed solution. To avoid misapprehensions, a workshop was held in Rome on May 5, 1986, in order to find a unique name for a process previously known by different names such as transmembrane distillation, thermo-pervaporation (PV), and membrane evaporation. Terminology committee consisted of six different members including V. Calabro (Universita della Calabria, Calabria, Italy), A.C.M. Franken (Twente University of Technology, Enschede, Netherlands), S. Kimura (University of Tokyo, Tokyo, Japan), S. Ripperger (Enka Membrana, Wuppertal, Germany), G. Sarti (Universita di

Bologna, Bologna, Italy), and R. Schofield (University of New South Wales, Kensington, Australia) who chose membrane distillation term for a distillation process in which two sides of membrane (liquid and gas phases) are detached by a porous membrane [1]. Generally, MD must be referred for nonisothermal membrane separation process in which the driving force is partial pressure difference induced by temperature gradient across the membrane that fulfills the following properties: (i) high porosity, (ii) high wetting resistance, (iii) does not change the VLE of the species, (iv) separates liquid and gas phases, and (v) condensation must not occur in membrane pores.

For the first time, on June 3, 1963, MD process was defined by Bodell to which he filed US patent describing an apparatus producing potable water from impotable aqueous mixture [2]. He invented an apparatus which was impermeable to water molecules but permeable to water vapor molecules. After Bodell's invention, on 1967, new findings were reported by Weyl (filed on May 14, 1964) to which he recorded a US patent describing an improved apparatus for recovery of water from impotable salty water [3]. Unlike Bodell who used silicon rubber as membrane (0.64 mm outer diameter and 0.30 mm inner diameter), Weyl used a polytetrafluoroethylene (PTFE) membrane (average pore size of 9 mm) to produce potable water. He also stated other hydrophobic polymers such as polyethylene (PE) and polyvinyl chloride (PVC), and also hydrophilic polymers coated by hydrophobic materials can be applicable for fabrication of MD membranes. After recording of the first MD patent, it took 4 years to publish the first MD paper by Findley on 1967 in the international journal *Industrial & Engineering Chemistry Process Design Development* [4]. Findley used different types of materials to fabricate MD membrane such as gumwood, aluminum foil, cellophane, and glass fibers. He also used silicone and Teflon to make the membranes more hydrophobic. According to the MD experimental results, some of the membranes fabricated by Findley had intra-pore condensation or intra-layer moisture adsorption. Based on his experimental

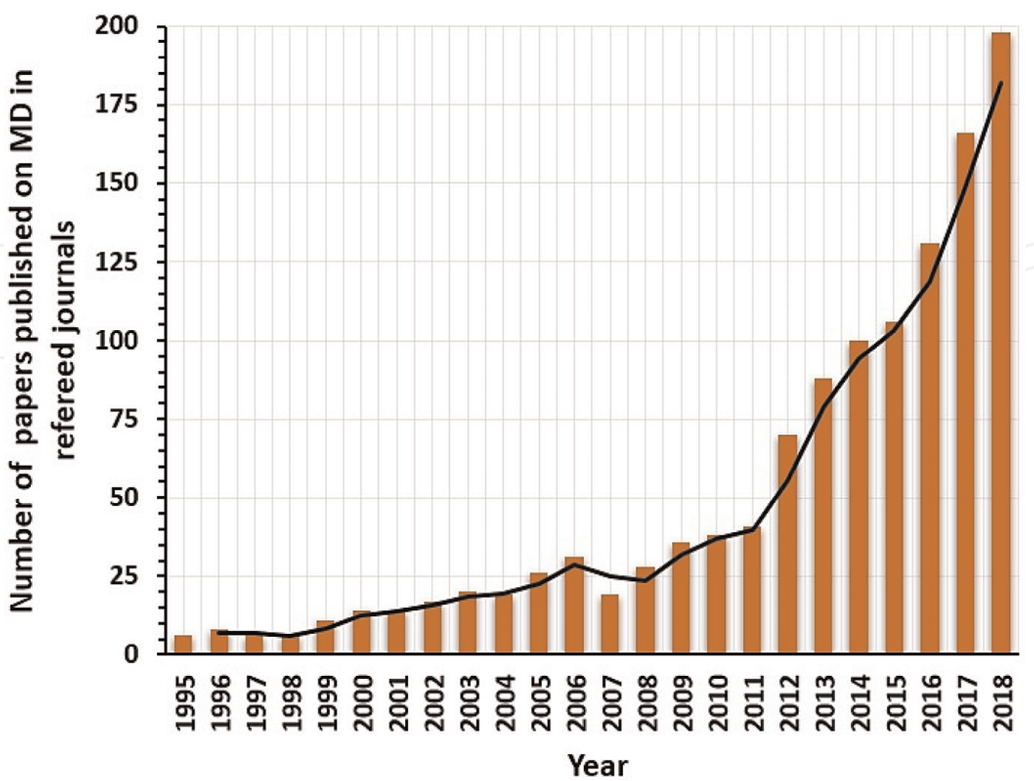

Figure 1.
Research interest on membrane distillation up to December 31, 2018, represented as a plot of number of papers published in refereed journals per year.

findings, Findley stated the highest efficiency will be achieved on high temperatures along with using low-cost membranes. After short couple of years, research interest on MD decreased unexpectedly due to lower obtained MD flux than other separation methods such as reverse osmosis (RO). After staying in shadows for several years, MD garnered attention once again in the early 1980s due to advances in membrane manufacturing techniques. Gore and Associated Co. [5], the Swedish National Development Co. [6, 7], and Enka AG [8–10] were the first to commercialize developed generation of MD membranes. Esato et al. developed a biologically inert membrane oxygenator which is later commercialized under the name Gore-Tex membrane distillation as spiral wound module [11]. Also, plate and frame membrane module was used by the Swedish National Development Co. in air gap membrane distillation (AGMD). In 1984 during the holding of Europe-Japan Joint Congress on Membranes and Membrane Processes, Enka presented the results of their direct contact membrane distillation (DCMD) experiments applying polypropylene (PP) hollow fiber membranes [12].

From an industrial viewpoint, MD has attracted little attention, yet, due to its rate of productivity which is not competitive enough compared with other industrial technologies. On the contrary, research interest in MD has grown considerably within the academic community. The number of MD publications in referred journals has increased almost 40 times in 2018 since 1995. **Figure 1** shows growth rate of MD publications from 1995 to 2018.

1.2 Fundamental of MD

MD is a well-suited technology for separation processes in which water is the major component of the feed solution. In MD, at least one side of a microporous hydrophobic membrane is in direct contact with an aqueous solution. Partial pressure difference induced by temperature gradient between two sides of membrane causes mass transfer through membrane pores. During MD process, liquid molecules are not allowed to infiltrate due to the hydrophobicity of the membrane, and only water vapor molecules are able to pass through the membrane walls. Based on partial pressure difference, evaporation of volatile compounds occurs; the vapor molecules pass across the pores and are condensed/evacuated on the permeate side of the membrane. Various MD configurations are applied to maintain the driving force on two sides of the membrane [13]. However these configurations can only be distinguished by their condensation procedure (**Figure 2**).

i. A condensing fluid (usually pure water) colder than feed stream flows across the permeate side of the membrane by means of circulating pump. At the time, the volatile component (water or volatile organic compounds) evaporates at the hot liquid/vapor interface, passes through the pores, and condense in the condensing fluid inside the MD cell. This type of configuration is known as direct contact membrane distillation due to direct contact between condensing fluid and the membrane surface. Among various MD configurations, DCMD is the most extensively investigated due to its ease of setup in laboratory scale and higher permeate flux than other configurations. Generally, DCMD is an appropriate method for desalination or production of fruit juice in which water is the main permeate component [14].

ii. In this configuration, vacuum is applied in the permeate side of the module by vacuum pumps in which vapor molecules are sucked out through membrane pores. To maintain driving force, the applied vacuum pressure must be lower than the saturation pressure of volatile components separating from the hot

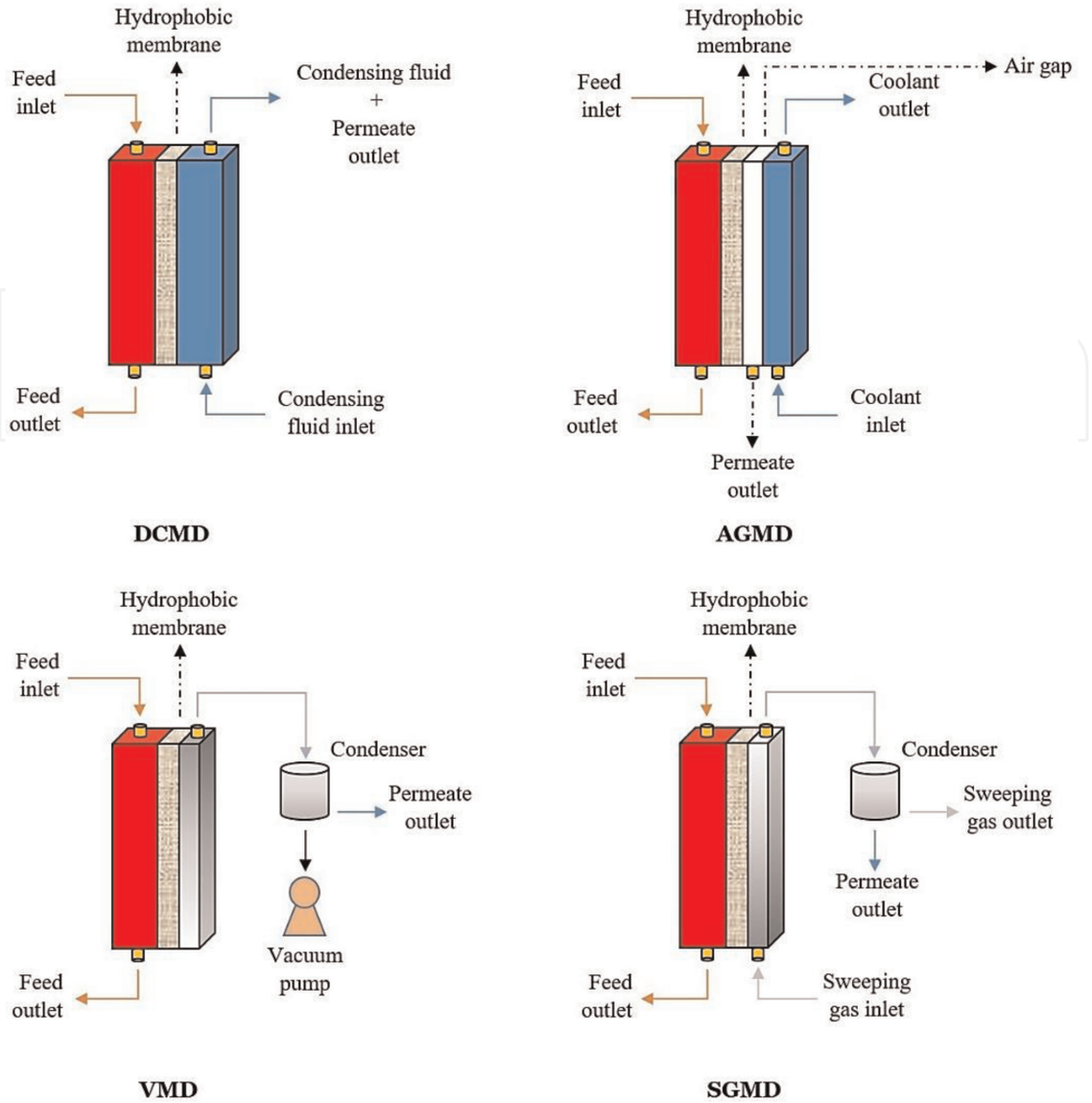

Figure 2.
Schematic of various MD configurations.

feed solution. In this type of MD, condensation occurs outside of the condensing chamber by means of an external condenser. This type of configuration is known as vacuum membrane distillation (VMD) due applied vacuum in the permeate side of the module.

iii. A stagnant air layer is placed between the permeate side of the membrane and condensing wall to reduce heat loss by conduction. In this configuration, vapor molecules pass across both the membrane wall and air layer and eventually condense over a cold surface of condensing wall inside the MD cell. At last, condensed component exits from the condensation chamber by the use of the gravity. This type of configuration is called air gap membrane distillation.

iv. In sweeping gas membrane distillation (SGMD), a cold inert gas is blown into the condensation chamber and sweeps permeated vapor molecules taking them out of the MD cell. In this method, condensation just like VMD takes place outside the module. Due to heat transfer between hot permeated vapor and blown inert gas, the temperature of sweeping gas increases continuously

MD configuration	Application area	Advantages	Disadvantages
Direct contact membrane distillation (DCMD)	• Seawater desalination • Crystallization • Treatment of dye effluents • Arsenic removal from aqueous solution	• High permeate flux • Considered at commercial scale	• High conductive heat loss
Vacuum membrane distillation (VMD)	• Seawater desalination • Treatment of alcoholic solution • Recovery of aroma compounds • Treatment of textile wastewaters	• High permeate flux • Considered at commercial scale	• High risk of membrane pore wetting • Process complexity
Air gap membrane distillation (AGMD)	• Seawater desalination • Concentration of fruit juices • Separation of azeotropic mixtures • VOC removal	• Low conductive heat loss • Process simplicity • Low risk of temperature polarization (TP)	• Lower flux than DCMD and VMD
Sweeping gas membrane distillation (SGMD)	• Brackish water desalination • Separation of azeotropic mixtures • Wastewater treatment • VOC removal	• Reduction of the barrier to the mass transport through forced flow	• High risk of temperature polarization (TP) • Process complexity

Table 1.
Properties of various MD configurations.

along the condensing chamber length. To minimize the effect of heat transfer between hot and cold stream, a cold wall is improvised in the permeate side of the module. This recently introduced method is called thermostatic sweeping gas membrane distillation (TSGMD). **Table 1** presents details of various MD configurations.

2. MD membranes fabrication techniques and design

2.1 Membrane fabrication

As stated earlier, the main characteristics of MD membrane are porosity and hydrophobicity. MD membrane can be supported and unsupported and also might

be fabricated in the form of single-layer membrane, composite dual-layer membrane (hydrophobic/hydrophilic), and composite triple-layer membrane (hydrophobic/hydrophilic/hydrophobic). The surface mean pore size of the membrane applied in MD is between 100 Å and 1 μm.

Generally, MD membranes can be fabricated by track etching, sintering, phase inversion, electrospinning, etc. Among these procedures, phase inversion is the most applied method. Also, several types of membranes are fabricated by combining the abovementioned methods. In 2013, Zhu et al. fabricated novel hollow fiber membrane by combining extrusion, sintering, and stretching [15]. Phase inversion method is based on solidification of a homogenous polymeric solution by such several procedure such as non-solvent-induced phase separation (NIPS), evaporation-induced phase separation (EIPS), thermally induced phase separation (TIPS), and vapor-induced phase separation (VIPS) in a controlled way [16]. NIPS and TIPS are the most commonly used techniques to fabricate MD membranes. In NIPS method, the polymer is dissolved in appropriate solvent, and then the polymeric solution is casted on a glass plate or non-woven support. After casting, the polymeric film is immersed into the non-solvent bath. After a while, two phases are formed: a polymer-rich phase and a solvent-rich phase. Solvent/non-solvent exchange continues until the whole polymer component becomes solid. To fabricate membranes by TIPS technique, a solution containing polymer/diluent must be prepared and then is casted via favorable procedure. After precipitation of polymer component by cooling method, diluent extraction causes pore formation [17–20]. In recent years, electrospinning technique has been suggested by many researchers to prepare well-suited MD membranes [21–23]. To prepare electrospun nanofibrous membranes (ENMs), a polymeric solution must be poured into a needle-equipped syringe. Electrospinning apparatus consists of a high-voltage electric source, needle-equipped syringe, syringe pump, and a collector. After overcoming the surface tension, polymeric jet is directed toward a collector (often rotating drum) in the shape of cylindrical nanofibers. To obtain uniform membrane structure, syringe pump has axial movement [13]. The schematic of electrospinning process is shown in **Figure 3**. The properties of commercial membranes used in MD are presented in **Table 2**.

2.2 MD module design

Membrane modules are one of the most important parts of MD process which control the operation parameters. Different types of MD module are manufactured so far especially for each kind of MD configurations. MD module must possess

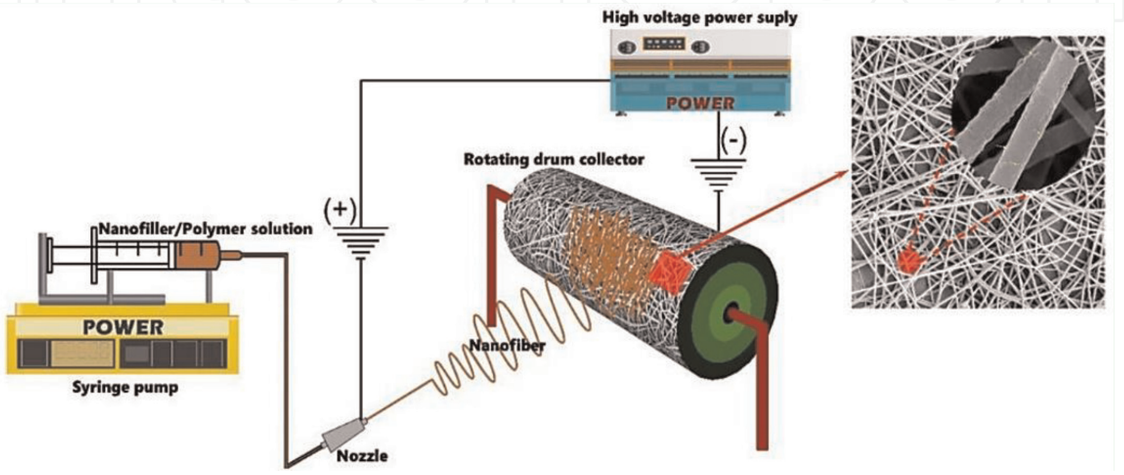

Figure 3.
Schematic of electrospinning process. Source: Reprinted from [24].

Membrane commercial code	Membrane type	Producer	Material	Porosity (%)	Membrane thickness (μm)	Reference
TF200	Flat sheet	Gelman	PTFE/PP	80	178	[25]
GVHP	Flat sheet	Millipore	PVDF	70–75	110	[26]
MD020TP2N	Tubular	Enka Microdyn	PP	75	1550	[27]
Celgard X-20	Tubular	Hoechst Celanese Co.	PP	35	25	[28]
G-4.0-6-7	Flat sheet	Gore-Tex Sep GmbH	PTFE	80	100	[29]
PP 50/200	Hollow fiber	Accurel Membrana	PP	0.5	200	[30]
3 MA	Flat sheet	3 M Corporation	PP	60	91	[31]

Table 2.
Commercial membranes recently used in MD.

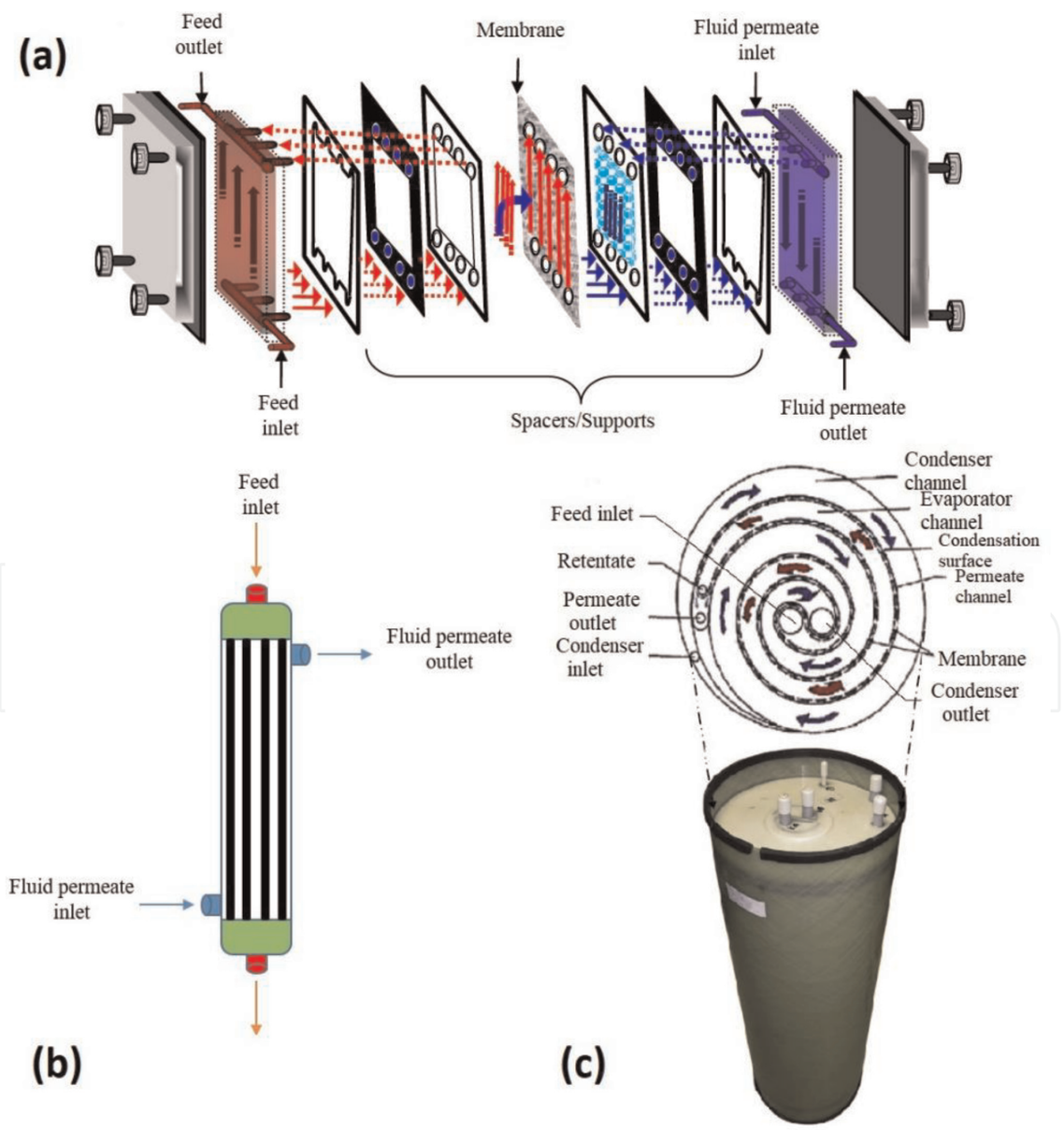

Figure 4.
Different MD modules: (a) plate and frame, (b) capillary, and (c) spiral wound. Source: Reprinted from [32].

Module producer	Effective membrane area (m^2)	Membrane material	Permeate flux (kg/m^2h)	MD configuration	Type of module	Reference
SEP GmbH	4	PTFE	2.5–12.5	DCMD	Spiral	[34]
GE Osmonics SEPA CF	0.014	PTFE	22.3	DCMD	Plate and frame	[35]
Microdyn	0.1	PP	3.6	VMD	Capillary	[36]
Enka-Microdyn	0.036	PP	4	DCMD	Tubular	[37]
Scarab development AB	2.8	PTFE	6.5	AGMD	Plate and frame	[38]
Microdyn	0.1	PP	13	DCMD	Hollow fiber	[37]

Table 3.
Commercial MD modules with different configurations.

required characteristics such as high packing density; high mechanical strength and chemical and thermal stability; low pressure drop; low heat loss; and user-friendly (for cleaning or membrane replacement). As presented in **Figure 4**, MD modules are divided into three major groups including plate and frame, spiral wound, and capillary (**Figure 4**).

i. Plate and frame module is the simplest one among all MD modules. It consists of a series of flat sheet membranes, spacers, and supports which are connected in axial direction. This type of MD module has shown good potential for commercialization due to its tangential flow in which the liquid stream is in direct contact with the membrane surface.

ii. In spiral wound module, supported or unsupported flat sheet membranes are wrapped around a central tube in a spiral formation. Spiral wound module can provide tangential flow and represent high surface to volume ratio which makes it the desirable choice for applying in MD process.

iii. Capillary modules are divided into three main categories: (1) capillary modules, (2) tubular modules, and (3) hollow fiber modules. Capillary, tubular, and hollow fiber membranes are distinguished by their inner and outer diameter which effects on their packing density. The membranes with diameter ranging from 5 to 25 mm are classified as tubular membranes (packing density 300 m^2/m^3). Capillary membranes often have pores with diameter between 1 and 3 mm (packing density 1200 m^2/m^3). The diameters of hollow fiber membranes are usually below 1 mm (packing density 500–9000 m^2/m^3) [33]. These types of membranes are typically assembled and bundled in shell and tube modules. **Table 3** summarizes some MD modules used in desalination process.

3. MD membrane characteristics

MD membranes should have such characteristics to show their best performance in MD process. Before conducting MD tests, the applied membranes must be

characterized by different methods to abstain from wetting during experiments. MD membrane characterization techniques are as follows: liquid entry pressure (LEP), porosity, thermal conductivity, water contact angle, and membrane thickness.

3.1 Liquid entry pressure (LEP)

To abstain from membrane wetting, the MD membrane should have three major properties, simultaneously: high water contact angle, high hydrophobicity, and narrow pore size distribution. However, membrane wetting may take place and effect on membrane performance when the feed solution is in direct contact with membrane surface. When the hydraulic transmembrane pressure oversteps LEP, aqueous solution components will prevail over the surface tension and wet membrane pores. Generally, LEP is the maximum pressure value applied onto the feed solution to be treated before the membrane pore wetting happens. Based on Cantor-Laplace equation, the LEP value depends on surface contact angle (θ), surface tension (γ_L), geometric coefficient (β), and maximum pore radius (r_{max}) [39]:

$$LEP = \frac{-2\beta\gamma_L cos\theta}{r_{max}} \tag{1}$$

As can be comprehended from Cantor-Laplace equation, increasing in surface contact angle or decreasing of maximum pore size will enhance LEP value.

3.2 Porosity

Porosity of MD membranes must be as high as possible until the wetting phenomenon does not occur. Porous surface can lead to higher permeate flux. Generally, the ratio of free volume to total volume of the membrane is called porosity. In MD, the ratio between the macrovoid volume and total volume of the membrane is calculated by gravimetric procedure [40]. This technique is based on measuring membrane weights applying a wetting liquid such as 2-propanol, which goes inside the pores, and weighing the membrane before and after wetting:

$$\varepsilon = \frac{(W_W - W_D)/\rho_{wl}}{[(W_W - W_D)/\rho_{Al}] + W_D/\rho_P} \tag{2}$$

where W_W, W_D, ρ_{wl}, and ρ_P are the weights of wet and dry membrane and the density of wetting liquid and hydrophobic polymer.

3.3 Water contact angle

Tendency of membrane surface to be wetted by liquids is often measured by liquid contact angle analysis. In MD, because water is the major component of the feed solution, water contact angle is calculated for determining surface tendency to water droplets. In this technique, the angle between water droplet and membrane surface is calculated. To minimize the errors of calculation, various locations of membrane surface are selected randomly, and the average contact angle is reported as water contact angle. It should be noted that the effect of mean pore size and surface roughness should be considered to specify the exact water contact angle.

3.4 Thermal conductivity

Thermal conductivity of MD membranes must be as low as possible. Heat loss in various MD configurations is attributed to the membrane material and existed gases in the membrane pores. Increasing in thermal conductivity could reduce mass flux which is undesirable for MD process. Since the water vapor thermal conductivity is one order of magnitude lower than polymeric materials to be used in MD, increasing membrane surface porosity could lead to heat loss reduction. So, the presence of macrovoids in the membrane surface will result in reducing thermal conductivity. As stated above, the thermal conductivity of MD membranes is related to both thermal conductivity of polymer (k_p) and gases (k_g):

$$k = \varepsilon k_g + (1 - \varepsilon) k_p \tag{3}$$

It is worth mentioning that most of the polymers used in MD membranes possess similar conductivity value. For example, thermal conductivity of PP, PTFE, and PVDF is about 0.11–0.16 (W/m^2 K), 0.25–0.27 (W/m^2 K), and 0.17–0.19 (W/m^2 K), respectively [41].

3.5 Membrane thickness

The membrane thickness is one of the most effective characteristics on MD membrane performance. The membrane thickness and membrane permeate flux are inversely related to each other. As the membrane becomes thinner, the permeate flux enhances due to the reduction of mass transfer resistance. On the other hand, when the membrane thickness increases, the heat loss decreases. So, there is a trade-off between advantage (lower heat loss) and disadvantage (lower permeate flux) of thicker membrane. It should be noted that the effect of membrane thickness in AGMD on mass transfer can be passed up, because the stagnant air layer controls mass transfer rate.

4. MD process conditions

The effects of various operational parameters on MD performance must be controlled to achieve the best results. Some of these parameters are as follows: (i) feed temperature, (ii) feed concentration, (iii) membrane type, (iv) feed flow rate, and (v) long operation.

4.1 Feed temperature

The feed temperature has a powerful effect on the permeate flux. Based on the Antoine equation, by increasing the temperature, the vapor pressure increases exponentially. So, the permeate flux will increase exponentially by increasing of the temperature [42]. When the temperature difference between the feed and permeate side of the membrane is kept constant, the distillate flux will enhance when the temperature of the feed side increases, which means the vapor pressure is more dependent to the higher temperature. In other words, the increase in vapor pressure gradient when the hot fluid temperature increases is more than the time which the cold fluid temperature decreases. Also, some researchers found out that increasing the temperature difference between the feed and permeate side of the membrane will increase diffusion factor positively [43–45].

4.2 Feed concentration

When the feed concentration increases, the permeate flux will decrease considerably due to the reduction of vapor pressure and increment of temperature polarization. Generally, when NaCl solution concentration was increased from 0 to 2 mol, about 12% decline was observed in permeate flux [45]. In fact, reduction of vapor pressure induced by concentration increment caused distillate flux reduction. Also, researchers demonstrated that there are three reasons for flux decline as a result of increasing feed concentration, reduction of water activity, reduction of mass transfer coefficient caused by concentration polarization, and reduction of heat transfer coefficient caused by decline in membrane surface temperature [46].

4.3 Membrane type

As discussed earlier, MD membranes should have porous surface with high mean pore size. The distillate flux is proportional to the surface pore size and porosity and inversely proportional to the thickness of the membrane and pore tortuosity. Also, membranes must present high LEP value to prevent membrane wetting. Furthermore, unsupported membranes with a certain pore size showed higher flux than supported membranes with the same pore size [47].

4.4 Feed flow rate

The effects of feed flow rate on SGMD are negligible, while it is considerable in DCMD and VMD. In general, increasing of feed flow rate leads to permeate flux increment. This is due to the improved mixing and the reduction of temperature boundary layer thickness on the feed side of the membrane. By increasing feed flow rate, the laminar flow regime turns into a turbulent regime, and the distillate flux reaches asymptotic values [48]. In fact, by increasing of feed flow rate, Reynolds number and heat transfer coefficient increase which lead to the reduction of temperature polarization.

4.5 Longtime operation

MD membranes must show stable performance during experiments for days and months. Actually, membrane stability is the most important challenge in MD commercialization. Several experiments showed after membrane compaction, the permeate flux increased at initial hours of the tests [49–51]. Then, the flux was reduced until reaching a steady state. Partial pore wetting and fouling were conveyed as reasons for the flux reduction during longtime MD experiments [46].

5. Transport mechanisms

5.1 Heat transfer

Measurement of heat transfer in MD is extremely complicated because of simultaneous heat and mass transfer. Based on the principal theory of heat transfer, a thermal boundary layer is formed at a fluid/solid interface with different temperatures. In MD module, a hot fluid is in direct contact with solid surface (membrane, with a thickness of δ) in which the thermal boundary layer will be formed adjacent to the membrane surface. Due to the existence of temperature gradient in MD module, two boundary layers will be formed on the feed side (with a thickness of δ_F)

and the permeate side (with a thickness of δ_P) of the hydrophobic membrane. Inside the thermal boundary layer, the feed temperature reduces from T_{bF} (feed bulk) to T_{mF} (membrane surface). Also, the permeate temperature increases from T_{bP} (permeate bulk) to T_{mP} (membrane surface). Since MD process depends on vaporization of a component, the latent heat should be transitioned from feed bulk to the membrane surface through the thermal boundary layer. Heat transfer coefficient (h_F) plays a key role in heat transfer across the boundary layer. So, the heat flux between the feed bulk and membrane surface is defined as

$$q_F = h_F(T_{bF} - T_{mF}) \tag{4}$$

When vaporization takes place at the membrane surface, the latent heat is transferred to the permeate side of the membrane with vapor stream:

$$q_L = N \times \Delta H_{vap} \tag{5}$$

where N (mol/m^2 K) is the vapor flux through the membrane pores, ΔH_{vap} (J/mol) is the latent heat of vaporization, and q_L (W/m^2) is the heat transferred because of volatile component evaporation. There are some other types of heat transfer in MD process including heat transfer via gas-filled pores (q_m) and heat transfer across the permeate side of the membrane (q_P):

$$q_m = h_m(T_{mF} - T_{mP}) \tag{6}$$

where h_m is the heat transfer coefficient of the membrane which depends on both the heat transfer coefficient of membrane material and the gas which fills the membrane pores. So, the heat transfer mechanism in MD process consists of three different steps: (i) heat transfer through the thermal boundary layer at the feed side, (ii) heat transfer through the membrane, and (iii) heat transfer through the thermal boundary layer at the permeate side.

5.2 Mass transfer

In general, mass transfer mechanism in MD consists of three major categories including Knudsen flow theory, viscous flow theory, and molecular diffusion theory. In MD, surface penetration is ignored because the penetration area of membrane matrix is much lower than the volume of the pores [46]. Moreover, as is stated earlier, MD membrane material has low affinity to water molecules. So, the contribution of transport through the membrane matrix can be ignored. The key parameter to recognize the governing mass transfer mechanism in MD module is Knudsen number (Kn) which is determined as

$$Kn = \frac{\lambda_i}{d_p} \tag{7}$$

where λ_i is the mean free path of the transferred vapor molecules through the pores with a size of d_p. When the Knudsen number is greater than one, the possibility of collisions between vapor molecule and pore wall is more than the collisions between vapor molecule and another one. In this case, the permeability through the membrane pores when a uniform pore size $d_{p,m}$ is assumed can be calculated from the following Equation [29]:

$$\beta_{k,m} = \frac{2}{3}\frac{\varepsilon d_{p,m}}{\tau\delta}\left(\frac{2}{\pi MRT}\right)^{0.5} \tag{8}$$

where ε, τ, and δ are membrane porosity, membrane tortuosity, and membrane thickness, respectively. When the Knudsen number is lower than 0.01, molecular diffusion is the governing mass transfer mechanism, and the membrane permeability is defined as [26]

$$\beta_{M,m} = \frac{\pi}{4RT}\frac{PD}{P_{air}}\left(\frac{{d_{p,m}}^2}{\tau\delta}\right) \tag{9}$$

where P, D, and P_{air} represent the total pressure within a pore, the diffusion coefficient, and air pressure within a pore, respectively. When hydrostatic pressure is used over a membrane owning pores with greater size than mean free path, viscous flow will be the governing mass transfer mechanism. In this situation, the possibility of collisions among vapor molecules is more than the collisions between vapor molecule and pore wall. When a uniform pore size $d_{p,m}$ is assumed for the membrane pores, the permeability can be measured with the following equation [44]:

$$\beta_{V,m} = \frac{\varepsilon}{32RT}\frac{P_m}{\mu}\left(\frac{{d_{p,m}}^2}{\tau\delta}\right) \tag{10}$$

where μ and P_m are the viscosity of transferred vapor molecules and average pressure of the pores.

6. MD applications

MD is going to be an attractive technology for separation processes due to its unique properties. Dealing with water as a key component of chemical and physical processes and high separation factor are the most attractive characteristics of MD technology. Nowadays, MD is used in environmental, food, pharmaceutical, and nanotechnology industries. Also, MD can be used as a single-step process or can be combined with other separation techniques as a last stage [52]. Some applications of MD are the following:

1. Desalination of seawater, brackish water, groundwater, and brines brought from other units.

2. Industrial wastewater treatment including radioactive waste treatment, concentration of nonvolatile acids, volatile acid recovery from industrial effluents, salt recovery by membrane distillation crystallization (MDC), and textile industry effluents.

3. Preparation of distilled water, pure water, and ultrapure water for medical and pharmaceutical purposes.

4. Production of liquid food concentrates such as mandarin juice, sucrose solution, whey, and apple juice.

5. Volatiles removal from fruit juice, alcohols, halogenated VOCs, and benzene by VMD and SGMD.

6. Dealcoholization of fermented beverages and enhanced ethanol production using DCMD.

The most important MD application is desalination of wastewaters including high percentage of salt molecules in order for safe discharge into the environment or to produce drinkable, pure, and ultrapure water. The theoretical 100% rejection of nonvolatile solutes, colloids, and biological matters by MD guarantees the elimination of all unwanted solutes that are often existing in water sources. The treated water by MD shows an electrical conductivity as low as 800 μS/cm with total dissolved solids (TDS) of 0.6 ppm [53].

7. Process challenges

The principal challenges of MD process are temperature polarization, concentration polarization (CP), and fouling of contaminants on the membrane surface. These challenges must be controlled to avoid underperformance in MD process. One of the most undesirable problems in MD is temperature polarization in which the temperature gradient is created between bulk feed and membrane surface at liquid/vapor interface. In fact, by vaporization of a component, liquid bulk temperature decreases, while vapor temperature increases instead. This phenomenon causes a reduction of temperature difference leading to permeate flux decline. Temperature polarization coefficient (TPC) is often defined as the ratio of boundary layer resistance to the total heat transfer resistance:

$$TPC = \frac{T_{mF} - T_{mP}}{T_{bF} - T_{bP}} \tag{11}$$

where superscripts m and b specify the temperature near the membrane surface and bulk. Based on scientific reports, a reasonable value for TPC to design MD systems lies between 0.4 and 0.7 [54]. Concentration polarization is another problem in MD process. When evaporation occurs, the solute concentration near the membrane surface becomes greater than that of the bulk feed. Similar to the temperature polarization effect, the concentration cannot be measured due to the simultaneous heat and mass transfer. Concentration polarization coefficient (CPC) is often defined as the ratio of the solute concentration near the membrane to the solute concentration in the bulk feed:

$$CPC = \frac{C_{mF}}{C_{bF}} \tag{12}$$

Fouling of contaminants on the membrane surface is also a problem in MD process. Although fouling has lower effect on MD than other pressure-driven membrane processes, it often causes underperformance in membrane process. Fouling and contaminant deposition on membrane surface cause the reduction of effective membrane area and membrane wetting resulting in distillate flux decline and low rejection. So, to reach maximum efficiency in MD process, the effects of these problems should be reduced as much as possible.

8. Recent developments and innovations in hybrid MD systems

MD can be combined with other membrane technologies such as RO, microfiltration (MF), and nanofiltration (NF) as well as common distillation systems (i.e., multistage flash (MSF)) and low-cost energy sources [55]. These hybrid systems will offer high-quality products and lower energy consumption both in the system installation and the discharging concentrated brine. In fact, MD hybrid systems are beneficial if they can rectify other system disadvantages.

Generally, MD hybrid systems can be divided into two major groups: (i) integrated MD systems with membrane processes and (ii) integrated MD systems with other processes. The combination of MD with ultrafiltration (UF) for treatment of oily wastewater was investigated by Gryta et al. [56]. DCMD was applied as final purification technique after UF. The hot UF permeate entered into the DCMD cell linked in parallel form. The MD permeate is collected outside the chamber, and the oil concentrate is returned to the UF modules as feed. The product collected from the UF module commonly contains less than 5 ppm of oil. An additional distillation process over the UF permeate leads to a complete elimination of oil from wastewater with a high removal percentage of 99.9% for total dissolved solids. As an another hybrid system, MD was integrated with RO for desalination by Drioli et al. [57]. MD was suggested to desalinate RO brine (75 g/l) at a temperature of 35°C to improve both efficiency and water recovery. Since MD is less sensitive to brine concentration than RO, more potable water can be obtained by RO/MD hybrid system. The results showed that the recovery factor of hybrid system was about 87% which was higher than that of MD (77%) and RO (40%). There are also some reports about using NF/MD and PV/MF/MD hybrid systems to produce high-quality products [53, 58].

As stated earlier, MD can be integrated with other chemical and physical separation processes. Gryta et al. studied the performance of hybrid bioreactor/MD system to produce ethanol [59]. The fermentation of sugar with *Saccharomyces cerevisiae* (commonly known as baker's yeast) results in the formation of by-products, which can be eliminated by MD. This integration leads to improve the efficiency of sugar conversion to ethanol. The results of the fermentation tests with and without integration with MD process corroborated the advantages of the fermentation carried out with continuous elimination of fermented products by the MD module. One of the interesting characteristics of MD process is its flexibility to use renewable energy source such as nuclear power and solar energy for heating the feed solution [60, 61]. Khayet et al. investigated the possibility of nuclear desalination by DCMD coupled with a nuclear reactor [62]. The results of experiments confirmed the feasibility of water desalination by consuming the heat and electricity generated in nuclear power plant. From the stated examples of MD hybrid systems, it is clear that all of the investigation was in laboratory or pilot scale. So, more investigation must be performed in order to remove the obstacles from commercialization of MD hybrid systems.

9. Economics and energy consumption in MD

As it was stated throughout this chapter, MD process requires an energy source for heating the feed to a specific temperature. The ability of coupling with renewable energy sources such as solar and geothermal energy or industrial waste heat converts MD from expensive laboratory scale process to beneficial industrial one. So, especially in desalination, the water production cost (WPC) will decrease by applying a low-cost energy source. It is worth mentioning that current seawater

Separation process	Production rate	Energy consumption (kWh/m^3)	Reference
RO standard	105,000 m^3/day	4.5	[63]
SPMD	5–27 l/m^2 h	200–300	[64]
AGMD	5.2 l/m^2 h	1	[65]
VMD	0.71 l/m^2 h	3.2	[66]
Brackish water RO (BWRO) with photovoltaic (PV) panels	0.2 m^3/day	1.3	[67]
Solar still	2–6 l/m^2 day	640	[68]

Table 4.
Estimated energy consumption of different separation processes used in desalination.

desalination capacity is about 27 million m^3/day which only meets 3% of freshwater demand. In fact, WPCs for industrial units are less than \$1/m^3, whereas it may vary between \$1/m^3 and 3/m^3 small-scale units. While solar energy-based processes are typically expensive due to the high capital cost, they could slowly become competitive with conventional energy sources in the future. It must be noted that even though the WPCs of solar-powered MD (SPMD) are considerably high, it could be an interesting alternative for water production in remote areas. Generally, lower energy consumption or using low-cost energy sources would reduce the WPC. **Table 4** summarizes energy consumption of different separation processes.

10. Conclusion and future prospects in MD

After several decades of persistent investigation for understanding the concept of MD and its difficulties, there are still many obstacles that must be eliminated for industrialization. Based on recent development, MD process is able to be used in a vast variety of applications such as desalination and wastewater treatment. Although MD process still suffers from some problems which limited its performance such as high-energy consumption, longtime operation, wetting and fouling, and lack of appropriate module, different reports have been presented to enhance permeate flux and solute retention and decrease energy consumption in MD process, including developed membrane modules and hybrid MD systems. So far, the effects of MD operational parameters have been studied over and over, but some areas related to commercialization field are still overlooked or investigated scarcely. Therefore, a vigorous motivation is required for research on the neglected areas such as membrane module design or scale-up variables both in experimental and modeling fields in which the obtained experimental data will be *extremely* beneficial.

Nomenclature

MD	membrane distillation
VLE	vapor-liquid equilibrium
PV	pervaporation
PTFE	polytetrafluoroethylene
PE	polyethylene

PVC	polyvinyl chloride
RO	reverse osmosis
AGMD	air gap membrane distillation
DCMD	direct contact membrane distillation
PP	polypropylene
VOCs	volatile organic compounds
VMD	vacuum membrane distillation
SGMD	sweeping gas membrane distillation
TSGMD	thermostatic sweeping gas membrane distillation
NIPS	non-solvent induced phase separation
EIPS	evaporation induced phase separation
TIPS	thermally induced phase separation
VIPS	vapor induced phase separation
ENMs	electrospun nanofibrous membranes
LEP	liquid entry pressure
Kn	Knudsen number
MDC	membrane distillation crystallization
TDSs	total dissolved solids
TP	temperature polarization
CP	concentration polarization
TPC	temperature polarization coefficient
CPC	concentration polarization coefficient
MF	microfiltration
NF	nanofiltration
MSF	multistage flash
UF	ultrafiltration
WPC	water production cost
SPMD	solar-powered membrane distillation
BWRO	brackish water reverse osmosis
PV	photovoltaic

Author details

Mohammad Reza Shirzad Kebria and Ahmad Rahimpour*
Department of Chemical Engineering, Babol Noshirvani University of Technology, Babol, Iran

*Address all correspondence to: ahmadrahimpour@nit.ac.ir

IntechOpen

References

[1] Smolders K, Franken A. Terminology for membrane distillation. Desalination. 1989;**72**:249-262

[2] Bodell BR. Silicone rubber vapor diffusion in saline water distillation, United States Patent Serial No. 285,032; 1963

[3] Weyl PK. Recovery of demineralized water from saline waters, United States Patent 3,340,186; 1967

[4] Findley M. Vaporization through porous membranes. Industrial and Engineering Chemistry Process Design and Development. 1967;**6**:226-230

[5] Gore D. Gore-Tex membrane distillation. In: Proc. of the 10th Ann. Convention of the Water Supply Improvement Assoc.; Honolulu, HI, USA. 1982. pp. 25-29

[6] Andersson S-I, Kjellander N, Rodesjö B. Design and field tests of a new membrane distillation desalination process. Desalination. 1985;**56**:345-354

[7] Carlsson L. The new generation in sea water desalination SU membrane distillation system. Desalination. 1983; **45**:221-222

[8] Schneider K, Hölz W, Wollbeck R, Ripperger S. Membranes and modules for transmembrane distillation. Journal of Membrane Science. 1988;**39**:25-42

[9] Schneider K, van Gassel TJ. Membrane distillation. Chemie Ingenieur Technik. 1984;**56**:514-521

[10] Van Gassel T, Schneider K. An energy-efficient membrane distillation process. In: Membranes and Membrane Processes. Boston: Springer; 1986. pp. 343-348

[11] Esato K, Eiseman B. Experimental evaluation of Gore-Tex membrane oxygenator. The Journal of Thoracic and Cardiovascular Surgery. 1975;**69**: 690-697

[12] Enka AG. Catalogue Presented at Europe-Japan Joint Congress on Membranes and Membrane Processes; Stresa, Italy; 1984

[13] Jafari A, Kebria MRS, Rahimpour A, Bakeri G. Graphene quantum dots modified polyvinylidenefluride (PVDF) nanofibrous membranes with enhanced performance for air gap membrane distillation. Chemical Engineering and Processing Process Intensification. 2018; **126**:222-231

[14] Lawson KW, Lloyd DR. Membrane distillation. II. Direct contact MD. Journal of Membrane Science. 1996;**120**: 123-133

[15] Zhu H, Wang H, Wang F, Guo Y, Zhang H, Chen J. Preparation and properties of PTFE hollow fiber membranes for desalination through vacuum membrane distillation. Journal of Membrane Science. 2013;**446**:145-153

[16] Lu W, Yuan Z, Zhao Y, Zhang H, Zhang H, Li X. Porous membranes in secondary battery technologies. Chemical Society Reviews. 2017;**46**: 2199-2236

[17] Gu M, Zhang J, Wang X, Tao H, Ge L. Formation of poly (vinylidene fluoride) (PVDF) membranes via thermally induced phase separation. Desalination. 2006;**192**:160-167

[18] Karimi H, Rahimpour A, Kebria MRS. Pesticides removal from water using modified piperazine-based nanofiltration (NF) membranes. Desalination and Water Treatment. 2016;**57**:24844-24854

[19] Kebria MRS, Jahanshahi M. Nanofiltration membrane synthesized

from polyethyleneimine for removal of $MgSO_4$ from aqueous solution. International Journal of Engineering. 2014;**27**:1173-1178

[20] Rajabzadeh S, Maruyama T, Sotani T, Matsuyama H. Preparation of PVDF hollow fiber membrane from a ternary polymer/solvent/nonsolvent system via thermally induced phase separation (TIPS) method. Separation and Purification Technology. 2008;**63**: 415-423

[21] Kebria MRS, Rahimpour A, Bakeri G, Abedini R. Experimental and theoretical investigation of thin ZIF-8/ chitosan coated layer on air gap membrane distillation performance of PVDF membrane. Desalination. 2019; **450**:21-32

[22] Kebria MS, Rahimpour A, Abedini R. Preparation and characterisation of new microporous Elvaloy4170 coated PVDF membrane for desalination by air gap membrane distillation. Micro & Nano Letters. 2019;**14**:551-555

[23] Lalia BS, Guillen-Burrieza E, Arafat HA, Hashaikeh R. Fabrication and characterization of polyvinylidenefluoride-co-hexafluoropropylene (PVDF-HFP) electrospun membranes for direct contact membrane distillation. Journal of Membrane Science. 2013;**428**:104-115

[24] Esfahani MR, Aktij SA, Dabaghian Z, Firouzjaei MD, Rahimpour A, Eke J, et al. Nanocomposite membranes for water separation and purification: Fabrication, modification, and applications. Separation and Purification Technology. 2019;**213**: 465-499

[25] Kiai H, García-Payo M, Hafidi A, Khayet M. Application of membrane distillation technology in the treatment of table olive wastewaters for phenolic compounds concentration and high quality water production. Chemical Engineering and Processing Process Intensification. 2014;**86**:153-161

[26] Martinez L, Rodriguez-Maroto JM. Membrane thickness reduction effects on direct contact membrane distillation performance. Journal of Membrane Science. 2008;**312**:143-156

[27] Khayet M. Membranes and theoretical modeling of membrane distillation: A review. Advances in Colloid and Interface Science. 2011;**164**: 56-88

[28] Drioli E, Ali A, Macedonio F. Membrane distillation: Recent developments and perspectives. Desalination. 2015;**356**:56-84

[29] Khayet M, Velázquez A, Mengual JI. Modelling mass transport through a porous partition: Effect of pore size distribution. Journal of Non-Equilibrium Thermodynamics. 2004;**29**: 279-299

[30] Li B, Sirkar KK. Novel membrane and device for direct contact membrane distillation-based desalination process. Industrial and Engineering Chemistry Research. 2004;**43**:5300-5309

[31] Moghaddam Kamrani P, Bakhtiari O, Kazemi P, Mohammadi T. Theoretical modeling of direct contact membrane distillation (DCMD): Effects of operation parameters on flux. Desalination and Water Treatment. 2015;**56**:2013-2022

[32] Tarleton ES. Chapter 3. In: Progress in Filtration and Separation. London: Academic Press; 2014. pp. 61-99

[33] Chiam C-K, Sarbatly R. Vacuum membrane distillation processes for aqueous solution treatment—A review. Chemical Engineering and Processing Process Intensification. 2013;**74**:27-54

[34] Zakrzewska-Trznadel G, Harasimowicz M, Chmielewski AG.

Concentration of radioactive components in liquid low-level radioactive waste by membrane distillation. Journal of Membrane Science. 1999;**163**:257-264

[35] Dow N, Zhang J, Duke M, Li JD, Gray SR, Ostarcevic E. Membrane Distillation of Brine Wastes; 2008

[36] Criscuoli A, Carnevale M, Drioli E. Modeling the performance of flat and capillary membrane modules in vacuum membrane distillation. Journal of Membrane Science. 2013;**447**:369-375

[37] Al-Obaidani S, Curcio E, Macedonio F, Di Profio G, Al-Hinai H, Drioli E. Potential of membrane distillation in seawater desalination: Thermal efficiency, sensitivity study and cost estimation. Journal of Membrane Science. 2008;**323**:85-98

[38] Guillén-Burrieza E, Blanco J, Zaragoza G, Alarcón D-C, Palenzuela P, Ibarra M, et al. Experimental analysis of an air gap membrane distillation solar desalination pilot system. Journal of Membrane Science. 2011;**379**:386-396

[39] Franken A, Nolten J, Mulder M, Bargeman D, Smolders C. Wetting criteria for the applicability of membrane distillation. Journal of Membrane Science. 1987;**33**:315-328

[40] Liao Y, Wang R, Tian M, Qiu C, Fane AG. Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation. Journal of Membrane Science. 2013;**425**:30-39

[41] Phattaranawik J, Jiraratananon R, Fane AG. Heat transport and membrane distillation coefficients in direct contact membrane distillation. Journal of Membrane Science. 2003;**212**:177-193

[42] Alklaibi AM, Lior N. Membrane-distillation desalination: Status and potential. Desalination. 2005;**171**:111-131

[43] Larimi YN, Mollahosseini A, Mohammadi P, Tabatabaei M. Waste polymers recycling in biodiesel as a strategy to simultaneously enhance fuel properties and recycle the waste: Realistic simulation and economical assessment approach. Biofuels. 2016;**7**: 559-570

[44] Mollahosseini A, Abdelrasoul A. Recent advances in thin film composites membranes for brackish groundwater treatment with critical focus on Saskatchewan water sources. Journal of Environmental Sciences. 2019;**81**: 181-194

[45] Qtaishat M, Matsuura T, Kruczek B, Khayet M. Heat and mass transfer analysis in direct contact membrane distillation. Desalination. 2008;**219**: 272-292

[46] Lawson KW, Lloyd DR. Membrane distillation. Journal of Membrane Science. 1997;**124**:1-25

[47] Izquierdo-Gil M, Garcıa-Payo M, Fernández-Pineda C. Air gap membrane distillation of sucrose aqueous solutions. Journal of Membrane Science. 1999;**155**: 291-307

[48] Khayet M, Godino M, Mengual J. Possibility of nuclear desalination through various membrane distillation configurations: A comparative study. International Journal of Nuclear Desalination. 2003;**1**:30-46

[49] Banat FA, Simandl J. Theoretical and experimental study in membrane distillation. Desalination. 1994;**95**:39-52

[50] Banat FA, Simandl J. Desalination by Membrane Distillation: A Parametric Study; 1998

[51] Drioli E, Wu Y. Membrane distillation: An experimental study. Desalination. 1985;**53**:339-346

[52] Van der Bruggen B. Integrated membrane separation processes for

recycling of valuable wastewater streams: Nanofiltration, membrane distillation, and membrane crystallizers revisited. Industrial and Engineering Chemistry Research. 2013;**52**: 10335-10341

[53] Karakulski K, Gryta M, Morawski A. Membrane processes used for potable water quality improvement. Desalination. 2002;**145**:315-319

[54] Schofield R, Fane A, Fell C. Heat and mass transfer in membrane distillation. Journal of Membrane Science. 1987;**33**:299-313

[55] Koschikowski J, Wieghaus M, Rommel M. Solar thermal-driven desalination plants based on membrane distillation. Desalination. 2003;**156**: 295-304

[56] Gryta M, Karakulski K, Morawski A. Purification of oily wastewater by hybrid UF/MD. Water Research. 2001; **35**:3665-3669

[57] Drioli E, Lagana F, Criscuoli A, Barbieri G. Integrated membrane operations in desalination processes. Desalination. 1999;**122**:141-145

[58] Johnson R, Sun J, Sun J. A pervaporation-microfiltration-osmotic distillation hybrid process for the concentration of ethanol-water extracts of the Echinacea plant. Journal of Membrane Science. 2002;**209**:221-232

[59] Gryta M. The fermentation process integrated with membrane distillation. Separation and Purification Technology. 2001;**24**:283-296

[60] Mollahosseini A, Abdelrasoul A, Sheibany S, Amini M, Salestan SK. Renewable energy-driven desalination opportunities—A case study. Journal of Environmental Management. 2019;**239**: 187-197

[61] Mollahosseini A, Hosseini SA, Jabbari M, Figoli A, Rahimpour A. Renewable energy management and market in Iran: A holistic review on current state and future demands. Renewable and Sustainable Energy Reviews. 2017;**80**:774-788

[62] Khayet M, Mengual J, Zakrzewska-Trznadel G. Direct contact membrane distillation for nuclear desalination, part II: Experiments with radioactive solutions. International Journal of Nuclear Desalination. 2006;**2**:56-73

[63] Meindersma G, Guijt C, De Haan A. Desalination and water recycling by air gap membrane distillation. Desalination. 2006;**187**:291-301

[64] Banat F, Jwaied N, Rommel M, Koschikowski J, Wieghaus M. Performance evaluation of the "large SMADES" autonomous desalination solar-driven membrane distillation plant in Aqaba, Jordan. Desalination. 2007; **217**:17-28

[65] Gazagnes L, Cerneaux S, Persin M, Prouzet E, Larbot A. Desalination of sodium chloride solutions and seawater with hydrophobic ceramic membranes. Desalination. 2007;**217**:260-266

[66] Cabassud C, Wirth D. Membrane distillation for water desalination: How to chose an appropriate membrane? Desalination. 2003;**157**:307-314

[67] Khayet M, Essalhi M, Armenta-Déu C, Cojocaru C, Hilal N. Optimization of solar-powered reverse osmosis desalination pilot plant using response surface methodology. Desalination. 2010;**261**:284-292

[68] Banat F, Jwaied N, Rommel M, Koschikowski J, Wieghaus M. Desalination by a "compact SMADES" autonomous solar-powered membrane distillation unit. Desalination. 2007;**217**: 29-37