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Membrane distillation: Recent developments and perspectives

Enrico Drioli [a,b,c,d,*], Aamer Ali [b,**], Francesca Macedonio [a,b]

[a] National Research Council Institute on Membrane Technology (ITM-CNR), Via Pietro BUCCI, c/o The University of Calabria, Cubo 17C, 87036 Rende, CS, Italy
[b] The University of Calabria, Department of Environmental and Chemical Engineering, Rende, CS, Italy
[c] Hanyang University, WCU Energy Engineering Department, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea
[d] Center of Excellence in Desalination Technology, King Abdulaziz University, Saudi Arabia

HIGHLIGHTS

- A research boom has been observed in the field of MD recently.
- Current developments in MD have been reviewed.
- The future perspectives have also been highlighted.

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ABSTRACT

Membrane distillation (MD) has gained significant regard from industrial and academic perspective in recent years, thus the frequency of publications related to the field has greatly accelerated. New perspectives have boosted the research activities related to deeper understanding of heat and mass transport phenomenon, novel applications and fabrication of the membranes specifically designed for MD. New efforts for module fabrication and understanding and control of non-traditional fouling in MD have also been highlighted in the recent literature. The current review summarizes the important and interesting recent developments in MD from the perspectives of membrane fabrication, heat and mass transport phenomenon, nontraditional fouling, module fabrication and applications. The future research directions of interest have also been pointed out.

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* Correspondence to: E. Drioli, National Research Council — Institute on Membrane Technology (ITM-CNR), Via Pietro BUCCI, c/o The University of Calabria, Cubo 17C, 87036 Rende, CS, Italy.
** Corresponding author.
E-mail addresses: e.drioli@itm.cnr.it (E. Drioli), aamer.ali@vscht.cz (A. Ali).

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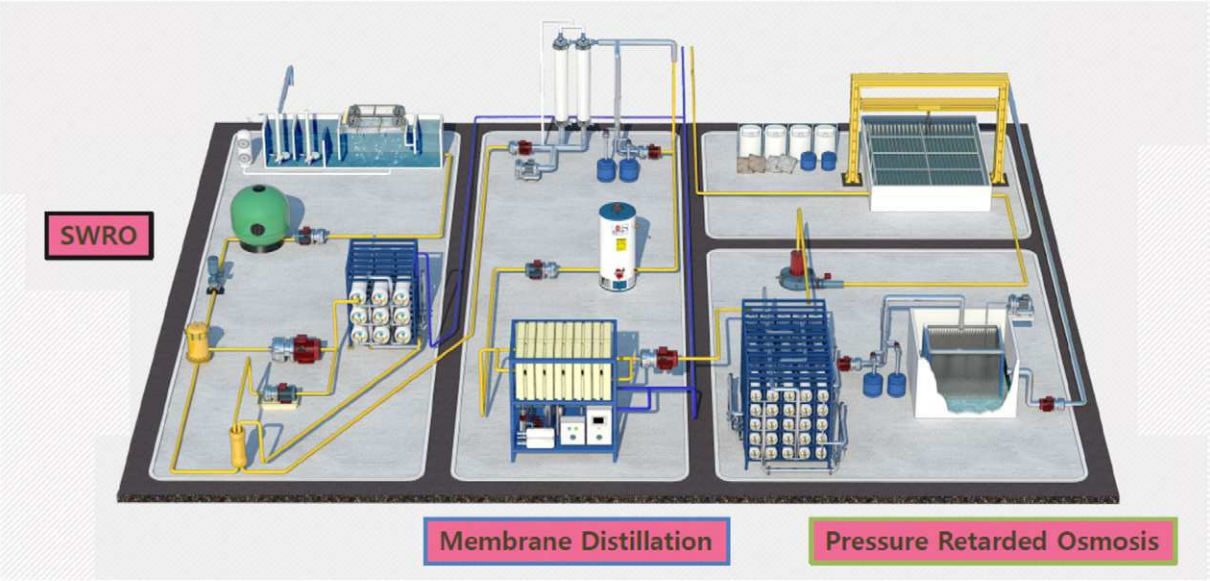


Fig. 1. A conceptual design of 3rd generation desalination scheme (www.globalmvp.org).

1. Introduction

Fresh water scarcity has emerged as a big challenge of the current era. Growing population, improved living standards, flourishing agricultural sector and industrialization have played a major role in making the problem worse. It has been estimated that more than one billion people on the earth don't have the access to clean fresh water [1]. On the other hand, conventional energy sources and fresh water reservoirs are becoming scarce quickly. Consequently, a strong need to develop less energy intensive and environment friendly water purification techniques has emerged. The overall volume of fresh water reservoirs might be enough to fulfill the current demand but unfortunately the distribution of these reservoirs does not match with population distribution across the globe. The ocean accounts for ~97% of the global water reserves whereas only ~3% is available as the fresh water the most part of which in form of glaciers and ice caps (2.06%), and a small part as ground water (0.90%) and surface/other fresh water resources (0.03%) [2,3]. Accordingly, seawater and brackish water desalination techniques have gained the popularity to fulfill the demand. As alternative to 1st generation thermal based desalination techniques, 2nd generation desalination technologies based on membrane operations (mainly reverse osmosis (RO)) gained popularity during last two decades or so [4]. Currently, RO accounts for 60% of desalination erections across the globe, thanks to its order of magnitude which requires less energy than its thermal counterparts. However, desalination technologies have to address the issue of disposal of produced brine and further decreasing of energy consumption for their sustainable growth.

To address these limitations, several other techniques are being investigated. These techniques mainly include membrane distillation (MD), forward osmosis and capacitive deionization and will be incorporated into 3rd generation desalination installations (for instance see Fig. 1 for the layout proposed by Global MVP, www.globalmvp.org). Among the main techniques under investigation, MD has gained popularity due to some unique benefits associated with the process. Conventionally, MD is based on a thermal gradient created across a microporous hydrophobic membrane and possesses the potential to concentrate the solutions to their saturation point without any significant flux-decline. At the same time, the process can be driven with waste grade heat including solar energy, geothermal energy and waste grade energy associated with low temperature industrial streams. The membrane used in MD process allows the passage of vapors only and retains all nonvolatile on retentate side, thus the product obtained is theoretically 100% pure from solid or nonvolatile contaminants [5,6]. Due to these attractive benefits, MD has emerged as a potential element of 3rd generation desalination technique to address the inherent drawbacks of conservative RO process.

Table 1
Merits and demerits of various configurations of MD.

Configuration	Pros	Cons
DCMD	The easiest and simplest configuration to realize practically, flux is more stable than VMD for the feeds with fouling tendency, high gained output ratio [8], it might be the most appropriate configuration for removal of volatile components [10].	Flux obtained is relatively lower than vacuum configurations under the identical operating conditions, thermal polarization is highest among all the configurations, flux is relatively more sensitive to feed concentration, the permeate quality is sensitive to membrane wetting, suitable mainly for aqueous solutions.
VMD	High flux, can be used for recovery of aroma compounds and related substances, the permeate quality is stable despite of some wetting, no possibility of wetting from distillate side, thermal polarization is very low.	Higher probability of pore wetting, higher fouling, minimum selectivity of volatile components [10], require vacuum pump and external condenser.
AGMD	Relatively high flux, low thermal losses, no wetting on permeate side, less fouling tendency.	Air gap provides an additional resistance to vapors, difficult module designing, difficult to model due to the involvement of too many variables, lowest gained output ratio [8].
SGMD	Thermal polarization is lower, no wetting from permeate side, permeate quality independent of membrane wetting	Additional complexity due to the extra equipment involved, heat recovery is difficult, low flux, pretreatment of sweep gas might be needed

Depending on the methods to induce vapor pressure gradient across the membrane and to collect the transported vapors from the permeate side, MD processes can be classified into four basic configurations. A common feature of all the configurations is the direct exposure of one side of the membrane to the feed solution used. Direct contact membrane distillation (DCMD) has been the most studied mode due to its inherent simplicity [7]. On the other hand, vacuum membrane distillation (VMD) can be used for high output while air gap membrane distillation (AGMD) and sweep gas membrane distillation (SGMD) enjoy the benefit of low energy losses and high performance ratio [8–10]. Some new configurations with improved energy efficiency, better permeation flux or smaller foot print have been proposed such as material gap membrane distillation (MGMD) [11], multi-effect membrane distillation (MEMD) [12], vacuum-multi-effect membrane distillation (V-MEMD) [13] and permeate gap membrane distillation (PGMD) [13]. A pros and cons analysis of conventional configurations has been explained in Table 1.

The slow progress of membrane distillation has been related with the unavailability of appropriate membranes for MD applications, high energy consumption with respect to RO, membrane wetting, low flux and limited investigations carried out on module designing. However, thanks to the recent and growing extensive research activities carried out in various areas of MD, the process has become much more attractive due to the availability of better membranes, the possibility to utilize alternative energy sources and uncertainty about the sustainability of fossil fuel. Furthermore, new rigorous separation requirements driven by the new regulations and needs have further highlighted the importance of the field. As a result, a "research boom" has been observed in various aspects of MD since the last one decade or so. Recently, a lot or interest in commercialization efforts for MD has been realized (Table 2). As an example Aquaver company has recently commissioned the world's first seawater MD based desalination plant in Maldives. The plant uses the waste grade heat available from a local power plant and has the capacity of 10,000 L/day (http://www.aquaver.com).

Recently, memsys have applied a patented concept of integrating vacuum with multi-effects in their module designing for MD. V-MEMD is a modified form of VMD that integrates the concept of state-of-the-art multi-effect distillation into the VMD. As a general principle of the process, the vapors produced in each stage are condensed during the subsequent stages. Vapors are generated in steam raiser working under vacuum by exchanging the heat provided by external source. The vapors are introduced in the 1st stage where these are condensed by exchanging the heat with feed via a foil. The vapors generated in the 1st stage are transported through the membrane and collected on the foil in the 2nd stage. The flow of different streams in a single stage has been illustrated in Fig. 2. It has been claimed that these modules have excellent gained to output ratio which is a crucial parameter for industrial applications [13]. A condenser is used to condense the vapors generated in the final stage. The vapor pressure in each stage is less than its preceding stage. A schematic diagram showing the module fabrication methodology has been illustrated in Fig. 3.

Starting from the first article by Bodell in 1963, substantial growth in the field has been observed over time. The progress and advancements have been reviewed in different review articles [14,5,15,16,6,17]. The number of scientists and researchers working on MD has increased tremendously in the recent years and a lot of research articles are coming out each year. Advent of commercialization era for the process has also contributed significantly in fueling the research in MD. DCMD is still dominant field for recent research, despite the fact that most commercializing companies are adopting VMD or AGMD for their plants.

The first patent related to MD was issued in 1963. Since then, 12 more patents have been registered as documented by Drioli et al. [18]. That number somehow shows slow progress of MD. The research momentum recently gained by the technology can be realized by the 8 patents published during 2013 and 2014. These patents cover the membrane preparation methods, application of MD in integration with the other processes to achieve complex separations, module designing, configurational modifications to improve process efficiency, oleophobic membranes, use of the process in steam production, etc. A list of the patents published recently has been provided in Table 3.

An interesting example of the fast growing of membrane distillation systems can be found also in the GMVP research program in progress in Korea in which membrane distillation, valuable resource recovery, and PRO are the main objectives and goals (Fig. 1). A first MD plant with a capacity of 400 m^3 per day will be realized together with a 200 m^3 per day PRO unit (www.globalmvp.org).

In this work, we aim to review the recent advances in MD technology in terms of membrane development, module design, heat and mass transport phenomenon, nontraditional fouling and applications. The future research directions of interest have also been pointed out.

2. Membranes for MD

One of the most crucial aspects of the membrane distillation is to have at disposal membranes with well controlled properties. Moreover, the final performance of a process is a direct consequence of the structural and physicochemical parameters of the utilized membranes. This aspect gains relevance when the proposed membrane technology is based on advanced systems where the use of well-structured and functionalized membranes becomes an imperative. Membrane distillation performance is intrinsically affected by the structure of the film in terms of thickness, porosity, mean pore size, pore distribution and geometry. Thus, the successful outcome of the process is reasonably expected to be depending upon the capability of the membrane to interface two media without dispersing one phase into another and to combine high volumetric mass transfer with high resistance to liquid intrusion in the pores. The membranes for membrane contactor application have to be porous, hydrophobic, with good thermal stability and excellent chemical resistance to feed solutions. In particular, the characteristics needed for membranes are as follows:

1. *High liquid entry pressure* (LEP), is the minimum hydrostatic pressure that must be applied onto the feed solution before it overcomes the hydrophobic forces of the membrane and penetrates into the membrane pores. LEP is a characteristic of each membrane and permits to prevent wetting of the membrane pores. High LEP may be achieved using a membrane material with high hydrophobicity and a small maximum pore size (see Eq. (a))

$$LEP_w = \frac{B\ \gamma_L \cos\theta}{d_{max}} \quad (a)$$

Eq. (a) has been proposed by Franken et al. [19] on the basis of Laplace equation. Here B is a geometric factor determined by pore structure with value equal to 1 for cylindrical pores, γ_L the liquid surface tension and θ is the liquid/solid contact angle.
However, as the maximum pore size decreases, the mean pore size of the membrane decreases and the permeability of the membrane becomes low.
2. *High permeability*. The flux will "*increase*" with an increase in the membrane pore size and porosity, and with a decrease of the membrane thickness and pore tortuosity. In fact, molar flux through a pore is related to the membrane's average pore size and other characteristic parameters by:

$$N \propto \frac{\langle r^{\alpha} \rangle \cdot \varepsilon}{\tau \cdot \delta} \quad (b)$$

[17]where ε is the membrane porosity, τ is the membrane tortuosity, δ is the membrane thickness, $\langle r^{\alpha} \rangle$ is the average pore size for Knudsen diffusion (when $\alpha = 1$), and $\langle r^{\alpha} \rangle$ is the average squared pore size for viscous flux (when $\alpha = 2$).

Table 2
Main suppliers and developers active in commercialization of MD.

Membrane trade name/ manufacturer	Material	Structural characteristic	Application	Bibliography reference	Contact
Fraunhofer Institute for Solar Energy Systems (ISE)					Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstr.2, D 79110 Freiburg, Germany
OEM GE Nylon-hydrophobic membranes	Hydrophobic membrane is a pure polymer internally supported with an inert polyester web. It is a supported, hydrophobic nylon impervious to aqueous-based solutions making it ideal for use in venting applications. GE Nylon-hydrophobic membrane is available in rolls up to 33 cm (13 in.) wide, as well as sheets, cut discs and pleat packs that can be customized to meet your application and size requirements. The GE Nylon-Hydrophobic membrane is manufactured on-site in GE Osmonics facilities.		-Bag vents -Bioreactor venting applications -CO_2 monitors -Fermentation air applications -Filtering gases to remove particulate -Insufflation filters -Lyophilizer venting or inlet air -Spike vents -Sterile process gases -Transducer protectors -Venting gases from sterile processes -Venting of sterile tanks -I.V. filter vents		
Donaldson Company Inc., Microelectronics Group	Donaldson Company Inc., Microelectronics Group Develops PTFE membrane				Donaldson Company Inc., Microelectronics Group Donaldson Europe B.V.B.A. Interleuvenlaan, 1 B-3001 Leuven, Belgium Tel.: 32 16 38 3811 Fax: 32 16 40 0077 e-mail: LeuvenRD@mail.donaldson.com Tetratec-Europe@mail.donaldson.com Website: www.donaldson.com
Liqui-Cel®			Liqui-Cel® Membrane Contactors are used for degassing liquids. They are widely used for O_2 removal from water as well as CO_2 removal from water. They have displaced the vacuum tower, forced draft de-aerator, and oxygen scavengers. Liqui-Cel®, SuperPhobic® and MiniModule® Membrane contactors are used extensively for de-aeration of liquids in the microelectronics, pharmaceutical, power, food & beverage, industrial, photographic, ink and analytical markets.		http://www.liqui-cel.com/ 13800 South Lakes Drive Charlotte, North Carolina 28273, USA Tel.: 704 588 5310 Fax: 704 587 8585
TNO					info-beno@tno.nl drs. A.E. (Albert) Jansen Business Developer Separation Technology Phone: +31 55 549 39 43

(continued on next page)

Table 2 *(continued)*

Membrane trade name/ manufacturer	Material	Structural characteristic	Application	Bibliography reference	Contact
Scarab Development AB			Invests in development of technology for water purification, solar power, poly-generation, recycling and sustainable systems		Street: Nybrogatan 12. 2 tr City: 114 39 Stockholm Country: Sweden Telephone: (+46) 8-660 39 70 Fax: (+46) 8-662 96 18
S6/2 MD020CP2N/AkzoNobel Microdyn	PP (polypropylene capillary membrane: number of capillaries in membrane module = 40; effective filtration area = 0.1 m2; inner capillary diameter = 1.8 mm; length of capillaries = 470 mm)	Thickness = 450 μm; average pore size = 0.2 μm; porosity = 70%.	Microdyn-Nadir produces polymeric membrane (in polyamide, polypropylene) and polypropylene hydrophobic membrane. applications include water and wastewater treatment, food and pharmaceutical industry.	M. Khayet, J.I. Mengual, T. Matsuura, Porous hydrophobic/hydrophilic composite membranes Application in desalination using direct contact membrane distillation, Journal of Membrane Science 252 (2005) 101–113	Microdyn-Nadir Microdyn Modulban Gmbh Öhder Straße 28-42289 Wuppertal, Germany Postfach 240252. 42232 Wuppertal Tel.: +49 (0) 202 26092-0 Fax: +49 (0) 202 26092-25 e-mail: sales@microdyn-nadir.de Web site: www.microdyn-nadir.de
Membranes from PP (Membrana GmbH, Germany) with microfiltration properties.			Commercial hollow fiber membranes from PP (Membrana GmbH, Germany) with microfiltration properties are often applied in gas/liquid contactors. Membrana GMBH produces polyethylene, polypropylene, polyetersulfon, cellulose and polymeric membranes.	W. Albrecht, R. Hilke, K. Kneifel, Th. Weigel, K.-V. Peinemann, Selection of microporous hydrophobic membranes for use in gas/liquid contactors: An experimental approach, Journal of Membrane Science 263 (2005) 66–76	Membrana GMBH Öhder Straße 28, D-42289 Wuppertal, Germany Postfach 200151, D-42201 Wuppertal Tel.: (0) 202 6099-651 Fax: (0) 202 6099 602 e-mail: info@membrana.de Web site: http://www.membrana.com http://www.pall.com/microe.asp
Pall-Microza PVDF fibers			Hollow-fiber modules containing Pall-Microza PVDF fibers used for VMD for water desalination.	Corinne Cabassud, David Wirth, Membrane distillation for water desalination: how to chose an appropriate membrane?, Desalination 157 (2003) 307–314	
Commercial Gelman polyvinylidene fluoride (PVDF) membranes			Commercial porous hydrophobic membranes for MD.	J.M. Ortiz de Zfirate**, L. Pefia, J.I. Mengual, Characterization of membrane distillation membranes prepared by phase inversion, Desalination 100 (1995) 139–148	
Millipore polytetra-fluoroethylene (PTFE) membranes and polyvinylidene fluoride (PVDF) membranes			Commercial porous hydrophobic membranes for MD	J.M. Ortiz de Zfirate**, L. Pefia, J.I. Mengual, Characterization of membrane distillation membranes prepared by phase inversion, Desalination 100 (1995) 139–148	
Durapore GVSP (PVDF)/Millipore UPVP (UHMWPE)/Millipore	GVSP: Surface modified polyvinylidene fluoride (PVDF), UPVP: Ultra high MW polyethylene (UHMWPE),	Nominal pore diameter = 0.2 μm, porosity 80%, thickness 108 μm. Nominal pore diameter = 0.2 μm, porosity 80%, thickness 90 μm.	These membranes are porous, hydrophobic and flat sheet. Commercial porous hydrophobic membranes for MD.	J.M. Ortiz de Zfirate**, L. Pefia, J.I. Mengual, Characterization of membrane distillation membranes prepared by phase inversion, Desalination 100 (1995) 139–148 J. Mansouri, A.G. Fane, Osmotic distillation of oily feeds, Journal of Membrane Science 153 (1999) 103 ± 120	

Celgard 2500 (PP/PE, Hoechst Celanese).	Celgar 2500: Polypropylene (PP/PE), Nominal pore diameter = 0.05 μm, porosity 45%, thickness 28 μm.		Commercial hydrophobic membranes, porous, hydrophobic and flat sheet	J. Mansouri, A.G. Fane, Osmotic distillation of oily feeds, Journal of Membrane Science 153 (1999) 103 ± 120	
Celgard Inc. — Membrana Underlining Performance Industrial Separations (a Division of Celgard)			This business develops membrane contactors SuperPhobic® e Liquicel®		Europe office: Erlengang 31 22844 Norderstedt, Germany Tel.: +49 4052 6108 78 Fax: +49 4052 6108 79 e-mail: Jschneid@celgard.net web site: www.liquicell.com www.membrane.com
memsys/memDist module	Polypropylene	The memsys technology is based on vacuum multi effect membrane distillation. The memsys modules, called “memDist”, consist of flat sheet membranes combined with a plate and frame design made of.	-Desalination -Wastewater treatment -Process water (Semi conductor, Boiler feed water, Food & beverage) -Aircon-desiccant cooling -Process engineering (Alcohol distillation) -Cooling towers		Production: memsys GmbH Frauenstr. 7 86830 Schwabmünchen Germany Principal: memsys clearwater Pte. Ltd. 51 Goldhill Plaza #23-11/12 Singapore 308900 T. +65 (0) 6354 0127 F. +65 (0) 6354 0128
Aquaver	PTFE	Aquaver membrane distillation systems (MDS) are modular and compact. They come in skid-mounted or containerized units. Each MDS has its own controls and can operate independently.	Seawater desalination Cogeneration Brine treatment Landfill leachate Industrial wastewater Difficult-to-treat waters		Aquaver info@aquaver.com Phone: +31 703 002 570 Oosteinde 114, 2271, EJ Voorburg, The Netherlands
Aquastill					Nusterweg 69 6136 KT Sittard The Netherlands http://www.aquastill.nl/index.html
SolarSpring		SolarSpring produces all MD-modules in cooperation with the Fraunhofer ISE in Freiburg. They operate a customized constructed winding-machine to produce spiral-wounded MD-Modules. They can vary many parameters like channel-length, channel-height, membrane-material, spacer geometry and material.	Drinking water Process and industry Research		SolarSpring GmbH Hanferstr. 28 79108 Freiburg Germany Tel.: +49 (0) 761-610-508-3 Fax: +49 (0) 761-610-508-50 E-mail: contact (at) solarspring.de www.solarspring.de

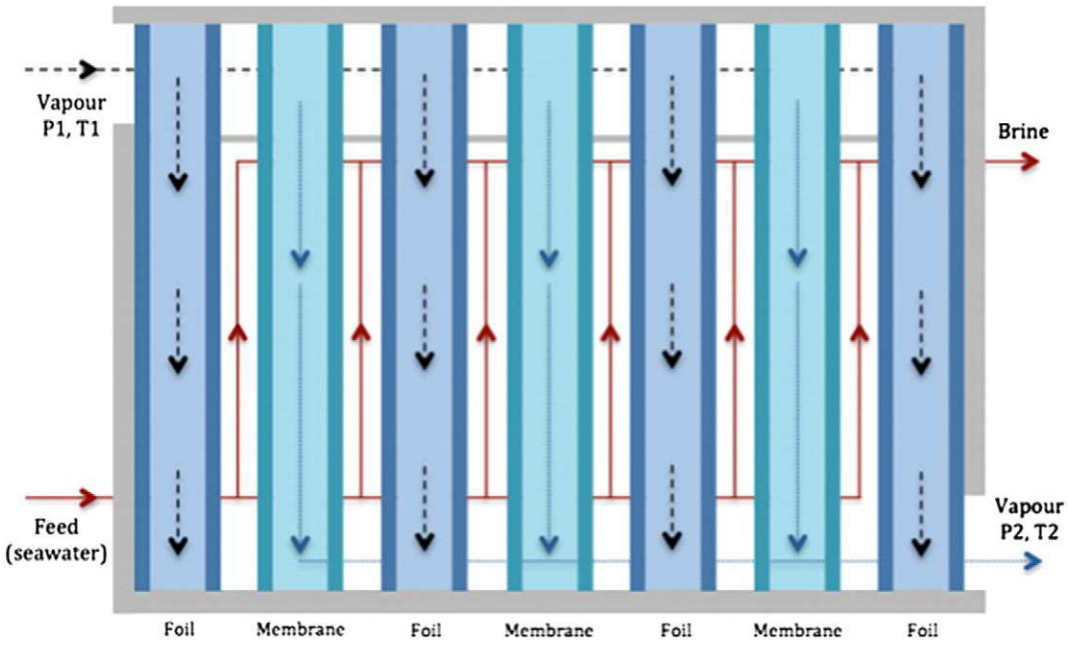


Fig. 2. Schematic illustration of streams in V-MEMD module [13].

Eq. (b) illustrates the importance (in terms of molar flux) of maximizing the membrane porosity and pore size, while minimizing the transport path length through the membrane, ($\tau\ \delta$). In other words, to obtain a high permeability, the surface layer that governs the membrane transport must be as thin as possible and its surface porosity as well as pore size must be as large as possible. However, a conflict exists between the requirements of high mass transfer associated with thinner membranes and low conductive heat losses achievable by using thicker membranes. In fact, as described in the following sections, thermal efficiency in MD increases gradually with the growing of membrane thickness and on optimization between the two requirements has to be found.

3. *Low fouling problem*. Fouling is one of the major problems in the application of porous membranes. Fortunately, in the gas–liquid contactor applications, the contactors are less sensitive to fouling since there is no convection flow through the membrane pores. However, in industrial applications, gas and liquid streams with large content of suspended particles can cause plugging due to the small hollow fiber diameter. Pre-filtration is necessary in such a case [51].
4. *High chemical stability*. The chemical stability of the membrane material has a significant effect on its long-term stability. Any reaction between the solvent and membrane material could possibly affect the membrane matrix and surface structure. Liquid with high load of acid gases are corrosive in the nature, which make the membrane material less resistance to chemical attack.
5. *High thermal stability*. Under high temperatures, the membrane material may not be able to resist to degradation or decomposition. Changing in the nature of membrane depends on the glass transition temperature T_g for amorphous polymers or the melting point T_m for crystalline polymers. Over these temperatures, the properties of the polymers change dramatically. In Table 4, the T_g for the polymers commonly used in membrane contactors is reported.

The transition temperature of a polymer is determined largely by its chemical structure, which includes mainly the chain flexibility and chain interaction. As it can be seen from Table 4, polytetrafluoroethylene has a much higher T_g compared to polyethylene and polypropylene. This contributes to the higher stability and less flexible polyvinyl chain of PTFE with respect to PE and PP. In general, the factors that increase the T_g/T_m or the crystallinity of a membrane can enhance both its chemical and thermal stability. Therefore, in terms of long term stability membrane material with suitable T_g needs to be applied. For operations at high temperatures, fluorinated polymers are good candidates due to their high hydrophobicity and chemical stability [20].

Traditionally, the membranes prepared for ultrafiltration and microfiltration through phase inversion processes have been utilized

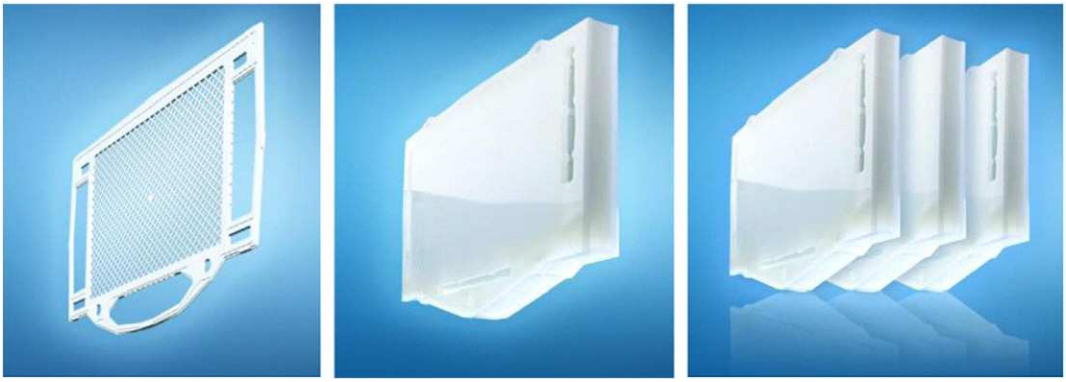


Fig. 3. Frame and stages used by memsys. (i) A simple frame, (ii) single stage consisting of welded frames and covering plates, (iii) multiple stages [13].

Table 3
List of MD-related patents published from October 2011 to August 2014.

Patent	Inventor/s	Remarks
Combined membrane-distillation-forward-osmosis systems and methods of use Publication number: US 8029671 B2 Publication date: Oct 4, 2011	Tzahi Y. Cath, Christopher R. Martinetti	Embodiments of the present disclosure provide combined membrane-distillation/forward-osmosis systems and methods for purifying a liquid, such as reducing its solute or suspended solids load.
Membrane distillation apparatus and methods Publication number: US 20110272354 A1 Publication date: Nov 10, 2011	Somenath Mitra, Ken Gethard	Methods based on MD for solvent removal, sample preconcentration and desalination employing hollow fiber porous hydrophobic membranes with carbon nanotubes are disclosed
Composite membranes for membrane distillation and related methods of manufacture. Publication number: WO 2012100318 A1 Publication date: Aug 2, 2012 Applicant: Membrane Distillation Desalination Ltd. Co.	Mohamed Khayet, Takeshi Matsuura, Moh'd Rasool Qtaishat	The present invention provides composite membranes for membrane distillation and related methods of manufacture.
Membrane and method Producing the same Publication number: US20120285882 A1 Publication date: Nov 15, 2012	May May TEOH, Na PENG, Tai-Shung Chung	The present disclosure relates to a membrane comprising a porous polymer body with a plurality of channels extending through the polymer body, a method of producing the same and a water treatment system comprising the membrane
Forward osmotic desalination device using membrane distillation method Publication number: US 20130112603 A1 Publication date: May 9, 2013	Sung Mo Koo, Sang Jin Lee, Sung Min Shim	The present invention relates to a fresh water separator using a membrane distillation method and a forward osmotic desalination device comprising the fresh water separator
Solar membrane distillation system and method of use Publication number: US 8,460,551 B2 Publication date: Jun. 11, 2013	Hisham Taha Abdulla El-Dessouky	The invention relates to distillation systems and, more particularly, to a solar driven membrane distillation system and method of use.
Forward osmosis system comprising solvent separation by means of membrane distillation Publication number: US 20130264260 A1 Publication date: Oct 10, 2013	Wolfgang Heinzl	The invention relates to a system for separating a product contained as solvent in a solution to be processed, comprising at least one forward osmosis device through which the solution to be processed and a draw solution flow, and a device connected downstream thereof for obtaining the product.
Polyazole membrane for water purification Publication number: EPA 13155093.1 Publication date: 14.08.2013	Nunes, Suzana, Pereira Thuwal, Maab, Husnul Thuwal, Francis, Lijo Thuwal	The method describes a membrane prepared for fluid purification comprising a polyazole polymer.
Method of converting thermal energy into mechanical energy, and an apparatus therefor Publication number: US 20140014583 A1 Publication date: Jan 16, 2014	Jan Hendrik Hanemaaijer	The invention relates to a method of converting thermal energy into mechanical energy wherein a working liquid such as is evaporated to generate a stream of a working fluid
Membrane distillation apparatus Publication number: US 20140138299 A1 Publication date: May 22, 2014	Pieter Nijskens, Bart Kregersman, Sam Puttemans, Chris Dotremont, Brecht Cools	The present invention relates to membrane distillation apparatus and is more particularly, although not exclusively, concerned with the production of desalinated water from seawater
Membrane distillation modules using oleophobically and antimicrobially treated microporous membranes Publication number: US 20130068689 A1 Publication date: Mar 21, 2013	Vishal Bansal, Christopher Keller	The present invention provides a system for liquid distillation which includes a vapor permeable–liquid impermeable microporous membrane having structures defining a plurality of pores, an oleophobic material that is applied to the structures of the vapor permeable–liquid impermeable microporous membrane
Membrane Distillation Device Publication number: 20140216916 Publication date: 2014-08-07	Wolfgang Heinzl	The invention describes a method to improve the efficiency of MD process by using the latent heat of condensation of the vapors to heat the feed during various stages.

for MD applications. Some examples from state-of-the-art literature on ultrafiltration membranes have been provided in Table 5. These membranes generally have low porosity, limited hydrophobicity, broader pore size distribution and pore size not engineered for MD requirements. The thickness of these membranes has been design to withstand relatively high pressure of UF and MF which is not encountered in MD. Accordingly, MD flux for such membranes is low and at the same time conductive losses are high.

Among membrane parameters, the role of thickness is not straightforward. On one side, low thickness offers less resistance to the mass transfer, while on the other hand, membranes with low thickness suffer from more energy losses due to heat flux flowing through conduction across the membranes [22]. In order to address the thickness issue, dual and even triple layer membranes have been introduced [23]. This membrane contains a hydrophobic active layer and a hydrophilic support layer. The support layer provides thermal insulation and ensures the required mechanical robustness of the membrane while the active layer retains the liquid. Care must be taken in selection of thickness of the active layer as too less thickness can allow the passage of the liquid through the pores and may not be sufficient to resist the chemical attack from the feed side during long term operations. According to Laganà et al. [24] optimum thickness of active layer is 30–60 μm. However, a broad look at thickness effect on MD performance reveals that the literature lacks of clear and conclusive statements. For example, for concentrated salt solutions, Gostoli et al. [25] have observed that the performance of thin membrane is more sensitivity towards concentration, however, no further investigations have addressed this issue. Wu et al. [26] have demonstrated that the optimal thickness for electrospun PVDF based

Table 4
Glass transition temperature T_g of polymers [20,21].

Polymer	T_g [°C]
Polyethylene (PE)	−120
Polypropylene (PP)	−15
Polytetrafluoroethylene (PTFE)	126
Polysulfone	190
Polyether sulfone	230
Polyimide (Kapton)	300

Table 5
Characteristic features of some state-of-the-art UF membranes mentioned in literature (for details of abbreviation used to describe the membranes, please consult the corresponding reference).

Membrane type	r_{min} (nm)	r_{min} (nm)	r_{av} (nm)	ε (%)	Ref.
XM 100A	5	12	9	0.75	[29]
XM 300	6	19	12.5	0.3	[29]
Milipore PTSG	1	15	3	7–12	[30]
PVDF	3	4	–	10	[31]
Polyimide UF	1.5	6	–	0.7–0.9	[32]
PCTE 10	134	258	181	6	[33]
PCTE 50	553	821	657	14	[33]
PCTE 100	98 5	1233	113 3	45	[33]
PTHK	16 8	33 6	22 1	34	[33]
YM	6.3	18	11.3	–	[34]
PM30	16.7	62.7	30.6	–	[34]
GVHP	–	–	283.2	70.1	[28]
PVHP	–	–	463.9	71.3	[28]

membrane increases with reduced heat transfer coefficient, decreased feed inlet temperature and increased permeability and salinity level. Contrary to this, Jansen et al. [27] have found that conduction losses are directly related with the temperature gradient at the membrane surfaces and inversely related with the membranes thickness.

For what concerns pore size, the utilized porous membranes don't show a single pore size; rather they exhibit a range of pore size distribution (PSD). A membrane with good PSD shows a Gaussian distribution curve with a sharp peak and very narrow width. As evident from Table 5, the membranes used for UF show quite a broad range of minimum and maximum pore sized which is somehow acceptable for UF applications. On the other hand, both mean pore size and pore size distributions are crucial for MD process. Although higher flux has been reported for the membranes with bigger pores, yet the large pore dimensions make the membrane vulnerable to wetting. The presence of even a few oversized pores can kill the efficiency of the entire process by allowing the passage of liquid through the pores. Therefore, for pore size, an optimization is required between the stable performance and high flux [28]. The commonly used pore size for MD is in the range of 100 nm to 1 μm [14]. The sensitivity of process performance towards pore size is different for different configurations of MD. The hydrophobicity of the membrane material and surface tension of the feed solution used will play a decisive role in deciding the pore size. The presence of pores with different dimensions gives rise to the involvement of different mass transport mechanisms in a single membrane [6].

Regarding the membrane material, it has to be hydrophobic to ensure the retention of liquid and the passage of only vapor phase through the membrane pores. PVDF, PP and PTFE are the most commonly used polymeric materials used for membrane preparation for MD applications. Among these, PTFE exhibits the best hydrophobic characteristics, yet the most research on membrane preparation has been carried out by using PVDF membranes due to its easy processability. PTFE is not soluble in any solvents and therefore, poses serious issues with processing. In order to render/improve the hydrophobic character, various techniques have been applied including the coating of different low energy fluoropolymers at the membrane surface, plasma modification, formation of various hierarchical structures, incorporation of nanoparticles into the dope solution during membrane synthesis, making the surface rough etc. Surface roughness is an interesting technique to render the super hydrophobicity to the membrane surface, however, its further effects on surface scaling/fouling and thermal polarization still need to be addressed.

In addition to the above all parameters, not only pore size but also membrane porosity plays crucial role in dictating the flux. More porous membranes offer more diffusion surface for the vapors and at the same time decrease the thermal conductivity of the membrane as the air trapped inside the pores has conductivity 10 times less than typical polymeric materials used. Overall porosity also dictates the mechanical stability of the membrane. It is not only the overall porosity that is important for the successful application but also the mechanism of achieving the porosity. The membranes having macrovoids usually show very good porosity or void fraction but on the other hand are more prone to the wetting. Related to the porosity is the tortuosity of the pores which indicates the effective length that vapors have to travel to move from feed side to the permeate side. The commonly used value for tortuosity factor is close to 2, though some studies have taken the tortuosity factor as the inverse of porosity [28].

Properties of some commercial membranes used for MD applications have been provided in Table 6. Comparison of Tables 5 and 6 indicates that the membrane properties required for two applications are very different. The second significant conclusion is that the required MD membrane properties have been incorporated to some extent in some commercial membranes (for example see the r_{av}, r_{min}, r_{max}, and porosity for TF1000, TF450,TF200, GVHP), however, the optimization of these features, further "engineering" of the membranes and additional improvement in module design can make them further attractive. Some approaches of great interest for the current and perspective trends in membrane fabrication for MD applications have been discussed in Section 2.1.

Table 6
Some features of the commercial membranes used for MD.

Membrane type	Manufacturer	Material	r_{min} (nm)	r_{max} (nm)	r_{av} (nm)	δ (μm)	LEP (bar)	ε (%)	Ref.
TF1000	Gelman	PTFE/PP	280	420	325	178	282	80	[6,35]
TF450	Gelman	PTFE/PP	180	300	235	178	138	80	
TF200	Gelman	PTFE/PP	120	210	155	178	48	80	
PV22	Millipore	PVDF	–	–	220	126 ± 7	2.29 ± 0.03	62 ± 2	[36]
PV45	Millipore	PVDF	–	–	245	116 ± 9	1.10 ± 0.04	66 ± 2	
					450				
PTS20	Gore	PTFE/PP	–	–	200	184 ± 8	4.63 ± 8??	44 ± 6	
PT20	Gore	PTFE/PP	–	–	200	64 ± 5	3.68 ± 0.01	90 ± 1	
PT45	Gore	PTFE/PP	–	–	450	77 ± 8	2.88 ± 0.01	89 ± 4	
Accurel® S6/2	AkzoNobel	PP	–	600	200	450	1.4	70	[37]
HVHP	Millipore	PVDF	280	680	451.23		105	33.64	[37]
GVHP	Millipore	PVDF	200	350	265.53		204	32.74	
MD080CO2N	Enka Microdyn	PP	–	–	200	650		70	[6]
MD020TP2N	Enka Microdyn	PP	–	–	200	1550		70	
Accurel®	Enka A.G.	PP		600		400		74	
Celgard X-20	Hoechst Celanese Co	PP	–	70	50	25		35	
EHF270FA-16	Mitsubishi	PE	–	–	100	55		70	

Table 7
Some examples of electrospun membranes synthesized for MD applications.

Technique	Membranes features				Operating conditions	Flux ($L/m^2 \cdot h$)	Ref.
	Material	Porosity (%)	MPS (μm)	Contact angle (°)			
Electrospinning with post treatment	PVDF	80	0.18 ± 0.01	>150	3.6% NaCL, T_{fin} 333 K, T_{pin} 293 K	31.6	[42]
Electrospinning followed by hot pressing	PVDF-HFP	58 ± 5	0.26	125 ± 2.41	T_{fin} 65 °C T_{pin} 40 °C, 10 g/L NaCl	20–22	[43]
Electro–spinning followed by hot pressing	PVDF	53.7–71.4	0.18–0.91	136–142	T_{fin} 323–353 K, T_{pin} 293 K 3.5% NaCL	20.6	[44]
Electro-spinning followed by sintering	PTFE	72–82		136.1–157.3	3.5% NaCl T_{fin} 80 °C	16	[45]
Electrospinning	PVDF	58.871.8–93.370.6	1.0070.02–2.2670.25	143.173.4–148.472.4	T_{fin} 80 °C, T_{pin} 20 °C, 30 g/L NaCl	38.88	[46]
Electrospinning	PVDF-HFP	~63–80	~0.27–0.37	~127	T_{fin} 60 °C T_{pin} 25 °C 10 g/L NaCl	~13	[47]

T_{fin}, feed inlet temperature; T_{pin}, permeate inlet temperature.

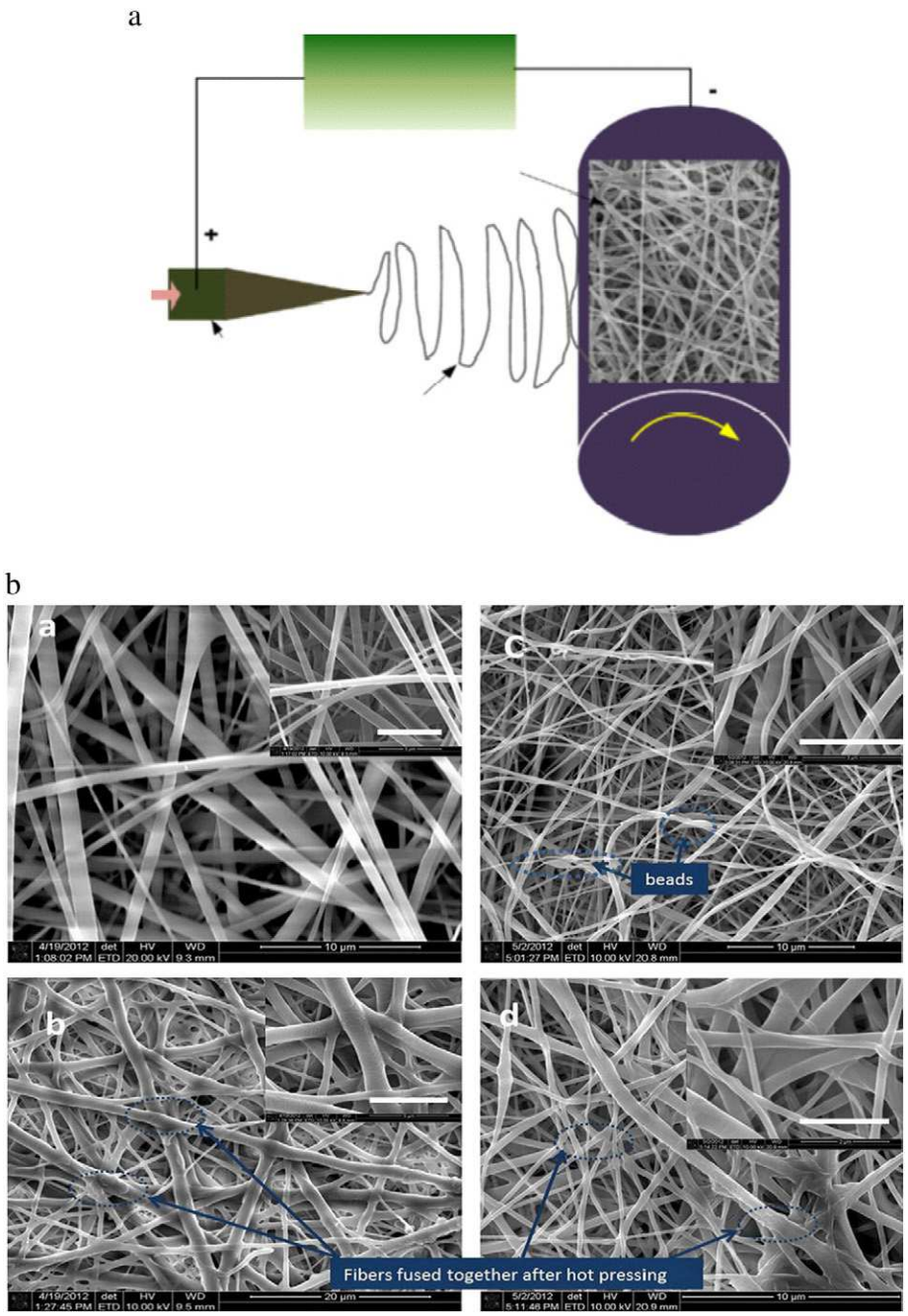


Fig. 4. (a) A schematic diagram of the electrospinning process [38], (b) SEM image of electrospun membranes [30].

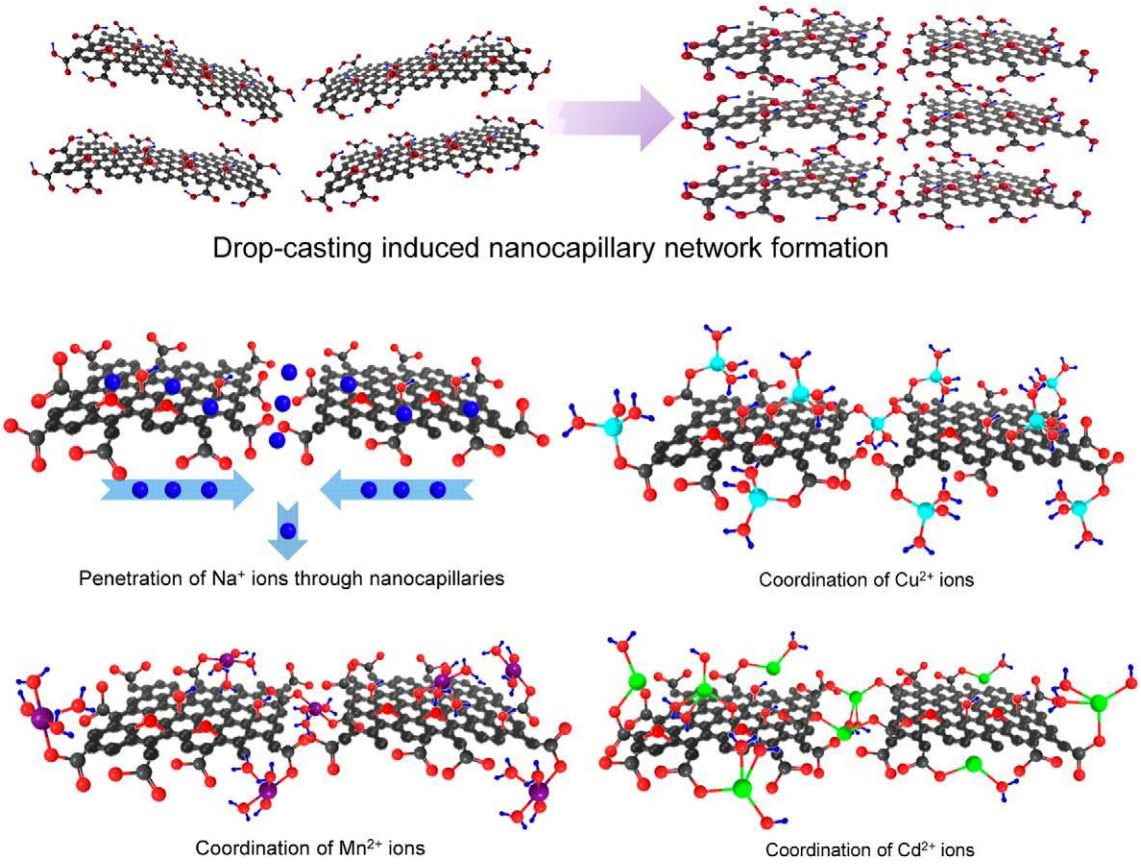


Fig. 5. Structure and ion selectivity mechanism of graphene oxide membranes [50].

2.1. Recent trends in membranes for MD

2.1.1. Use of nanotechnology

Nanotechnology has a significantly potential role in membrane based desalination techniques including MD. For instance, electrospun nanofiber membranes have been reported in many studies recently and have shown very interesting results (Table 7). As illustrated in Fig. 4(a), in electrospinning process, the fibers are spun under the pressure and electric field applied and form non-woven mat at the grounded rotating collectors. The mat formed shows very high porosity, excellent hydrophobicity, very good interconnectivity and very high surface to volume ratio making them interesting candidates for desalination applications. Eletrospinning can be performed with polymer solution or melt and the properties of the mat can be tuned by changing the process parameters, material used and the post treatment step applied [38–40]. Due to the possibility to use polymer melt, instead of

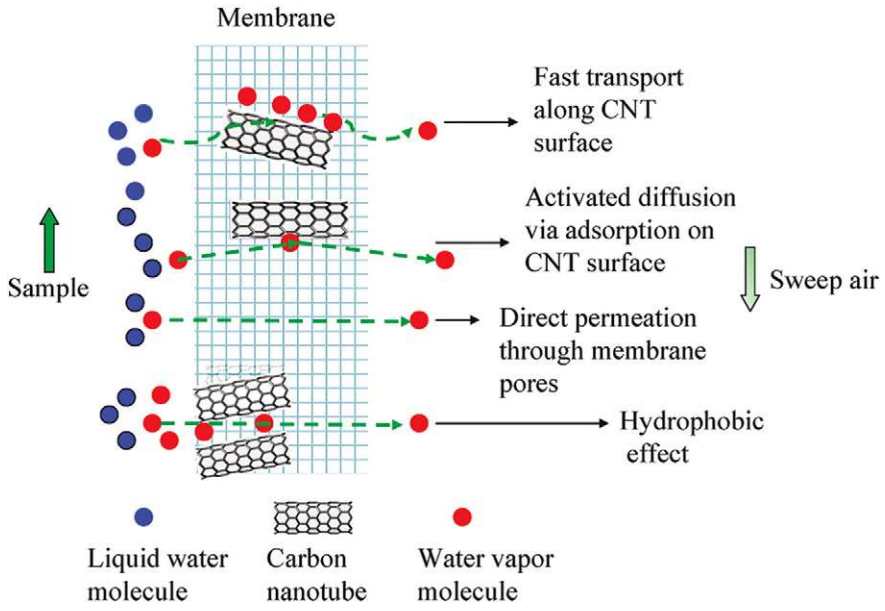


Fig. 6. MD mechanism for the membranes containing CNTs in their matrix [57].

Table 8
Various attempts to modify the membrane surfaces.

Base polymer	Modification applied	Objective	Ref.
PVDF	Immobilization of detonation nanodiamonds	To avoid wetting	[65]
PVDF	Grafting of polyethylene glycol followed by deposition of TiO_2 particles	Incorporation of anti-oil fouling properties	[66]
PVDF	Hydrophobic modified $CaCO_3$ nanoparticles	Improvement in pore size distribution, surface roughness and porosity	[67]
PVDF	Deposition of TiO_2 nanoparticles on microporous membrane followed by flourosilanization	Improvement in hydrophobic character	[68]
CNT bucky-paper membranes	Thin layer coating of PTFE	Improvement I hydrophobicity and mechanical strength	[58]
PVDF	Grafting of CF4 through plasma technique	Incorporation of super hydrophobic character	[69]
Polyetherimide	Blending followed by surface segregation of surface modifying macromolecules	Fabrication of hydrophobic/hydrophilic membrane	[70]

solution, electrospinning provides opportunities to make the membranes with vast variety of polymers. Different functional materials can be incorporated into the nanofibers during or after their spinning thus incorporating multi-functionality into the fibers. Some examples of membrane prepared through the electrospinning process along with their characteristics have been provided in Table 7. Some lab scale applications of electrospun nanofiber membranes have also been reported in recent literature [40,39,41].

Graphene is an interesting material with several applications due to its very high strength to weight ratio. In addition to its use in various fields (foldable electronics, biological engineering, composite materials, energy storage), the new research has shown that it exhibits amazing selective permeability towards various components (Fig. 5). For example, a sub-micron thin graphene oxide membrane can retain all gases and liquids through the membrane except water molecules [48]. The separation of water from organic mixtures has been demonstrated excellently by these membranes [49]. Similarly, graphene membranes can selectively permeate some metals ions present into a solution containing different types of ions [50]. Graphene membrane with thickness near to 1 nm has shown excellent selectivity towards various gases [51]. Due to these facts combined with their high strength, it is possible to tremendously reduce the thickness of the graphene based membranes that can open broad opportunities for these membranes in desalination applications including MD. The applications of graphene membranes in water treatment sections are being tested by different researchers [52–54].

Biomimic membranes like aquaporin have shown a great potential for desalination applications due to their high permeability and selectivity towards water molecules. Under the right conditions, aquaporin membranes form the water channels allowing the passage of only water molecules and exclusion of all ions. It has been postulated that aquaporin based membranes can achieve a water flux as high as 601 $L/m^2 \cdot h\ bar^{-1}$ which is an order of magnitude higher than conventional RO process [55]. The commercial application of such membranes for water desalination is however still far away due to insufficient stability of the membranes, difficult associated with commercial scale production and limited rejection of salts exhibited by the existing membranes [56].

The use of carbon nanotubes (CNTs) in water desalination is also emerging in lab scale investigations. CNTs comprise of rolled up cylinder of graphene with nanoscale dimensions. Their exceptional mechanical strength, chemical resistance and thermal properties are well known. As illustrated in Fig. 6, very high transport of water molecules inside the CNTs and their potential to change the water–membrane interaction to stop the permeation of liquid water molecules while favoring the preferential transport of vapors through the pores have encouraged their incorporation into the membrane matrix [57,58]. On the other hand, for desalination through MD, CNT based membranes provide excellent porosity and hydrophobicity. The initial studies to demonstrate the potential of CNT membranes for desalination through MD have been provided in [59] and [60]. The application of CNT based membranes in MD has caused considerable increase in flux enhancement for salt solution [58].

2.1.2. Enhancement of hydrophobicity

Considerable efforts have been devoted to improve the hydrophobicity of the membranes by incorporating various modifications. The main objective of the modification is to incorporate/enhance hydrophobic character to the membrane surface. The use of fluoropolymers has gained popularity for such modifications. High thermal stability, mechanical strength and low surface energy are the main attractions for use of these polymers. Xing Wei et al. [61] have introduced CF4 plasma surface modification on hydrophilic asymmetric PES membrane. The modified membranes showed a contact angle of 120° and transmembrane flux of ~45 $L/m^2 \cdot h$ for 4% NaCl solution at feed inlet temperature of ~63 °C. Zhang et al. [62] used a spray of polydimethylsiloxane (PDMS) and hydrophobic SiO_2 on PVDF membrane to render hydrophobic character. A water contact angle of 156° was achieved for 1.5% particles in the spray. The modification ensured the operational stability of the process and a permeate of very high quality was achieved during long time operational run. Zhang and Wang [63] modified the surface of polyetherimide hollow fiber membrane with fluorinated silica layer. A dramatic increase in hydrophobicity of the membrane was observed due to increased surface roughness and decrease surface energy of the membrane. Fang et al. [64] used fluoroalkylsilane to render hydrophobic character to the surface of porous alumina ceramic hollow fiber membrane for MD applications. The modified membrane was tested for vacuum MD and showed the performance comparable with the polymeric membranes. A summary of various modifications applied has been provided in Table 8.

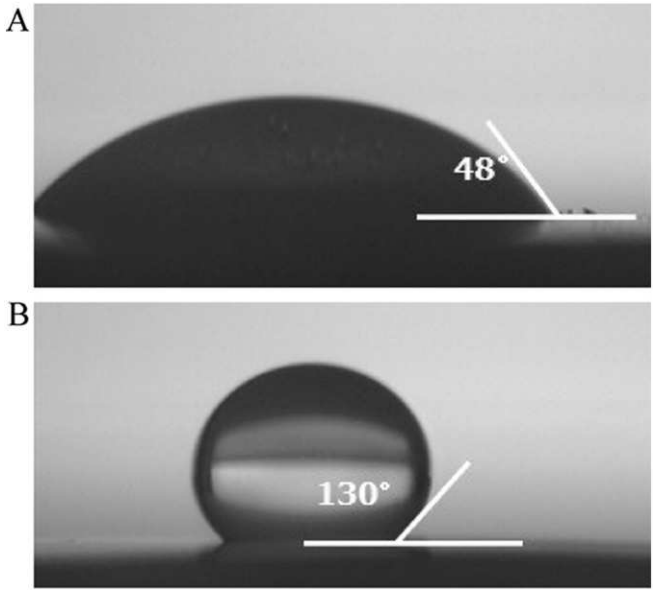


Fig. 7. Water contact angle at alumina based ceramic membrane before and after hydrophobic modification [64].

Table 9
A brief overview of various modifications applied to ceramic membranes for MD applications.

Base Material	Modifier	Attachment technique	Contact angle (°)	Comment	Ref.
Porous alumina	Polydimethylsiloxane oil	Thermal grafting	–	No water permeation was observed	[74]
Zirconia and $KTiOPO_4$ based mesoporous membranes	Fluorinated silanes	Grafting through condensation reaction	140–150	No results for water are quoted	[75]
γ-Alumina membrane	Different alcohols	Adsorption	–	Ethanol shows the strongest chemisorption	[76]
Mesoporous γ-alumina	Organochlorosilanes	Grafting via Soaking	–	Short chain organochlorosilanes are more effective	[77]
Zirconia membranes	Fluoroalkylsilanes	Grafting via soaking	116–145		[78]
Zirconia and alumina	Fluoroalkylsilane	Grafting via soaking	116–145	The flux is quite poor	[79]
Zirconia and alumina based	Fluorosilanes	Grafting via soaking	–	Flux is ~6 $L/m^2 \cdot h$ at feed temp. of 95 °C	[80]
Zirconia, alumina and alumino-silicate	Fluorodecyltriethoxysilane	Grafting via soaking	–	Flux is very low	[81]
Alumina HF	FAS solution	Grafting via soaking	100	No change in hydrophobicity after 96 h of operation	[82]
Alumina Anodisc™	Various silanes	Grafting via soaking	141	Expected thermal losses are too high	[83]
Alumina hollow fiber	Fluoroalkylsilane	Grafting via soaking	130	Obtained flux is comparable to that for polymeric membranes, no results for long term performance	[64]
Tubular and planar TiO_2 ceramic membranes	Perfluoroalkylsilanes	Grafting via soaking	130–140	The flux obtained is quite low as compared to polymeric membranes	[84]

Fluoropolymers possess very attractive features for MD. Their excellent hydrophobicity, chemical resistance and mechanical stability make them suitable candidates for MD membranes. Although several methods have been applied to prepare the membranes by using fluoropolymers and their copolymers, the widespread use is somehow restricted mainly to PVDF due to its low cost and easy processing [71]. As previously described, PTFE shows an excellent hydrophobic character and is very resistant to chemical and mechanical degradation but it possesses very high melting temperature (317–337 °C) and is not soluble in any solvent, thus limiting the workable membrane preparation techniques. The current path to prepare PTFE membranes relies on extrusion, followed by rolling and stretching or sintering. The easy way to enjoy the benefits of unique properties of fluoropolymers is the membrane modification incorporated through surface grafting, coating, blending and filling. There is a strong demand to incorporate the hydrophilic feature to the existing fluoropolymer based membranes and to increase the hydrophobicity

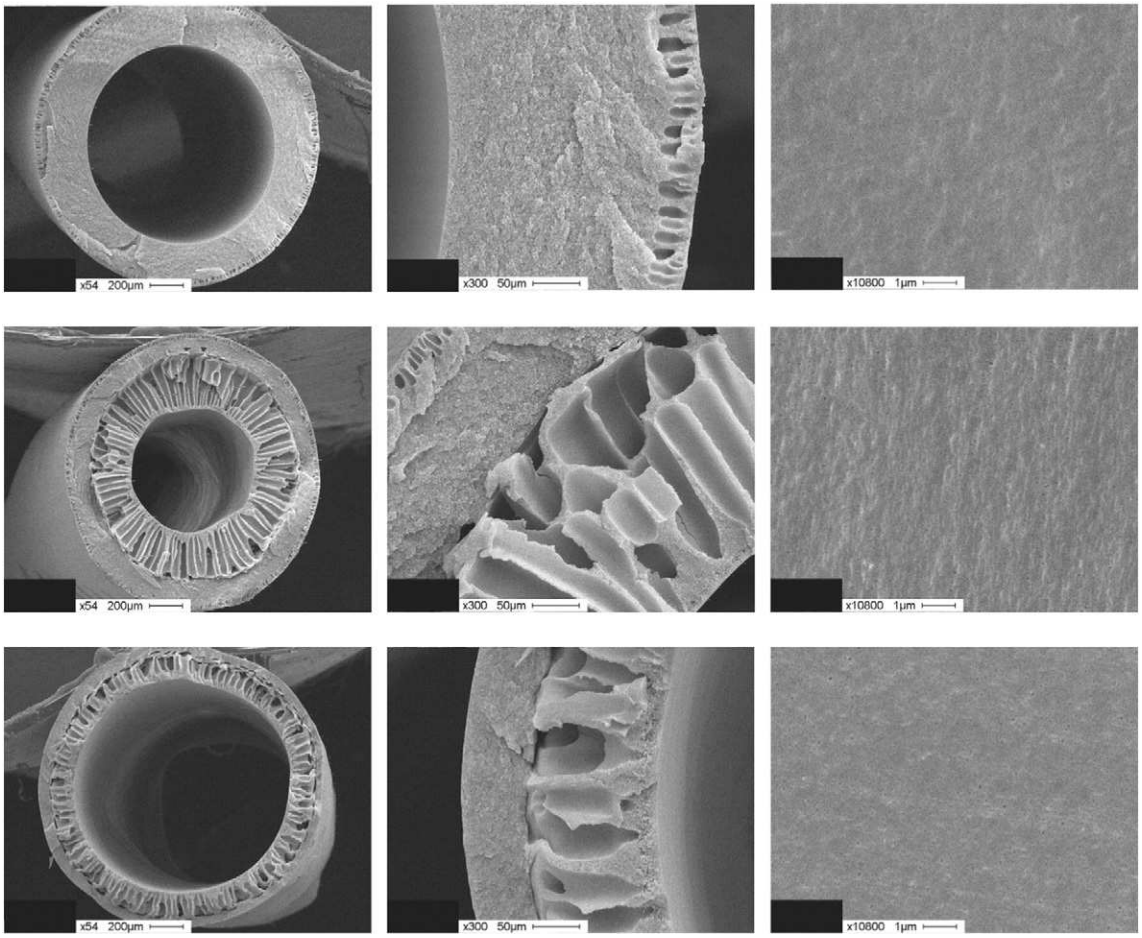


Fig. 8. Structure of different PVDF membranes prepared under different operating conditions and dope compositions [85].

of the membranes by using fluoropolymers with outstanding water repellence. In addition to the other familiar fluoropolymers such as poly(ethylene chlorotrifluoroethylene) and poly(ethylene-alt-tetrafluoroethylene), innovative fluoropolymers including Hyflon® AD introduced by Solvay Specialty Polymers and Cytop® from Asahi Glass have promising potential to induce high hydrophobicity at membrane surface when applied in the form of coating. Application of Hyflon® AD coating on PVDF membrane narrows down the pore size distribution and improves mechanical resistance and contact angle of the base membrane [72]. Besides the surface coating, these polymers can also be used for membrane synthesis [73], though that will increase the economics of the process.

Ceramic membranes are known for their mechanical, thermal and chemical stability. The application of ceramic membranes ensures the long operational life and robustness of the process. The ceramic membranes mainly comprise of TiO_2, alumina, silica and zirconia and have hydroxyl group at the surface that renders hydrophilic character to the membrane. Due to their hydrophilic nature, these membranes have not gained much popularity for MD applications. In parallel to the polymeric membranes, some attempts to modify the hydrophilic surface of the ceramic membranes can be seen. The water contact angle at unmodified and modified ceramic structure has been shown in Fig. 7. The most common approach to change the hydrophilic character is based on the use of fluoroalkylsilanes as the surface modifier.

A list of various attempts made to modify the hydrophilic ceramic membrane has been given in Table 9.

2.1.3. Optimization of features and structural design

Non-solvent induced phase separation is the most widely studied method to synthesize the membranes for MD. The overall characteristics of the produced membranes are function of operating conditions, dope and coagulant composition, thus providing vast opportunities to tune the properties of resultant membranes. An example of the effect of various variables on membrane structure has been shown in Fig. 8 [85]. Thomas et al. [86] have applied two stage coagulation bath phase inversion technique to fabricate PVDF based hollow fiber membranes with narrow pore size distribution and high wetting resistance. Simone et al. [87] have investigated the effect of composition and flow rate of inner coagulant on properties of hollow fiber PVDF membranes. Tao et al. [88] have investigated the effect of solvent power on polymorphism for four different solvents. Different phases were found to be formed depending upon the solubility of PVDF into the solvents. The effect of compositions of bore fluid and dope solution and operational parameters on characteristics of the membrane formed and their performance in membrane distillation has been studied in other studies [89,85,90].

Besides optimizing the features (pore size, pore size distribution, overall porosity etc.), some efforts have also been devoted to engineer the structure of membrane. Wang and Chung [91] have fabricated multi-bore PVDF hollow fiber membranes by using especially designed spinneret. The membranes are claimed to have better mechanical strength and provide easy module fabrication. Edwie and Chung [92] have investigated the "layer effects" on performance of MD process. The authors have prepared and compared the performance of single layer PVDF membrane, dual layer hydrophilic/hydrophobic PVDF membrane and dual layer hydrophobic/hydrophilic PVDF/PAN membrane. The most stable performance was achieved by using the single layer membrane with small pore size having cellular morphology.

Thermal induced phase separation (TIPS) is another interesting technique to synthesize the membranes with narrow and controlled pore size distribution. Recently, some investigations have been performed to fabricate and analyze the performance of PP membranes prepared through TIPS. Tang et al. [93] have prepared isotactic polypropylene based membranes with narrow pore size distribution by using TIPS. The factors affecting the structure and performance of these membranes were studied. The method seems to be very promising to fabricate the membranes with specific features for MD applications.

Several miscellaneous studies have been carried out with the aim to study the effect of different parameters on membrane features and performance. Wang et al. [94] have investigated the effect of stretching ratio and heating temperature on characteristics of PTFE membranes. High stretching ratio increased the pore size and overall porosity. The membrane performance was improved by increasing the stretching ratio and heating temperature. Hou et al. [95] have investigated the effect of non-woven fabric support on performance of PVDF membranes prepared through coating and wet phase inversion process. The prepared membranes have shown promising results for desalination through MD. Wang et al. [96] have proposed and tested a strategy based on membrane morphology of dual layer membranes for improving the performance of MD process. The finger like inner layer and a sponge like outer layer minimize the resistance to mass transfer. Consequently, a permeate flux as high as 98 $L/m^2 \cdot h$ was observed at feed inlet temperature of ~80 °C. Shirazi et al. [97] have investigated the performance of nine different commercially available PTF membranes under different operating conditions. The authors have highlighted the importance of selecting the appropriate membrane features for the successful DCMD operation.

2.1.4. Use of green solvents

In addition to the innovations introduced in membrane design, a significant interest has been seen in using the green solvent for membrane preparation. In boarder sense, the term "green chemistry" has been coined by US Environmental Protection Agency to describe the sustainable processes and designs that eliminate or mitigate the use of hazardous solvents, reagents and chemicals. Membrane operations have demonstrated their potential to meet the requirements of sustainable growth in various industrial sectors. However, in order to fully realize the sustainable and green growth by using membrane technology, the membrane synthesis process itself must also be "green". Additionally, environmental regulations are also exerting increasing emphasis on using the environmental friendly solvents. It implies that the materials used for the membrane synthesis must be renewable and the solvents used must not be hazardous or toxic and must be derived from bio based renewable resources in order to ensure the sustainable growth of membrane processes.

Potential green solvents used for membrane preparation through non-solvent induced phase separation include methyl lactate, ethyl lactate, triethylphosphate, dimethyl sulfoxide, γ-butyrolactone and ionic liquids. Similarly, for thermal induced phase separation, the list of green solvent includes triethylphosphate, dimethyl sulfoxide, tributyl O-acetyl citrate (ATBC), tributyl citrate (TBC), triethyl citrate (TEC), triacetate ester of glycerol, γ-butyrolactone (γ-BL), propylene carbonate, dioctyl sebacate, triethylene glycol (TEG), polyethylene glycol (PEG), 2-methyl-2,4-pentanediol and 2-ethyl-1,3-hexanediol [98].

3. Heat and mass transfer

A lot of recent publications aim to address the understanding of heat and mass transport phenomenon in MD from different perspectives. Like past, the most of the studies are based on theoretical approaches. New modeling tools and computational software such as CFD, ASPEN and MATLAB have also been introduced to better elucidate the phenomenon. The most published literature discusses the heat and mass transfer in DCMD and VMD with some evolving significance devoted to AGMD. The main challenge is to incorporate quantitatively the thermal polarization and concentration effect in heat and mass transport analysis. This section describes the different general mathematical approaches applied to elaborate heat and mass transfer analysis while a general overview of heat and mass transfer in various configurations of MD has been provided in Fig. 9.

3.1. DCMD

The flux in membrane distillation can be represented by the following simple correlation

$$N = C\left(P_{fm} - P_{pm}\right) \tag{1}$$

where C is the membrane characteristics parameter and can be calculated by using various models, depending upon the membrane features and operating temperature applied. Three well known models include Knudsen diffusion model, molecular diffusion model and transitionary (also known as combined Knudsen and molecular diffusion) model. According to the Knudsen diffusion model, membrane resistance to mass transfer can be expressed as following.

$$R_{Km} = \left[\frac{2\varepsilon r}{\tau\delta}\left(\frac{8M_v}{\pi R(T_m + 273.15)}\right)^{0.5}\right]^{-1}. \tag{2}$$

Mass transfer according to the molecular diffusion model can be expressed as follows

$$R_{Mm} = \left[\frac{\varepsilon DP_t}{T\delta P_{a,log}}\frac{M_v}{R(T_m + 273.15)}\right]^{-1}. \tag{3}$$

In the above equations, ε, δ, τ, and r represent the membrane porosity, membrane thickness, tortuosity and mean pore radius, respectively. M_v is the molar mass of water molecules, T_m is the average temperature across the membrane, D is the water vapor diffusion coefficient through the air present into the pores, $P_{a,log}$ is the log mean air pressure calculated at the membrane surface temperatures and P_t is the total pressure of air and water vapors.

If the ratio between the mean free path of water molecules and membrane pore diameter is between 0.01 and 1, the mass transport through the pores can be expressed in terms of the combined Knudsen and molecular diffusion models.

$$R_m = R_{Km} + R_{Mm} \tag{4}$$

In the case of DCMD, the total resistance to heat and mass transfer arises from feed side boundary layer resistance, membrane resistance and permeate side boundary layer resistance and the flux can be expressed through the following

$$N = \frac{P_f - P_p}{R_f + R_m + R_p} \tag{5}$$

where P_f and P_p represent the vapor pressure at bulk feed and permeate temperatures, respectively.

The net heat transported through conduction and convection in DCMD can be calculated by using the following well acknowledged relationships

$$Q = Q_c + Q_v = \frac{K_m}{\delta}\left(T_{fm} - T_{pm}\right) + N\lambda. \tag{6}$$

At steady state

$$Qf = Qp \Rightarrow h_f\left(T_f - T_{fm}\right) = h_p\left(T_{pm} - T_p\right). \tag{7}$$

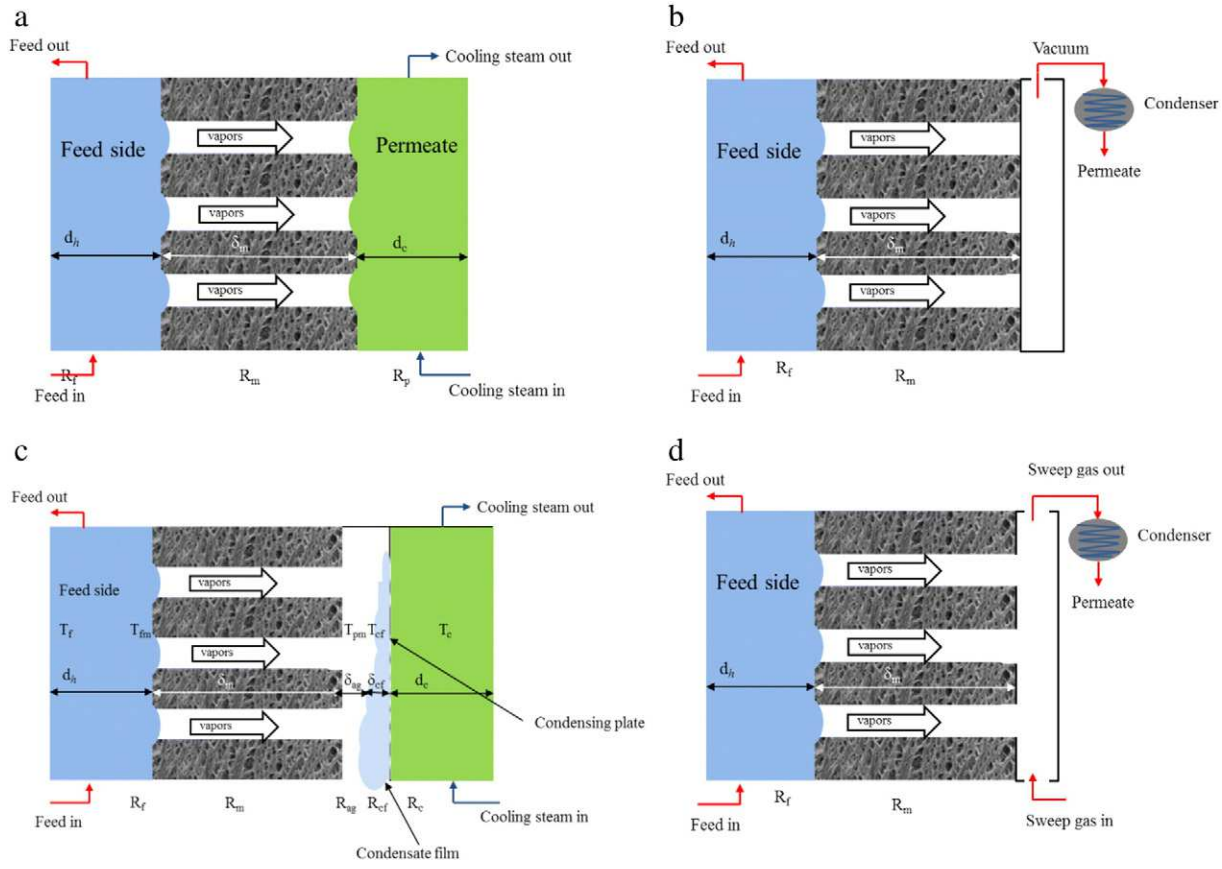


Fig. 9. Different resistances to heat and mass transfer in (a) DCMD, (b) VMD, (c) AGMD, (d) SGMD.

The real challenge is to calculate the temperatures at membrane surfaces (T_{fm} and T_{pm}). To realize this, various approaches have been used [99–101]. The initial pathway was provided by Schofield and Fane [99]. If the transmembrane surface temperature difference is not greater than 10 °C, then the pure water flux can be represented by the following simple relation

$$N = C\frac{\mathrm{dP}}{\mathrm{dT}}\bigg|_{T_m}\left(T_{fm}-T_{pm}\right) \tag{8}$$

where $\frac{dP}{dT}|_{T_m}$ can be expressed according to the Clausius equation

$$\frac{\mathrm{dP}}{\mathrm{dT}}\bigg|_{T_m} = \frac{M\lambda P}{\mathrm{RT}^2}\bigg|_{T_m}. \tag{9}$$

Assuming the same temperature polarization on up and downstream

$$T_m = \frac{T_f + T_p}{2}. \tag{10}$$

Thus Eq. (6) can be written in the following form

$$Q = \left(\frac{K_m}{\delta} + C\frac{\mathrm{dP}}{\mathrm{dT}}\bigg|_{T_m}\lambda\right)\left(T_f - T_{fm}\right) \tag{11}$$

$$Q = H\left(T_{fm}-T_{pm}\right). \tag{12}$$

Combining Eqs. (7), (11) and (12)

$$\left(T_{fm}-T_{pm}\right) = \frac{T_f - T_p}{1 + \frac{H}{h_f} + \frac{H}{h_p}} \tag{13}$$

$$\left(T_{fm}-T_{pm}\right) = \mathrm{TPC}\left(T_f - T_p\right) \tag{14}$$

where TPC represents temperature polarization coefficient. From Eq. (8) and (13)

$$\frac{\Delta T}{N\lambda} = \frac{1}{\mathrm{dP}/\mathrm{dT}}\frac{1}{\lambda C}\left(1 + \frac{K_m/d_m}{h}\right) + \frac{1}{h}. \tag{15}$$

The permeability C and overall heat transfer coefficient h ($1/h_f + 1/h_p$) can be determined by plotting $\frac{\Delta T}{N\lambda}$ vs $\frac{1}{\mathrm{dP}/\mathrm{dT}}$ as illustrated by Eq. (15).

The Eq. (12), was originally developed for $T_{fm} - T_{pm} \leq 10$ °C and for pure water as feed and permeate [99].

A more general approach for the determination of up and downstream heat transfer coefficients is based on the use of various correlations to calculate heat transfer coefficients at different feed flow velocities. The main drawback of this approach is the very different values predicted by the different correlations even under the same conditions and averaged predicted value of heat transfer coefficient across the fiber. Once the heat transfer coefficients are known, the corresponding surface temperatures can be calculated by using the known flux and membrane heat transfer coefficient.

In order to overcome the problems associated with the determination of heat transfer coefficients by the above mentioned approaches, the use of different numerical approaches has been introduced. By applying the heat, mass and momentum balance under the given boundary conditions, the temperature at the membrane surfaces can be predicted. Al-Sharif et al. [102] have modeled the effect of three different spacer types on heat and mass transport in DCMD by using open source computational fluid dynamic (CFD) code. [103] have investigated local heat flux, membrane surface temperature, thermal polarization and thermal efficiency of DCMD system in counter current configuration. The effect of hollow fiber microstructures on hydrodynamic, thermal polarization and flux for wavy and geared shaped geometries by using CFD analysis has been provided by [104]. Manawi et al. have developed a predictive model for MD incorporating the effect of various operating parameters including feed and permeate temperatures and flow rates, flow configurations and flow regimes [105]. The membrane has divided into n control volumes on each hot and cold side, exchanging heat and mass transfer with each other. The experimental results have been claimed in good agreement with the model predictions. Kurdian et al. [106] have used mass and energy balance to model the flux behavior of GVHP hydrophobic membranes operating on aqueous solution of sodium chloride and sodium sulfate.

Recently some ambitious attempts have been observed in measuring the membrane surface temperature directly by using different techniques. Tamburini et al. [107] have used a technique based on thermochromic liquid crystals and digital image analysis tool to investigate the thermal polarization in spaced filled channels used in MD studies. The hot and cold channels were fabricated between plexi glass chambers and a polycarbonate thin sheet that mimics the membrane. Thermochromic liquid crystals were incorporated at the hot feed side adhering with the polycarbonate sheet by using silicon grease. The surface of TLC was illuminated and images were recorded at various experimental conditions for further analysis of temperature distribution along and across the channels by using MATLAB image processing toolbox. On the basis of experimental results obtained, a correlation between Nusselt number and Re and Pr was proposed for the system. Ali et al. [108] have used a cell equipped with 16 temperature sensors to measure the temperature profiles on feed and permeate side in DCMD. The effect of different parameters on thermal polarization has been investigated by directly monitoring the bulk and interfacial temperatures. The authors have concluded that heat transfer coefficient can be predicted by using the relationship predicted by [101].

3.2. AGMD

For AGMD, the mass transport across the membrane can be described by general Eq. (1), however, the presence of the air gap offers an additional resistance to the water vapors before these are condensed at the condensing plate. The water flux in the air gap can be written as

$$N = \frac{P_{pm} - P_{cf}}{R_{ag}} \tag{16}$$

$$R_{ag} = \left[\frac{\varepsilon\,\mathrm{DP}_t}{\delta_a P_{ag,log}}\frac{M_v}{R\left(T_{ag,avg} + 273.15\right)}\right]^{-1}. \tag{17}$$

In the above expression, δ_a is the air gap width while $P_{ag,log}$ and $T_{ag,avg}$ represent the log mean pressure and temperature within the air gap. The other terminologies are according to those illustrated in Fig. 9c.

Thus the total resistance to mass transfer can be represented as the sum of membrane resistance and air gap resistance

$$R_{AGMD} = R_m + R_{ag}. \tag{18}$$

If the membrane resistance is defined by combined Knudsen and molecular diffusion model, then the total resistance to mass transfer in AGMD can be expressed in the following way.

$$R_{AGMD} = R_{Mm} + R_{km} + R_{ag} \tag{19}$$

Introducing R_{Mm}, R_{Km} and R_{ag} from Eqs. (2), (3) and (17) into Eq. (19) yields the following simplified expression

$$R_{AGMD} = \left(\frac{\tau\delta}{\varepsilon} + \delta_a\right)\frac{P_{ag,log}}{DP_t}\frac{R\left(T_{ag,avg} + 273.15\right)}{M_v} + \left[\frac{2\varepsilon r}{\tau\delta}\left(\frac{8M_v}{\pi R(T_m + 273.15)}\right)^{0.5}\right]^{-1} \quad (20)$$

and the net flux can be written as

$$N = \frac{P_{fm} - P_{cf}}{R_{AGMD}} \quad (21)$$

where P_{pm} and P_{cf} are the water vapor pressures at membrane surface on permeate side and at condensing film, respectively, according to the nomenclature used in Fig. 9(c) and R_{AGMD} is the net resistance offered and can be determined by using Eq. (20).

Heat transfer across the membrane can be expressed by Eq. (6) while for the air gap it can be calculated by the following expression

$$Q_{ag} = \frac{K_{ag}}{\delta_a}\left(T_{pm} - T_{cf}\right) + N\lambda \quad (22)$$

where K_{ag} is the thermal conductivity of air/water mixture present in the air gap. The condensed vapors form a film at the condensed plate that offers an additional resistance to the heat transfer across the plate. The heat transferred across the falling film can be calculated by the following expression

$$Q_{cf} = \frac{K_{cf}}{\delta_{cf}}\left(T_{cf} - T_{cw}\right) \quad (23)$$

where K_{cf}, δ_{cf} and T_{cw} represent the thermal conductivity of condensed water, thickness of the condensed film and temperature at the interface of condensed film and condensing plate.

The heat transferred across the condensing plate can be expressed by the following relation

$$Q_{cp} = \frac{K_{cp}}{\delta_{cp}}(T_{cw} - T_{cc}) \quad (24)$$

where K_{cp} and δ_{cp} represent the thermal conductivity and thickness of condensing plate while T_{cc} is the temperature at the interface of condensing plate and cold fluid. Heat transfer for the coolant channel can be determined by using the flowing equation.

$$Q_c = h_c(T_{cc} - T_c) \quad (25)$$

where h_c and T_c represent the convective heat transfer coefficient and temperature of the cooling fluid, respectively.

The temperature polarization coefficient in AGMD can be defined as

$$TPC = \frac{T_{fm} - T_{cf}}{T_f - T_c}. \quad (26)$$

It should be noted that the condensed film, condensing plate and thermal polarization in cold fluid increase the value of P_{cf} and thus decrease the effective driving force.

Various activities can be seen in recent literature to optimize and understand the AGMD process. The effect of removal of air from the membrane pores and feed water deaeration has been discussed in [109]. The air entrapped in the pore and air gap can significantly reduce the mass transfer in AGMD. The use of deaerated water has been claimed to increase the flux and reduce the thermal energy demand. It was further claimed that the additional energy consumed in deaeration can be compensated by the additional product obtained. The concept of directly heating the composite membrane for desalination purposes through AGMD has been introduced in [110]. The top surface of the composite membrane can absorb the solar energy while the underneath hydrophobic surface ensures the required non-wettability. The important of reducing the pressure in air gap has also been highlighted in the same study. Geng et al. [111] have used the energy recovery hollow fiber to directly heat the feed by using the latent heat of vapors condensed at the surface of heat exchanger hollow fiber. Alsaadi et al. [112] have used the mathematical equations applied to explain heat and mass transfer phenomenon in single stage AGMD to develop a one dimensional AGMD model. The model was validated for various operating conditions, process parameters and membrane features. It was also claimed that the model can predict the upscale AGMD installation too.

3.3. VMD

In the case of VMD, the cold permeate is replaced with vacuum, therefore, the resistance offered by the permeate vanishes. Therefore the flux can be expressed by the following simplified expression

$$N = \frac{P_f - P_v}{R_f + R_m}. \quad (27)$$

Furthermore, the removal of air from inside the pores due to the vacuum facilitates the mass transport. In VMD, Knudsen diffusion model is commonly used to describe the diffusion through the pores [113,114], though combined Knudsen and Poiseuille flow has also been applied [115]. The existences of a broader pore size distribution can result into the coexistence of all mass transport mechanism simultaneously. In this case, the pore size distribution can be applied to accurately elaborate the mass transport mechanism. Due to the absence of contact of cold permeate with the membrane surface, thermal polarization effect is relatively less than DCMD.

Neglecting the conductive heat transport through the membrane, the heat balance reduces to

$$Q = N\lambda = h_f\left(T_f - T_{fm}\right). \quad (28)$$

The membrane surface temperature used in Eq. (28) can be calculated by assuming an initial value of T_{fm} followed by the calculation of transmembrane flux for a given permeability of the membrane, the trial and error procedure of assuming the temperature and calculating the corresponding flux is continued until the experimental flux and theoretical flux become equal [116]. The other approach involves the determination of flux as function of the feed flow rate. At infinite feed velocity, the temperature at the membrane surface becomes equal to its value in the bulk. Thus, the effect of thermal polarization on flux at lower feed velocities can be quantified through the relationship established between the feed velocity and flux [117].

Zhang et al. [115] have proposed a new method based on gas permeability data to measure the properties of hollow fiber membranes to be used in modeling of VMD. The modeling predictions agree well with the experimental flux, although the difference diverged at high temperatures. Zuo et al. [113] have built and solved a two dimensional model with finite element method for VMD by using hollow fibers. The model incorporates the effect of feed inlet temperature, feed flow rate, fiber length and degree of vacuum applied on temperature, velocity and pressure distribution along and across the fiber. It has been predicted that water production cost through VMD can be reduced to ~38% by using the optimized design and conditions. Similarly, [118] have proposed a one dimensional model to predict the performance of hollow fibers in VMD by simultaneously solving the energy, mass and momentum conservation equations. Kim [119] has modeled the temperature distribution across the feed and permeate channels by using perturbation theory and method of separation of variables.

Table 10
A summary of research articles describing different aspects of heat and mass transfer in various MD configurations.

Configuration	Nature of work	Brief description	Ref.
DCMD	Theoretical	Effect of feed and permeate inlet temperatures, flow rates and feed concentration on characteristics of MD flux curve has been studied.	[109]
DCMD	Theoretical, experimental	The effect of membrane compression on its performance under applied pressure	[110]
DCMD	Theoretical	Modeling the thermal efficiency and flux behavior of compressible and incompressible membranes	[111]
MCr	Experimental	Effect of microwave irradiation on crystallization of NaCl and $CaCO_3$ salts	[112]
MCr	Experimental, theoretical	Effect of process conditions on performance of crystallizer, crystal size distribution, mean crystal size etc.	[113]
MCr	Experimental, theoretical	Effect of operating conditions on NaCl crystallization from RO brine, simulation of crystallization order by using PHREEQC	[114]
General	Experimental	Investigation of flow dynamic in different fiber configurations by using low-field nuclear magnetic resonance imaging (MRI)	[115]
DCMD	Experimental, theoretical	Effect of PTFE membrane characteristics including pore size, porosity, thickness, tortuosity and support structure on their performance	[116]
DCMD	Experimental	Fabrication of mechanically robust, chemical resistant and super hydrophobic membranes and effect of their surface energy on MD performance	[117]
DCMD	Theoretical and experimental	Effect of introducing the surfaces with different roughness on performance of MD process	[118]
VMD	Theoretical	Development of a ballistic transport model to describe mass transfer in VMD	[119]
VMD	Theoretical and experimental	Use of gas permeability data to predict the membrane performance	[115]
VMD	Theoretical and experimental	Development of simultaneous heat and mass transport model to simulate the effect of operating conditions on VMD performance	[114]
Multi-VMD	Theoretical	Performance evaluation of multi-VMD process by using a one dimensional model	[120]
AGMD	Theoretical and experimental	Use of response surface methodology to optimize AGMD process	[121]
AGMD	Experimental	Effect of feed and air gap deaeration of AGMD (PGMD) performance	[109]
AGMD	Theoretical and experimental	Effect of direct solar heating of composite membrane and air-gap-deaeration on performance of AGMD	[109]
AGMD	Experimental	Effect of operational and membrane parameters and energy recovery on AGMD process	[111]
AGMD	Theoretical and experimental	Development of validation of model for FS membranes for counter current and co current configurations	[112]
AGMD	Experimental	Effect of membrane pore size and hydrophobicity on its performance against high concentration saline solutions	[122]
SGMD	Experimental	Effect of operating parameters on performance of SGMD	[123]
SGMD	Theoretical	Modeling and optimization of SGMD process	[124]

Lovineh et al. [114] have developed a simultaneous heat and mass transport model to predict the effect of operating conditions and membrane characteristics on the performance of VMD process. The authors have concluded the insensitiveness of the process performance towards membrane materials when the pore size is tiny.

In addition to the above mentioned investigations, different tactics have been used to better elucidate the heat and mass transport phenomenon in MD. A list of different attempts has been provided in Table 10.

4. Module designing for MD

After the availability of appropriate membranes for any application, the next most important step is to assemble these membranes in a particular configuration to ensure the required membrane area enclosed in a particular module volume. In addition to provide compactness, an appropriate module design can reduce the thermal/concentration polarization, fouling and energy consumption of the process. These advantages can be realized by disturbing the normal flow pattern that develops along the fiber. Adequate module design can improve the hydrodynamic on shell and lumen side, thus imparting a positive impact on the process. In this context, the module designing provides an economical alternative of the active techniques to change the hydrodynamic conditions in the membrane. Despite of these benefits, the investigations on module design are limited in number generally for membrane operations and particularly for MD.

Similar to the other membrane based processes, module design for MD is crucial to use the process more rationally. An appropriate module design for MD applications should take into consideration the minimization of thermal polarization on up and downstream, appropriate packing density to ensure the module compactness, robustness, achievement of high energy efficiency, suitable length, high volume based enhancement factor and relatively easy fabrication with the flexibility to apply for the maximum configurations. In addition, the material implied for module fabrication must ensure the minimum thermal losses and must be heat resistance. There are several different industrial sectors looking at MD with different demands that further underline the importance of flexibility in module design. In MD, several possibilities have been considered to design an appropriate module:

- use of appropriate flow scheme to maximize the temperature gradient along the membrane (counter flow, cross flow, concurrent)
- use of baffles and spacers (Fig. 10) to homogenize the temperature distribution within a stream
- use of different fiber geometries to ensure the uniform heat distribution within the module
- use of heat recovery devices

He et al. [125] have provided the concept of heat recovery by interstate heating of the cold feed by using the permeate of previous stage in a cascade of modules. A schematic of the concept used by the author has been shown in Fig. 11. The authors have provided a theoretical analysis of countercurrent cascade of cross flow DCMD modules. Such cascades can be useful in improving the recovery and energy efficiency of

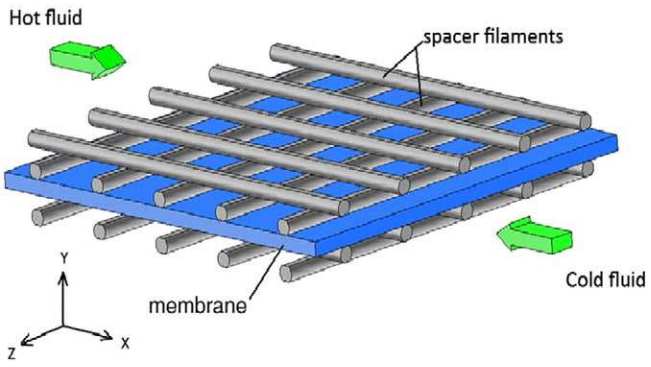


Fig. 10. Space filled channels used to improve the hydrodynamic conditions at the membrane surface in MD [128].

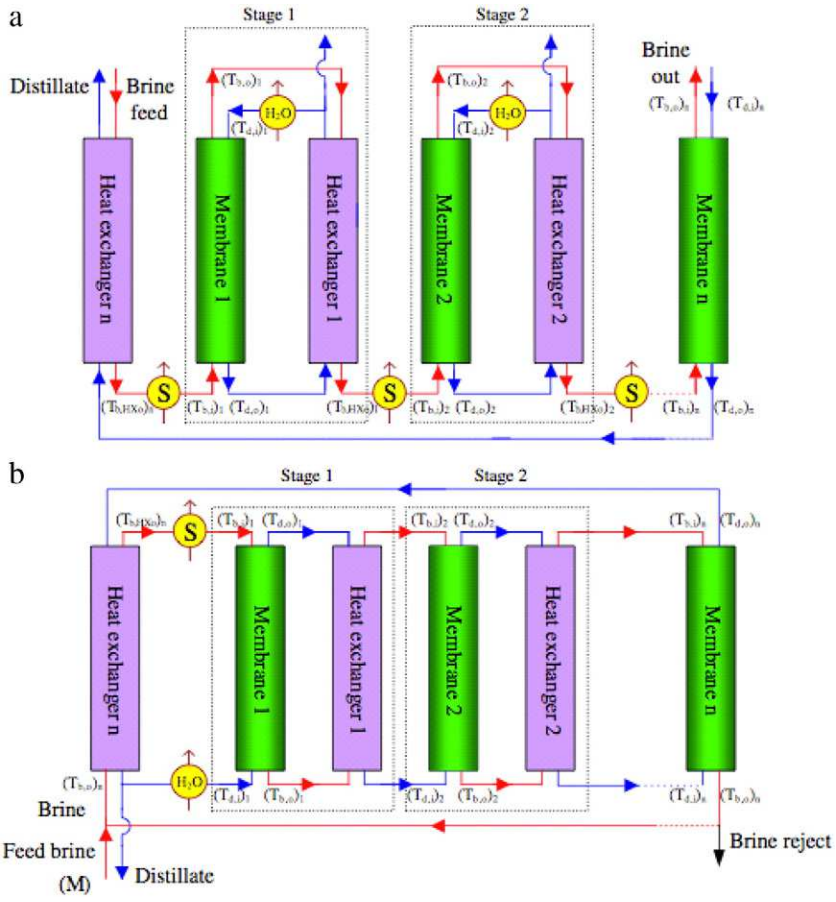


Fig. 11. Cascade module design used by [125].

the system. The authors have claimed a recovery of 60% and gain output ratio of more than 60% for appropriate configurations and temperature difference. Yang et al. [126] have investigated the effect of various fiber geometries (Fig. 12) on performance of DCMD both experimentally and theoretically. The flux enhancement as high as 300% has been claimed due to reduced thermal boundary layer resistance. Experimental and theoretical feasibility of roughened surface for DCMD process has been demonstrated by Ho et al. [127].

Rotational and tangential to the membrane surface flow have been proven very affective in increasing the performance of the AGMD [129]. Such flow combined with the partial contact of membrane with condensing surface in AGMD has caused synergetic effects. The authors have claimed the permeate flux as high as 119 kg/m^2·h at feed inlet temperature of 77 °C. The claimed flux is ~2.5 times higher than the flow observed in traditional AGMD studies carried out under the identical conditions. The authors have associated the improvement with improved heat and mass transfer due to the specific flow patter generated and due to the contact of membrane with the cooling plate. AGMD module designing involves bulky modules in order to incorporate the air gap, condensing plate and cooling channel. In their proposed configuration as illustrated in Fig. 13, Singh and Sirkar [130] have introduced porous and non-porous hollow fibers in the same lab scale modules to compact the module volume. The vapors from hot feed passing through the porous fibers are condensed at the outer wall of non-porous fiber which has been cooled by the circulation of a cold fluid inside the fiber. On the similar lines, Geng et al. [131] have designed a module with the heat exchanging

Fig. 12. Various hollow fiber configurations used by [126].

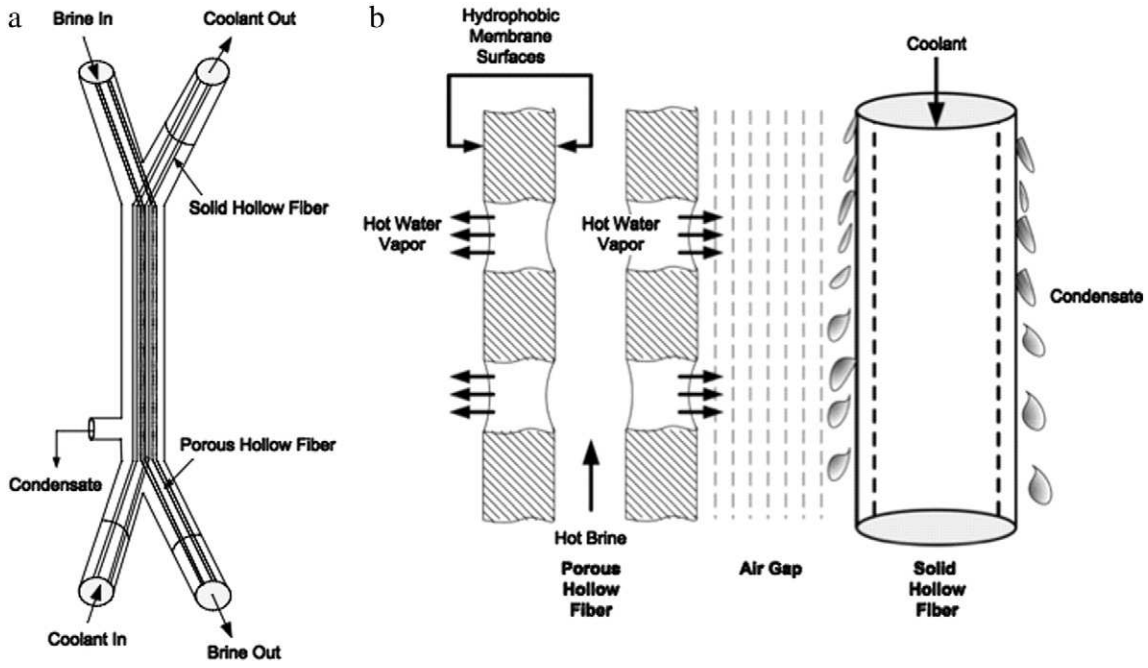


Fig. 13. Conceptual mechanism of hollow and heat recovery fibers used in [130].

hollow fibers that collect the latent heat of vapors and transfer to the cold feed. The authors have claimed a thermal efficiency of 80% or higher in all the studied cases.

Zhao et al. [13] have explored the performance of a V-MEMD module introduced by memsys under solar and diesel heating arrangements. The authors have identified the number of stages and the size of each stage as the key parameters for optimizing the module performance for large scale applications. The module efficiency is mainly controlled by the hot and cooling fluid temperatures. From optimization results, it was concluded that the module has a very attractive gain output ratio. Zhang et al. [132] have explored the effect of fiber packing density and module length on their performance in VMD. The initial flux decay under constant operating conditions was attributed to the membrane compression that took place due to the hydraulic pressure. The shorter modules with compact packing have been recommended by the authors for a high yield per unit module volume. The authors have also pointed out that increase in flux at high feed flow rate is due to increased average temperature instead of enhanced thermal polarization coefficient. The effect of liquid distributor on the performance of VMD process has been investigated theoretically by Wang et al. [133]. The authors have claimed that the appropriate design of distributor plays a significant role in optimizing the performance of VMD process. The liquid distribution in dome-like and pyramidal distributor was better than plate-like distributor.

In the recent years, a further MD enhancement was developed and produced by Fraunhofer Institute for Solar Energy Systems (ISE) which works on the development of energy self-sufficient desalination systems based on solar driven MD technology since many years. Recently, studies and productions of spiral wound MD-modules in permeate gap membrane distillation (PGMD) have been carried out (Fig. 14a).

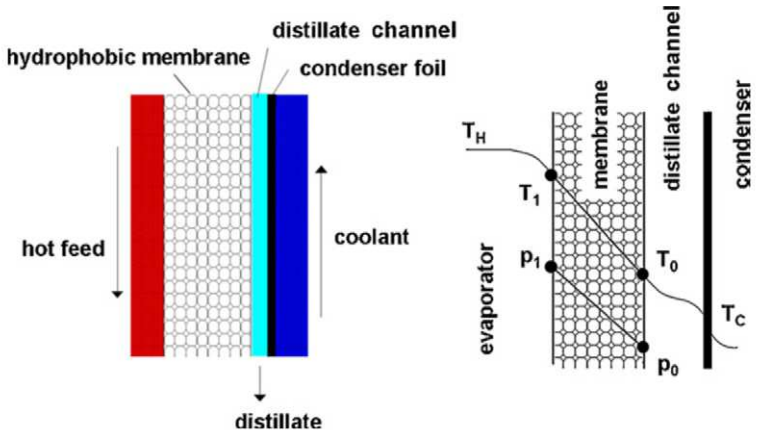
PGMD is one of the possible MD configuration in which a third channel is introduced by an additional non-permeable foil. The advantage of this arrangement is the separation of the distillate from the coolant. Therefore the coolant can be any other liquid, such as cold feed water. Winter et al. [109] report that the presence of the distillate channel reduces sensible heat losses due to an additional heat transfer resistance; the disadvantage is the reduction of the effective temperature difference across the membrane, which slightly lowers the permeation rate [109]. In module development, PGMD opens the opportunity to integrate an efficient internal heat recovery system as can be seen in Fig. 14b.

Water vapor passes through the membrane and condenses in the distillate channel. The latent and sensible heat is transferred through the condenser foil to preheat the feed water in the condenser channel by internal heat recovery. An external heat source (e.g. solar collector) heats the feed water until the desiderated temperature (only from 73 to 80 °C in Fig. 14b). The activities carried out by Winter et al. [109] prove that, in this configuration, the main effect of the active membrane area increase is the significant reduction in the specific energy demand. This justifies the transfer of the PGMD channel configuration into a compact spiral package where, even without module insulation, only minimal heat losses to ambient occur.

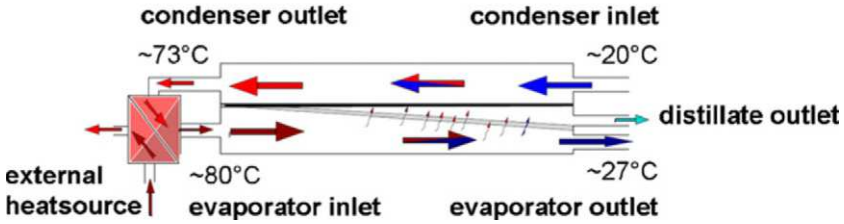
5. Fouling in membrane distillation

Due to different transport phenomena, generally rigorous feed characteristics and use of hydrophobic membranes, the nature of fouling in MD is different from other low pressure membrane processes. A summary of various types of fouling observed in MD has been provided in Table 11. Scale formation at the membrane surface is the most common form of fouling observed in MD process when applied to concentrated salt solutions. With the advent of novel applications of MD, other types of fouling can also be seen in various studies. For example, the fouling phenomenon becomes more significant and severe while treating the solutions containing macromolecules that have tendency to adsorb at the membrane surface [134]. Protein-type macromolecules have special tendency to adsorb at the membrane surface. The initial fouling layer in such cases can be associated with the adsorption of molecules at the hydrophobic surface. Once built, such layer will tend to accumulate more solute molecules at the membrane surface and ultimately, a thick cake layer can establish under high convective flux conditions. The initial adsorption at the membrane surface followed by the further buildup of fouling cake layer can decrease the flux due to increase in net resistance to heat and mass transfer. The thickness of the fouling layer can play a decisive role in controlling the heat and mass transfer across the membrane [135].

In addition to the typical fouling, some other parameters also affect the MD performance. The mass transfer rate across microporous



a) Basic channel arrangement and temperature profile for PGMD [109].



b) Module arrangement for PGMD [109].

Fig. 14. a. Basic channel arrangement and temperature profile for PGMD [109]. b. Module arrangement for PGMD [109].

hydrophobic membrane in MD is driven by the temperature gradient across the membrane surfaces. The heat losses attributed to the conduction through the membrane and convection associated with the vapor transport reduce the surface temperature at the feed side and increase the corresponding temperature at the permeate side, thus inducing the thermal polarization at both sides. The effect of temperature polarization on flux reduction in membrane distillation has been well acknowledged in several studies [17,99,136]. For a well-designed system, the value of thermal polarization coefficient has been indicated in the range of 0.4 to 0.7 [17].

The scale formation at the membrane surface has been observed in the studies addressing the MD applied to solutions containing salts. Gryta [137] has investigated the membrane distillation performance in treating the spent solution from heparin production. The rapid flux declined was reported due to the fouling and scaling. The presence of salt deposits on distillate side confirms the occurrence of wetting as well. The removal of foulants by boiling the feed followed by the separation of the deposits was found to be an affective pretreatment to reduce the fouling during the membrane distillation process. The problem of scale formation at the distribution channel of the membrane modules and at the membrane surface was observed in a study conducted by Kullab and Martin [138] for production of water for cogeneration power plants. The permeate quality and the operation stability were dependent upon the nature of the feedstock. Ca and Mg were identified as the main scale forming salts. In another study, Gryta [139] has analyzed the performance of MD against several different types of feed solutions including brine, bilge water and water containing protein. The strength and nature of fouling were dependent upon the feed and operating conditions used. The formation of Ca and protein based deposits on the membrane surface was detected. The scale formation in MD was pointed out as one of the major responsible factors for wetting, flux reduction and damage to the membrane structure. The formation of porous deposits decreases the flux by lowering the heat transferred to the membrane surface while the non-porous deposits increase the resistance to the mass transfer. The scaling occurred at membrane surface and in distribution channels observed in various studies has been shown in Fig. 15.

More recently, some further focus has been devoted for deeper understanding of scaling in MD process. Burrieza et al. [142] have studied the effect of intermittent MD operation at the surface scaling. The intermittent operation has been simulated by exposing the PTFE and PVDF membranes to wet/dry cycles. A decrease in contact angle and scaling

Table 11
Different types of fouling observed in MD studies.

Feed type	Membrane used	Type of fouling observed	Reference
Wastewater from heparin production	PP capillary membranes	Wetting, deposition, scaling, biofouling	[137]
NaCl solution	Accurel PP S6/2 membrane	Wetting, surface scaling	[156]
Synthetic wastewater	PVDF flat sheet MILLIPORE® Durapore GVHP)	Wetting, thick layer of biofouling	[145]
Bilge water, saline water from meat processing industry, tap water	Accurel S6/2 PP, Membrana, Germany	Deposit layer formation at the surface, bio fouling, surface and internal crystallization	[139]
Skim milk and whey solution	PTFE flat sheet membranes with woven PP support, GE Osmonics, Minneapolis, MN, USA	Layer of deposits at the membrane surface	[147]
Municipal water and flu gas condensate	PTFE flat sheet, SCARAB AB.	Scale formation at the membrane surface	[138]

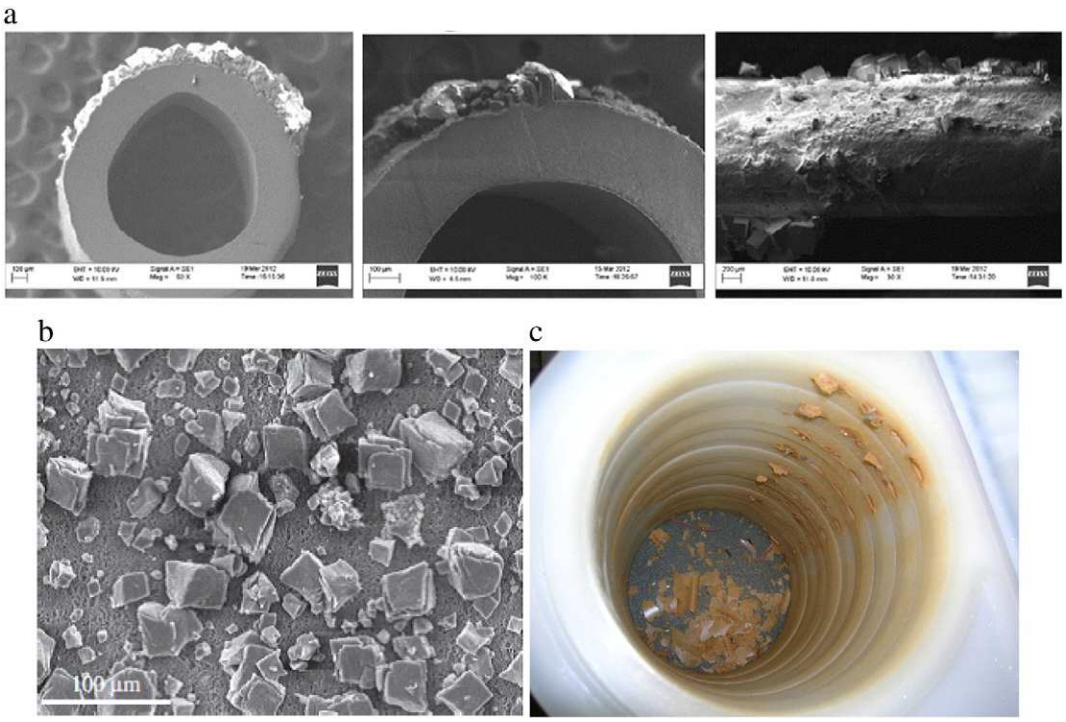


Fig. 15. Scale formation observed at the membrane surfaces and in distribution channels (a, b and c taken from [140,141,138] respectively).

inside the pores was observed. The scaling inside the pores was more prominent for PVDF based membranes due to their low contact angle. The scaling reduced the surface roughness and promoted the calcium carbonate adhesion with the surface. The effect of coating on surface scaling of heat exchanger has been investigated by Al-Janabi et al. [143]. The authors have developed and applied various coatings at the surface of heat exchanger to be used in MD to minimize the surface energy and to impart anti-scaling properties. The electron donor coating materials have shown the best performance. Ge et al. [144] have investigated the surface scaling and wetting behavior of PVDF membrane under different operating conditions. The authors have observed that scaling and wetting increase with temperature. Chen et al. [140] have demonstrated the efficacy of gas bubbling in controlling the surface scaling in DCMD process. A significant increase in flux and delayed flux decline were observed under the gas bubbling conditions. Similarly, the use of polyphosphate has been proven effective in decreasing the $CaCO_3$ scaling at membrane surface in another study [141].

Due to the emerging use of MD process in membrane bioreactors, the importance of understanding and control of bio fouling in MD has gained more significance. Goh et al. [145] have highlighted the importance of bioprocesses in controlling the membrane wetting of MD present at downstream. The authors have shown that biofouling formed at the membrane surface does not only cause membrane wetting but can also increase the resistance to heat and mass transfer. MD integrated at downstream of bioreactor is less prone to wetting and fouling due to the removal of nutrient in the bioreactor. The effect of sludge hydrophilicity on biofouling and transport characteristics in membrane has been studied by Goh et al. [146]. The microporous structure of the biofilm has been held responsible for vapor pressure depression and further addition of resistance to heat and mass transport. The membrane with high thermal resistance and a hydrophilic layer facing to the feed can mitigate the vapor pressure reduction. A detailed understanding of fouling of dairy products on hydrophobic membranes applied in MD can be found in the work by Hausmann et al. [134,147] (see Fig. 16).

The knowledge and tactics used to control biofouling in traditional MBRs can be utilized to address the biofouling issue in MD. Widespread applications of MBRs in various fields have been hampered due to the problem of biofouling. In traditional MBRs, several strategies have been applied to mitigate the biofouling. The use of additives ([148] and specific media ([149] has been effective in reducing the biofouling from membrane surface. Specific designing of the membrane systems and membrane modifications have also been useful in controlling the biofouling [150,151]. Likewise conventional MBRs, the use of emerging bio based approaches has great potential to control biofouling in MD process too. One prominent example of such approaches is quorum quenching that is based on interrupting the quorum sensing between the microorganisms responsible for cell to cell communication, formation of biofilm and excretion of extracellular polymeric substances [152], as illustrated in Fig. 17. The immobilized quorum quenching enzymes have proven very useful in controlling the biofilm formation by interrupting the quorum sensing. Due to the problems associated with enzyme based quorum quenching (difficult extraction and purification and instability), the new efforts focus on the utilization of bacteria that produce quorum quenching enzyme [152,153]. Such techniques can be very beneficial to alleviate biofouling in MD too.

The successful application of the membrane distillation has been associated with the fulfillment of non-wettability criteria of membrane pores. When the hydraulic pressure exceeds the liquid entry pressure, the membranes are prone to wetting. The effect of wetting is not only possible reduction in flux and degradation of permeate quality but also a severe fouling inside the pores caused by the precipitated/adsorbed materials. Recently, Gilron et al. [154] have investigated the effect of silica scaling and membrane pore wetting on MD process. In the case of partial wetting, it has been shown by the authors that the temperature at the pore mouth can be significantly less than that at the membrane surface and can decrease the temperature polarization coefficient. For a given feed and membrane combination, the wetting can be controlled by selecting the appropriate conditions of temperature and flow rate (hydraulic pressure). More comprehensively, feed temperature, feed composition, pore size and hydrophobic character of the membrane combined with the hydraulic pressure

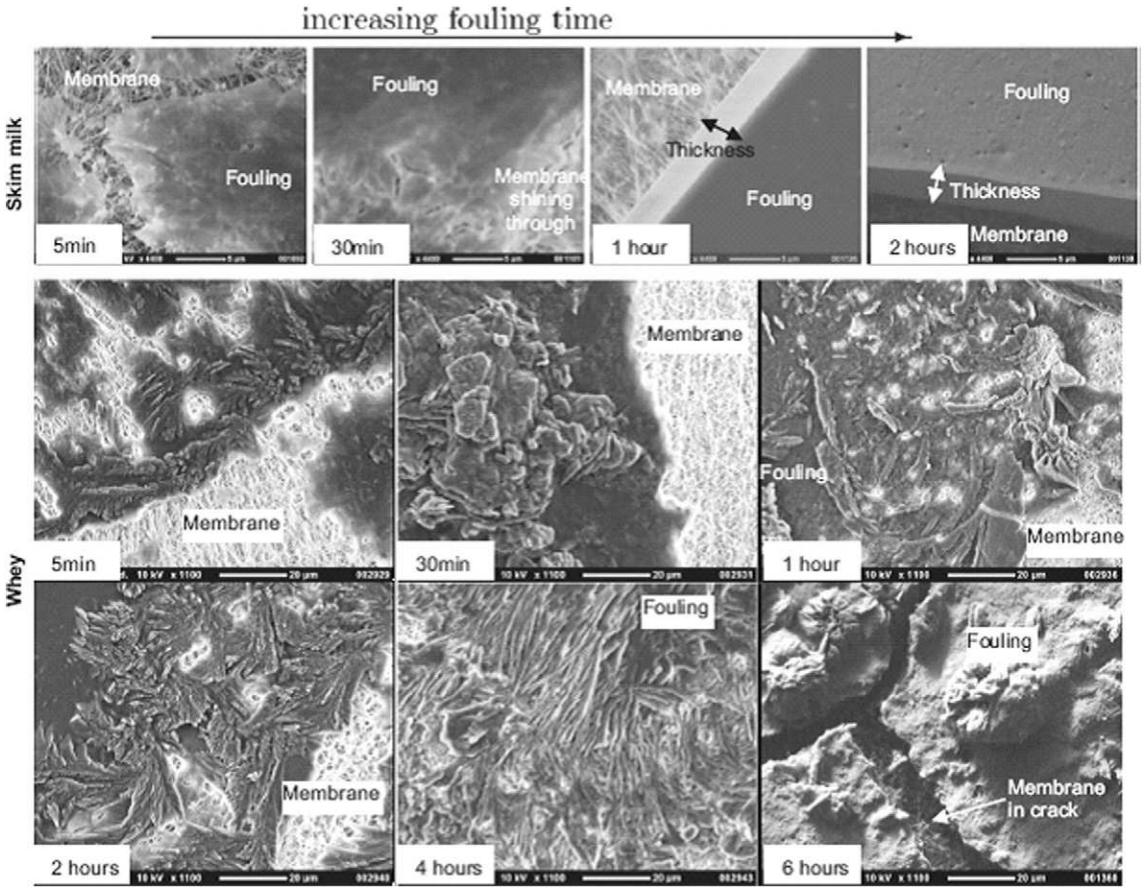


Fig. 16. Fouling caused by skim milk (top) and whey solution (bottom) as function of time [134].

applied at the membrane surface will dictate the wetting phenomenon in MD.

6. Emerging applications of MD

Traditionally, MD has been utilized for desalination purposes as an alternative to RO or to overcome limited recovery of RO and other thermal desalination techniques [157]. Moreover, MD has been considered as a viable candidate in arid areas which lie in the region with abundant solar energy available, thus further confining its application mostly for desalination [158]. However, a lot of other interesting applications of MD have been explored due to less fouling tendency of the process, the potential to treat the complex feed solutions and due to the fact that the separation is driven by the temperature induced phase

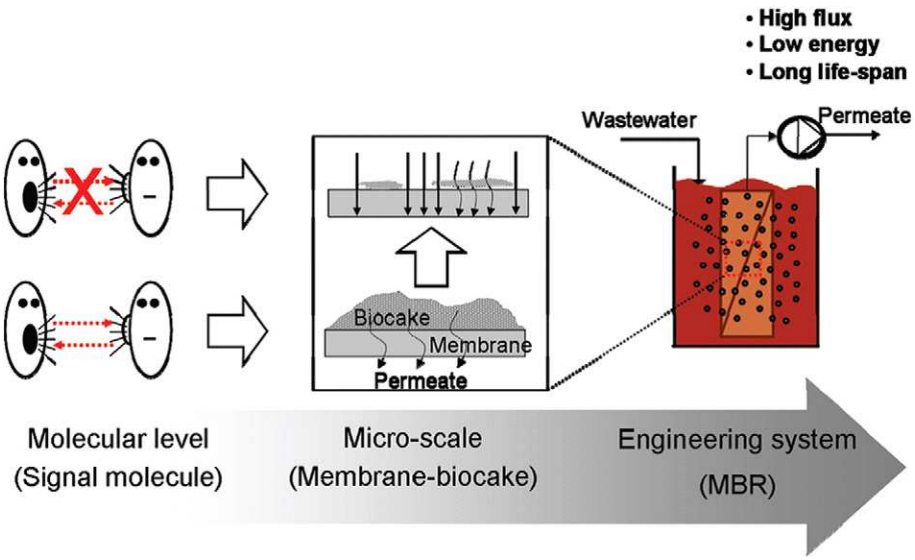


Fig. 17. Schematic diagram of quorum sensing mechanism for biofouling control in MBRs [155].

equilibrium establish at a particular temperature. The temperature gradient base nature of the process also opens new novel opportunities to use it for vapor/gas separation applications where the equilibrium composition at any temperature is enriched with the more volatile component. Consequently, the sphere of applications of the process has extended beyond the traditional use of desalination.

In addition to the traditional membrane based processes, MD has potential for temperature sensitive products such as pharmaceutical compounds, juices, dairy products, natural aromatic compounds and solutions of several chemicals. The process can be applied in the fields where a very high rejection of certain component is required such as the treatment of nuclear waste or radioactive water and water for semiconductor industry. In oil and gas sector, shale gas has been identified as the game changer due to its abundant availability in various regions across the world [159]. However, the detrimental environment impacts of shale gas exploration are big hindrance in its wide spread adaptation. The fracturing or produced water is one of the major causes responsible for the hazardous environmental impact of exploring shale gas. Produced water contains very high level of salts, various hydrocarbons and production chemicals. Treatment of such complex steam through state-of-the-practice processes is really challenging [160]. Moreover, high pressure and temperature of the produced water during the production process provide additional complexity for its immediate treatment. MD has proven a feasible candidate for the treatment of this water after certain physical processes that remove hydrocarbons from the stream [161]. Similarly traditional MBRs suffer from the major fouling issues. MD as standalone process or in integration with some other processes (such as FO) has provided very interesting results [162]. Similarly the removal of heavy metals that acts as a micropollutant is challenging for existing RO plants. For example, due to its existence as boric acid under normal pH conditions, the boron can diffuse through the RO membrane and thus traditional RO cannot meet the required removal criteria (0.5–2.5 ppm). The current alternative techniques are either costly or not robust as the operating conditions change. MD has been applied successfully to remove the boron well below the set limits. Similarly, the removal of chromium has been successfully achieved to the desired level by using MD.

Another potentially interesting field for MD is the recovery/removal of phosphorous from agricultural, household and industrial runoffs. The presence of phosphorous in soil is essential for growth of crops. On the other hand, the access of phosphorous gives rise to the condition known as eutrophication, characterized by the excessive growth of algae inside the water thus reducing the oxygen level and causing an adverse effect on marine life. As the phosphorous reservoirs are limited, MD as standalone process or in integration with other membrane based processes can be utilized not only to control the level of phosphorous in water runoffs but also to recover phosphorous crystals from the phosphorous rich-streams [163]. Similarly, during protein crystallization and crystallization of pharmaceutical compounds via membrane crystallization (which is just an extension of MD, a process in which the evaporative mass transfer of volatile solvents through the microporous hydrophobic membranes is utilized to concentrate feed solutions above their saturation limit, thus attaining a supersaturated environment where crystals may nucleate and grow), the level and rate of supersaturation can be finely tuned and membrane surface creates heterogeneous nucleation providing the opportunity to selectively crystallize various polymorphs [15]. Similarly, the recovery of various valuable components from waste streams and RO brine has been reported in several studies [164–166]. The crystals recovered through MD process show better quality in terms of crystal size, crystal size distribution, coefficient of variance and nucleation kinetics.

A list of innovative and potential uses of MD for various applications mentioned in the recent literature has been provided in Table 12.

Besides the lab scale applications, various activities can be seen at the commercial scales too. Jensen et al. [27] have demonstrated the potential of membrane distillation modules at large scales for desalination purposes. The authors have used a total membrane area of 300 m^2 and have observed no problem of scaling or biofouling over a period of 4–14 months. Burrieza et al. [185] have compared the performance of two pilot scale AGMD modules over a period of two years against NaCl solution of 1 and 35 g/L. The modules have produced excellent and constant quality distillate throughout the process. On the similar lines, Raluy et al. [186] have compiled the 5 years' experience and data analysis of a solar collector MD unit installed in Instituto Tecnológico de Canarias (ITC) in Playa de Pozo Izquierdo (Gran Canary Island—Spain). The authors have reported a specific thermal energy consumption in the range of 140–350 kW h/m^3 while the distillate quality was very good (20–200 μs/cm). Asadi et al. [187] have demonstrated desalination of deoiled stream coming from the oil refinery by using a MD module with an area of 40 m^2. The water produced fulfills the local irrigation standards.

7. Conclusions

Membrane distillation is a relatively new process, investigated worldwide as a low cost and energy saving alternative with respect to

Table 12
Applications of MD mentioned in different recent studies.

Feed	Target	Membranes used	MD configuration	Ref.
Seawater	Boron removal	PVDF	DCMD	[167]
Simulated water	Chromium removal	PTFE	DCMD	[168]
Produced water	Desalination	PTFE	DCMD	[169]
Aqueous solution of N-methyl-2-pyrrolidone	Concentration of N-methyl-2-pyrrolidone solution	PP	VMD	[170]
Cooling tower blow down water	Desalination	FS PP	DCMD	[171]
Aqueous ammonia solution	Removal of ammonia	PVDF capillary	DCMD and MDCMD	[172]
Olive oil waste mill water	Concentration of phenolic compounds	FS PTEF	DCMD	[162]
Produced water	Desalination	FS PTFE	AGMD	[173]
Model lactose solution	Ethanol production	PP capillary membrane	DCMD	[174]
Synthetic solution of trace OC	Removal of complex trace organic compounds	FS PTFE	DCMD	[175]
Aqueous H_2SO_4 solution	Concentration of H_2SO_4 solution	PP hollow fiber	Multi effect MD	[176]
Retentate of NF and RO	Improvement of water RF and salt crystallization	PVDF hollow fibers	DCMD	[177]
Water from great salty lake	Recovery of minerals	FS PTFE and PP	DCMD	[178]
Zabłocka Thermal Brine	Brine concentration	PP hollow fiber Accrual	DCMD	[179]
Glycerol fermentation broth	Separation of acetic acid from the broth	Accurel PP hollow fiber	DCMD	[180]
Synthetic radioactive wastewater	Removal of radioactive elements	Hydrophobic ally modified FS PS or PES	DCMD	[181]
Wastewater containing arsenic in different concentrations	Removal of arsenic	PP and FS PVDF	VMD	[182]
Dilute glycerol wastewater	Concentration of glycerol	FS PTFE	SGMD	[183]
Ethanol–water mixture	Ethanol separation	FS PTFE	SGMD	[184]

conventional separation processes (such as distillation and reverse osmosis). It is one of the few membrane operations based on a thermal process. Energy consumption therefore is, in principle, the same as the traditional evaporative process. However, the required operating temperature is much lower than that of a conventional distillation column because it is not necessary to heat the process liquids above their boiling temperatures. In fact, the process can be conducted at temperatures typically below 70 °C, and driven by low temperature difference (20 °C) of the hot and the cold solutions. Therefore, low-grade waste and/or alternative energy sources such as solar and geothermal energy can be coupled with MD systems for a cost and energy efficient liquid separation system. Consequently, this operation might become one of the most interesting new membrane techniques. It can overcome not only the limits of thermal systems but also the ones of membrane systems such as RO or NF. Concentration polarization does not affect significantly the driving force of the process and therefore high recovery factors and high concentrations can be reached in the operation, when compared with RO process. All the other properties of membrane systems (easy scale-up, easy remote control and automation, no chemicals, low environmental impact, high productivity/size ratio, high productivity/weight ratio, high simplicity in operation, flexibility, etc.) are also present. This technology can be used practically in a large variety of industrial and bio-medical processes as for the purification, extraction, concentration (to very high values), and final formulation of organic and inorganic species. More recently, membrane bioreactors (MBRs) with membrane distillation membranes (MDBR) have been developed for the treatment of industrial and municipal waters in order to exceed the limits of the existing MBR systems (i.e., the difficulty to retain effectively small size and persistent contaminants) [188,189]. Another novel application with the vision of water separation and recovery from industrial gaseous waste steams is *membrane condenser* [190–193]. In this membrane technology, the hydrophobic membranes are utilized for water condensation and recovery in the retentate side of the membrane module, whereas the dehydrated stream is recovered on the permeate side of the membrane. The water obtained by condensation assisted by membranes represents a new and promising source of water. Membrane condenser, moreover, might be considered of interest in various gas streams treatments, with membrane as an appropriate pre-treatment for dehumidification or reduction of ion concentration.

It is also important to recall the potentiality of MD in acting as a precursor of the membrane crystallization and membrane dryer systems, other interesting new membrane operations very consistent with the process intensification strategy [194–197,15,198,192–197] and whose main principles are those of MD.

Membrane crystallization (MCr) is conceived as an alternative technology for producing crystals and pure water from supersaturated solutions. MCr is able to promote crystals nucleation and growth in a well-controlled pathway, starting from undersaturated solutions. In a membrane crystallizer the membrane matrix acts as a selective gate for solvent evaporation, modulating the final degree and the rate for the generation of the supersaturation. Hence, the possibility to act on the trans-membrane flow rate, by changing the driving force of the process, allows to modulate the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution). Membrane dryer is a system able to dry solid particles contained in liquid streams, while producing a liquid particle-free. In a membrane dryer the liquid stream (feed) to be treated is in contact with one side of a microporous membrane and the liquid permeates as vapor thanks to a driving force that can be established across the membrane in different ways: by applying vacuum; by creating an air gap; by sending a cold liquid or a sweep gas. This technology offers the possibility to work with feeds of different concentrations, containing solid particles of different sizes and allows to produce liquid particle-free without the need of a separation step downstream.

Despite its great potential, membrane distillation is still far to fulfill all the expectations. To overcome the existing barriers, new and better membranes, improved design of the membranes and of modules and an overall better engineering are necessary for a further industrial exploitation of this technology. For example, the investigation of the complex correlations between physicochemical properties of the membrane and MD performance confirms the need for a customized hardware, i.e. high porosity hydrophobic membranes with appropriate thickness and made by low-heat conductive polymers in order to reduce the amount of waste energy. New amorphous perfluoropolymers are becoming available. Moreover, clear protocols and comparison indexes for the choice of the best materials and operative conditions, accurate modeling for an easy scale-up or scale-down, and significant multidisciplinary research efforts are needed and might contribute to the development of the technology.

Symbols and abbreviations

AGMD	air gap membrane distillation
B	geometric factor determined by pore structure
CFD	computational fluid dynamic
CNTs	carbon nanotubes
DCMD	direct contact membrane distillation
H	over all heat transfer coefficient
K	thermal conductivity
LEP	liquid entry pressure
M	molecular weight
MD	membrane distillation
MEMD	multi-effect membrane distillation
MF	Microfiltration
MGMD	material gap membrane distillation
MPS	mean pore size
N	flux
P	vapor pressure
PGDM	permeate gap membrane distillation
PRO	pressure retarded osmosis
PSD	pore size distribution
Q	heat flux
R_f	feed side boundary layer resistance
R_m	membrane resistance
R_p	permeate side boundary layer resistance
RO	reverse osmosis
SGMD	sweep gas membrane distillation
T	temperature
T_g	glass transition temperature
T_m	melting temperature
UF	ultrafiltration
VMD	vacuum membrane distillation
V-MEMD	vacuum-multi-effect membrane distillation
γ_L	surface tension of the liquid
d_{max}	maximum pore diameter
ε	porosity
λ	latent heat of vaporization
τ	tortuosity
δ	membrane thickness

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