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Membrane Distillation Design Configuration, Development and Application Processes

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Abstract**—** Rapid population growth has resulted in imbalance in the supply and demand of fresh water for human consumption. As the sources of fresh water from surface water and fresh groundwater have been consistently depleting at an alarming rate, alternative sources such as seawater and brackish water are sought out. Desalination of water is considered as one of the most sustainable and best water resource alternatives. Membrane distillation (MD) is a separation process based on the vapor transport across the hydrophobic microporous membrane driven by the vapor pressure gradient across the membrane. This process can be used for various applications such as seawater desalination, wastewater treatment, separation of volatile compounds, and concentration of non-volatile compounds and processing of dairy fluids. Comparing with other separation processes, the MD process possesses unique characteristics such as 100% (theoretical) rejection, mild operation conditions, insensitive to feed concentration and stable performance at high contaminant concentrations. Due to high oil prices in recent years, extensive research has been devoted to MD in the areas of materials, module configurations, process applications and hybrid systems.

Keywords: Membrane, Distillation, Microporous, Desalination

I. INTRODUCTION

Membrane distillation (MD) is an emerging membrane technology based on the vapor pressure gradient across the porous hydrophobic membrane. Since only volatile vapor molecules can transport across the membranes, the feed liquid directly contacting the membrane must not be allowed to penetrate into the dry pores of the hydrophobic membranes [1–3]. As illustrated in Fig. 1, the hydrophobic nature of the MD membrane prevents the feed liquid from entering membrane pores due to the surface tension. Meanwhile, the volatile components in the hot feed vaporize at the liquid/vapor interface and diffuse across the dry membrane pores. The vapors are then collected or condensed by different methods.

Fresh water shortage for human consumption and irrigation is one of the major problems faced globally today. Nowadays, more than 1 billion people lack access to drinking water [1]. Seawater comprises majority of the world's water resources and only 2.5% is fresh water, but only a portion of this fresh water is available for human consumption. Finding alternative ways to provide fresh water is of utmost importance. Since seawater is widely available, many research studies have been focused on converting seawater into drinking water [2, 3] or for irrigation [4]. Other alternative ways are to treat brackish or wastewater into potable water [5, 6].

Membrane technology plays an important role in desalination, and in water and wastewater treatment. Several membrane-based technologies such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) are currently being used [7]. In desalination, multi-stage flash distillation (MSF) and RO are the most widely used methods globally with a salt rejection higher than 98% [8]. Extensive research about RO has been conducted by several group and many review papers are widely available in literature. RO presents an efficient way of desalination; however, it is an energy-intensive process, so there is a need for an alternative cost-effective process to turn seawater into drinking water. In recent years, several groups have focused on studying alternative methods for RO such as NF, electrodialysis, capacitive deionization, forward osmosis (FO), and membrane distillation (MD). Among the current water desalination and purification technologies, MD process presents many attractive features compared to other technologies. Increasing array of research is being conducted to optimize the performance of MD in desalination focusing both on theoretical and experimental studies. Several experimental parameters are investigated on their effect on MD flux performance such as the feed and permeate temperature, salt concentration, and membrane properties (morphology, hydrophobicity, porosity, pore size and pore size distribution, etc.). There has been a surge of MD studies in the past 10 years. In 2013 alone, as of the writing of this paper, the number of MD publications as searched through the Web of Science with the topic „membrane distillation‟ is already more than 200 publications, and it still continues to rise. Recently, an increasing number of studies is geared on modifying or entirely changing the MD membrane. Khayet [9] reviewed the fabrication and MD performance evaluation including experimental and theoretical studies of several commercial and laboratory-made MD membranes. Alkhudhiri et al. recently reported a comprehensive review on MD performance addressing membrane characteristics, fouling, heat and mass transfer concepts, and effects of operating conditions.

Comparing with other membrane separation processes, MD offers a number of advantages: (1) 100% (theoretical) rejection of inorganic ions, macromolecules and other non-volatile compounds, (2) relatively low operating temperatures,

(3) lower operating pressures than conventional pressure-driven membrane separation processes, (4) insensitive to feed concentration for seawater desalination, and (5) less requirements on membrane mechanical properties. With these unique advantages, MD processes have demonstrated promising results in seawater desalination, wastewater treatment and many other applications.

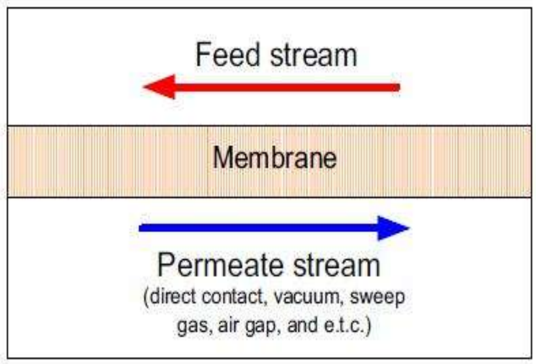

Fig. 1 Illustration of the MD process

The first MD patent was issued in 1963. Lawson et al. conducted an in-depth review on MD and its historical development. Comprehensive reviews were then made by Alklaibi and Lior [10], Tomaszewska, Curcio and Drioli, El-Bourawi et al.. The applications of MD process for desalination and water purification have been reviewed by Gryta, Camacho et al. [10] and other research teams. Khayet has reviewed the theoretical modeling of MD process. The commercialization of MD process has been constrained mainly by two factors; namely, 1) the lack of commercially available high performance membranes and 2) high energy consumption. To expand and fully harvest the advantages of MD process, new MD applications and hybrid systems must also be explored. In this work, we aim to review the recent advances in MD technology in terms of membrane development, energy-saving configuration design, system hybridization and exploration of new applications. Firstly, design of suitable MD membranes will be reviewed from the aspects of membrane materials and fabrication. As a microporous physical barrier, the desired MD membrane must have excellent anti-wetting properties, high flux and resistance towards high temperature, potential fouling and scaling [11,12].

The rest of the paper is structured as follows: In Section II we define different configurations for Membrane Distillation process. In Section III we present the related work regarding Membrane development process. Section IV presents the application of Membrane Distillation processes. Section V presents the conclusions of our work.

II. MEMBRANE DISTILLATION CONFIGURATIONS

Unlike pressure-driven membrane processes where permeate can be directly collected at the lower pressure side, the permeated vapor needs to be condensed via different methods. 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. The MD configuration plays an important role in determining the separation performance and operation cost. Some new configurations with improved energy efficiency, better permeation flux or smaller foot print have been proposed by many research teams [13-15]. In this chapter, we will review both basic and newly developed MD configurations.

2.1. *Basic MD configurations*

The mechanisms of these four basic configurations:

(a) Direct contact membrane distillation (DCMD): An aqueous solution with a lower temperature is in direct contact with the permeate side of the membrane. The temperature difference across the membrane induces the vapor pressure difference.

Consequently, volatile molecules evaporate at the hot liquid/vapor interface, transport across the membrane pores in vapor phase and condense in the cold liquid/vapor interface at the permeate side. As the most simplified configuration, DCMD is widely studied in literature and laboratories for desalination and concentration of aqueous solutions. As membrane is the only barrier to separate the hot feed and cold permeate solutions, DCMD has the highest conductive heat loss among four basic configurations.

(b) Air gap membrane distillation (AGMD): A thin air gap is designed between the membrane and a condensation surface (typically a thin dense polymer or metal film). The evaporated volatile molecules pass through both the membranes and the air gap and then condense on the cold surface [16]. As the air gap provides a significant vapor transport resistance, the flux of a typical AGMD is lower than DCMD or VMD configurations.

Utilizing the integrated cooling plate in the AGMD configuration, extensive works have been carried on the multi-effect or multistage membrane modules with improved thermal efficiency.

(c) Sweep gas membrane distillation (SGMD): A cold inert or sweep gas sweeps through the permeate channel and collects vapor molecules from the membrane surface. In most cases, the vapors are condensed outside the membrane module by an external condenser. This could result in an additional equipment cost.

(d) Vacuum membrane distillation (VMD): Vacuum is applied at the permeate side of the membrane module. To provide the driving force, the applied vacuum must be lower than the saturation pressure of volatile molecules in the feed solution.

Condensation may or may not occur outside of the membrane module. SGMD and VMD are often used to remove VOCs from aqueous solutions.

2.2. New MD configurations

Comparing with RO, nanofiltration (NF) or MSF, MD can be operated at ambient pressure and lower temperature. However, the low thermal efficiency has limited the commercialization of MD process [17]. For example, the specific energy consumption of traditional MD configurations without heat recovery design can be easily higher than 1256 kwh/m3 (estimated from gain output ratio). Hence, extensive works have been carried out to develop new MD configurations and membrane modules with higher thermal efficiency. Some of these new configurations are introduced in this section.

2.2.1. *Multi-stage and multi-effect membrane distillation (MEMD)*

The AGMD module consisting of internal heat recovery based on the concepts of multi-stage and multi-effect distillation for seawater desalination. The cold feed solution was placed beneath the condensation surface as a coolant to condense the permeated vapors as well as to gain heat. The pre-heated feed solution is further heated before it enters the feed channel. The AGMD Memstils MD module with heat recovery was developed in the late 1990 s by Netherlands Organization for Applied Scientific Research (TNO) and later licensed to Aquastil and Keppel Seghers for commercialization. The module was designed with a spiral wound configuration. A heating source of 50–100 1C is supplied to the system. A micro-porous PTFE membrane was used in the module. The Memstills module was designed for seawater and brackish water desalination [18]. Pilot desalination plants have been tested in Singapore, Netherland and other countries to address the technical issues. After the pilot trials, Memstills claimed to have a very low specific energy consumption of 56 to 100 kWh/m3. Besides AGMD modules, DCMD modules with heat recovery were also developed based on the same technology [10].

The Sweden Company, Scarab Development AB, developed the heat recovery AGMD module with a plate and frame design. A microporous PTFE membrane from Gore-tex has been used in this module. The energy consumption of this module was reported as 810 kWh/m3.

The Fraunhofer Institute for Solar Energy Systems (ISE) developed a full-scale multi-effect spiral-wound MD module with a membrane area of 5 or 14m2 and named it as permeate gap membrane distillation (PGMD). A typical PGMD module consists of a feed channel, hydrophobic membrane; permeate channel, condensation surface and condensate. The system enables feed pre-heating and permeates condensation within the membrane module. The schematic and photos of spiral wound PGMD module. With the aid of heat recovery design and optimal operation conditions, the specific energy consumption of this module for desalination can be as low as 130 kwh/m3.

III. MEMBRANE DEVELOPMENT PROCESS

One of major difficulties in MD processes is the lack of commercially available MD membranes with high performance, sufficient wetting resistance and minimized fouling/scaling tendency. Without a suitable membrane, it is hard to materialize MD as a viable separation technology. Among the materials investigated or utilized for MD membranes, hydrophobic polymers are preferred due to their characteristics of easy fabrication, modification, and scale-up as well as low costs [19, 20]. Different fabrication processes such as non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS), melt extrusion stretching, sintering, electro-spinning and other technologies have been employed to fabricate MD membranes depending on polymer properties and applications. In recent years, ceramic, carbon nanotubes (CNTs) and metals have also been explored as membrane materials for some MD studies.

3.1. Membrane materials and fabrication

Since hydrophobicity is the essential requirement for MD membranes in most applications, the membranes must be made from intrinsic or modified hydrophobic polymers with low surface energy. Materials such as silicone coated glass fibers and nylon were investigated in the early stage of MD development but showed unsatisfactory wetting resistance

[21]. The characteristic properties of commercially available low surface energy polymers commonly used for MD membranes. So far, the most popular polymers used in MD membranes are still polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF) [10]. PTFE has the lowest surface energy of around 9_20_10_3 N/m . It is a highly crystalline polymer with excellent thermal stability and chemical resistance. Since PTFE is a non-polar polymer, it is difficult to fabricate PTFE membranes by common NIPS and TIPS processes. The hydrophobic PTFE membranes used for MD applications are normally produced using sintering method or melt-extrusion method. PTFE membranes are most often used in the commercial and pilot MD systems because of their good wetting resistance, satisfactory water flux and excellent stability in various operation conditions.

The sintering process begins with a mixture of very fine PTFE powders and volatile lubricating agents (e.g. hydrocarbon)

[22]. The formed paste is then extruded into a sheet or hollow fiber forms which is then heated and expanded in order to produce a microporous membrane. The membrane needs to be stabilized in an amorphous locking step by thermal annealing. As an example of the sintering process, Gore fabricated a highlyporous PTFE membrane using a paste with PTFE powder and volatile lubricant Isopar™ isoparaffinic fluids

(ExxonMobil Chemical). After removing the volatile lubricant by drying, the paste was bi-axially stretched for five times at 225 1C to generate the highly-porous structure. The final amorphous locking process was carried by annealing the membrane at 370 1C for 5 mins.

The polymer melt extrusion method followed by stretching is also used for PTFE membrane fabrication. PTFE films are obtained by extruding PTFE melt coupling with a rapid draw down during the stretching. After the annealing and cooling processes, a mechanical stress is applied to the direction of drawing so that a relatively uniform porous structure is formed with a pore size distribution in the range of 0.2–20 µm . PP also has a highly crystalline structure but higher surface energy (30.0_10_3 N/m) than PTFE [10]. Porous PP membranes such as Celgards have been fabricated by the melt-extrusion stretching method by taking the unique hard elastic properties of PP. Besides, PP membranes are also fabricated by the TIPS process [22]. In this method, a homogeneous solution is firstly formed by dissolving PP in diluents at a temperature above Tm. Inert gas such as nitrogen is often introduced to avoid oxidation.

Once the membranes are fabricated by casting or spinning, solid liquid separation and liquid-liquid separation as well as diluents extraction take place. Eventually, a porous membrane is formed. In some cases, the resultant membranes are further stretched from single/dual directions to re-align the crystal structure and balance the mechanical properties. Recently, circular pores were also obtained by a bi-axially stretching after the melt-extrusion process. As compared with other MD membranes, PP membranes are relatively advantageous in material and manufacturing costs.

However, the membrane performance is generally lower due to the symmetric structure and the moderate thermal stability at elevated temperatures. These may limit PP potential for MD applications. PVDF is a semi-crystalline polymer with a surface energy of 30.3_10_3 N/m. Unlike PTFE and PP, it can be easily dissolved in common solvents such as n-Methyl-2-Pyrrolidone (NMP), dimethylacetamide (DMAC) and dimethylformamide (DMF). Meanwhile, it has a relatively low melting temperature of 170 1C. Therefore, PVDF membranes can be fabricated either by NIPS, TIPS or a combination of TIPS and NIPS process [23]. The SEM images of micro-porous PVDF membranes fabricated by the two methods. PVDF membranes fabricated via TIPS tend to have a relatively uniform porous structure without macrovoids, while most of PVDF membranes fabricated via NIPS possess an asymmetric structure consisting of a dense surface and many macrovoids in the crosssection. Utilizing the aforementioned polymers, membranes with flat sheet and hollow fiber configurations have been fabricated by both membrane manufacturers and researchers. For example, flat sheet PTFE membranes with polyester (PET) or PP supports have been produced by companies such as PALL, Gore, Membrane Solutions and GE [10].

Hollow fiber PTFE membranes have been produced by Toyobo and several research groups. Similarly, flat sheet and hollow fiber PP membranes are commercially available as Celgards (Pollypore) and ACCURELs (Membrana). Gryta and his co-workers have thoroughly evaluated the application of PP hollow fiber membranes for MD applications. In addition to homo-polymers of PP, PVDF and PTFE, MD membranes can be made from their copolymers with enhanced hydrophobicity and durability. Hyflons AD (Solvay Plastics), the copolymer of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy- 1,3-dioxole (TTD), has been used by Gugliuzza and Drioli and Arcella et al. to prepare asymmetric membranes with a contact angle large than 1201. Garcio-Payo et al. fabricated a series of hollow fiber membranes using poly (vinyldiene fluoride- co-hexafluoropropylene) (PVDF-HFP). Nunes and her co-workers fabricated MD membranes from aromatic fluorinated polyoxadiazoles and polytriazoles by both phase inversion and electro-spinning methods. The resultant membranes exhibited high porosity and super-hydrophobicity with an apparent contact angle up to 1621.

Besides using intrinsic hydrophobic polymers, MD membranes can also be made from hydrophilic polymer materials that have undergone hydrophobic modifications. Plasma polymerization provides a powerful technology to modify the membrane surface. Fluorine-containing monomers can be activated with plasma sources to form a branched polymer and adhere to membrane surface. For example, hydrophilic polyethersufone (PES) ultrafiltration (UF) hollow fiber membranes can be plasma modified by CF4 monomer and converted to hydrophobic membranes for MD. Theplasma modified membranes displayed a contact angle of around 1201.

During the 54 h DCMD test, the modified PES membrane exhibited a stable water flux of 66.7 l m_2 h_1 (LMH) and a salt rejection as high as 99.97% at 73.8 1C. Similarly, Kong et al. modified a cellulose nitrate (CN) membrane via plasma polymerization of octafluorocyclobutane [23]. In another work, surface modified poly(phthalazinone ether sulfone ketone) (PPESK) membranes were used for vacuum membrane distillation (VMD). After surface-coating modifications by silicone rubber and sol-gel polytrifluoropropylsiloxane, the PPESK hollow fiber membrane exhibited a more hydrophobic surface with a contact angle of 1101 and a higher liquid entry pressure (LEP) of 0.12 Mpa. The permeation flux of silicone rubber composite membranes was affected by the formulation of coating solutions and the membrane with the optimal formulation exhibited a high salt rejection of 99%.

Aside from polymeric materials, metal, glass, CNTs and inorganic based materials were also evaluated for MD applications. Similar with the hydrophilic polymers used in MD processes, ceramic membranes (i.e., zirconia, alumina and titanium) need to be modified for improved hydrophobicity. For example, surface modified zirconia membrane with a pore diameter of 50 nm exhibited a high rejection and a reliable air gap membrane distillation (AGMD) flux of around 4.7 LMH and close to

100% salt rejection (converted from the original unit) at a feed temperature of 95 1C. Recent works also investigated the assembly of CNTs into paper-like structures called Bucky-Papers (BP) as selfsupporting membranes, where the CNTs were held together solely by Van der Waals forces. The ultra-thin BP membranes with a narrow pore size were processed by vacuum filtration of CNTs dispersed in 99.8% pure 2-propanol. The self-supporting CNT BP membrane showed a DCMD flux of 12 LMH with 99% salt rejection at a water vapor partial pressure difference of 22.7 kPa. However, aging and delamination were observed, improvements such as surface grafting and coating have to be carried out to improve membrane durability.

Hydrophobic materials have been used in the MD process for seawater desalination and alcohol/water separation due to its large surface energy gaps with water. However, in the case of oillike liquids, either hydrophilic or super-hydrophobic materials are preferred to produce an oleophobic surface. Qu et al. compared the VMD performance of hydrophobic PVDF and hydrophilic polyacrylonitrile (PAN) membranes for the recovery of petroleum ether from the solanesol extracting solution. The hydrophilic PAN membrane showed a good VMD flux (415 LMH) and solute rejection (498%), while the hydrophobic PVDF membrane was easily wetted and lost its selectivity. There are transport mechanisms of a feed mixture of solanesol and organic solvents across hydrophilic and hydrophobic membranes in MD processes. A hydrophobic membrane will be easily wetted due to the high affinity between the organic solution and the hydrophobic membrane material. Yet in a hydrophilic membrane, the volatile solvent evaporates from the liquid-vapor interface on the feed side and then diffuses across the membrane pores.

IV. APPLICATIONS OF MEMBRANE DISTILLATION PROCESSES

4.1. Applications of MD processes

The water availability for human consumption is continuously decreasing due to rapid industrialization and population growth. MD was originally designed for seawater desalination, but the studies of MD for brackish water desalination have gradually attracted interests from both academia and industry.

4.1.1. Seawater/brackish water desalination

A small pilot plant was set up by Song et al. for DCMD based desalination and operated successfully on a daily basis for three months [3]. The hot brine tested was either city water containing salt at the level of 3.5, 6 or 10%, or seawater. The plant was operated successfully with a very limited flux reduction at salt concentrations up to 19.5% from sea water. Pilot desalination plants have been built with the commercialized MD systems [24]. Guillén-Burrieza reported an optimal operation using a multi-stage AGMD module which showed a specific energy consumption of 294 Kwh/m3. The AGMD Scarab AB system with heat recovery design has been tested in different desalination projects worldwide. Bench and pilot Memstills modules with heat recovery were tested in Singapore and Netherland before being commercialized. Demonstration desalination plants with VMEMD Memsys systems were also tested in Singapore and China.

4.1.2. Removal of small molecule contaminants

Membrane technologies such as NF, RO and electro-dialysis (ED) have been widely used for wastewater treatment. In recent years, concerns on poor removal efficiency of small molecule contaminants and heavy metal ions are growing. Hence, MD has received attention because it may provide better rejections towards these contaminants.

Boron-containing compounds are commonly found in wastewater or saline water in Asia, North America and Australia [25]. However, rejections of toxic boron-containing compounds by a RO or ED process are only 30–50% depending on the pH value of feed solutions. MD has demonstrated its superior performance in the removal of boron contaminants with a rejection 499.8%. Almost complete rejections were also reported on other heavy metals such as arsenic, chromium or gold.

The treatment of colored wastewater is of big importance. Usually, a combined coagulation/flocculation, adsorption and UF or NF are applied. Criscuoli et al. reported a complete dye removal using VMD [26]. Khayet et al. also investigated the use of MD to treat wastewater containing radioactive substances. By using both laboratory and pilot systems, MD was found to be an alternative for liquid nuclear waste treatment. Oil-water separation has received worldwide attention recently due to large amounts of discharged oily wastewater from industries.

Free oily wastewater and dispersed oily wastewater have commonly been treated by gravity and skimming, dissolved air flotation, deemulsification, coagulation and flocculation techniques. However, there is lack of an effective method to treat stable emulsified oily wastewater. Since no hydraulic pressure is applied, MD shows less fouling tendency and has potential for oily wastewater treatment. Using a plasma-modified PVDF membrane, a stable MD performance was reported over 24 h with oily feed water. pH and solution hydrodynamics were found as important parameters affecting oil fouling behavior. The Memsys systemwas also evaluated for oil-water separation. By modifying the Memsys PTFE membrane with fluoride to improve its oil resistance, the Memsys system showed a stable 6-h operation with feed seawater containing 0.1 wt% oil.

Produced water is a byproduct wastewater stream normally associated with the hydraulic fracturing process in the oil and gas industry. Produced water contains dispersed oils, suspended particles, chemicals as well as salty water. They must be treated prior to being discharged. Due to the high salinity, it's difficult to treat the produced water with RO. MD has been proven as a promising technology for desalting highly saline water with or without pretreatments [27]. As an example, produced water from the steam assisted gravity drainage (SAGD) process is typically at 80–130 1C and 2–3 atm. Singh and Sirkar utilized this residue heat to process the produced water by DCMD comprising PTFE membranes. The highest water vapor flux achieved was 195 LMH. Zhang et al. designed an integrated forward osmosis and MD process to recover water and acetic acid from produced water. In 2013, GE and Memsys have successfully tested its MD system to concentrate produced water from the hydraulic fracturing process. The field test results showed no noticeable decline in performance and stable performance with brine concentrations near saturation. Besides the contaminants mentioned above, MD operations were carried to remove organic contaminants such as ammonia, aromatic compounds, trichloroethane and halogenated VOCs.

4.1.3. Recovery of valuable components

Due to the unique transport mechanism, MD processes have been widely explored for the recovery of valuable components. Based on the volatility and vapor pressure, these components can be concentrated either in the feed stream or permeate stream. Examples include mineral acids, fruit juices, sugar, alcohols and others [28]. Specifically, concentration of sulfuric acid from 16% until 40% was reported with a separation coefficient of above 98%. Studies were conducted to concentrate the fruit juices as well as sugar, herbal extracts and small organic molecules by MD. Substances that are more volatile than water, such as volatile acids and alcohols, are enriched in the permeate stream of MD processes. One of most studied applications is the separation of volatile acid from its aqueous solutions. Waste streams containing volatile acids such as hydrochloric acid (HCl) are commonly generated from rare earth mining and metallurgical industry. The MD process has demonstrated its capability in volatile acid recycles. MD was also widely explored for the separation of alcohols and volatile organic compounds. The permeate flux was found to be strongly affected by the feed temperature and ethanol/organic concentration in the feed. Hence, only dilute aqueous solutions were tested by AGMD and VMD configurations.

4.2. MD based Hybrid separation processes

MD has been recognized as one of the most preferred membrane processes for hybrid separation technologies. On one hand, with a minimum capital cost, MD can be readily integrated into the existing plant as it is not a pressure-driven process. On the other hand, the separation performance of the MD process is less affected by the high salt concentration. As a result, it can significantly enhance the total water recovery (TWR). This section reviews various MD based hybrid processes.

4.2.1. Integration with the existing desalination process

Incorporation of MD into the desalination process can dramatically reduce brine discharge and therefore enhance water recovery. Several works have reported positive results by integrating MD with NF or RO desalination. De Andres et al. integrated MD with an existing multi-effect distillation (MED) unit [29]. The overall production of fresh water and energy efficiency has increased by 7.5% and 10%, respectively.

The scaling of inorganic salt crystals is the main concern when MD is integrated into current desalination processes. Inorganic salts in the brine such as Ca2þ will cause severe scaling in the MD process. Qu et al. integrated an accelerated precipitation softening process with DCMD with a high recovery for the desalination of RO brine. Freeze desalination (FD) refers to the process in which fresh water is extracted by harvesting and melting the ice crystal from saline water. It is a promising desalination technology that could utilize waste cold energy such as liquefied natural gas (LNG) cold energy. However, the low water recovery has severely limited the application of FD technology. In order to enhance the water recovery and the utilization efficiency of the cold energy, Wang and Chung proposed the FD-MD process for seawater desalination. The brine from the FD process was further concentrated in the MD process; clean water was obtained from both processes. A high total water recovery of 71.5% was achieved.

4.2.2. Forward osmosis-membrane distillation (FO-MD)

Besides the combination of membrane process and traditional separation technologies, researches have been carried out to integrate the MD process with other membrane processes. For instance, several research groups have worked on the hybrid forward osmosis-MD (FOMD) process. FO refers to the spontaneous transport of water across a semi-permeable membrane driven by an osmotic pressure gradient. Credit to the anti-fouling properties of FO processes, the hybrid FO-MD process can be sustainable under robust feed conditions. A typical FO-MD process.. The FO process draws clean water from the feed solution to the draw solution side, while the MD process is utilized to re-concentrate the diluted draw solution.

The concept of combining FO and MD was firstly proposed in a U.S. patent application. Yen et al. pioneered the real demonstration. Later, Wang et al. explored the process for the concentration of proteins. It could preserve the proteins or pharmaceutical compounds while maintaining high rejections. Other applications that have been explored included heavy metal removal, wastewater treatment, oil removal, dye removal and others. One of the major challenges faced by the combined FO-MD process is the invention of the suitable draw solution. The ideal draw solution should have a high FO flux, low reverse salt leakage and should not cause severe concentration polarization in the MD process. Draw solutes such as inorganic salt and sugars, were used in early stages [30].

However, similar to the standalone FO process, the current FO-MD hybrid process is affected by the high reverse draw solute flux (i.e., draw solute leakage). Recently, novel draw solutes were proposed and synthesized based on different chemical structures. Ge at al. synthesized the draw solutes based on polyelectrolyte which had good solubility in water, high water flux and low salt leakage. When used in a standalone FO process, polyelectrolytes showed a lower flux due to its high viscosity. In the FO-MD process, the flux was significantly enhanced as the polyelectrolytes viscosity decreased with increasing temperatures.

V. CONCLUSION

With the rapid changes in energy price and clean water shortage, the end use of MD has been expanded from initially seawater desalination to many other applications including wastewater treatment and recovery of valuable compounds. To meet the demands from new applications, breakthroughs in material development and membrane fabrication have been made for MD membranes. Materials from traditional hydrophobic materials such as PVDF, PTFE and polyolefins have been extended to new materials including inorganic materials, carbon nano-tubes, and modified hydrophophilic materials. Fabrication methods for MD membranes have also been advanced to comprise dual-layer hollow fiber spinning, multi-bore fiber spinning, and electro-spinning.

Currently, the microporous PTFE membrane dominates the applications in the commercial and pilot MD modules because of its high hydrophobicity and excellent resistance towards harsh operation conditions. However, its high cost and difficulties in module sealing are the major drawbacks. MD membranes made from low cost are urgently needed. In addition to continuously use aforementioned methods to fabricate MD membranes, focuses should also be given to revolutionary fabrication technologies such as nonwoven supported PVDF hollow fiber spinning process, combined thermal-nonsolvent induced phase separation (TNIPS) process, hydrophobic ceramic membrane fabrication, and others. Considering the increasing MD application in contaminated water purification, attentions might be drawn on the fabrication of membranes with better resistance towards fouling/scaling of organic matters and other contaminants.

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