Membrane distillation: recent technological developments and advancements in membrane materials

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Abstract
Membrane distillation (MD) is a novel desalination technology that has potential to produce distilled quality water from high salinity brine streams. The driving force for MD is the vapor pressure difference across a hydrophobic membrane resulting in transfer of water vapor from hot to cold side. This vapor contacts a cold surface and condenses to produce distillate. This paper reviews recent and/or multi-year research programs that focused on MD pilot or field testing. The various investigations concluded that while MD can produce distilled water quality, the energy efficiency remains the key bottleneck for future deployment of MD. Membrane wetting and fouling also presents key challenges for desalination due to both the high salinity and the presence of organics in the feed water. The authors contacted several MD vendors requesting updates on their latest products and technology developments. MD vendors with innovative module designs, some of which promise a step change in performance, have recently emerged on the market. In addition to water desalination, MD has a wide range of industrial applications such as hydrogen sulfide removal, the treatment of wastewater from the pharmaceutical, metal finishing industries, direct sewer mining, oily wastewater, and water recovery from flue gas. This paper also reviews novel membrane chemistries with emphasis on membranes prepared by phase inversion and electrospinning techniques to which nanomaterials have been added. The primary objectives in adding various nanomaterials (e.g., carbon nanotubes, graphene, silicon dioxide, fluorinated compounds) are to increase hydrophobicity (to reduce wetting) and increase mass transfer rates (to increase flux and lower cost).

Keywords Membrane distillation · Pilot studies · Desalination · Nanomaterials · Phase inversion · Electrospinning

1 Background
Membrane distillation (MD) is a hybrid thermal-membrane process driven by the vapor pressure difference between hot and cold sides of a hydrophobic membrane, resulting in the passage of water vapor through the membrane, followed by condensation on the cold side producing distilled quality water [1, 2]. The different MD configurations and its advantages and disadvantages are widely reviewed in the literature [3–9].

The hydrophobic membrane chemistries [10] used in MD are polypropylene (PP), polyvinyl difluoride (PVDF), and polytetrafluorethylene (PTFE). The PTFE membrane is the material most commonly used in MD process and was introduced to the market by Gore and Associates [11].

The target application of MD is the desalination of saline waters such as seawater or brines. MD can also be integrated with other advanced water treatment technologies such as forward osmosis (FO) and humidification-dehumidification (HDH) to achieve either zero liquid discharge (ZLD) or minimum liquid discharge (MLD) [12]. The other niche applications of MD and hydrophobic membranes are fruit juice concentration in the food industry [13], treatment of wastewater from electronic industry [14], metal finishing and pharmaceutical industries [15], and removal of specific gas streams such as hydrogen sulfide from process water [16]. These industries focus more on recovering the value-added products or removal of key contaminants which can justify the energy consumption.

To understand the recent MD developments, a candid search in scientific databases such as Scopus, ScienceDirect, and Google Scholar was carried out for “membrane distillation” and they all showed significant increases in MD citations.
in the past 20 years. Based on the literature findings, ScienceDirect was considered a reliable source for assessing key technological developments of MD [10]. Figure 1 is a cumulative plot of the number of MD publications at 5-year intervals since 2000. By 2010, a total of 693 publications had been recorded and this number jumped > 3-fold by July 2020. Most of the MD research papers focused on the preparation of novel membranes using nanomaterials, synthesis, characterization, modelling, and simulations.

Numerous MD bench studies were published showing improvements in distillate flux and fouling reduction. Despite the large number of published literatures, there is a wide spread between the number of bench-scale results and pilot/field studies. While significant research papers focused on bench-scale testing and/or modeling of MD process, there were limited studies (~35) which address MD technology implementation at pilot and/or demonstration scale (Fig. 1). Nevertheless, various investigations were conducted worldwide to advance the MD technology readiness level (TRL) from 3 up to 8 to facilitate full-scale applications [18]. The challenge, however, is that each field study was conducted on one specific design of MD technology, and not many side-by-side evaluations of various configurations were conducted to determine the pros and cons of the different systems.

Commercial MD vendors initially focused on the development of flat sheet modules based on either direct contact or air gap mode. To improve the energy efficiency, vacuum was introduced and further optimized by preheating the feed stream [19]. MD vendors developed innovative cost-efficient designs in the form of hollow fiber and spiral wound configurations to leverage the higher membrane area leading to larger volumes of water production at lower footprints. In addition, the membrane chemistries were modified by adding more proprietary fluorinated compounds to improve hydrophobicity and reduce membrane wetting.

Several investigators addressed different membrane fabrication methods such as phase inversion and electrospun techniques by modifying the membrane surface with addition of nanomaterials in the form of silicon dioxide, zinc oxide, carbon nanotubes, and graphene to improve membrane performance. The modified membranes have shown superior performance for the treatment of high saline water containing oil, surfactant, and stabilized emulsion [20].

1.1 Objectives

Recent MD reviews lack information on the various pilot field tests/demonstration and technology developments from commercial vendor perspectives. Hence, the main objectives of this paper are to provide:

- Overview of recent pilot/field testing evaluations of various MD technologies
- Update on commercial MD vendors and their technology developments
- Highlights on niche novel applications of hydrophobic membranes
- Synopsis on latest developments on synthesis of advanced membrane materials

This review will allow academic/industry professionals gain a comprehensive assessment on the status of MD technology and its feasibility for full-scale installation. It also sheds light on promising MD vendors, innovative applications, and recent advances in membrane nanomaterials.

2 Field testing of MD technology

The key pilot/field investigations of MD technology for water desalination conducted in the past decade are listed in Table 1. Various research organizations in different countries were involved in these efforts with the primary goal to advance the MD to TRL scale of 8 or 9 and thereby facilitate full-scale applications of the technology. Detailed process performance parameters of all pilot/field studies are presented in Table 2 for comparison purposes and to identify common trends and range of MD operation. In addition, the authors reviewed representative case studies to highlight specific applications, vendors, module configurations, and key process performance issues.

2.1 MD for seawater desalination

A nine-party consortium led by Netherlands Organisation for Applied Scientific Research (TNO) with Keppel was formed to field test the patented Memstill air gap flat sheet MD technology (Fig. 2) under direct contact mode. A single Memstill design consists of an array of hydrophobic PTFE membranes and impermeable condensers placed parallel to each other.
The seawater is initially preheated in the condenser, followed by supplementary heat addition. The water vapor from the seawater passes through the hydrophobic membrane and produces freshwater by condensation. Extensive investigations with a 24 m³/day pilot system (Fig. 2) were carried out in different locations: Rotterdam, Antwerp, and Singapore.

### Table 1 Pilot investigations of MD for seawater desalination application

| Case history | Description | Technology developer | Location | Year | Discussed |
|--------------|-------------|----------------------|----------|------|-----------|
| 1            | MD for seawater desalination [21, 22] | Memstill | Netherlands | 2010 | ✓         |
| 2            | MD coupled with solar energy for seawater desalination [23] | Fraunhofer | Spain | 2012 | ✓         |
| 3            | MD for desalinating brines from thermal desalination plants [24] | Memsys, Xzero | Qatar | 2014 | ✓         |
| 4            | MD for desalinating hypersaline groundwaters [25] | Memsys | USA | 2016 | ✓         |
| 5            | MD with air gap configuration for seawater desalination at pilot scale level [26] | Aquastill | Australia | 2016 | ✓         |
| 6            | MD system with hybrid solar-power operation [27] | Memsys | Saudi Arabia | 2016 | ✓         |
| 7            | MD with vacuum multi effect configuration for saline water desalination [28] | Memsys | Greece | 2017 | ✓         |
| 8            | MD methodical design and operation for desalination [29] | Fraunhofer | Germany | 2017 | ✓         |
| 9            | MD for concentration of hypersaline brines [30] | Solarspring | Germany | 2018 | ✓         |
| 10           | MD for desalinating seawater with enhanced heat recovery [31] | Memsys | Spain | 2018 | ✓         |
| 11           | MD pilot testing using solar energy [32] | Solarspring | Spain | 2019 | ✓         |
| 12           | MD for desalinating brines with vacuum-enhanced air-gap configuration [33] | Aquastill | Spain | 2020 | ✓         |

### Table 2 Results of various pilot investigations of MD technology

| Case history | Vendor | Year | Membrane material | Membrane configuration | Application | Feed TDS (mg/L) | Product water TDS (mg/L) | MD flux (L/m²h) | Recovery (%) | GOR | Energy consumption (kWh/m³) |
|--------------|--------|------|-------------------|------------------------|-------------|----------------|-----------------------|----------------|--------------|-----|---------------------------|
| 1            | Memstill [21, 22] | 2010 | PTFE | DCMD | Seawater | 35000 | <2 | 0.25–3 | 10 | 10–17 | 154–38 |
| 2            | Fraunhofer [23] | 2012 | PTFE | AGMD | Seawater | 43,600 | 21 | 1.5 | 18–44 | 3.4 | 140–350 |
| 3            | Memsys [24] | 2014 | PTFE | VMD | Thermal brine Seawater | 71,031 | 6 | 5.7 | 52 | 2.5 | 260 |
| 4            | Memsys [24] | 2014 | PTFE | VMD | Seawater | 44,701 | 9 | 4.8 | NA | 2.5 | 260 |
| 5            | Xzero [24] | 2014 | PTFE | AGMD | Thermal brine | 68,529 | 1472 | 2.5 | NA | 0.74 | 1031 |
| 6            | Memsys [25] | 2016 | PTFE | VMD | Hypersaline ground water | 62,592 | <5 | 5 | 40 | 2.5 | 260 |
| 7            | Aquastill [26] | 2016 | LDPE | AGMD | Seawater | 35,000 | 50 | 1.0 | 5 | 6–7 | 90–95 |
| 8            | Memsys [27] | 2016 | PTFE | VMD | Brackish water | 1000 | 2 | 1.6–2.5 | NA | NA | ND |
| 9            | Memsys [28] | 2017 | PTFE | VMD | Seawater | 15,000 | NA | 1.7 | 76 | 2.0 | 340 |
| 10           | Fraunhofer [29] | 2017 | PTFE | AGMD | Seawater | 35,000 | <1 | 1.1 | 4–10 | 3.18 | 207 |
| 11           | Solarspring [30] | 2018 | PTFE | AGMD | Seawater | 240,000 | 128 | 0.7 | NA | 3.64 | 200–800 |
| 12           | Memsys [31] | 2018 | PTFE | VMD | Seawater | 25,600 | <2 | 8.5 | 36 | 3.3 | 200 |
| 13           | Solarspring [32] | 2019 | PTFE | AGMD | Seawater | 35,000 | <1 | 1.5 | NA | NA | NA |
| 14           | Aquastill [33] | 2020 | LDPE | VEMD | Hypersaline solution | 35,000–292,000 | 508 | 1–3 | NA | 8.5–13.5 | 48–77 |
The product water of all MD systems was of excellent quality with more than 99.9% salt rejection achieved. A wide range in energy consumption was reported from pilot testing (Table 2). Different operational challenges, including membrane wetting, were experienced during the testing and the field evaluation was completed without follow up full-scale implementation of the technology.

2.2 MD coupled with solar energy for seawater desalination

An MD system with a capacity of 5–120 l/h (Fig. 3) was developed by Fraunhofer for a European Union sponsored “MEMDIS” project and field tested in Spain [36]. The system was integrated with solar energy (collectors and photovoltaic modules) to supply the heat energy and required electricity for the MD system. Pretreated seawater using cartridge filters was used as feed to the pilot unit. The unit was operated intermittently for approximately 2 years. The hydrophobic PTFE membrane channels were arranged in a spiral wound configuration for efficient heat transfer with a constant temperature difference established throughout the entire membrane surface area. The water vapor passed through the membrane and condensed in the distillate channel. Overall, the MD unit was operated at a feedwater recovery rate up to 44% and the membranes achieved > 99% salt rejection. A range of energy consumption was reported with a gain output ratio (GOR) of up to 3.4 was reported (Table 2).

2.3 MD for desalinating brines from thermal desalination plants

Water production from seawater desalination is vital for sustainability in Middle Eastern region [37]. The most widely used desalination processes are multistage flash (MSF), multieffect distillation (MED), and RO, many of which are coupled with power plants to leverage the thermal energy and electricity requirements.

The desalination plants in Middle East produce large volumes of relatively hot concentrated brine which are returned to the sea. MD has the potential to recover additional water from the concentrated brine of existing desalination plants without incurring significant additional capital costs. ConocoPhillips Global Water Sustainability Center (GWSC) embarked on an ambitious MD research program in 2012 with an industrial-academic consortium including Qatar University (QU) and Qatar Electricity and Water Company (QEWC) to demonstrate pilot scale MD performance at a full-scale thermal desalination plant in Qatar. The long-term performance, process economics and specific field condition challenges were addressed.

Five MD technology vendors, Fraunhofer, Scarab, TNO, Memsys GmbH, and Keppel, were identified and a global request for proposal (RFP) to supply of 1 m³/day pilot [1] was issued. After a technical evaluation, 2 MD vendors, Memsys (Germany, multieffect VMD) and Xzero (Sweden, AGMD), were selected for the field investigation. The pilot units were designed and built by the vendors and shipped to be operated at a full-scale thermal desalination plant in Qatar (Fig. 4). The study presented a unique opportunity for side-
by-side MD system testing under relevant field conditions [24]. While both units were operated at similar membrane flux, the Memsys system was more reliable in consistently achieving high-quality distillate and > 99.9% salt rejection. Lower energy consumption and higher GOR was also achieved by Memsys as compared to Xzero system (Table 2). The testing identified pretreatment as key challenge due to the presence of anti-foaming chemical agent in the brine which resulted in membrane wetting. Granular activated carbon proved to be effective pretreatment. The study findings were shared with the vendors to help optimize their designs for future applications.

2.4 MD for desalinating hypersaline groundwaters

The Memsys pilot unit from the above study was sent to Texas (USA) for the treatment of inland hypersaline groundwater for potential use in fracking of shale reservoirs. The MD pilot unit was integrated with a multieffect humidification–dehumidification (HDH) unit to demonstrate a ZLD process (Fig. 5) [25]. The HDH pilot unit was supplied by Saltworks Technologies Inc. Canada. HDH is an emerging desalination process which mimics natural water cycle by heating water to produce vapor streams and condensing the vapor to produce distilled water. Air serves as a carrier gas for both heat and mass transfer. The high-quality water can be either blended with low saline solution or produced water for hydraulic fracturing. The feed water salinity to MD system was at 6.3% total dissolved solids (TDS) and the MD brine contained 10.2% TDS and both units achieved > 99.9% TDS rejection. The specific energy consumption (SEC) for MD and HDH were 260 kWh/m³ and 220 kWh/m³, respectively.

2.5 MD for concentration of hypersaline brines

A spiral wound AGMD module manufactured by Solarspring (Fig. 6) was tested with sodium chloride solutions ranging in concentration from 0 to 240 g/L NaCl in Germany [30, 32]. The pilot unit distillate capacity was 25 L/h (Fig. 6). The novelty in their AGMD module was the blowing of pressurized air into the air gap which improved the drainage of the stagnant distillate which reduced membrane wetting and improved distillate conductivity. The hydrophobic membrane is PTFE with PP backing. In the pilot investigation, the feed flow rate, condenser inlet, and outlet temperatures were kept at 300 L/h, 25 °C, and 80 °C, respectively. The membrane flux decreased from 2.1 to 0.7 LMH when the feed salinity was increased from 0 to 240 g/L. The blowing of air reduced the distillate flux and GOR by 1.4% and 4.1%, respectively.

2.6 MD for desalinating seawater with enhanced heat recovery

A pilot investigation of VMD based on Memsys design was evaluated for seawater desalination in Spain (Fig. 7). The 1 m³/day pilot unit was coupled with solar energy collectors to
provide thermal energy. Innovative modifications were carried out in the condenser section to preheat the seawater and improve energy efficiency. The other novelty was vapor transfer between effects by internal channels rather than external siphon. This helped to increase the distillate flux and removal of non-condensable gases. The membranes were PTFE, and the module was constructed of PP. While the system was able to achieve relatively high flux (8.5 LMH) at hot feed temperature (75 °C), a drop of ≈40% in productivity was observed due to seasonal variations in seawater temperature. Also, membrane fouling due to calcium scaling reduced production by 50% but cleaning with citric acid was able to restore the flux.

2.7 MD for desalinating brines with vacuum-enhanced air-gap configuration

Aquastill’s spiral wound MD module with multieffect configuration was tested at a pilot scale (~2 m³/day) in Spain to concentrate brines with salinities ranging from 35 to 292 g/L (Fig. 8). A low-density polyethylene (LDPE) hydrophobic membrane was used in the module. The novelty in their design was the vacuum application on the permeate side to decrease the mass transfer resistance and improve the removal of non-condensable gases. The inlet temperatures in the evaporation and cooling channels were kept at 80 and 25 °C, respectively.

The absolute pressure in the permeate gap was maintained at 150–200 mbar. While the product water of the MD system was of excellent quality, it was observed that as the feed salinity increased, the salt rejection declined from 99.8 to 97.9%. Results also showed that the distillate flux of vacuum enhanced AGMD was superior to normal AGMD by 31%. The MD system demonstrated GOR values between 8.5 and 13.5 which are relatively high compared to other system designs.

2.8 Key outcomes from MD field evaluations

Table 2 summarizes the results from the various pilot and field tests, including water quality, membrane performance, and energy consumption. The most critical outcome of all MD pilot-scale evaluations for field implementation is that various designs exist for this technology with different membrane materials, module configurations, and energy efficiencies. This makes the results from these evaluations very specific to the vendors’ specifications rather than general technology assessment. Very limited studies were conducted where multiple MD designs were tested side-by-side to identify the pros and cons of each system based on a level playing field. Although the pilot and field studies used modules from various vendors with different chemistries and designs, the key outcomes are summarized as follows:
1. MD can be applied to desalinate saline waters in the range of 1.5 up to 29%.
2. MD is technically feasible and can consistently produce permeate of distilled water quality.
3. MD flux is usually in the range of 1–5 L/m² H, with few exceptions.
4. MD product recovery is typically less than 50% for seawater applications.
5. MD energy consumption and GOR values are variable depending on system design and membrane configuration.
6. Pretreatment is critical for stable operation as the presence of field chemicals in the brine may potentially lead to MD membrane pore wetting.
7. PTFE is the most widely used material in MD membranes.
8. Development of novel membrane chemistries and module designs is necessary for commercialization.

3 Recent MD technology developments

Scientific publications and gray literature were searched for the latest developments in MD technology. In addition, vendors were contacted to discuss their latest products and module designs. Table 3 lists various MD technology developers and providers [38]; some of whom are no longer in business. One full-scale 10 m³/day MD system has been installed by Memsys in the Maldives. The process harnesses waste heat released from an 80-kW diesel generator. The heat from the diesel generator coolant (~87 °C) was used to preheat the seawater feed to the MD [39], and seawater is used for cooling. MD vendors are currently at different stages in promoting their technology, and those who responded to our requests for updates are highlighted with specific sections. Other vendors appear to be less active in marketing their MD technology for water desalination or could be developing their technology but were reluctant to share information at this stage.

3.1 Aquastill [40]

Aquastill, a company based in The Netherlands, offers different MD configurations. Aquastill holds the license of Memstill MD technology, and in 2011, research focus shifted towards the development of a spiral wound configuration (low-density polyethylene membrane (LDPE)) to improve energy efficiency [41]. The system can be integrated either with low-grade waste heat or solar energy to lower operating costs. The system has achieved a performance ratio in the range of 10–14 due to a multi-effect design which significantly lowers energy consumption compared with single-effect MD. The application of vacuum to the permeate side enhances productivity and performance ratio. Numerous pilot investigations (Fig. 9) were carried out on seawater desalination by integrating with solar energy and treatment of seawater RO concentrate [42].

3.2 Scarab [43]

Scarab, a Swedish company has been developing MD technology for more than decade. The AGMD modules mimic plate and frame heat exchanger designs with condensation...
Table 3 MD technology developers

| Technology Developer | configuration   | Type           | Country            | Logo |
|----------------------|-----------------|----------------|--------------------|------|
| Fraunhofer           | Spiral wound    | Air gap        | Germany            | ![Fraunhofer](image) |
| Solarspring          | Spiral wound    | Air gap        | Germany            | ![Solarspring](image) |
| Scarab / Xzero       | Flat sheet      | Air gap        | Sweden             | ![Scarab](image) |
| TNO / Memstill       | Proprietary     | Air gap        | Netherland         | ![TNO](image) |
| Memsys GmbH          | Flat sheet      | Vacuum air gap | Germany, China     | ![Memsys](image) |
| Keppel / Memstill    | Flat sheet      | Air gap or direct contact | Singapore | ![Keppel](image) |
| Aquatech             | Flat sheet      | Vacuum         | USA                | ![Aquatech](image) |
| Aquastill            | Multichannel Spiral wound | Air gap | Netherland | ![Aquastill](image) |
| KmX corporation      | Hollow fiber    | Vacuum         | Canada, USA        | ![KmX](image) |
| Econity              | Hollow fiber    | Vacuum         | Korea              | ![Econity](image) |
| Mem sift Innovation  | Hollow fiber    | Vacuum (Joule Thomson) | Singapore | ![Mem sift](image) |

Fig. 9 Aquastill pilot unit [41]  
Fig. 10 Xzero pilot unit [44]
plates alternating with microporous hydrophobic PTFE membranes (Fig. 10). The PTFE membranes are attached to the polyethylene (PE) frame by thermal welding to avoid leakages and to cope with higher pressures inside the membrane [44]. The system requires relatively larger footprints and the membrane modules are heavy. However, the vendor has been working to optimize their system designs for future field-testing opportunities. The technology was applied for desalination of seawater, RO concentrate, and brine from thermal desalination plants, in addition to application on flue-gas condensate water and pharmaceutical residues. Recently, Scarab has been exploring the integration of their technology with concentrated solar power to leverage the waste heat dissipated from a steam turbine.

3.3 Aquatech [45]

Aquatech, a US-based new entrant in this field, offers vacuum MD in a flat sheet configuration (Fig. 11) with specialized proprietary hydrophobic membranes. The membrane serves as a demister in their evaporators, i.e., only vapor passes through the membrane and there is no contact of water with the membrane surface. This reduces significantly possible wetting and fouling of membrane surface [46]. The SEC for the process is claimed by the vendor to be 100 kWh/m³ with evaporators in a multieffect configuration. For the cooling purpose, the system uses radiators to remove heat from the process. Distilled water is sprayed intermittently to clean the membrane surface. While full-scale installations are limited, it is expected that Aquatech’s position in the industry should generate opportunities to promote the technology. Their target niche applications include reducing the volume of RO concentrate and the pharmaceutical sector.

3.4 KMX Technologies LLC (formerly KmX Membrane Technologies) [47]

KMX Membrane Technologies, a Canadian company, developed a hollow fiber (HF) vacuum MD technology and was recently acquired by Texas-based Antelope Water Management and renamed KMX Technologies LLC [48]. Antelope focuses on infrastructure, technology investment, and sustainable development. PTFE and proprietary membrane chemistries were used in fabricating the HF membranes (Fig. 12). The vendor claims the cost of membrane manufacturing is lower than competitors and that hollow-fiber configuration allows higher membrane surface area per module when compared to flat sheet configurations. Various investigations have been conducted related to lithium recovery, acid mine drainage, and produced water. Heat pumps are integrated into their systems to reduce or eliminate cooling water requirements.

3.5 Memsift Innovation [49]

Singapore-based Memsift was formed to transfer the results of academic MD research into a commercial product. Memsift developed two commercial proprietary HF membranes which
provide a compact lower footprint system (Fig. 13). Higher concentrations of fluoride compounds are added to the membrane surface to increase the membrane hydrophobicity [49, 50]. The process uses a Carnot cycle based on the Joule-Thomson effect to control the temperatures inside the system [51]. The SEC for the process is in the range of 110–150 kWh/m³. The vendor targets niche applications including opportunities where water disposal cost is very high such as semiconductor industry and metal cleaning. The vendor is actively pursuing optimization options to reduce the energy consumption.

4 Innovative applications for hydrophobic membranes

In addition to saline water desalination, hydrophobic membranes used in MD processes also have a wide range of industrial applications. Hence, various MD vendors are continuously looking for niche applications where deploying hydrophobic membranes can be cost-effective for removing target contaminants regardless of energy requirements. Below are selected examples of such innovative applications.

4.1 H₂S removal

PP hollow fiber hydrophobic membranes, typically used as membrane contactors to deoxygenate water in vacuum deaerators [52] can be applied to remove hydrogen sulfide (H₂S) from sour water from the oil and gas industry. As such, the GWSC team investigated H₂S removal from sour water collected from Qatari gas field using hydrophobic membrane contactors (Fig. 14). The process schematic consisted of a membrane contactor, UV oxidizer and followed by aeration [16]. The membrane allowed only H₂S gas from the sour water to pass through while preventing the water passage. The driving force was the concentration gradient, and H₂S gas then dissolved in the receiving sodium hydroxide solution channel which immediately converted the H₂S gas into a non-hazardous form of sodium sulfide. The experimental data was validated with a mathematical model. The results showed the mass transfer coefficient was independent of the H₂S concentration [53]. The investigation revealed no immediate short-term fouling from the organic moieties present in the sour process water. The research team also investigated the feasibility of combining the membrane contactor with UV oxidation and followed by aeration. The sodium sulfide was converted into sulfate for safe disposal. This technology offers several advantages over other H₂S removal methods such as reduced health and safety concerns, lower energy consumption, cheaper materials of construction, and overall system compactness [16].

4.2 Pharmaceutical industries

MD technologies with hydrophobic membranes are also applied to treat pharmaceutical wastewater for removal of toxic organic contents. A pilot trial with Xzero AGMD modules (Fig. 15) was carried out, and the removal efficiency of organics (diclofenac, atenolol, ibuprofen, etc.) was greater than 90% [15]. The thermal energy for the pilot system was provided by district heating. In another investigation, trace organics from pharmaceutical residues were removed by coupling the MD with an enzymatic bioreactor. The combination removed 99% of 4-tert-octylphenol, octocrylene, 4-tert-butylphenol, benzophenone, and oxybenzone. The distillate was non-toxic and membrane properties were not affected [54].

4.3 Metal finishing industries

Metal finishing industries such as electronic, automotive, and heavy equipment manufacture generate wastewater with high concentration of organic and inorganic constituents. Discharge regulations for heavy metals (nickel, zinc, tin, chromium, and cadmium) generated by those industries have become stringent. The traditional wastewater treatment methods (flocculation and clarifiers) consume large quantity of chemicals and form heavy metal sludge which leads to disposal challenges. MD offers a
unique advantage of treating those wastewaters and offers an MLD solution. MD recovered > 90% of water in one step and the treated water met discharge regulations without further post polishing. MD pilot studies (Fig. 16) showed promising results by producing an effluent quality of 31 μS/cm from a feedwater of 6615 μS/cm [51].

4.4 Hybridization of FO/MD

Hybridization of FO with MD was applied to treat the streams such as direct sewer mining, reclamation from shale gas drilling flow back water, and oily wastewater [55]. The application of FO-MD for direct sewer mining resulted in removal of 91–98% trace organic contaminants [56]. The hybrid system recovered 90% of water from real shale flowback water (Fig. 17). The FO functioned as pretreatment to the MD process. Potassium chloride (KCl) was identified as suitable draw solution for the FO process. The MD process produced high-quality distillate of 5 μS/cm [57]. Fouling was observed for the oily wastewater stream in FO, and the process achieved 90% of water recovery [58].

4.5 Other MD applications

AGMD technology was also investigated to treat wastewater generated from nanoelectronics industries to comply with environmental regulations. The feed consisted of inorganic constituents: silicon (95.16 mg/L), aluminum (9.9 mg/L), copper (3.5 mg/L), and lower concentrations of other ions. The high-quality distillate showed that silicon, aluminum, and copper concentrations were below the detection limit and met regulation requirements. Separation efficiency for other inorganic ions was greater than 99% [14].

MD was also investigated for other applications including bioethanol recovery from fermentation of off-gas water [59], boron removal from geothermal groundwater [60], industrial dyeing wastewater [61, 62], anaerobic digestion effluent [63], recovery of minerals from produced water [64], metabolic wastewater for space application [65], and removal of toxic metals [66].

Another application of MD for water recovery from flue gas includes:

- Coupling of wet scrubber and integration with MD [67]
- Cooling the gas using humidifier followed by hydrophobic membrane condenser [68, 69]
5 MD energy considerations

To minimize energy consumption, module designs must include the recovery of both specific heat and latent heat. To recover specific heat, heat exchangers are used to recover energy from the brine and the distillate to preheat the feed. Recovery of the latent heat, i.e., the heat of vaporization, is more difficult and requires multieffect designs. It is important to remember that in MD, the energy needed to produce vapor must also be removed in the condenser. Typical specific energy consumption of single-effect MD with seawater cooling is 650 to 750 kWh/m³ of distillate produced. Some MD vendors offer multieffect designs and the energy consumption decreases sharply. In a 10-effect system, the energy input is expected to be 50 to 80 kWh/m³ depending on operating conditions. In designing an MD, increasing the number of effects will reduce energy consumption but will increase the amount of membrane area needed and hence capital cost. Identifying the number of optimum number of effects is dependent upon feed composition and operating conditions.

The energy consumption for seawater desalination by RO is ≈ 5 kWh/m³, significantly less than MD. But electricity, at $0.10/kWh, is 30× higher in cost on a $/kWh basis when compared with natural gas which sells for ≈ $0.0034/kWh ($2/MMBTU). On a $/m³ basis, a 5-effect MD with an energy consumption of 140 kWh/m³ has a specific energy cost comparable to RO at ≈ $0.50/m³ while a 10-effect MD has an energy cost of $0.24/m³, about 50% that of RO (Table 4). Although MD is not as energy efficient as RO, it can be cost-effective against seawater RO desalination with improvements in membrane chemistry, module design, and multieffect process configurations. Incorporating solar energy can reduce energy consumption, but because solar energy is highly variable, and storage is not practical, solar-powered MD is better suited for smaller-scale seawater desalination applications. For inland applications of MD, i.e., without seawater available for cooling, the energy consumption increases as condensing water vapor typically requires chillers, generally powered by electricity.

6 Membrane material chemistries

Most commercial MD membranes are produced using PTFE and synthesized by “stretching” [70]. To improve module sealing capabilities, membranes are also produced by the “phase inversion” method with a variety of polymers. Table 5 illustrates preparation techniques, physical properties, and performance of various commercial MD membranes. Limited new membrane development produced through stretching has been reported.

As noted in Section 5, MD can have comparable or even lower specific energy costs than RO, but novel membrane chemistries and module designs are required. MD membrane chemistry research strives to:

Table 4 MD vs. RO energy cost comparison

|                | RO          | MD          |
|----------------|-------------|-------------|
| Fuel source    | Electricity | Natural gas |
| Unit energy cost | $/kWh 0.10  | 0.0034      |
| # of effects   | ---- 10     | 5           |
| Energy consumption | kWh/m³ 5    | 70 140     |
| Energy cost    | $/m³ 0.50   | 0.24 0.48   |
a) Increase hydrophobicity (reduce pore wetting)
b) Reduce mass transfer resistance (improve flux)
c) Improve energy efficiency (reduce cost)

To increase hydrophobicity and/or reduce mass transfer resistance, research efforts apply emergent materials into the membrane chemistry. To improve energy efficiency, research focuses on membrane construction (hollow fiber and spiral wound) and module designs that enable energy reuse through multieffects within a module.

The majority of MD material chemistry development revolves around the phase inversion method with PVDF as the key polymer material and either (i) adding nanoparticles or other materials or (ii) process modifications. In addition to advancing the phase inversion chemistries, electrospun and inorganic MD membranes are also under development.

Nanoparticles can be incorporated directly into the solvent or, more easily, applied to the surface in a thin functional layer [78–80]. The challenge with a surface coating is providing good adhesion to the base membrane to ensure that the coated layer does not peel off during operation or cleaning. Crosslinking [81] or sulfonation are the main mechanisms used to apply the nanoparticle coating to the base membrane.

The range of nanoparticles being evaluated includes:

- Carbon nanotubes (CNT) [82]
- Graphene [83]
- Lithium chloride [84]
- Titanium oxide [85]
- Silicon dioxide (SiO2) [86]
- Fluorinated compounds [87]
- Polyethylene glycol (PEG) [88]
- Polyvinylpyrrolidone [89]

Membrane surface grafting can be achieved using different methods:

- Plasma posttreatment [90]
- UV photo irradiation [91]
- High energy irradiation [92]
- Chemical vapor deposition [93]

While increasing hydrophobicity is a target for many scientists, there is also active research in developing “omniphobic” membranes. The objective of this research is to create a surface that repels liquids with a wide range of surface tensions, thereby reducing possible wetting by both hydrophilic and hydrophobic materials. Omniphobic membranes can be inorganic or polymeric and can be created by various methods, including by phase inversion and electrospinning [94].

Another area of research is the development of “Janus” membranes with tailored hydrophobic and hydrophilic surfaces, i.e., asymmetric [3]. This promotes mass transfer in one direction only.

The developments to improve energy efficiency generally focus on membrane construction or module design. While hollow fiber membranes cost less to produce than flat sheet membranes on a $/m^2$ basis, flat sheet membranes have the advantage that they can be incorporated into spiral wound modules with multi-effect capabilities internal to the module. Membrane development efforts are proceeding in both areas.
6.1 Phase inversion membranes

Phase inversion is based on interfacial polymerization and converts a polymer solution into solid phase by one of three methods:

- Non-solvent induced phase separation (NIPS)
- Thermally induced phase separation (TIPS)
- Vapor-induced phase separation (VIPS)

Adding nanoparticles to PVDF membranes and casting by the NIPS method dominates development efforts although TIPS is also re-emerging as a promising method [95].

The addition of CNT is of interest to developers. CNTs consist of hollow graphene cylinders with nanoscale-sized pores. CNTs promote faster water vapor transport across membranes due to slippage effect and reduce the friction in the pore walls [96]. Figure 18 shows the mechanism to synthesize functionalized CNT with addition of silica and fluorinated compounds to enhance hydrophobicity. CNTs increase the partitioning of the water vapor while rejecting hydrogen bonded salt-water phase thereby improving performance. PVDF flat sheet membranes blended with CNTs showed smaller pore sizes but a very low contact angle of 87° [97].

The alignment of CNTs still remains a concern to lot of researchers [98].

Other examples of recent developments incorporating nanoparticles include:

1. PEG-1500 added to PVDF hollow fiber membranes produced a membrane with a contact angle of 118.5° [99].
2. PTFE microparticles and fluorinated silica particles were added to PVDF hollow fiber membranes and led to superhydrophobic membrane surface with contact angles ranging from 130° to 147° [100, 101].
3. Adding octadecyl amine functionalized graphene oxide to a PVFD flat sheet membrane yielded a contact angle of 146° and increased mechanical strength and porosity [102]. Other researchers experimenting with different forms of graphene oxide produced PVDF membranes with low contact angles of 70° [103], 59° [104], and 84° [105].

In addition to PVDF, other polymers employed in the development of advanced MD membranes include:

- Polyethylene imide [106]
- Polysulfone (PS) [107]
- Ethylene chlorotrifluoroethylene (ECTFE) [108]
- PP [109]

Examples of other membrane formulations producing highly hydrophobic MD membranes include:

1. A blend of Hyflon AD60 and PVDF produced a hollow fiber membrane with a contact angle of 138° [110].
2. PVDF grafted with triethoxysilane produced a flat sheet membrane with a contact angle > 150° [111].
3. A flat sheet membrane produced by blending PTFE with ECTFE had a contact angle of 144° [112].

6.2 ENM

The process of electrospinning transforms any of a variety of polymers into nanofibers which are laid out to produce a non-woven mat or membrane. In electrospinning, the polymer solution is stretched by electrostatic forces and nanofibers are deposited on a receiver with rapid evaporation of the solvents [113–115]. The fabrication method can be optimized through coaxial electrospinning, dual electrospinning, and electrospraying. Electrospun nanomembranes (ENMs) offer high surface area to volume ratios, high porosity, tunable pore size, and good mechanical strength in comparison to membranes produced by phase inversion [113]. Important parameters in electrospinning are applied voltage, tip-to-collector distance, chamber humidity, chamber temperature, spinning time, and polymer feed rate [3]. The heat pressing of ENM reduces the membrane thickness and increases permeate flux compared to ENMs produced without heat treatment [116]. Production-to-date has focused on lab-scale ENMs; to the author’s knowledge, commercial ENMs are not currently available.
Various polymers have been used in ENMs, including:

- PVDF [117]
- Styrene-butadiene styrene [118, 119]
- PS [120]

To improve mechanical strength and mass transfer, dual-layer ENMs have also been developed, e.g., with a polyacrylonitrile (PAN) support layer under a PVDF/hexafluoropropylene active separation layer [121]. In another investigation, the PVDF ENM served as the separation layer and PS served as the support, and together, they showed superior performance in comparison to PVDF ENMs without PS support [122].

In a third investigation, an active separation layer of polyvinyl alcohol/Triton X-100 was electrospun onto a PP mat to obtain dual-layer ENMs. The Triton X-100 improved the homogeneity of nanofiber [123] and the dual-layer membrane exhibited 2× times water flux in comparison to neat PP mats [123].

Recently, a triple-layer membrane was fabricated by electrospinning which consisted of a PVDF-PTFE hydrophobic layer, PET intermediate layer, and PEO hydrophilic layer. This membrane is claimed to offer superior flux and rejection in comparison to dual-layer membranes [124].

Nanoparticles have also been incorporated into ENMs (Fig. 19) including:

- Clay nanocomposites [125]
- SiO₂ [126]
- CNT [96]
- Graphene [127]

Surface heating membrane distillation is fabricated by nanocoating hexagonal boron nitride (hBN) (white graphene) on a stainless-steel wire cloth followed by attachment to the commercial PVDF spiral wound membranes. This phenomenon offers superior vapor permeability, thermal conductivity, electrical insulation, and anticorrosion properties in comparison with membrane without coating [128].

### 6.3 Ceramic MD membranes

Ceramic MD membrane development is also being investigated, albeit at a much smaller scale than polymeric membranes and only at lab-scale. Primary materials of construction include silicon carbide and aluminum oxide (alumina). Secondary materials include titanium oxide and zirconium oxide. These membranes are inherently hydrophilic and surface modifications are required to prevent membrane wetting in MD. A highly hydrophobic or omniphobic layer was synthesized with fluorination yielding a contact angle of 160° [129].

CNTs were deposited on nickel aluminate substrates via chemical vapor deposition and the highly hydrophobic membranes produced also showed improved fouling resistance [130]. Other developments in ceramic MD membranes include:

- Depositing zinc oxide nanoparticles on glass membranes followed by a coating of fluoralkylsilane [131]
- Silica/alumina nanoparticles on an alumina membrane [132]
- Alkoxysilane/silica nanoparticles on a glass membrane [133]

Figure 20 illustrates the various methods to convert the ceramic membrane surface into a hydrophobic surface for MD application.

### 7 Summary and conclusions

MD is a hybrid thermal-membrane process driven by the vapor pressure differential across the hot and cold sides of a hydrophobic membrane resulting in passage of water vapor through the membrane, followed by condensation to produce...
distilled water. The target application of MD is the desalination of saline waters such as seawater or brines. This paper provides an overview of recent pilot/field testing evaluation of various MD technologies, an update on commercial MD vendors and their technology developments, highlights on novel applications of hydrophobic membranes, and presents the latest developments on synthesis of advanced membranes incorporating emergent materials. The key outcomes from the review include the following:

- While significant research papers over the past decade focused on bench-scale testing and/or modeling of MD process, there were limited studies that addressed MD technology implementation at pilot and/or demonstration scale.
- Various research organizations in different countries have been involved in pilot/field testing of MD to facilitate full-scale applications of the technology.
- MD pilot-scale evaluations covered various system designs with different membrane materials, modules configuration, and energy consumption. This makes the results from these evaluations very specific to the vendor’s specifications rather than general technology assessment.
- Pretreatment is critical for stable operation of MD as the presence of chemicals in the feed can lead to MD membrane pore wetting.
- Various MD vendors are at different stages of technology development with Aquastill, Scarab, Aquatech, KMX Technologies, and Memshift Innovations currently lead the commercial market.
- Although MD total energy consumption is high compared to RO, since natural gas on a per unit energy basis is only a small fraction of the cost of electricity, the energy cost of multieffect MD can be comparable with RO.
- The lack of full-scale industrial applications for water desalination is primarily due to the low energy efficiency inherent with current module designs.
- To improve MD’s commercial potential, a key direction for future research lies in the development of multieffect membrane configuration.
- MD vendors are continuously looking for niche applications where MD technology can be cost-effectively applied for removing target contaminants regardless of energy requirements.
- Advancements in membrane chemistry research target the addition of nanomaterials (e.g., carbon nanotubes, graphene, silicon dioxide, fluorinated compounds) to membranes produced by phase inversion or electrospinning techniques.
- These emergent materials can increase hydrophobicity (to reduce wetting) and/or increase mass transfer rates (to increase flux and lower cost).

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