



Membrane Distillation Configurations and Hybrids: A Review

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ABSTRACT

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Membrane Distillation (MD) is constantly acknowledged in the research literature as a promising technology for the future of desalination, with an increasing number of studies reported annually. MD processes encompass various configurations designed for liquid separation applications. Four primary MD configurations are Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Vacuum Membrane Distillation (VMD), and Sweeping Gas Membrane Distillation (SGMD). However, real MD applications still lag with only a few universal pilot-plant tests. The absence of technology transfer from academia to industry is caused by important gaps between its fundamental basis and the process design. MD has the potential to recover both chemicals and water. This review paper describes the background and properties of interest for desalination processes and reviews the recent literature for novel compounds used in membrane processes. The advantages and disadvantages of using particular methods, examples of applications, and integrated processes are presented. Perspectives, benefits, and limitations are also discussed.



Introduction

An ever-increasing amount of research is being conducted to improve water desalination processes, largely focused on decreasing specific energy requirements for water production, increasing product water quality, and eliminating hazardous waste. MD is constantly acknowledged in the research literature as a promising technology for the future of desalination, with an increasing number of studies reported annually. The present research provides an overview of MD configurations and recent advancements in this field [1]. MD is a process in which a microporous, hydrophobic membrane is applied to separate aqueous solutions at different temperatures. The MD process is similar to conventional distillation: requires heating of the feed solution to obtain the necessary latent heat of vaporization and MD is based on the vapor/liquid equilibrium. MD is acknowledged as an alternative membrane-based approach that could potentially alleviate the aforementioned high CO₂ emissions in the desalination industry and allow efficient operation at high salt concentrations. Early work on MD was reported in the late 1960s, yet it is still considered an emerging technology [2].

MD has four primary configurations as outlined below:

- 1- **DCMD:** Involves direct contact between the feed solution and a hydrophobic membrane, suitable for heat-sensitive solutions.
- 2- **AGMD:** Utilizes an air gap between the membrane and the cold side to minimize fouling risks.
- 3- **VMD:** Operates under reduced pressure, making it energy-efficient.
- 4- **SGMD:** Used for gas separation, employing a sweep gas to pass volatile components through a membrane [3].

However, the MD process did not receive much interest until the early 1980s when membranes such as Gore-Tex Membrane (expanded polytetrafluoroethylene, PTFE, porous membrane supplied by Gore and Associated Co.) and modules with better characteristics became available [4].

Recent MD innovations can be summarized as follows: enhance permeate flux and minimize heat loss by using various materials to fill the air gap (MGMD); replace the air gap with permeate water, improving performance and energy efficiency (PGMD); and immerse the membrane module in a feed solution or coolant stream (SMD). Hybrid MD simplifies design while achieving comparable performance. Configurations are gaining prominence across industries, offering improved water recovery, ion removal, minimal brine volume, resource and energy recovery, and mitigation of scaling and fouling issues [5]. These include:

- **Hybrid MD-crystallizer:** Combines MD with crystallization processes for enhanced efficiency in various industries.

- **Hybrid MD-FO (Forward Osmosis):** Integrates MD with fouling-resistant FO technology for efficient wastewater treatment.
- **Hybrid MD-RO:** Combines MD with RO to improve energy efficiency in desalination.
- **Hybrid MD-UF (Ultrafiltration):** Combines MD with UF to enhance separation efficiency in desalination and wastewater treatment.

One important factor to consider when determining whether a new technology or material is likely to become industrially important in the future is the economics of running a process or producing a material. Gryta [6] established properties of batch fermentation producing ethanol with MD recovery method. They used porous capillary polypropylene (PP) membranes to separate volatile organic compounds from the fermentation broth, which was supposed to increase the efficiency of the fermentation process. In addition, when MD is compared with full-scale thermal distillation approaches, MD can be carried out at lower operating temperatures and pressures because it requires lower vapor space (due to membrane barrier), has good compatibility with waste heat sources or renewable energy, and can be used for decentralized applications because of its less complex configurations. Banat and Simandl [7] studied the recovery of acetone, n-butanol, and ethanol from aqueous solutions by air gap MD with polyvinylidene fluoride membrane. The authors discovered that n-butanol was the most effectively removed compound. It was also shown that temperature, air gap width, and compound concentration affect the flux and selectivity of compounds recovery.

Alkhudhiri et al. [8] tested the use of air gap MD to treat highly saline water samples comprising salts similar to those found in CSG brines. Water flux rates were found to decrease when the brine concentration was elevated and enhanced when membrane pore sizes were increased. Likewise, Singh and Sirkar [9] studied both concentrated brines and produced water by direct contact membrane distillation.

Duong et al. [10] recently conducted pilot plant trials using an air gap MD to treat brines from reverse osmosis-treated coal seam water. High water recovery rates were obtained and performance was stable over a reasonable time. Concerns were expressed concerning the possibility that membrane fouling due to silica and calcium scaling may restrict efficiency during long-term operation.

Tavakkoli et al. [11] executed a techno-economic analysis at Aspen Plus and estimated the cost of produced water as 0.73 \$/m³ feed when waste heat is utilized. However, Zuo et al. [12] simulated the DCMD process at Aspen Plus and calculated optimum energy recovery and water production cost (WPC) as \$1.1

per m³ at a 6 °C temperature difference on the hot side with a minimum membrane area of 4 m².

Moore et al. [13] formulated a model for the solar-driven sweeping gas membrane distillation for the desalination of water in MATLAB and optimized the unit cost of water as \$84.7 per m³ to recover the capital, operation, and maintenance costs for a capacity of 240 L/day. Shirazi and Kargari [14] and Wu et al. [15] reviewed CFD opportunities and simulation techniques for membrane distillation systems. Undoubtedly, desalination and wastewater treatment provided valuable opportunities to avoid the complete depletion and diminishment of freshwater resources [16].

Desalination has particularly been recognized as the essential contributor to reducing water stress in coastal and inland regions through the production of fresh water from seawater, saline groundwater, drainage water, and treated wastewater. Desalination and wastewater treatment based on membrane technology is one approach extensively explored to address the challenge of increasing access to clean drinking water to sustain the rapidly growing global population as well as to ensure economic progress [17].

The research and industrial community have been thinking strategically and looking beyond the fence line to fully utilize membrane technology as a cost-effective candidate for an expanding range of purification and separation needs such as water and wastewater treatment, and brackish and seawater desalination. Recent signs of progress have witnessed the potential and reliability of applying commercially available membranes and membrane systems to relieve water issues [18].

Conventional configurations

MD has been the subject of worldwide academic studies by many experimentalists and theoreticians and from the commercial standpoint, MD has gained only little acceptance and is yet to be fully implemented in the industry [19]. Although MD processes can be primarily categorized into four major configurations, each of which relies on specific methods to create a vapor pressure difference across the membrane and how the permeate is collected on the cold side. These configurations are DCMD, AGMD, VMD, and SGMD [20].

Table 1. MD conventional configurations and their advantages, disadvantages, and applications [21].

Configuration	Advantages	Disadvantages	Applications
DCMD	Simple design and operation, high flux	High conductive heat loss, low non-volatile rejection	Desalination of seawater, and brackish water, removal of various contaminants
VMD	Negligible heat loss, high flux	Risk of membrane wetting due to high-pressure difference	The concentration of fruit juice, inorganic acids, recovery of volatile organic compounds, concentration of RO brine

Configuration	Advantages	Disadvantages	Applications
SGMD	Low conductive heat loss, high flux	Requires large condenser, expensive	Concentration of fruit juice, removal of non-volatile organics, ethanol processing
AGMD	High non-volatile rejection, high purity Low membrane wetting, low heat loss	High mass transfer resistance, low permeate flux	Wastewater produced in water treatment, separation/removal of inorganic acids and organic compounds

DCMD

DCMD is a membrane separation process used for desalination and other liquid separation applications. In DCMD, the feed solution and the cold side are brought into direct contact with each other on opposite sides of a hydrophobic membrane [22]. Heat is applied to the feed solution, causing it to evaporate. The vapor molecules, being smaller and able to pass through the membrane's pores diffuse through the membrane. On the cold side of the membrane, the vapor condenses into liquid, forming the permeate [23]. One of the key advantages of DCMD is its ability to operate at relatively low temperatures and pressures compared to traditional distillation processes, making it energy-efficient and suitable for treating heat-sensitive solutions. The hydrophobic nature of the membrane prevents liquid from passing through, allowing only vapor molecules to transfer, thereby achieving the desired separation [24].

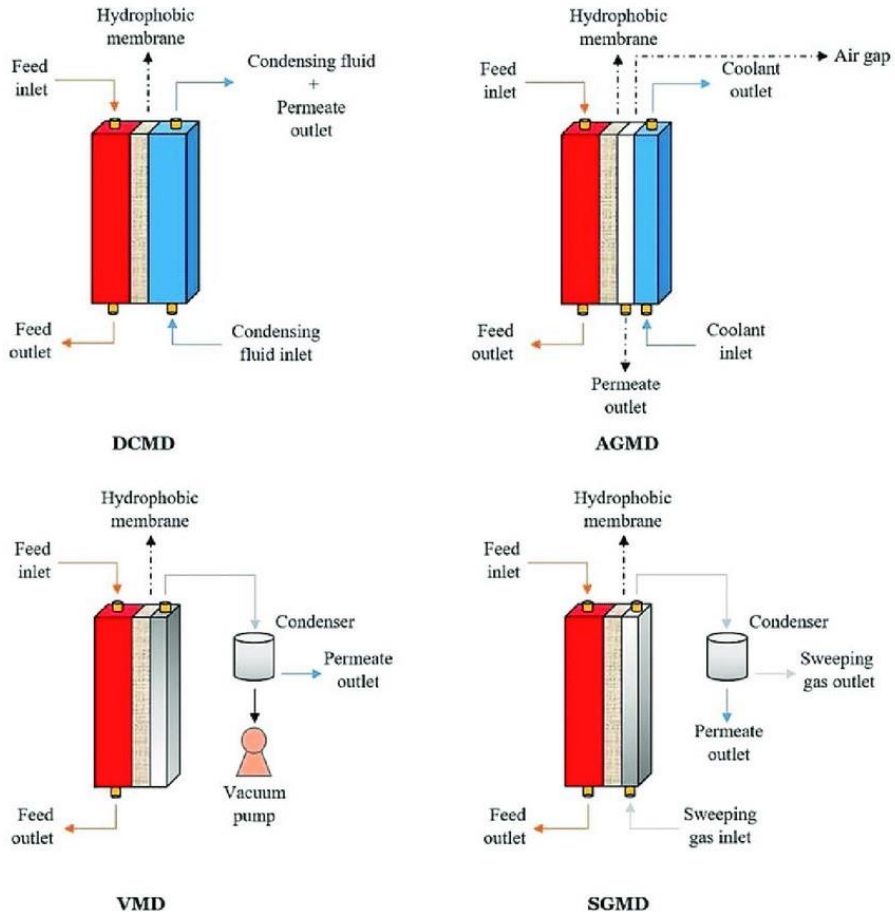


Figure 1. Conventional configurations of membrane distillation [25].

AGMD

AGMD is a specialized form of membrane distillation used for liquid separation applications. In AGMD, a hydrophobic membrane separates the feed solution from the cold side, with an air gap in between. Heat is applied to the feed solution, causing it to vaporize. The vapor molecules, being smaller than the pores in the membrane, can pass through it. However, instead of condensing directly on the cold side of the membrane, the vapor condenses on the outer surface of the membrane. The condensed vapor forms a liquid layer on the membrane's surface, which is then collected as the permeate. The air gap between the membrane and the cold side aids in maintaining a temperature gradient, which is essential for the distillation process. Because the vapor condenses outside the membrane, it minimizes the risk of wetting or fouling the membrane, making AGMD suitable for treating challenging feed solutions [26].

VMD

VMD is a membrane separation process employed for various liquid separation applications. In VMD, a hydrophobic membrane separates the feed solution from the cold side, and a vacuum is created on the cold side. Heat is applied to the feed solution, causing it to vaporize even at lower temperatures due to the reduced pressure in the vacuum chamber. The vapor molecules, being smaller than the pores in the membrane, can pass through it. On the cold side of the membrane, the vapor condenses into a liquid, forming the permeate. The key advantage of VMD is its ability to operate at relatively low temperatures compared to traditional distillation processes. This makes it suitable for separating heat-sensitive solutions or processing temperature-sensitive compounds. The vacuum environment aids in reducing the boiling point of the feed solution, making it an energy-efficient distillation method [27].

SGMD

SGMD is a specialized form of membrane distillation used for gas separation and purification applications. In SGMD, a hydrophobic membrane is employed to separate a gas mixture. Unlike liquid-phase membrane distillation, SGMD is applied to separate volatile components or gases. In SGMD, a sweep gas, often an inert gas such as nitrogen or helium, is introduced on one side of the hydrophobic membrane while the gas mixture to be separated is on the other side. The sweep gas carries the volatile components or target gases through the membrane, while the less volatile or unwanted components are left behind. On the other side of the membrane, the volatile components in the sweep gas are condensed, resulting in the desired purified gas stream, known as the permeate [28].

Recent configurations

MGMD

In the pursuit of further advancements, various materials are being employed to fill the air gap in AGMD. These materials can be categorized into two groups: thermally conducting and non-conducting materials. Examples of these materials include metal mesh, polypropylene mesh, polyurethane sponge, and sand [29]. The primary objective following these endeavors is to enhance the permeate flux and/or reduce the conductive heat loss experienced across the membrane. An alternative configuration, known as CGMD, involves the incorporation of a conducting plate within the gap. This configuration is expected to exhibit higher heat loss, similar to DCMD. However, it also offers the potential advantage of effectively rejecting non-volatile compounds at lower temperatures [29].

PGMD

PGMD is an innovative distillation configuration that combines features from both airgap and direct contact membrane distillation modules to enhance efficiency. In PGMD, the air gap in AGMD is replaced by permeate water, leading to advantages in performance and energy consumption. Vapor generated on the membrane surface immediately condenses in PGMD, and the condensed vapor is further cooled by a coolant, which can even be cold-feed water. PGMD offers lower mass transfer resistance and enhanced thermal conductivity compared to traditional AGMD and DCMD setups. This improved thermal conductivity is used to preheat the cold feed solution, reducing energy consumption. Importantly, PGMD does not require pre-cooled permeate water, simplifying the process and saving energy. Overall, PGMD is a promising advancement in membrane distillation technology, offering improved efficiency and energy savings in desalination and other separation processes [30].

SMD

The SMD technique represents an innovative approach within the realm of membrane distillation. In this method, the membrane module is immersed either within a feed solution tank or a coolant stream. This unique configuration offers a straightforward design and construction when juxtaposed with other membrane distillation setups. What sets SMD apart is its remarkable adaptability, as it seamlessly integrates with other traditional MD configurations such as DCMD, VMD, and SGMD. This inherent flexibility opens up a myriad of possibilities for SMD's application. Francis et al. delved into the intricacies of this process [31]. Through a series of laboratory-scale experiments employing hollow fiber membranes, they ascertained that the permeate flux attained in SMD was on par with that achieved in other conventional MD setups. This compelling observation suggests that SMD holds the promise of delivering comparable performance while simplifying module design and construction [32].

Hybrid MD configurations

The increasing focus on hybrid MD in diverse sectors such as seawater desalination, wastewater treatment, food processing, mining, and pharmaceutical industries is driven by the potential to improve the overall efficiency of treatment processes and to address the limitations and obstacles hindering the widespread commercial adoption of MD. Across the globe, many industries are actively working on developing sustainable treatment technologies. Hybrid systems offer the flexibility to integrate and optimize specific processes that complement each other effectively. In terms of enhancing the sustainability of the overall treatment process, hybrid MD is noticeable for its

ability to improve water recovery and remove ions from complex solutions including micropollutants; to minimize brine volume, ultimately achieving zero liquid discharge; to recover valuable resources and energy, potentially generating revenue to offset treatment costs; and finally, to mitigate scaling and fouling issues (see Figure 2). The following section will focus on evaluating various MD hybrid approaches based on these contributing factors [33].

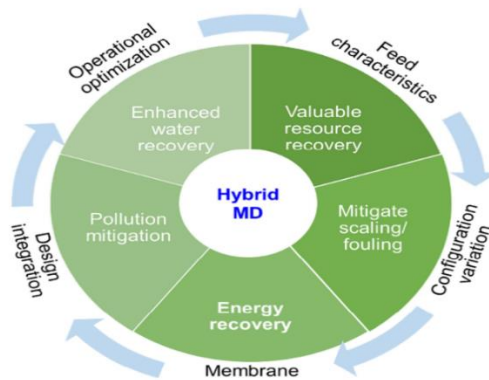


Figure 2. Hybrid MD configurations - major advantages and factors influencing its performance [33].

Hybrid MD-crystallizer

Crystallization, a crucial process employed in industries such as pharmaceuticals, chemicals, and food production, plays a pivotal role in separating and purifying substances. This method entails the creation of ordered crystal structures from solutions or melts, ultimately ensuring the production of high-quality products. On the other hand, Molecular Dynamics Simulation (MDS) is a computational technique utilized to investigate molecular behavior at the atomic level. Through the solution of motion equations, MDS provide valuable insights into molecular interactions and the dynamics of a system. The Hybrid MD-crystallizer represents an integration of these two components, yielding remarkable advantages:

- 1- **Predictive Modeling:** MDS can predict the behavior of crystallization processes, contributing to process optimization and tailored outcomes.
- 2- **Understanding Molecular Interactions:** MDS unveil molecular-level interactions, facilitating the optimization of crystallization processes for purity and yield.
- 3- **Process Optimization:** The combination of real-world equipment with MDS enables precise control of conditions, leading to the achievement of ideal crystal size, shape, and quality.

- 4- **Cost-Efficiency:** Reduced experimentation requirements, thanks to MDS, resulting in cost savings and a reduced environmental footprint.

In conclusion, the Hybrid MD-crystallizer harnesses the power of MDS to enhance the comprehension, control, and efficiency of crystallization processes. This innovation offers significant benefits to industries relying on crystallization techniques. While conventional methods such as evaporation-crystallizers have been widely used for resource recovery, they are energy-intensive and challenging to control. In contrast, the hybrid MD-crystallizer, which combines MD with a crystallizer, offers a practical solution to achieve supersaturation levels in solutions through water recovery instead of energy-intensive evaporation. This approach offers advantages such as faster induction times, more efficient energy consumption, and better control over supersaturation due to well-defined membrane mass transfer. Moreover, the hybrid MD-crystallizer is expected to mitigate membrane scaling issues, which can be a significant drawback in standalone MD processes [33-36].

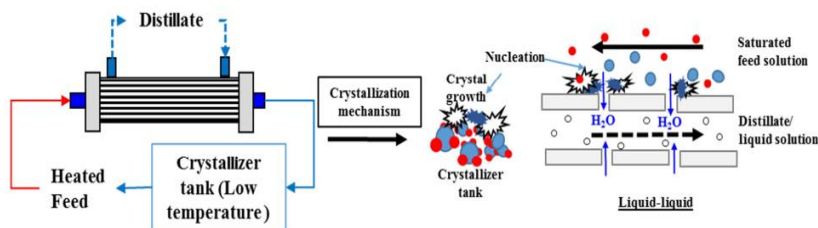


Figure 3. Hybrid MD-crystallizer schematic [33].

Hybrid MD-FO

Forward osmosis (FO) has attracted attention from both the research community and industry due to its potential as an energy-efficient and fouling-resistant membrane separation technology [37]. FO relies on the osmotic pressure difference between two sides of a semi-permeable membrane, created by varying solution concentrations. This process pulls water molecules from a less concentrated feed solution toward a more concentrated draw solution. As water permeates the membrane, the feed solution shrinks in volume and becomes more concentrated, while the draw solution becomes diluted, lowering its osmotic pressure [38]. Compared to pressure-driven membrane processes such as RO, FO operates without the need for applied hydraulic pressure, resulting in significantly lower energy requirements and reduced membrane fouling. However, FO faces limitations in that the diluted draw solution requires

further treatment after mixing with the extracted water, or it must be re-concentrated to maintain its osmotic pressure [39].

Hybrid MD-RO

Hybrid systems that combine RO and MD elements are designed to take advantage of the strengths of each process while mitigating their weaknesses. The primary goal of such systems is to improve energy efficiency and reduce fouling or scaling issues associated with conventional RO systems, particularly when dealing with challenging feed solutions such as brackish or seawater.

The way a hybrid RO-MD system typically works is outlined below:

- **Pretreatment:** The feed solution is first pre-treated to remove large particles, suspended solids, and scaling agents that could foul the membrane surfaces.
- **(RO)Stage:** The feed solution is pressurized and passed through an RO membrane. This stage removes a significant portion of dissolved solids and impurities from the feed water.
- **MD Stage:** The RO permeate is then subjected to the MD process. It is heated, and water vapor is separated from the solution by passing through a hydrophobic MD membrane. This step further purifies the water and concentrates the remaining impurities in the MD reject stream.
- **Integration:** The purified water from the MD stage can be collected as the final product, while the reject stream from both the RO and MD stages might be combined and treated separately or disposed of.

The hybrid RO-MD system benefits from the high rejection capabilities of RO and the capability of MD to handle challenging feed solutions with high salinity or fouling potential. It can potentially reduce energy consumption compared to traditional RO processes while providing high-quality purified water.

Hybrid MD-UF

- The hybrid MD-UF process combines the advantages of both MD and UF to achieve better separation efficiency and improved overall performance.
- Typically, the process commences with the feed solution entering an ultrafiltration system. In this step, UF removes larger particles, suspended solids, and macromolecules from the feed, resulting in a cleaner and more concentrated solution.
- The clarified and concentrated solution from UF is then directed to the MD system.

- In the MD unit, the feed solution undergoes the thermal-driven separation process. Heat is applied to one side of the hydrophobic membrane, causing water vapor to pass through it and leaving behind concentrated solutes and contaminants.
- The permeate from the MD unit contains purified water vapor, which can be condensed and collected as a product stream.
- By using UF as a pretreatment step, the MD process encounters fewer fouling issues, as larger particles and contaminants have already been removed, leading to improved MD performance and longer membrane lifespan.

The hybrid MD-UF process is particularly useful in various applications such as desalination, wastewater treatment, and concentration of heat-sensitive or high-value products. It allows for efficient separation and purification while mitigating fouling and enhancing overall system reliability. In the process presented, the UF permeate is heated in a heat exchanger prior to the MD installation. The hot feed flows through the MD modules connected in a parallel mode. The evaporation of water through the membrane causes an increase in the concentration of the oil phase in the feed. The concentrated emulsion is returned to the feed of the ultrafiltration plant. Pure water (MD distillate) and an oil concentrate (UF retentate) are produced in the hybrid system.

Conclusion

MD processes offer various configurations for liquid separation. The primary MD configurations are DCMD, AGMD, VMD, and SGMD. DCMD is suitable for heat-sensitive solutions, AGMD minimizes fouling risks, VMD is energy-efficient, and SGMD is used for gas separation. MD has been in the inflated expectations stage for a considerable time, and no major signs of enlightenment demonstrated. Thus, it is probably at the disillusionment stage currently. Efforts to reach technological maturity must be put on the right track, avoiding missed opportunities and wasting resources in expensive iterative pilot assays. Recent advancements include MGMD, CGMD, PGMD, and SMD. MGMD enhances permeate flux and minimizes heat loss, PGMD improves performance and energy efficiency by replacing the air gap with permeate water, and SMD simplifies design while achieving comparable performance. Hybrid MD configurations are gaining prominence. These include Hybrid MD-crystallizer, Hybrid MD-FO, Hybrid MD-RO, and Hybrid MD-UF (Ultrafiltration). They offer improved water recovery, ion removal, minimal brine volume, resource and energy recovery, and mitigation of scaling and fouling issues. In conclusion, MD has diverse configurations and hybrid options, offering advantages for liquid separation and gas purification, supported by recent advancements in the field.

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