

**MANIPULATING MEMBRANE ANTI-WETTING
TENDENCY THROUGH PHASE INVERSION**

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MANIPULATING MEMBRANE ANTI-WETTING TENDENCY THROUGH PHASE INVERSION

by

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LIST OF SYMBOLS

ε	Bulk porosity of membrane	%
m_b	Wet mass of the membrane after immersing in 2-butanol	g
m_m	Dry mass of the membrane	g
ρ_b	Density of 2-butanol	g/cm ³
ρ_m	Density of the PVDF	g/cm ³
J	Permeate flux	kg/m ² h
Δm	Mass of permeate	kg
A	Membrane effective area	m ²
Δt	Time interval	h
R	Salt rejection	%
c_p	Permeate concentration	$\mu\text{S/cm}$
c_f	Feed concentration	$\mu\text{S/cm}$

LIST OF ABBREVIATIONS

CA	Contact angle
DCMD	Direct contact membrane distillation
NIPS	Non-solvent induced phase separation
NMP	N-Methyl-2-pyrrolidone
SEM	Scanning electron microscope
TIPS	Thermal induced phase separation
L-L	Liquid-liquid
S-L	Solid-liquid

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- Appendix A **MATLAB CODING FOR PORE SIZE IDENTIFICATION**
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ABSTRAK

Penyulingan membran (MD) adalah suatu teknologi pemisahan yang mana fasa umpan cecair dan fasa meresap cecair bersentuhan secara langsung dengan membran hidrofobik bermikropori dan pemisahan berlaku atas keseimbangan termodinamik pada antara muka cecair-wap. Dalam MD, perbezaan tekanan wap adalah daya pendorong untuk menggerakkan wap air melintasi membran. Membran MD yang unggul mempunyai ciri-ciri peresapan dan peratusan penolakan yang tinggi, dengan kecenderungan anti-pembasahan yang sangat baik. Dalam kajian ini, morfologi membran PVDF yang diperbuat daripada pemisahan fasa yang berbeza parameter (suhu pelantar dan suhu larutan dope) dianalisis kerana dipercayai bahawa morfologi membran akan dipengaruhi oleh parameter fabrikasi yang akan seterusnya mempengaruhi kecenderungan membasahi membran. Dalam pendapatan kami, manipulasi suhu larutan dope mempunyai pengaruh yang lebih keseluruhan pada morfologi membran berbanding dengan suhu pelantar. 60 °C suhu larutan dope mampu menghasilkan membran yang lebih hidrofobik di mana sudut kontak terbesar iaitu 143.36°, manakala larutan dope 90 °C dapat menghasilkan membran yang fluks meresap tertinggi (19.72 kg/m²h) dan kadar penolakan sempurna (100%) ketika menjalani MD kontak terus pada suhu panas dan sejuk 60 °C dan 20 °C dan fluks tertinggi ini disebabkan oleh ketebalan membrannya yang nipis. Berdasarkan gambar SEM, penambahan pada sudut kontak dapat dikaitkan dengan pembentukan globula

sfera skala nano yang lebih banyak dan taburan globula sfera yang seragam pada permukaan membran (interfasa plat membran-kaca) untuk membran yang disediakan pada suhu larutan dope 60 °C.

MANIPULATING MEMBRANE ANTI-WETTING TENDENCY TROUGH TIPS

ABSTRACT

Membrane distillation (MD) is a separation technology which liquid feed phase and liquid permeate phase are in direct contact with a microporous hydrophobic membrane and the separation occurs based on the thermodynamic equilibrium at the liquid-vapour interface. In MD, the vapour pressure difference is the driving force to drive the water vapour transport across the membrane. An ideal MD membrane has the characteristics of high permeate flux and rejection percentage, with an excellent anti-wetting tendency. In this study, the morphology of PVDF membrane fabricated at different phase separation parameters (casting platform temperature and dope solution temperature) was analysed as it is believed that the morphology will be affected by the casting parameters which in turn influence the membrane wetting resistance. From our findings, manipulating of dope solution temperature has a more overall effect on membrane morphology instead of casting platform temperature. 60 °C dope solution temperature able to produce the membrane with enhanced hydrophobicity with largest contact angle at 143.36° while 90 °C dope solution results in membrane with highest average permeate (19.72 kg/m²h) flux and perfect rejection rate (100%) when running DCMD at a hot and cold temperatures of 60 °C and 20°C and this highest flux is mainly due to its least membrane thickness. Based on the SEM images, the gain on the contact angle is related to the more formation of nano-scale spherical globules and the uniformity of spherical globules distribution at membrane surface (membrane-glass plate interface) for membrane prepared at 60 °C dope solution temperature.

CHAPTER 1

INTRODUCTION

In this chapter, the overview of this research as well as the importance of membrane anti-wetting properties in direct contact membrane distillation (DCMD) will be introduced. This chapter also covers the research background on membrane distillation (MD), anti-wetting and hydrophobicity, thermally induced phase separation (TIPS), problem statement and the objectives of this final year project.

1.1 Membrane distillation

Membrane distillation (MD) is a process which use the principles of both the thermal and membrane technologies. MD is a process which liquid feed phase and liquid permeate phase are in direct contact with a microporous hydrophobic membrane and the separation occurs based on the thermodynamic equilibrium at the liquid-vapour interface (Ashoor *et al.*, 2016). In MD, vapor pressure difference across the membrane is the driving force and a porous hydrophobic membrane is used as a vapour-liquid interface. By creating a higher temperature difference between the feed and permeate phase, the vapor pressure difference across the membrane increases. Heat is transferred from the feed stream to the permeate side by conduction through the membrane as well as evaporation of bulk water in feed stream.

The basic schematic of the MD process is shown in Figure 1.1. Based on the Figure 1.1, the liquid feed phase which has higher temperature will evaporate and turns into vapours. By then the vapours will diffuse through the pores of the membrane. The vapours will condense when they reach the cold interface and turns into liquids (distillate). As a result of mass transfer of water vapours, the mass of feed phase will decrease while the mass of the permeate phase will increase. In MD, only water vapour molecules in the hot feed are permeable to the hydrophobic membrane whereas the

liquid feed is prevented from passing through the membrane pores. Hence, the high hydrophobicity and low surface energy membrane is preferred in MD in order to keep the membrane pore from wetting phenomena. As the nature of water is polar with high surface tension, membrane with low surface energy has outstanding performance in keeping the membrane pores dry (Ahmed *et al.*, 2020).

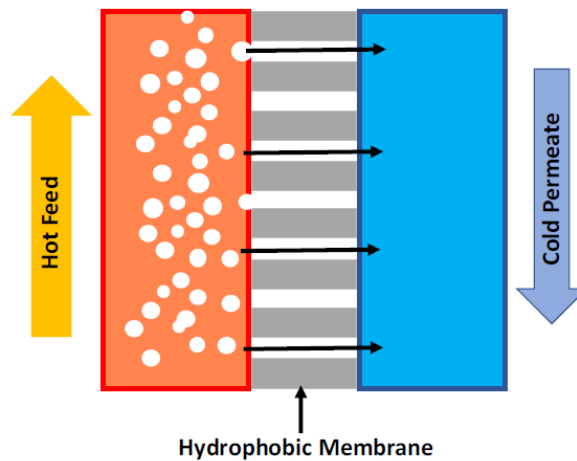


Figure 1.1 Schematic of the MD process ((Ahmed *et al.*, 2020)

MD mainly has four main types of configurations which are direct contact (DCMD), air gap (AGMD), sweep gas (SGMD) and vacuum (VMD). The difference between these techniques is that the condensate permeate is collected in different configurations (Ahmed *et al.*, 2020).

MD has been widely used in various applications such as water desalination, wastewater treatment, food industries (e.g.: milk and juice concentration), chemical and pharmaceutical industries, textile industry as well as in medical applications (Ameen *et al.*, 2020). Compared to conventional membrane technologies such as reverse osmosis (RO), MD has lower operating pressure. Heating in MD forms a significant component of total energy consumption. In order to solve this issue, researchers are focusing on the reduction of thermal energy used in MD and the use of low-cost alternative energy

sources. For example, MD can be operated with alternative energy sources such as solar, wave or geothermal energy (Ashoor *et al.*, 2016).

MD is a more sustainable method in desalination compared to RO as the separation can be conducted at a lower pressure under the vapor pressure gradient. By understanding the distribution of heat energy at different depth of sea zone, the thermal energy of the seawater can be utilised to sustain the thermal energy consumption of MD. To increase the vapor pressure of feed phase in DCMD, the thermal heat can be derived by heat exchanging between the seawater at the epipelagic zone (sunlight zone) which has a higher temperature. Or as an alternative, by heat exchanging between the seawater below the epipelagic zone with the permeate phase, permeate phase with lower vapor pressure can be achieved.

1.2 Anti-wetting and hydrophobicity

Anti-wetting is one of the crucial requirements of a MD membrane. The main prerequisite to be fulfilled by the membranes in MD is the membrane pores must remain dry and not wet by the solutions on both side of the membrane. The chosen of membrane material and properties undeniable able to mitigate the membrane wetting. Materials such as polyvinylidene fluoride (PVDF), polypropylene (PP), polytetrafluoroethylene (PTFE) and polyethylene (PE) are widely used in fabricating intrinsic hydrophobic microporous polymeric membrane in MD. However, these membranes are still prone to wetting if the LEP is exceed (Rezaei *et al.*, 2018). PVDF membranes has higher surface free energy with 30.3 mN/m which indicates that PVDF is less hydrophobic as compared to PE, PP and PTFE membrane with surface energies of 20-25mN/m, 30mN/m, and 9-20 mN/m respectively. However, PVDF membranes are still widely used in MD due to its easy processability.

Even though the intrinsic CA of the PVDF membrane is less than 90° , the contact angle (CA) can be improved and enhanced by increasing its surface roughness. Surface roughness is more important than low surface energy in the hydrophobicity of the membrane. Increase the surface roughness of two membranes with different hydrophobicity able to convert both membranes into superhydrophobic.

The anti-wetting properties of the membrane depends on three main parameters including: (1) CA (2) surface roughness (3) the surface morphology or topography (re-entrant structure) (Wae AbdulKadir *et al.*, 2020). A hydrophilic membrane has a CA $<90^\circ$ while a hydrophobic membrane has a CA $>90^\circ$. A superhydrophobic membrane is defined as membrane which has very large water CA ($>150^\circ$) and very low sliding angle ($<10^\circ$) (Su *et al.*, 2019).

There are different approaches to control wetting in MD and most of the research emphasise on advancement in membrane fabrication. Most of the studies has investigated on the modifying of membrane surface geometrical structure and surface chemistry. In order to improve the super hydrophobicity or pore wetting resistance of the membranes, the morphology of MD membranes can be modified chemically and physically (Wang *et al.*, 2014; Ashoor *et al.*, 2016; Tijing *et al.*, 2016; An A. K. *et al.*, 2017; Lu *et al.*, 2017; Ray *et al.*, 2017; An S. *et al.*, 2017; Zhang *et al.*, 2017; Zuo *et al.*, 2017; Huang *et al.*, 2018; Rezaei *et al.*, 2018; Kharraz and An, 2020; Kumar *et al.*, 2020).

One of the common hydrophobic membrane fabrication techniques is Thermal Induced Phase Separation (TIPS), due to a series of its benefits and excellent properties of the membranes produced. Hence, the fabrication parameters of the TIPS process such as the temperature of coagulation bath and casting temperature as well as their

respective difference in cooling rates will be having different level of impact on the membrane morphology, and they will be further discussed in the later section.

1.3 Thermal Induced Phase Separation (TIPS)

In general, TIPS process involves five basic steps to fabricate microporous membrane. Firstly, a polymer of interest is dissolved in a high-boiling, low molecular weight solvent at an elevated temperature (typically close to the melting point of the polymer) to obtain a homogenous solution. Next, the dope solution is casted into the desired shape such as flat-sheet or hollow fibre. Then, the cast solution is cooled in a controlled manner to induce phase separation and precipitation of the polymer. Finally, the membrane is dried (Roh *et al.*, 2010; Kim *et al.*, 2015). In TIPS, the phase separation is driven by the heat transfer coupled with mass transfer rather than a complex multi-component mass exchange.

Phase separation of TIPS mainly occur via two mechanisms which are liquid-liquid (L-L) and solid-liquid (S-L). During cooling process of the cast solution, L-L separation is induced if the cooling temperature reaches a binodal line. Two mechanisms which are nucleation growth (NG) and spinodal decomposition (SD) must be considered when the L-L separation occur. NG mechanism occurs in a metastable region (region between the spinodal and binodal lines in the phase diagram) while SD mechanism occurs in an unstable region (region under the spinodal lines in the phase diagram). If cooling temperature reaches the crystallization curve of the polymer/solvent system, S-L separation will occur (Gu *et al.*, 2006). In TIPS, the main driving force is the removal of thermal energy from the dope solution. There are many factors that will influence the resulting morphology of the PVDF membrane such as the selection of solvents, the cooling rate, and the quenching temperature.

TIPS process has been widely applied in fabrication membrane such as poly(ethylene chlorotrifluoroethylene) (ECTFE) membrane, poly(vinylidene fluoride) (PVDF) (Cui *et al.*, 2008; Rajabzadeh *et al.*, 2009), polysulfone (PSf) (Tiron *et al.*, 2017), polyacrylonitrile (PAN) (Wu *et al.*, 2012) and so on.

As mentioned, a membrane can be formed by removing the thermal energy to induce the phase separation. Therefore, phase separation is related to the polymer-solvent interaction, cooling media, cooling rate, as well as the thermal gradient. One of the highlighted properties of TIPS is its ability to fabricate membrane from semi crystalline polymers (e.g.: ECTFE) that are generally insoluble in solvents at ambient temperature. Besides, TIPS process is usually used as a binary system compared to the non-solvent induced phase separation (NIPS) process in a ternary system, making the TIPS process inherently simpler than the NIPS process with fewer variables to be controlled (Kim *et al.*, 2015).

According to Zhao *et al.* (2019), they proposed a modified N-TIPS method by using mixed solvents in fabricating the PVDF hollow fiber membranes. The mixed solvents contain a water-insoluble poor solvent and water-soluble neutral solvent. By using this approach, they able to tune the surface pore structure without the forming of mechanical weak micro voids. The membrane produced by this approach shows increased water permeability from 389 ± 30 to 922 ± 36 L m⁻² h⁻¹ bar⁻¹ in a cross-flow filtration process, with overall porosity improved from 50 ± 2.2 to $69 \pm 2.9\%$. The membrane also exhibits a good tensile strength ranging from 5.6 ± 0.1 to 6.5 ± 0.2 MPa (Zhao *et al.*, 2019). From the study of Jung *et al.* (2018), N-TIPS method also used to fabricate the PVDF hollow fibre. They have applied a transient coating layer to prevent the polymer dope solution from directly contacting the nonsolvent which is regarded as the main cause of dense skin layer formation (Jung *et al.*, 2018).

In another work, Hou *et al.* (2014) has prepared a PVDF flat-sheet membranes for DCMD. They investigate the effects of some important factors such as polymer concentration, solvent and non-solvent additive, non-woven fabric support on the flat-sheet membrane structure and properties. They concluded that the PVDF/non-woven fabric composite membrane using 5 wt.% acetone and 3 wt.% H₃PO₄ as the mixed additive gave the highest stable flux during the desalination of 35g/L NaCl solution. This composite membrane has high potential to be utilised in DCMD process (Hou *et al.*, 2014).

In the study of Fan *et al.* (2020), they have developed a method of fabricating surface-patterned microporous membrane which combining soft lithography and TIPS process. The membrane fabricated via this method has enhanced the water CA and pure water flux because of the presence of surface pattern on the membranes which increases the active surface area. This patterned PVDF membrane has similar pore structure, mechanical characteristics and crystallinity as compared to the non-patterned PVDF membrane (Fan *et al.*, 2020).

By optimising the dope composition and temperature in TIPS, it is able to fabricate membrane which is less prone to defects and with narrow pore distribution. Besides, TIPS process allows for fabrication of membrane with high mechanical strength because the high temperature TIPS dope solution allows for high polymer concentration. However, the surface pore size of TIPS membranes cannot be tuned or controlled easily as compared to other phase inversion methods. Hence, researchers are trying to fine-tune the TIPS processes for better pore size control in membrane fabricating without compromising the mechanical integrity (Jung *et al.*, 2018).

1.4 Non-solvent Induced Phase Separation (NIPS)

PVDF membrane can be fabricated via NIPS method (immersion precipitation) due to its ease of dissolution in common organic solvents such as N,N-Dimethylacetamide (DMAc), N,N-Dimethylformamide (DMF), Dimethylsulfoxide (DMSO), Hexamethyl phosphoramide (HMPA), N-Methyl-2-pyrrolidone (NMP), Tetramethylurea (TMU), Triethyl phosphate (TEP), Trimethyl phosphate (TMP), Acetone (Ac), DMF/Ac, methyl ethyl ketone (MEK) and Tetrahydrofura (THF). In NIPS, the behavior of a mixture of the components which are polymer, solvent and non-solvent can be presented in a three-component phase diagram to have a better understanding on the mechanism of membrane formation. Since PVDF is a semi-crystalline polymer, hence its phase separation behavior is far more complicated than an amorphous polymer such as polysulfone, polyamide and cellulose acetate (Wienk *et al.*, 1996).

Currently, supercritical carbon dioxide was utilized in NIPS method to prepare PVDF membrane. This method is to improve the traditional phase inversion process because it is more eco-friendly and has lower cost (recovery). Besides, the membrane prepared via supercritical carbon dioxide can form and dry without experiencing structure collapse due to the absence of liquid-vapor interface. Via this technology, membranes with “sponge-like” and asymmetric structure, cellular pores surrounded by interlinked PVDF particulate crystallites as well as leafy-life sub-morphology are obtained (Cao *et al.*, 2005; Huang *et al.*, 2007).

In general, at least a polymer and a solvent are mixed to obtain a homogeneous solution. Then, then dope solution is cast into a thin film to get flat sheets structure on a support or extruded through a die to obtain a hollow fibers structure. After casting the dope solution into desired shapes, the cast film is immersed into a coagulation bath

which consist of a non-solvent or poor solvent for the polymer. Hence, phase separation occurs under the mutual diffusion of solvent and non-solvent and precipitation of cast film takes place (Tan and Rodrigue, 2019).

Typically, two types of demixing which are S-L demixing and L-L demixing accompanying crystallization will occur phase inversion mechanism of PVDF polymer and the type of demixing will control the membrane morphology. L-L demixing has a significant effect in NIPS process. Instantaneous demixing represents the demixing of solution followed by further changes of polymer rich phase composition going through the glass transition. This demixing will give finger-like pore structure, fine gravimetric porosity and thin skin layers of membrane due to the rapid precipitation of polymer after immersion in non-solvent bath. Delayed demixing represents the composition of the interface through the vitrification boundary without demixing. This type of demixing usually produce membrane with sponge-like substructure and a relatively dense top layer due to the slow membrane formation (Tan and Rodrigue, 2019).

1.5 Problem Statement

Global desalination capacity has increased sharply in order to mitigate the freshwater scarcity issue. The membrane-based technologies exist as an alternative in desalination. However, the current membrane technologies with high operating pressure require high energy intensity and consumption. Hence, MD with operating pressure at ambient conditions is developed with better separation efficiency and lower energy consumption. However, one of the main challenges of utilizing MD in desalination is the wetting of membrane. Membrane pore wetting can cause the deterioration of separation efficiency due to the increase of mass transfer resistance to water vapors

passing through the membrane pores. Therefore, a superhydrophobic membrane is the main pre-requisite.

TIPS is one of the techniques to tune the membrane hydrophobicity. However, there is always a challenge in application where the surface pores of the resulted membrane are hard to control. Hence, this paper is to study on the effect of the temperature of casting platform and dope solution in TIPS process on the membrane hydrophobicity. Furthermore, a membrane with rough surface will not necessarily has anti-wetting property due to the parahydrophobic effect. Thus, the correlation between the physical and chemical properties of the membrane will be studied as well. The fabricated membrane will be tested in DCMD to treat high saline water in order to determine its anti-wetting capability.

1.6 Objectives

1. To explore the membrane anti-wetting tendency via thermally induced phase inversion (TIPS) by manipulating the membrane fabrication conditions (casting platform temperature and dope solution temperature).
2. To characterise the physical and chemical properties of the membrane.
3. To investigate the membrane anti-wetting capability via testing the membrane with Direct Contact Membrane Distillation (DCMD) to treat a high salinity water.

1.7 Scope of study

In this study, the PVDF membrane is cast under two different TIPS conditions. The first condition is to cast the membrane under different casting platform temperature (25 °C and 70 °C). In the second TIPS condition, the phase inversion is studied by casting the membrane under different dope solution temperature (25°C, 60 °C and 90 °C) before immersed in the coagulation bath. The characteristics of the membrane such

membrane morphology under SEM, water CA of the membrane, water sliding angle of the membrane, porosity, pore size distribution and thickness of the membrane are analysed and the viscosity of dope solution at different temperature are measured. The performances of the fabricated membranes are tested via DCMD in desalination of high salinity water.

CHAPTER 2 LITERATURE REVIEW

In Chapter 1, the major challenge in MD which is membrane wetting and hence a hydrophobic membrane is required in MD have been discussed. In this Chapter, the review and research papers that are related to this final year project are included. Further details on water crisis and desalination, MD, challenges of MD (membrane wetting), techniques to control membrane wetting, choice of polymer material to manipulate the membrane hydrophobicity as well as the effect of parameters in TIPS on membrane morphology and membrane performance have been emphasised.

2.1 Water crisis and desalination

Undeniably, water is the paramount for life, and it covers about $\frac{3}{4}$ of the earth's surface. Even though almost 75% of earth surface is covered with water, 97.5% of earth's water exists as salt water and only 2.5% remain as fresh water. Hence, freshwater scarcity is still a menace in many countries worldwide including the developing countries as well as Middle East region countries. According to World Health Organisation, the salinity of a safe drinking water is limited at 500ppm. Most of the seawater on earth may be range in 35000 to 45000 ppm due to the presence of dissolved salts. Owing to the unbalanced distribution of rain water and drought results from the climate change and the degradation of water quality results from industrial revolution, the existing freshwater resources has decreased at an alarming rate (Thimmaraju *et al.*, 2018).

Desalination can be defined as process which remove the mineral components and contaminants or dissolved salt from seawater, brackish water and wastewater effluent (Asadollahi *et al.*, 2017). It has emerged as a promising technology to provide water security for future generations and offers solutions to freshwater scarcity.

According to statistical analysis by Eke *et al.* (2020), the global desalination capacity has increased steadily at a rate of around 7% per year from 2010 to the end of 2019. Figure 2.1 shows the rising trend of cumulative (installed) desalination capacity in Africa and Europe. Based on Figure 2.1, even in the least expected regions, the desalination capacity of Europe and Africa increases sharply over 1600% (from 604 274 m³/d in 1990 to 10.6 million m³/d in 2019) and over 1700% (from 425 455 m³/d in 1990 to 7.6 million m³/d) respectively. This drastically increasing in desalination capacity is related to the growing need of fresh water caused by the climate change as well as the population growth. Figure 2.2 (a) shows the desalination capacities across world's continents in terms of contributions to the global installed capacity of 97.2 million m³/d. According to Figure 2.2 (a), Middle East countries account for 39% of the global desalination capacity, followed by Asian region countries and Americas countries with 21% and 18% respectively (Eke *et al.*, 2020). Middle East has the largest operational desalination plants due to the limited natural freshwater resources (Eke *et al.*, 2020). Primary desalination technology utilised in Middle East region countries mainly thermal desalination due to the easily accessible fossil fuel resources and poor water quality of local feed water which contributes to membrane fouling (Asadollahi *et al.*, 2017). Figure 2.2 (b) shows the desalination capacities in terms of cumulative installed capacity and year-on-year increase. Based on Figure 2.2 (b), the cumulative capacity of the operational desalination plants worldwide has increased from 27 252 m³/d in 1969 to 97.2 million m³/d in 2020.

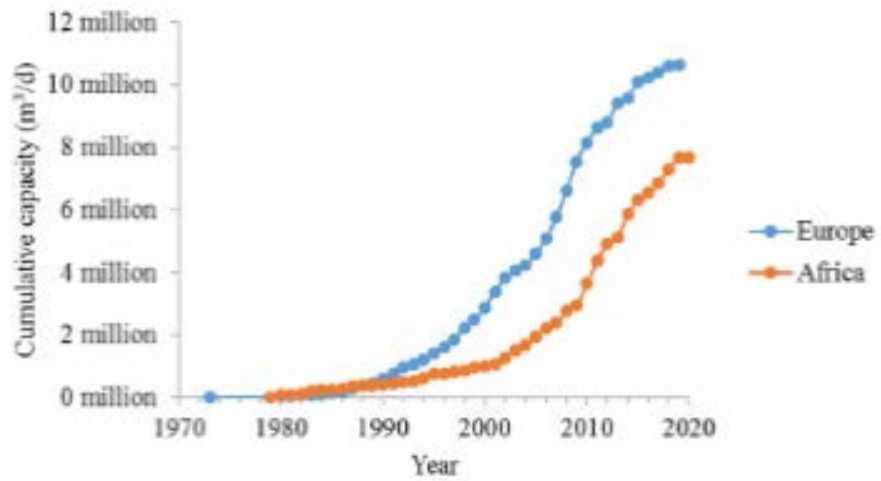
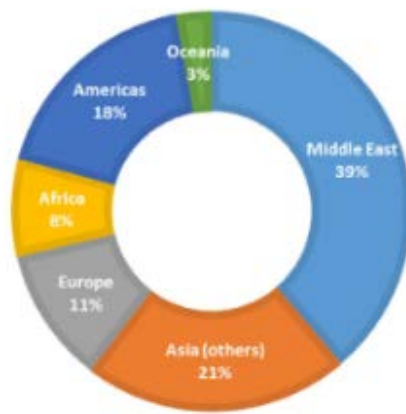


Figure 2.1 Rising trend of cumulative (installed) desalination capacity in Africa and Europe (Eke *et al.*, 2020)



(a)

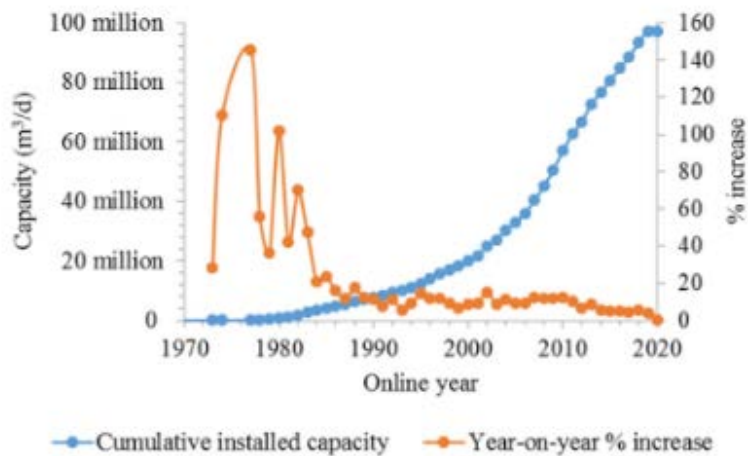


Figure 2.2 Desalination capacities (a) across world's continents in terms of contributions to the global installed capacity of 97.2 million m³/d (b) in terms of cumulative installed capacity and year-on-year increase (Eke *et al.*, 2020)

Desalination processes are categorised into thermally driven process (e.g.: multi-stage flash (MSF) and multi-effect distillation (MED)) as well membrane process (e.g.: RO, nanofiltration (NF), and MD) (Greenlee *et al.*, 2009). Thermal desalination utilises thermal energy to evaporate the saline water and collect the condensed water vapour to obtain high purity water. Usually, this technology is high in cost as it consumes high energy in the process. Membrane desalination generally use a relatively permeable membrane to separate water and salt under different driving forces, depends on its configuration (e.g.: pressure, concentration and vapour pressure gradient) to produce pure water. Thermal desalination is a phase change process while membrane desalination can be a non-phase change or hybrid process (Gude and Fthenakis, 2020). In membrane desalination, the most common membrane module utilised is spiral wound membrane followed by hollow fibre types and its dual configurations. Spiral wound membrane is widely used in desalination due to its flexibility in feed water sources including seawater, brine, river water and wastewater. Besides, it has large active area density, more physical resilience to pressure and longer life span (Eke *et al.*, 2020).

Table 2.1 shows the energy requirement of desalination process for thermally driven process and membrane process in desalination. In the early stage, thermally driven technologies have been widely applied in desalination industry and these thermal desalination technologies have a high separation efficiency because of the involvement of phase change during the separation process. However, referring to Table 2.1, these technologies which involve high complexity in operating require high energy intensity especially in terms of both thermal and electrical energy to vaporise the seawater into distillate. In order to solve the issue of high energy consumption in the thermally driven

desalination, several emerging membrane technologies such as Reverse Osmosis (RO) and Nanofiltration (NF) have been evaluated. These pressure-driven membrane technologies have a relatively simple operating mechanism as compared to the thermally driven desalination technologies. However, these membrane technologies still can't mitigate the issue of high energy intensity in desalination because they also require high amount of energy in terms of electrical energy to overcome the osmotic pressure of seawater during the separation process (Eke *et al.*, 2020).

Table 2.1 Energy requirement of desalination processes (Gude and Fthenakis, 2020)

		MED, MSF	MED-TVC, MED-MVC	RO
Electrical energy consumption (kWh/m³)		1.5-3	8-15	1.5-4
Thermal energy consumption (kWh/m³)		45-320	45-128	None

Therefore, researchers are gradually focusing on the use of other membrane technologies such as MD and forward osmosis (FO), which have high separation efficiency as well as lower energy consumption (lower operating pressure) in desalination over the high pressures driven membrane technologies. Nowadays, MD is proven as a promising solution to solve the energy consumption issue in desalination due to the reasons such as its lower operating temperature and operating pressure at ambient condition, the use of renewable energy which is solar thermal energy as heating source in MD and smaller modular design and space required than conventional thermal desalination (Susanto, 2011).

2.2 Membrane Distillation (MD)

MD is a combination of both thermal and membrane. In MD, a temperature difference is created between the feed and permeate which are in contact with either side of a microporous membrane. This temperature difference will create a vapour pressure difference which is the driving force for the transportation of the evaporated volatile components in hot feed side through the membrane pores to the condensation cold permeate side. In MD, the membrane used must pose high hydrophobicity or anti-wetting properties, which is only permeable to water vapour instead of liquid water (Thimmaraju *et al.*, 2018). MD has mainly four types of configurations, includes direct contact MD (DCMD), air gap MD (AGMD), sweep gas MD (SGMD) and vacuum MD (VMD). The difference between techniques is that the condensate permeate is collected in different configurations (Ahmed *et al.*, 2020).

2.2.1 Direct contact MD (DCMD)

DCMD has the simplest and basic configuration. In DCMD, separation occurs due to the vapour pressure gradient which induced mainly by the temperature difference of liquids between the feed and permeate side. There are three main steps in mass transfer of DCMD. (1) diffusive transport of water vapor from the feed stream to the membrane interface (2) both diffusive and convective transport of vapours through the pores of membrane (3) vapours condense on the membrane interface at the cold permeate side of the membrane (Cath *et al.*, 2004). Although the configuration of DCMD is considered as simplest, the heat loss due to conduction in DCMD is large as compared to other MD configurations. Therefore, DCMD has lower heat efficiency as the heat used for water evaporation at the membrane interface is highly lost in the form of conduction heat. (Ahmed *et al.*, 2020). DCMD was proposed in the treatment of water produced from the source of Steam Assisted Gravity Drainage (SAGD). Singh *et*

al. (2013) has developed a SAGD process which operates in the range of temperature from 80-130 °C, which is observed to have elevated desalination performance of a saline feed with 10,000 ppm TDS. In the system, the membrane used was a porous flat sheet PTFE in a range of pressure from 2 to 3 atm. The feed solution composition includes NaCl, phenol, cresol and naphthenic acid, at 3000, 45, 45, 10ppm respectively. The water vapor flux that is observed was 195 kg/m²h, which is significantly larger than the flux from seawater RO process (Singh *et al.*, 2013). Figure 2.3 shows the schematic of DCMD.

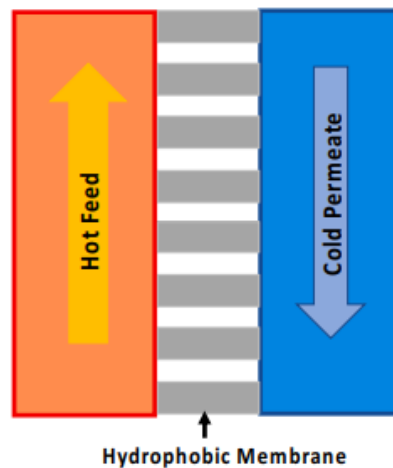


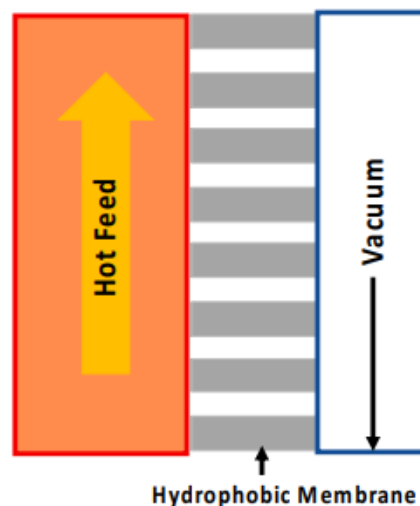
Figure 2.3 Schematic of DCMD (Ahmed *et al.*, 2020)

2.2.2 Vacuum MD (VMD)

In VMD configuration, the feed solution is also brought into contact with one side of a microporous membrane which is similar to DCMD. However, vacuum is applied at the permeate side which create a driving force for the water vapour transportation. By applying vacuum on the permeate side, the pressure will be lower at the permeate side and hence the volatile molecules from the feed side with higher saturation pressure will be separated (Ahmed *et al.*, 2020). Then condensation of water

vapour will occur outside the membrane module (An S. *et al.*, 2017). Therefore, VMD will require an external condenser generally.

VMD has wide applications in various field such as in wastewater treatment, desalination of brackish sea water, concentration of sucrose solution during beverage production and etc. Compared to DCMD, VMD can achieve a higher water vapour flux if reasonable high vacuum is maintained at the permeated side. Also, the heat loss via heat conduction is less significant in VMD. Temperature polarization effect in VMD is less significant due to the quick removal of water vapour permeate (Deng *et al.*, 2020). For example, in a work carried by EL-Bourawi *et al.* (2007), VMD had been studied for ammonia removal from its aqueous solution and the effects of different operating parameters on the ammonia removal from aqueous solutions of different concentrations has been investigated. Based on their results, VMD operation under the conditions of high feed temperature, low downstream pressures and high initial feed concentrations and pH levels will give enhanced ammonia removal efficiency. They also found out that the temperature and concentration polarisations within feed boundary layer can be minimised by increasing the feed flow velocity. This study has achieved ammonia removal efficiencies greater than 90% as well as separation factors larger than eight (EL-Bourawi *et al.*, 2007). Figure 2.4 shows the schematic of VMD.



2.2.3 Sweep gas MD (SGMD)

SGMD is a MD configuration that using a stripping gas (inert gas) as a carrier to sweep the vapour transferred from the hot feed solution through a microporous membrane. The volatile molecules at the hot feed side will evaporate and move through the membrane pores, where they will be swept and carried away by the stripping gas to outside of the membrane module. Then condensation of the vapour occurs in external condensers (Tomaszewska, 2015). This configuration has a higher cost as a leak-proof gas system is required (Ahmed *et al.*, 2020). The SGMD configuration has a less significant conductive heat loss through the membrane. SGMD is more suitable in applications that involve the removing volatiles from an aqueous solution. For instance, desalination of aqueous solution with practically 100% of salt rejection factors, separation of isopropanol/water mixtures and wastewater treatment by removal of organics (ethanol, acetone) (Deng *et al.*, 2020). SGMD also can be applied in glycerol recovery from wastewaters. In the work by Shirazi *et al.* (2014), a SGDM process system was used to recover the glycerol from wastewater by using a flat-sheet PTFE membrane. They had studied on the effects of various operating parameters such as the feed temperature, concentration of glycerol in the aqueous phase, flow rate of feed as well as flow rate of sweeping gas on the permeate flux by performing a Taguchi analysis. Based on their experimental results, the feed temperature is found as the dominant factor on permeate flux followed by the sweeping gas flow rate. This study also has achieved a solute rejection of more than 99% (Shirazi *et al.*, 2014). Figure 2.5 shows the schematic of SGMD.

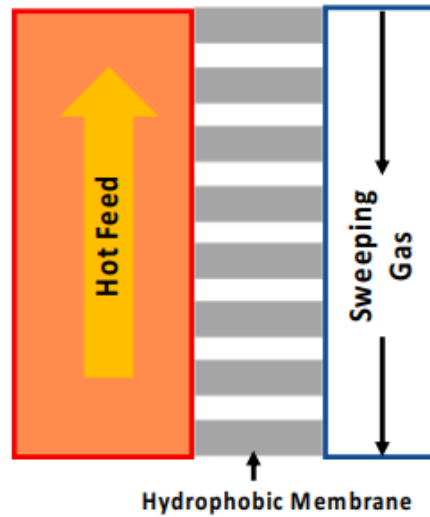


Figure 2.5 Schematic of SGMD (Ahmed *et al.*, 2020)

2.2.4 Air gap MD (AGMD)

AGMD is a MD configuration which water vapour from the hot feed side is transferred to the cold condenser surface via an air gap. The air gap which is created between the membrane and the condensing surface functions as an insulator to mitigate the conductive heat loss in DCMD. However, the permeate flux in AGMD is lower than DCMD due to the additional mass transfer resistance caused by the separating air gap (Attia *et al.*, 2018). A proper design that narrowing the air gap is able to reduce the mass transfer resistance to a certain extent. The permeate in AGMD is not in direct contact with the membrane, hence membrane wetting will not occur at the permeate side in AGMD. In general AGMD is suitable in MD applications especially those with low energy availability (Ahmed *et al.*, 2020). AGMD can be applied in desalination and treatment of wastewater such as removal of dyes from textile wastewater and treatment of oil-produced water (Attia *et al.*, 2017). Alkhudhiri and Hilal (2017) have conducted a study on the application of AGMD in treating high saline solutions by using different PTFE membranes. In this work, the effect of salt concentration on permeate flux, the rejection factor and the energy consumption of different membrane pore sized was

investigated. They had found out that the energy consumption of the AGMD increases when the concentration of the salt increases due to the higher boiling point of the salt solution under higher concentration. Besides, the energy consumption also increases when membrane pore size decreases because of the negative effect of pore size on flux, which decreases (Alkhudhiri and Hilal, 2017).

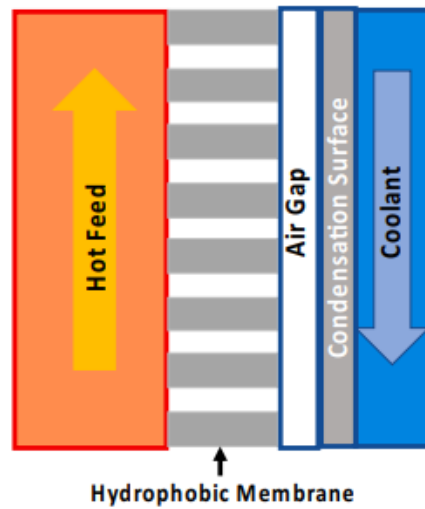


Figure 2.6 Schematic of air gap MD (AGMD) (Ahmed *et al.*, 2020)

2.3 Challenge of MD: Membrane wetting

Wetting is one of the major challenges in MD. Wetting of membrane will increase the mass transfer resistance to the water vapours and causes MD to slow down. These pores wetting phenomena will reduce the permeate flux or even deteriorate the permeate quality. Hence, superhydrophobic membrane plays an important role in MD as it exhibits high anti-wetting properties which only permeable to water vapours through the membrane but impermeable to bulk water (Mohammad Reza Shirzad Kebria, 2020). Membrane wetting can be categorised into four wetting degrees which are non-wetted, surface-wetted, partially wetted and completely wetted.

The pressure of liquid on the feed side of the membrane is the main cause of membrane wetting. For a given pore size, a critical penetration pressure exists. The

liquid phase will only penetrate across the membrane if the applied pressure is larger than the critical penetration pressure. This pressure is known as the liquid entry pressure of water (LEP_w) and used to interpret membrane wetting. By breaking the surface tension at the interface between the liquid and vapour on the membrane surface, water can enter the larger pores of the membrane and cause membrane wetting (BURGOYNE and VAHDATI, 2000).

Membrane wetting not only occurs when the hydraulic transmembrane pressure is larger than the LEP, it may also occur when the feed solutions containing organic, inorganic and amphiphilic components. When the feed solution consists of low surface energy surfactants, the hydrophobic moiety will adsorb onto the hydrophobic membrane surface while the hydrophilic part of the surfactant stays in the water phase. As a result, the hydrophobic membrane surface will convert into hydrophilic and results in a decrease in CA. This will decrease the LEP value and leads to membrane wetting easily because the LEP is linearly proportional to the surface tension (Rezaei *et al.*, 2018; Li *et al.*, 2020).

The occurring of membrane wetting also causes by the membrane degradation during long-term operation. Chemical oxidative degradation of membrane will form hydrophilic groups (e.g.: hydroxyl (OH), carbonyl (C=O) and unsaturated (C=C) groups) which reduce the CA from 90° to 61.4° (Gryta *et al.*, 2009).

2.3.1 Techniques to control membrane wetting: Physical Modification

There are different approaches to control wetting in MD and most of the researches emphasise on advancement in membrane fabrication. Most of the studies has investigated on modifying of membrane surface geometrical structure and surface chemistry.

In order to improve the super hydrophobicity or pore wetting resistance of the membranes, the polymeric MD membranes can be modified chemically and physically. Chemical membrane modification is mainly aimed to decrease the surface free energy of the membrane itself, and physical modifications are purposed to increase the surface roughness of the membrane (Rezaei *et al.*, 2018).

For example, the chemical grafting of the SiO₂ nanoparticles on polypropylene (PP) membrane surface has increased the surface roughness and hydrophobicity of the membrane. By comparing to an uncoated membrane, the nano-coated membrane exhibited higher surface roughness which has higher anti-wetting tendency (Ashoor *et al.*, 2016). Moreover, the modification of polyvinylidene fluoride (PVDF) nanofiber membrane with silver nanoparticles or dopamine also improve the anti-wetting property of the membrane as compared to the unmodified membrane (Liao *et al.*, 2013). According to the study from Liao *et al.* (2013), water droplets on this nanostructured membrane surface are easy to slide off along the membrane surface (Liao *et al.*, 2013). The membrane has achieved high and stable MD flux of 31.6 L/m²h by using a 3.5 wt% NaCl as feed solution. This chemical modified I-PVDF membrane has shown some elevation in terms of its anti-wetting properties. As the chemical modification will not affect the pore size distribution, the main determinant factor for anti-wetting in this case is the surface property of the modified membrane. The chemical modification process mentioned has lower the adhesive force between the water molecule and the membrane, which enhances the anti-wetting properties of the membrane.

There is also another approach to increase the overall surface roughness of the membrane, which is the layer-by-layer assembly. A combination of hydrophobic/hydrophilic layer can be done with the co-extrusion method, for example, the production of the PVDF/UltemTM hollow fiber membrane (Zuo *et al.*, 2017).