Development of highly porous flat sheet polyvinylidene fluoride (PVDF) membranes for membrane distillation

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ABSTRACT
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With the increase of population every year, fresh water scarcity has rapidly increased and it is reaching a risky level, particularly in Africa and the Middle East. Desalination of seawater is an essential process for fresh water generation. One of the methods for desalination is membrane distillation (MD). MD process separates an aqueous liquid feed across a porous hydrophobic membrane to produce pure water via evaporation. Polyvinilidene fluoride (PVDF) membranes reinforced with a polyester fabric were fabricated as potential candidates for MD. Non-solvent induced phase separation coupled with steam treatment was used to prepare the PVDF membranes. A portion of the prepared membrane was coated with Teflon (AF2400) to increase its hydrophobicity. In the first study, the fabricated membranes were characterized using scanning electron microscopy and other techniques, and they were evaluated using direct contact MD (DCMD). The fabricated membranes showed a porous sponge-like structure with some macrovoids. The macrovoid formation and the spongy structure in the membrane cross-sections contributed significantly to a high permeate flux as they provide a large space for vapor water transport. The modified PVDF membranes with steaming and coating exhibited a permeate flux of around 40 L/h m² (i.e. 27-30% increase to the control PVDF membrane) at temperatures of 60 °C (feed) and 20 °C (permeate). This increase in the permeate flux for the modified membranes was mainly attributed to its larger pore size on the bottom surface. In the second study, the control PVDF membrane was tested in two different module designs (i.e. semi-circular pipe and rectangular duct module designs). The semi-circular module design (turbulent regime) exhibited a higher permeate flux, 3-fold higher than that of the rectangular duct module design (laminar
regime) at feed temperature of 60 °C. Furthermore, a heat energy balance was performed for each module design to determine the temperature polarization coefficients (TPC). The turbulent module design showed higher TPC (0.5-0.58) than the laminar module (0.1-0.14) (i.e. a poor module design). This indicates that the effect of temperature polarization on the laminar flow was significant, which is below the reported TPC range of 0.4-0.70.
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CHAPTER 1: INTRODUCTION AND OBJECTIVE

1.1 Introduction

The large need for fresh water and high energy cost of conventional desalination technologies have driven scientists to develop membrane technologies such as membrane distillation (MD). One way to meet the demand of freshwater, and save energy is through the desalination of seawater or brackish water using membrane technologies. Membrane popularity has gradually increased for separation applications such as seawater desalination. Examples of membrane technologies used for desalination of seawater include reverse osmosis (RO), and membrane distillation (MD) [1].

RO is almost entirely developed but it is still considered an energy intensive process due to the need to overcoming the osmotic pressure (~28 bar for seawater). Also, aggressive fouling caused by hydrocarbons and Red Tide algae slows its rapid use in Gulf of Arabian countries. Furthermore, RO comprises of many units increasing its capital cost, it emits greenhouse emissions associated with its energy use (fossil fuel), and it generates brine disposal at waste streams [2].

In contrast, MD is under development and not commercialized yet due to the lower flux and wettability issue. It differs from pressure driven processes since it requires a thermal gradient to allow water vapor to travel across a hydrophobic membrane using a lower temperature than conventional thermal distillation and lower pressure (about 1 bar). Key advantages of the MD process is that the permeate water quality is insensitive to feed-water salinity, it has less fouling than pressure-driven membranes, and it does not require a large footprint. The membrane should be porous and hydrophobic, allowing only vapor to pass while preventing the liquid from passing through the membrane [1, 2].

In this research, flat sheet polyvinylidene fluoride (PVDF) membranes supported with a polyester fabric material prepared by steaming-immersion precipitation method were
characterized using various techniques and evaluated by direct contact membrane distillation (DCMD) experiments with a feed of 1 M NaCl solution at different temperatures. Moreover, heat transfer analysis was performed for two different module designs with two different DCMD setups to investigate the effect of temperature polarization.

This thesis starts with a comprehensive literature review about polymeric membranes and membrane distillation. The third chapter contains the main experimental part of this research in which steam vapors was applied to the casting solution before immersion in the coagulation bath during. Steam exposure to the casting solution was varied in which top and bottom surfaces were considered. Furthermore, a Teflon (AF 2400) solution was used to coat one of the membranes to improve its hydrophobicity. This research ends with a comparison of two different DCMD setups using heat transfer analysis by estimating the interfacial temperatures in the feed and permeate sides. It is worth stating that each DCMD setups contains different module design, where the prepared membranes can be placed.
1.2 REFERENCES


CHAPTER 2: LITERATURE REVIEW

2.1 General overview of membrane technology

The word membrane comes from the Latin language, which means skin. It is defined as a thin film or sheet or layer that acts as a barrier between two bulk phases. The membrane itself can be a homogenous or heterogeneous solid, a liquid or gel and its structure can be symmetric or asymmetric [1]. Moreover, membranes can be found in nature “biological membranes” or synthesized “synthetic membranes.” The main feature that distinguishes a biological membrane from a synthetic membrane is that the biological membrane is very selective, precise, and efficient as it can recognize, regulate the passage of various molecules that have different physical and chemical properties as well as block or eliminate the passage of harmful components effectively. Also, other features include self-regulating, self-healing, and self-cleaning [2].

![Figure 2.1: A typical membrane separation process flow diagram](image)

Synthetic membranes are thin layers usually made of organic or inorganic materials or both. These membranes are divided into porous and non-porous membranes. The transport through the non-porous membranes can be described by the solution-diffusion mechanism whereas porous membranes depend on pore flow mechanism [3].

Membrane processes can be classified according to the driving force that causes the flow of the permeant in the membrane process such as pressure, concentration, temperature, and electrical potential difference (Table 2.1) [4]. Membranes can also be classified according to their
pore size, and in general there are three pore size classifications including microporous (dp < 2 nm), mesoporous (2 nm < dp < 50 nm) and macroporous (dp>50 nm) [3].

Table 2.1: Classification of different membrane processes according to their driving force [4]

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Driving force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse osmosis</td>
<td>Pressure difference</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td></td>
</tr>
<tr>
<td>Microfiltration</td>
<td></td>
</tr>
<tr>
<td>Membrane distillation</td>
<td>Temperature difference (partial pressure difference)</td>
</tr>
<tr>
<td>Dialysis</td>
<td>Concentration difference</td>
</tr>
<tr>
<td>Membrane extraction</td>
<td></td>
</tr>
<tr>
<td>Electro-dialysis</td>
<td>Electric potential difference</td>
</tr>
</tbody>
</table>

A schematic representation of a typical membrane process is shown in Figure 2.1 where the feed stream is separated into a retentate and permeate stream. Depending on the process used, the product can be either the retentate or permeate stream or both. For example, in reverse osmosis, pervaporation, fractionation processes, the desired stream is either permeate, retentate, or both streams, respectively [5].

2.2 Membrane distillation background

The term membrane distillation (MD) was extracted from the conventional distillation process since both processes rely on the vapor-liquid equilibrium as a method of phase separation. In 1963, Bodell invented the MD where he first described a desalting process for seawater. In the patent (published in 1968), Bodell provided apparatus and methods to convert seawater to fresh water, consisting of a tank through which a brine solution was allowed to flow around a parallel array tubular silicon rubber membrane. Bodell did not describe the structure of the membranes or their pore geometry, stating only that they were vapor permeable and liquid impermeable [6].

Membrane distillation is a thermally driven process with driving force of vapor pressure difference caused by the temperature gradient. There are a number of features of the MD process,
which include low operating temperatures that the liquid feed is not necessarily heated up to the boiling point and also, the pressure used is lower compared to conventional processes [7].

Several configurations can be used to carry out the MD process, but the general procedure is that the feed solution is heated up to a desired temperature, usually 60°C, after that it will be brought into contact with one side of the hydrophobic membrane surface. Thus, the water vapor molecules will pass through the membrane pores and condenses in the other cold side of the membrane. Particularly, the difference in temperature creates vapor pressure difference, which allows the water vapor to move from the hot side of the membrane to the cold side of the membrane [8, 9].

Membrane distillation process is classified into four basic configurations. MD configurations include direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), air gap membrane distillation (AGMD), and vacuum membrane distillation (VMD) [7].

AGMD has lower heat lost by conduction because of the presence of the air gap thickness. However, the main drawback of this configuration is the generation of additional mass transfer resistance caused by the width of the air gap, which leads to producing the lowest permeate flux among the MD configurations [7].

SGMD is similar to the AGMD technique, but the difference is that a cold permeate sweep gas (inert gas) is applied. The sweep gas carries the vapors to an external condenser where condensation occurs [10]. Since the sweep gas carries the vapors outside the membrane system, there is no additional mass resistance, which is advantageous. However, there is an increase of temperature of the sweep gas along the membrane configuration because of the heat transfer from the feed to the permeate side [11].
VMD process gives the highest flux in comparison to the other configurations because the downstream pressure is reduced. Moreover, the heat loss in this module is insignificant which is advantageous. However, the main problem with this configuration is the high probability of wetting the pores of the membrane because the permeate side pressure can be negative [8, 12].

The simplest configuration among the four techniques is the DCMD, which is usually used in research laboratory for desalination processes. DCMD modules contain a hot feed side, and cold permeate side, and between them is a porous hydrophobic membrane as shown in Figure 2.2. The hot feed solution is brought in direct contact with membrane surface. The hot solution evaporates at the feed side, and vapor molecules are thermally driven to diffuse to the permeate side.

![Figure 2.2: Schematic representation of DCMD configuration](image)

Temperature gradient causes a vapor pressure difference between the two sides, which enhances the overall driving force. After that, the vapor molecules get condensed in the permeate side. Since the membrane used is hydrophobic, liquid feed (usually seawater) cannot pass through the membrane, only vapors penetrate through the pores of the membrane. The main disadvantage of this design is the heat loss by conduction [11, 10].
2.2.1 Material Considerations for Membrane Distillation

Polymeric materials are most frequently used to make different types of membranes for membrane distillation. Poly (vinylidene fluoride) (PVDF) is considered one of the most common polymeric materials used to fabricate MD membranes because they are naturally hydrophobic and thermally and chemically stable with good mechanical strength [13, 14, 15]. PVDF has a semicrystalline structure that typically consists of 59.4 wt% fluorine and 3 wt% hydrogen with repeating unit of –CH$_2$-CF$_2$- as shown in Figure 2.3. Up to this moment, most of the commercial PVDF membranes are manufactured using phase inversion method because of its simplicity and high production scale [13, 15].

![Polyvinylidene fluoride (PVDF) structure.](image)

PVDF is a flexible material that can be used to make flat sheet, hollow fiber or tubular membranes. PVDF is less hydrophobic compared to polytetrafluoroethylene (PTFE), but it is still the best selection for membrane distillation since it can be easily dissolved in common organic solvents such as N, N-dimethyl acetamide (DMAc), and dimethyl formamide (DMF). In contrast, PTFE and PP do not dissolve easily in common organic solvents limiting its use in phase inversion approach. Thus, the phase inversion method by immersion precipitation can be used to create a hydrophobic porous PVDF membrane. Phase inversion is demixing process whereby the initial homogeneous polymer solution is converted from a liquid state to solid state in a controlled manner [13].
PVDF membranes have been widely utilized in ultrafiltration, and microfiltration processes, and are currently being investigated as a potential candidate for membrane distillation process [13]. Consequently, in the literature, several researchers have been trying to develop a highly porous PVDF membrane suitable for membrane distillation (MD) process to desalinize seawater. The main requirement of this MD membrane is a high porosity and hydrophobicity. Porous membrane helps to increase the permeate flux, whereas, high hydrophobicity prevents the occurrence of pore wetting.

2.3 Polymeric Membrane Formation
2.3.1 Membrane Formation Techniques
Various formation techniques are used to make polymeric membranes such as sintering, stretching, track etching, phase inversion, interfacial polymerization, and electrospinning. The selection of these fabrication methods depends on the membrane materials, desired structure of the membrane and final application [16, 17, 18]. The most commonly utilized polymeric membrane fabrication method is phase inversion. Phase inversion is a process at which a polymer is converted from a liquid to solid in a controlled manner. The phase separation can be induced by different processes:

- **Thermally induced phase separation (TIPS):** In this method, cooling or lowering the temperature of a polymer solution induces the phase separation. The dope solution is cast hot while cooling causes the formation of the membrane. After the demixing process, the solvent is eliminated by extraction, evaporation or freeze drying. TIPS is mainly employed for polymers that are not soluble at room temperature such as polyolefins [16, 17, 18, 19].

- **Evaporation induced phase separation (EIPS):** In EIPS, phase separation is made by the evaporation of a volatile solvent from the casting solution. A polymer solution is prepared in a single volatile solvent or mixture of solvents, and a non-solvent. Once the polymer solution
is prepared, it can be cast on a glass plate using a doctor blade; the cast polymer solution is exposed to air at room temperature, leading to the evaporation of the volatile solvent and thus precipitation occurs. [17, 18].

- **Vapor induced phase separation (VIPS):** In VIPS method, a dope solution consisting of a polymer and solvent can be cast on a glass plate and placed in a vapor atmosphere where the non-solvent vapor penetrates the polymer solution. The absorption of non-solvent into the cast solution leads to precipitation [5].

- **Immersion precipitation (IP):** Immersion precipitation is the most commonly used method by membrane manufacturers due to its high production and simplicity. In the IP process, precipitation takes place inside a coagulation bath containing a non-solvent (usually water). In particular, to prepare a porous membrane using IP, the polymer must first dissolve in a suitable solvent, and once the dope solution is ready, it can be cast on a glass plate using a doctor blade with/without support followed by immersion in a coagulation bath (non-solvent). An exchange between the solvent in the casting solution and the non-solvent from the coagulation bath results in the formation of the membrane [17].

![Figure 2.4: Schematic process of the immersion precipitation process](image)

In particular, mass transport takes place between the solvent and non-solvent in which the non-solvent concentration in the polymer film increases. Specifically, the first step is a thin porous
skin layer is formed at the top of the cast membrane due to the diffusion of solvent out from the casting solution whereas, in the second step, the non-solvent diffuses into the cast film (Figure 2.4). The top porous skin layer governs the performance of membrane while the porous sub-layer provides the mechanical strength to the membrane. It was found that a porous top skin layer is favored at a low polymer concentration with short solvent evaporation time [12].

In this study, immersion precipitation technique is carried out to prepare PVDF membranes with slight modification using steaming process to increase its performance for membrane distillation application. In the following sections, membrane preparation and different parameters affecting the structure and performance of flat sheet polymeric membranes will be described.

2.3.2 Polymeric Membranes Fabrication & Immersion Precipitation (IP)

Polymeric membranes were mainly fabricated by the phase inversion process, particularly using IP due to the low cost of production and ease of dissolution in common organic solvents [13]. Flat sheet membranes can be manufactured into a plate and frame and spiral wound modules, while tubular membranes are employed for hollow fiber, capillary, and tubular shapes [5]. A typical flat sheet membrane fabrication process is depicted in Figure 2.5. The first step for preparing a membrane is to dissolve the polymer in an appropriate solvent at a specified temperature and stirring modes which depends on the type of the polymer. Modifying agents such as lithium chloride (LiCl) can also be added to make the membrane more open. Once the dope solution is ready, it can be degassed to remove air bubbles to avoid pinholes later when casting the membrane [5].
As it is shown in Figure 2.5, flat sheet membranes in a large-scale production can be obtained by pouring the polymer solution on the supporting material after adjusting a suitable casting thickness. The poured polymer solution is cast using a doctor blade (with/without evaporation) followed by immersion in the non-solvent bath. During the immersion process, the phase separation occurs between the solvent and non-solvent leading to the formation of the membrane. After precipitation, the membranes are washed to remove the remaining solvent then rolled and collected for drying process [5, 19]. The viscosity of the polymer solution is a critical parameter, which depends on the molecular weight of the polymer, its concentration, solvent and additives used. The casting thickness can vary between 50 and 500 µm. Liquid water is frequently used as non-solvent since it is environmentally friendly as well as it is a strong non-solvent liquid [5, 19].

There are a number of important preparation parameters including polymer concentration, evaporation time, coagulation bath temperature, humidity, temperature, and composition of the dope solution (e.g. additives) that determine the ultimate membrane performance and final structure of the prepared membrane. It should be noted that all phase separation processes are
based on the thermodynamic principles since the starting point in all cases is a thermodynamically stable solution, which is subjected to demixing. Moreover, the selected solvent and non-solvent must be miscible with each other [5].

There are three basic structures of asymmetric polymeric membranes which include (i) integral asymmetric with a porous skin layer, (ii) integral-asymmetric with a dense skin layer, and (iii) thin-film composite membranes. Porous integral-asymmetric membranes are most often prepared by the phase inversion approach and applied in various applications such as dialysis, ultrafiltration, microfiltration, and membrane distillation while integral asymmetric membranes with a dense skin layer are applied in reverse osmosis and gas separation applications. Thin-film composite membranes comprise a thin, selective polymer layer located at the top of a porous support [20].

Furthermore, it should be noted that there are two demixing speeds for the IP process which include instantaneous demixing and delayed demixing. These two demixing processes generate different morphologies. In general, instantaneous demixing produces membranes with porous top layer while the delayed demixing produces a dense top layer. This is attributed to the precipitation rate of the polymer by the non-solvent induced phase separation. Precipitation rate is defined as the time between immersing the casting solution in a coagulation bath and formation of the membrane. Usually, slow precipitation rates result in a sponge-like structure where high precipitation rates produce finger-like structures with macrovoids. These membranes normally have a high salt rejections and low water fluxes. Membranes with finger-like structure tend to have higher flux and lower solute rejection than spongy-like structure membrane [21].

Asymmetric membranes have a thin layer on top of a porous sublayer. This porous sublayer supporting the top layer usually contains macrovoids, and depending on the kinetic and
thermodynamics of phase inversion; two different morphologies can be obtained either finger like or sponge-like structures. Having macrovoids in the substructure can be advantageous for low-pressure driven processes as more space is available for mass transfer. However, macrovoids containing membranes are not suitable for high-pressure processes such as reverse osmosis as it might result in compaction and collapse of the membrane. [22].

2.4 Effect of Various Parameters on polymeric membrane properties and performance by Immersion Precipitation

Several parameters that influence the morphology and performance of polymeric membranes during membrane formation by immersion precipitation. Selection of the solvents, polymer, additives and coagulation bath for polymeric membranes is critical for obtaining great membranes for such applications. Although there are many different polymeric membranes, PVDF membranes will be mainly considered in the following sections.

2.4.1 Effect of solvents

Various solvents can be used to prepare PVDF casting solutions, and the choice of suitable solvents is of great importance. Selection of solvents for PVDF membranes depends mainly on the formation method used. For example, N, N-dimethyl acetamide (DMAc), N, N-dimethyl formamide (DMF) are applicable solvents for PVDF when using immersion precipitation while for thermal induced phase separation (TIPS), dimethyl phthalate (DMP), and diethyl phthalate (DEP) are applicable [23].

Miscibility of solvent with the non-solvent for immersion precipitation is a key factor for the morphology of the cast membrane. If the miscibility between the solvent and non-solvent is low, a non-porous membrane is obtained whereas, more porous membranes are produced when the miscibility is high. Fast precipitation (instantaneous demixing) requires high miscibility between the solvent and non-solvent to have anisotropic membrane with high porosity [17].
Inappropriate selection of solvent for PVDF results in aggregation of polymer molecules, while appropriate solvents produce a homogenous solution. Table 2.2 shows good solvents and their boiling point for PVDF that are mostly used in the immersion precipitation process. It can also be recognized from Table 2.2, the boiling point of each solvent differ and can be classified as a high boiling point solvent and low boiling point solvent. DMAc, DMF, and NMP have been extensively used as a high boiling point in casting PVDF membrane [16].

**Table 2.2: Common solvents for PVDF [16]**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N-Dimethylacetamide (DMAc)</td>
<td>165</td>
</tr>
<tr>
<td>N,N-Dimethylformamide (DMF)</td>
<td>153</td>
</tr>
<tr>
<td>Dimethylsulfoxide (DMSO)</td>
<td>189</td>
</tr>
<tr>
<td>Hexamethyl phosphoramidine (HMPA)</td>
<td>232.5</td>
</tr>
<tr>
<td>N-Methyl-s-pyrrolidone (NMP)</td>
<td>202</td>
</tr>
<tr>
<td>Tetramethylurea (TMU)</td>
<td>176.5</td>
</tr>
<tr>
<td>Triethyl phosphate (TEP)</td>
<td>215.5</td>
</tr>
<tr>
<td>Trimethyl phosphate (TMP)</td>
<td>197.2</td>
</tr>
<tr>
<td>Acetone (Ac)</td>
<td>56.1</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>65</td>
</tr>
</tbody>
</table>

Different structures of PVDF membranes can be obtained depending on the solvent used and other casting conditions. For example, when using water as coagulant medium, and TEP as a solvent to prepare PVDF membranes, a uniform sponge symmetric structure could be produced while when using DMAc with same coagulant medium, asymmetric finger-sponge like structures could be obtained. This is attributed to the weak solvent power of TEP and low interactions with water, whereas the opposite is true for DMAc [13]. Based on literature, high power solvents result in rapid precipitation rates leading to less membrane shrinkage and longer finger-like structures, whereas, shorter finger structures are obtained when using low power solvents [16].
2.4.2 Effect of polymer concentration, viscosity, and grades

Polymer concentrations in the dope solution play a crucial factor for the prepared membrane’s morphology as well as its performance. Various variables such as porosity, permeate flux, pore size, thickness, and viscosity depend on the polymer concentration used in the casting solution [16, 12, 17]. In general, increasing the polymer concentration produces membranes with smaller pore size and porosity, and in this case, the permeate flux is decreased. Lower porosity is attributed to the increase in the volume fraction of the polymer. Further, it is evident that decreasing polymer concentration in casting solution will produce a smaller thickness since the cast membrane thickness is always smaller than the adjusted thickness gap of the doctor blade during immersion precipitation. The adjusted thickness gap considers the solvent, while the thickness that matters is after the removal of the solvent. For instance, casting PVDF/DMAc membranes with concentrations of 25 wt%, and 10 wt% and casting gap of 400 µm, forms PVDF membrane with thickness ranges between 85 and 54 µm, respectively [12, 21].

PVDF membranes have various grades with different molecular weights, meaning that the viscosity of each grade differs from each other. In spite of the grade used, increasing the polymer concentration results in an increase in the viscosity of the casting solution, which affects the final structure and performance of the cast membranes. Moreover, it is worth stating that there is a concentration limit for each PVDF grade where it becomes challenging to prepare a homogenous PVDF casting solution. Consequently, the viscosity of the casting solution is as important as the concentration when it comes to controlling the morphology of PVDF membranes. Moreover, using too low polymer concentration, (which in turn, low viscous casting solution) causes penetration of casting solution inside the supporting materials, leading to a damaged membrane structure [16].
2.4.3 Effect of additives on casting solution

Membrane properties and morphology can be improved by the addition of small amounts of additives, sometimes called modifying agents. As it is well known, a normal casting solution consists of polymer, solvent, and non-solvent, but sometimes modifying agents can be added such as inorganic salts (e.g. lithium chloride, LiCl), polymeric additives (e.g. polyvinyl pyrrolidone, PVP or poly(ethylene glycol), PEG). These modifiers can work as pore opening agents, viscosity increasers or phase inversion accelerators [17].

The effect of LiCl on the preparation of flat sheet PVDF membrane was studied by Tomaszewska [24], his study showed that increasing LiCl content in the casting solution results in a more porous structure with larger cavities and high porosity, but with lower mechanical strength. Another study was done by Fontananova et al [25], where the addition of small amounts of LiCl (i.e. 2.5 wt. %, LiCl) in PVDF/DMAc contributed to increasing the permeation flux, while the addition of large LiCl amounts (i.e. 7.5wt. %, LiCl) reduces the membrane permeation flux. The latter case was attributed to the suppression of macrovoid formation at high LiCl concentration [24].

The previously mentioned observations were linked to thermodynamic and kinetic changes in the casting solution or during the immersion process. It was found that adding LiCl to the casting solution could increase the thermodynamic instability of the casting solution by reacting with water, which enabled a fast demixing rate. In this case, the macrovoid formation is favored. In contrast, LiCl has strong interactions particularly at high LiCl concentrations with the polymer and solvent, which leads to an increase of the casting solution viscosity compared to a LiCl-free casting solution. Consequently, kinetic effect outweighs the thermodynamic effect, which induces delayed demixing and therefore, a decreased size of macrovoids is observed in the prepared membranes [13, 17].
For the case of polymeric additives, many researchers have investigated the influence of the addition of PVP to the casting solution. Saljoughi et al. noticed that formation of macrovoids was favored at 1.5 wt.% PVP concentration which led to an increase in permeation flux, whereas, more than 1.5 wt.% PVP concentration showed smaller macrovoids and thus lower permeation flux. Another study was reported by Ngang et al [26] to investigate the effect of PEG 2000 on PVDF membrane, their result showed that the pore size distribution of PVDF increases as the PEG 2000 concentration increases, which led to an enhancement in the water permeation flux. Moreover, their PVDF membranes exhibited a finger like structure with micorovoids in the substructure layer. Despite the advantages of this membrane, the contact angle was reduced to due to the hydrophilicity nature of PEG, which limits its use in membrane distillation, but the membrane is a good candidate for ultrafiltration [26].

Other types of additives can be used in the casting solution such as glycerol and water. For the case of glycerol, it was found that the glycerol effect on membrane morphology varies depending on the solvent used. For example, when TEP was utilized as a solvent, an increase in glycerol concentration results in an increase in the mean pore size, and effective porosity with a formation of a thin skin layer of the fabricated membranes while a decrease in the effective porosity was observed when DMSO was used as a solvent. This observation was attributed to the different affinity of the solvents inside the water coagulation bath [27, 13]. Khayet and Matsuura examined the influence of water addition to the casting solution. Their results showed that using water as additive offers a PVDF membrane with larger pore radius and high effective porosity. Also, they found that the mass transfer resistance of the membrane was reduced at high water concentrations [13].
2.4.4 Effect of evaporation time

The evaporation time process is the time between casting and immersion into the coagulation bath. An increased evaporation time might lead to a remarkable changes in the morphology of the fabricated membranes especially when a low boiling cosolvent has been applied. The influence of evaporation time on the membrane structure is associated with the increase of polymer concentration in the top part of the membrane as well as with the entanglement of polymer macromolecules. In general, increasing the evaporation time provides membranes with a denser skin layer. For instance, PVDF membranes were prepared at different evaporation times, and the results showed that longer evaporation time produces membranes with lower porosity, pore size, which in turn leads to a lower permeate flux [12].

Another study was conducted by Munari et al., [28] where evaporation time was varied between 5 and 480 s during casting of PVDF flat sheet membranes using two different high boiling point solvents (i.e. NMP and DMF) and with/without low boiling point cosolvent (i.e. THF and acetone, Ac). Their study showed that there was no a remarkable effect on the structure of prepared PVDF membranes at different evaporation time. However, the structure of PVDF membrane was influenced by the evaporation time when THF and Ac were added as cosolvents in the PVDF/DMF or PVDF/NMP casting solution. They concluded that the membrane mechanical strength and properties were adversely affected at longer exposure time.

2.4.5 Effect of coagulation bath medium

PVDF membrane formation is dominated by two mechanisms, liquid-liquid demixing and crystallization (or liquid-solid demixing) which is attributed to the semicrystallinity of this polymer. Consequently, the non-solvent coagulation bath is one of the main factors in controlling the system of liquid-liquid demixing or crystallization of the PVDF membrane formation through immersion precipitation process. Water is mainly employed as the non-solvent coagulation
medium as it is a strong non-solvent medium. Also, its presence in coagulation bath enhances rapid precipitation or liquid-liquid demixing resulting in asymmetric finger like membranes [13].

In the meantime, other solvents could be used alone or mixed with water such as 1-octanol inducing a delayed liquid-liquid demixing. Tai-Horng et al. [29] investigated the use of 1-octanol and water as coagulation bath mediums in the fabrication of flat sheet PVDF membranes. In their study, they used PVDF as polymer and DMF as the solvent, but with two different non-solvent coagulants. PVDF membranes prepared when using water as the coagulation bath exhibited an asymmetric finger like structure with a dense skin layer. On the other hand, with the use of 1-octanol as the coagulation bath, a symmetric PVDF membrane with a uniform cross-section of identical spherical particles was observed. This latter observation was dominated by crystallization mechanism [29].

A recent study was conducted by Siamak et al, [30] where they engineered a flat sheet microporous PVDF films for membrane distillation process via the addition of 2-propanol in a water coagulation bath medium. In their experimental part, PVDF was as the polymer, triethyl phosphate (TEP) the solvent, and a mixture of water and 2-propanol was the coagulation bath. The employed volume ratio of 2-propanol to water was from 0 to 30 v/v%. In general, the addition of co-non-solvent, 2-propanol to the water bath contributed to an increased surface porosity due to the increase of the exchange rate between the solvent and the non-solvents.

Moreover, as the concentration of 2-propanol in the coagulation bath was increased from 0 to 30 v/v%, the PVDF membrane top surface became more open, with gradual reduction in the fiber-like structure. Contact angle, surface roughness were also influenced by the addition of 2-propanol into the coagulation bath. It was observed increasing the concentration of 2-propanol from 5% to 20v/v% increases the contact angle from 100±4 to 125±, and from 0 % to 20 v/v%, the
average surface roughness was increased from 150 to 450 nm. Their best fabricated PVDF membrane for membrane distillation (i.e. 1 M NaCl feed solution at 60 °C and DI water permeate solution at 20 °C) was found to have a vapor water flux of 40 L/hr m² at thickness of ~60 µm and porosity of ~75 % under the case of using 30 v/v% 2-propanol in the water coagulation bath [30].

2.5 Hydrophobic Surface Coating Technique
Hydrophobic surface coating is a technique used to deposit certain materials on the top surface of a membrane to decrease its surface tension. For example, Teflon® AF2400, and Hyflon® AD were used to coat PVDF membranes leading to higher contact angles. In recent studies, Taghreed et al. coated 4wt.% Hyflon® AD on PVDF membrane surface and found the contact angles increased from 91.7° ± 0.8 to 119.6° ±0.8, [31] and Kang-Jia, et al. also found that coating Teflon AF2400 with concentration of 0.025 wt.% offered hollow fiber PVDF membrane with a contact angle of 151° ± 1. The latter study showed that increasing Teflon concentration above 0.025% did not further increase the contact angles of the PVDF membranes. For instance, the contact angle was found to be 140° ±1 when the Teflon concentration increased from 0.025% to 0.5%. This reduction in contact angles was attributed to the disappearing of hierarchical structure in PVDF membrane surface, where air could not be trapped under the skin layer of the membrane at higher Teflon concentrations [32].

Despite the advantages of the coating process, it has two disadvantages; the first one is that the coated layer could be washed away under operation process due to the weakness of physical adsorption between the membrane and the coated layer. The second drawback is that the coated layer might add resistance to membrane surface or might block or lower the pores of the membrane or permeate flux. However, increasing or improving the weakly physical adsorption interaction between the membrane and the coated layer may be achieved by chemical treatments such as sulfonation or crosslinking [23, 13].
2.6 Membrane Distillation (MD) Parameters and Characterization

Several membrane characteristic parameters should be taken into account when selecting MD membrane. These parameters include liquid entry pressure (LEP), mean pore size, pore size distribution, and thickness of the membrane. Also, surface porosity, pore tortuosity, and material or membrane thermal conductivity are important. In 1986, a conference held in Italy, ‘Workshop on Membrane Distillation’ reviewed the characteristics of the membranes utilized in MD and reported that the membrane should be characterized by five parameters. These parameters include the polymer membrane material, thickness, porosity, nominal pore size and liquid-entry-pressure of water (LEP) [12].

The objective of membrane characterization tools is to examine the morphological properties of fabricated membranes and measure some of the previously mentioned parameters. Membrane distillation characterization tools can include, but are not limited to, scanning electron microscope (SEM), atomic force microscope (AFM), contact angle measurement, pore size distribution, and gas permeation test.

SEM is commonly used to study the surface and cross-sections of the prepared membrane, whereas, AFM is most often employed to measure the surface roughness of the membrane for membrane distillation application. The Porolux 1000 machine is used to obtain two important parameters which include pore size distribution, and mean pore size. Porosity can be calculated using gravimetric method based on weight of dry and wet samples which can be carried out in the laboratory.

2.6.1 Liquid Entry Pressure

One of the main prerequisite for MD is that the membrane should not be wetted by the feed solution. Liquid entry pressure (LEP) is an important parameter that can provide an indication of the membrane performance towards pore wetting issue. In principle, LEP is defined as the
minimum trans-membrane pressure needed for the liquid feed to overcome the hydrophobic forces of the membrane. Overcoming the hydrophobic forces means that the liquid feed has penetrated the membrane pores, and thus causes a decrease in the permeate flux. This challenging behavior is a common problem in membrane distillation and known as pore wetting or wettability issue. In particular, pore wetting occurs when the applied pressure in the feed liquid is greater than the liquid entry pressure, so the LEP must be as high as possible [11].

Liquid entry pressure (LEP) can be determined by experimentally or mathematically. A few LEP experimental methods have been reported in the literature, and most of them are based on the paper published by Smolders et al. A typical LEP measurement set-up comprises of a nitrogen gas cylinder, manometer, regulator, statistic stainless steel testing cell, and a digital flowmeter. The membrane is placed in the static cell, which is loaded with pure water. Nitrogen gas can then be used to apply pressure the static cell, and once the LEP can be recorded from the first water drop coming from the cell. For more details of this testing method, refer to [33, 34]. Mathematically, The LEP value can be determined using the Laplace-Young equation [12]:

\[
LEP = \Delta P_{entry} = P_f - P_p = \frac{-2B\gamma \cos(\theta)}{r_{max}}
\]  

(2.1)

P\(_f\) and P\(_p\) are the hydraulic pressure on the feed and permeate sides, respectively, B is a geometric pore coefficient ranges between 0 and 1 (B=1 for cylindrical pores), \(\gamma\) is the surface tension of the liquid (for pure water = 72 mN/m), \(\theta\) is the contact angle, and \(r_{max}\) is the maximum pore radius [8].
This concept is explained in Figure 2.6 above, which shows the feed liquid flux against the pressure drop in a microporous hydrophobic membrane. As the pressure increases, the feed liquid does not pass through the membrane, but when the LEP is exceeded, the feed liquid starts to pass through the membrane pores. When all the pores are filled with liquid, then liquid flux follows Darcy’s law (i.e. \( N = K \Delta P \)), which indicates that reducing the pressure leads to a linear decrease in flux [8]. Consequently, the LEP get high for membranes that have a high contact angle (high hydrophobicity), and small pore size.

### 2.6.2 Pore size, thickness, and porosity of Membrane Distillation

Membrane distillation can have a pore size in the range of 100 to 1000 nm. In general, increasing the pore size results in a high flux. Increasing the membrane pore size, and porosity leads to a higher flux, whereas, it is essential to reduce the vapor transport path distance by \( \tau \delta \). However, there are two conditions must be followed when choosing a pore size for MD membrane. The pore size must be as large as possible to obtain a high flux, and at the same time, the pores must be small enough to avoid pore wetting. Thus, there is a tradeoff between the flux and pore size in MD [8, 11]. As a result, careful adjustment of the membrane to meet the requirement of a good membrane for MD application is important.

Membrane thickness is another critical characteristic, when the thickness is very thin, the
permeate flux is very high, so there is an inversely proportional relationship between them. The permeate flux decreases when the membrane thickness is large because the mass transfer resistance gets higher [8, 11]. Lagans et al. examined the membrane morphology such as the thickness and pore size distribution and they reported the optimum membrane thickness ranges between 30-60 µm [35]. However, as thin as 5 µm of hydrophobic layer in composite membranes were used in DCMD [36]. Membrane thickness can be determined by SEM from cross-section.

Furthermore, porosity is one of the main parameters for membrane distillation and also reported by El-Bourawi et al. that the porosity in membrane distillation ranges between 30 and 85% [36]. As a definition, porosity is the volume of the pores divided by the total void volume of the membranes [11].

Moreover, membrane porosity is a critical factor for minimizing the heat lost by conduction. This indicates that high porosity membranes exhibit a larger evaporation surface area which can be explained by correlating the membrane porosity with heat coefficients [8]:

\[ Q_m = h_m \Delta T_m \]  
\[ h_m = \varepsilon h_{mg} + (1 - \varepsilon) h_{ms} \]

Where, \( Q_m \) is heat flux by conduction through the membrane material and vapor (W/m²), \( \varepsilon \) is the membrane porosity, \( h_{mg} \) is the heat transfer coefficient of the vapor transferred through the membrane pores (W/m² k), and \( h_{ms} \) is the heat transfer coefficient of the solid membrane materials. It is worth noting in Eq. (4) that \( h_{ms} \) is generally an order of magnitude larger than \( h_{mg} \), meaning that \( h_m \) can be controlled or minimized by increasing the porosity [8].

Porosity of the membrane is commonly determined using gravimetric method by measuring the volumes of membranes pores over the total volume of membrane that is usually
carried out in the laboratory. In particular, a membrane sample’s porosity can be estimated by weighing a dry membrane sample using an accurate balance then it can be wetted with a low boiling solvent such as 2-propanol (IPA), then measuring the wetted sample’s weight. After that, the volume of the wetted and dried membranes can be estimated by using the following Equation [30]:

\[
\varepsilon = \frac{V_{pore}}{V_{total}} = \frac{m_{sol}}{\rho_{sol}} = \frac{m_{sol}}{\frac{m_{sol}}{\rho_{sol}} + \frac{m}{\rho_{m}}} = \frac{V_{sol} + V_{m}}{V_{sol} + V_{m}}
\]

(2.4)

Where, \( V \), \( m \), and \( \rho \) is the volume, mass, and density, respectively. Sol indicates solvent used, and \( m \) is the membrane (e.g. PVDF’s density = 1.78 g cm\(^{-3}\)). IPA is commonly used as the wetting fluid for the membrane and its density is 0.786 g cm\(^{-3}\) [30].
2.7 REFERENCES


CHAPTER 3: EXPERIMENTAL, CHARACTERIZATION, AND RESULTS AND ANALYSIS OF THE DCMD PROCESS

3.1 Introduction

Lacking access to safe drinking water is one of the main problems affecting people throughout the world. More than 1 billion people suffer from various water based diseases, and more than 3000 children die per day in the world due to the lack access of safe water [1]. Consequently, development of existing desalination processes such as membrane distillation is of great importance to meet the water requirements all over the world. Membrane distillation is an emerging membrane separation technology that has attracted researchers’ attention in the last few decades. It is a thermally driven process with a driving force of a vapor pressure gradient induced by the temperature difference across a porous hydrophobic membrane [2]. It can be combined with solar energy or waste heat since the operating conditions (i.e. temperatures and pressure) are low; the liquid feed is not necessarily heated up to the boiling point. Moreover, the applied pressure is much lower (about 1 bar) compared to conventional seawater desalination processes [3, 4].

Membrane distillation (MD) process can be classified into four basic configurations. MD configurations include direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), air gap membrane distillation (AGMD), and vacuum membrane distillation (VMD) [5]. The simplest configuration among the four techniques is the DCMD which many researchers use it in laboratories for desalination purposes. DCMD modules contain a hot feed side, and a cold permeate side, and between them is a porous hydrophobic membrane. The hot feed solution is brought into a direct contact with the membrane surface. The hot solution evaporates at the feed side, and vapor molecules are thermally driven to the permeate side. In particular, the temperature gradient causes a vapor pressure difference between the two sides, which enhances the overall driving force. After that, water vapor molecules get condensed in the permeate side.
Since the membrane used is hydrophobic, liquid feed (usually seawater) cannot pass through the membrane; only vapors penetrate through the pores of the membrane. The main disadvantage of this design is the heat lost by conduction [5, 6].

Key benefits of the MD process include less fouling than pressure driven membrane process, the permeate quality is insensitive to the feed salinity, and it requires a small footprint. However, MD is still under development stages and not commercialized yet due to the lower permeate flux, and wettability issue [4, 7]. The ideal MD membrane should be highly porous within the range of 100-1000 nm to enhance water vapor transport [2, 5, 7]. Thus, the pore size should not be too large (>1000 nm) to avoid pore wetting. Moreover, MD membrane must be hydrophobic with a reasonable liquid entry pressure (LEP) to prevent the penetration of liquid feed in the pores of the membrane. According to the Young-Laplace equation, the liquid entry pressure (LEP) increases as the pore size decreases, but this reduces the permeate flux. Consequently, the pore size should be optimized for membrane distillation process [8].

The selection of suitable materials and development of fabrication techniques for membrane distillation process are key elements for further advancement. MD membranes are mostly prepared from hydrophobic polymers due to their lower heat conductivity, lower surface energy, sufficient mechanical stability, and better processability. However, most hydrophobic polymers are not easily prepared by immersion precipitation method because common solvents cannot dissolve them [9].

Poly (vinylidene fluoride) (PVDF) is one of the most common polymeric materials used in membrane distillation process due to its thermal stability, sufficient processability, high chemical resistance, high hydrophobicity, and excellent mechanical strength [9, 10, 11]. PVDF is a flexible material that can be used to make flat sheet, hollow fiber or tubular membranes and it is still the
best selection for membrane distillation since common organic solvents can easily dissolve it such as N, N-dimethyl acetamide (DMAc), and dimethyl formamide (DMF) [9]. Up to this moment, most of the commercial PVDF membranes are manufactured using phase inversion methods, particularly by immersion precipitation because of its simplicity and high production scale [9, 10].

In this work, we propose a simple new technique to fabricate a high-performance flat sheet PVDF membrane supported with a polyester material for immersion precipitation process coupled with an external steaming process. In other words, fabric steamers attached to the immersion precipitation-casting machine (Figure 3.2) were utilized to steam the surface of the membranes before immersion in the coagulation bath. This new fabrication approach immersion precipitation combined with an external direct steam process for the preparation of PVDF membranes has never reported previously according to our best of knowledge. Moreover, Teflon AF2400 with a concentration of 0.01% was used to coat a portion of the prepared membranes. Various characterization techniques were employed to analyze the prepared membranes. The performance of the fabricated membranes was evaluated using the direct contact membrane distillation (DCMD) process.

3.2 Material and Methods

3.2.1 Materials

Poly (vinylidene fluoride) PVDF (Kynar HSV 900, powder, Arkema Inc.) was used in this study as the main polymer. Kynar HSV 900 PVDF is a homopolymer that has the highest viscosity among other Kynar grades due to its high molecular weight. N, N-dimethylacetamide (DMAc) was used as the solvent, with purity of 99.9% purchased from Sigma-Aldrich. RO or tap water was employed as the non-solvent in the coagulation bath. The supporting material of the PVDF membrane was a non-woven polyester fabric with an average thickness of 150 μm, which was purchased from Sojitz Europe, Germany. Normal upright fabric and handheld steamers were used
to steam the membranes during the casting process, which was filled with Mill-Q deionized water produced by a Millipore unit. Teflon coating material (AF2400) was acquired from Sigma Aldrich. Galden, Solvay was used to prepare the Teflon coating solution. Lithium chloride (LiCl) was used as an additive, which was purchased from Fisher Scientific, USA. Sodium chloride (NaCl, 99.5%) was used in the preparation of saline solution for DCMD process.

3.2.2 Casting Solution Preparation

The preparation of the dope solution started by placing a certain amount of lithium chloride (4 wt.% LiCl) inside an empty clean conical flask followed by the addition of the solvent (i.e. 88 wt.%, DMAc) (Figure 3.1). The mixture of LiCl/DMAC was allowed to stir at 200 rpm and 80 °C until the lithium chloride was completely dissolved. Afterward, certain amounts of PVDF powder (i.e. 8 wt. %) were added and overnight stirred to ensure dissolution of the polymer at the same temperature and stirring mode.

![Figure 3.1: Dope solution preparation process with stirring speed of 200 rpm and temperature of 80 °C.](image)

After obtaining a clear viscous casting solution, it was let to degas on the bench to remove air bubbles generated during the preparation process to avoid possible pinholes during the casting
The concentration of the Kynar PVDF HSV 900 was fixed to a relatively low 8 wt% due to its high viscosity. At low PVDF concentration, membranes with high porosity and large pore sizes can be obtained, which is desirable for membrane distillation [12, 13].

3.2.3 Flat Sheet Membrane Fabrication and Coating Processes

PVDF membranes were fabricated using immersion precipitation in a pilot scale production by a flat sheet membrane-casting machine with coagulation bath water capacity of 600 Liters. Figure 3.2 shows a schematic of the casting machine coupled with fabric steamers. The casting gap thickness was adjusted to 150 µm when casting the membranes. More than 5 meters long PVDF membranes with an effective membrane width of 20 cm were successfully produced.

Figure 3.2: Flat sheet membrane casting machine process using immersion precipitation.

In this study, different modification techniques were employed during the casting process (i.e. steaming process), and after the casting process (i.e. coating with AF2400 Teflon) to improve PVDF membranes. Steaming process was used to modify the surface of PVDF membranes except when preparing the control PVDF. An upright fabric steamer was used to generate the steam. It was adjusted manually and gently exposed to the top surface of the PVDF membrane for about 5 seconds before immersion the membrane into the coagulation bath. The dope solution was gently
poured into the provided space in the casting machine. The polyester non-woven was moving with a speed of 2 m/min. The coating was followed by steaming the front side facing the top part of the polymer solution for one run. It should be mentioned that when exposing the top surface of the membrane, the mouth of the steamer was tilted 45 °C to avoid damaging the surface of the membrane. Another run was attempted where both sides of the membranes were steamed using another handheld steamer device. The handheld steamer produces a high flow of steam hitting the bottom side of the membrane surface horizontally. The steam could penetrate the highly porous polyester support due to its large pore size and high direct steam flow, which in turn influences the bottom surface of the PVDF membrane. Since the casting process was performed in a large casting machine we were able to find a location to steam the bottom surface of the membrane (Figure 3.2). A schematic diagram showing the steaming process of both sides of the fabricated membrane during casting process prior to immersion in the coagulation bath is depicted in Figure 3.3.

![Figure 3.3: A schematic diagram of steaming both sides of the PVDF membrane during solution casting process particularly before immersion precipitation process. The steamer hitting the top side was tilted 45 °C and high flow of steam hitting the polyester support.](image)

After phase separation took place, the fabricated PVDF membrane roll was collected and moved into a washing bath filled with DI water and left overnight. The following day, the prepared membranes were stretched out on clean plastic sheet for drying.
Figure 3.4: Teflon coating method carried in open air at room temperature

In particular, three PVDF membranes were prepared with/without steaming. These PVDF membranes include a control PVDF coded as M1, top sided steamed PVDF coded as M2, and both sided steamed PVDF membrane coded as M3. The exposure steaming time was about 5 seconds. It should be noted that the evaporated steam from the upright steamer was not close to the surface of the membrane during steaming process to avoid oversteaming which may lead to destroying the structure of the membrane or making the membrane too porous (i.e. undesirable for membrane distillation “wettability issue”). Further, a portion of the prepared M3 was collected and coated with 0.01% AF2400 Teflon where a sponge paint brush was dipped in the Teflon solution then gently applied to the surface of M3 (Figure 3.4). The prepared four membranes with and without modification processes are shown in Table 3.1.

Table 3.1: Prepared membrane solution composition and specifications

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Polymer concentration (wt. %)</th>
<th>Solvent concentration (wt. %)</th>
<th>Additive concentration (wt. %)</th>
<th>Exposure Steaming Time (s)</th>
<th>Steaming Top Side</th>
<th>Steaming Bottom Side</th>
<th>Teflon Coating (0.01%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>8% PVDF</td>
<td>88% DMAC</td>
<td>4% LiCl</td>
<td>0</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>M2</td>
<td>8% PVDF</td>
<td>88% DMAC</td>
<td>4% LiCl</td>
<td>5</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>M3</td>
<td>8% PVDF</td>
<td>88% DMAC</td>
<td>4% LiCl</td>
<td>5</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>M3C</td>
<td>8% PVDF</td>
<td>88% DMAC</td>
<td>4% LiCl</td>
<td>5</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
3.3 Characterization and measurement

3.3.1 Surface Morphology and Cross Sections

Cross-sections and top and bottom surfaces of the prepared membranes were investigated by scanning electron microscopy (SEM) (GeminiSEM, ZEISS). Membranes were coated with iridium and mounted before the observation of the SEM. For surface analysis, small squared pieces from each membrane were cut and placed on SEM stubs followed by fixing them using a copper tape. After taping, the samples were coated with iridium for two reasons, first, to avoid charging, and second, to increase the signal and surface resolution. For cross sections analysis, the supported prepared membranes were half cut by scissor from one edge followed by tearing it by hand, then small pieces were fractured using liquid nitrogen and sputtered using iridium, respectively.

3.3.2 Contact angle

The contact angles of the fabricated membranes were measured using a sessile drop technique (Easy-Drop, Kruess). A 5 μL DI water droplet was deposited on the membrane sample and imaged using a digital camera. At least five measurements for two different samples for each membrane were recorded at different positions, and the average was considered.

3.3.3 Gas permeation test

The gas permeation test for all prepared membranes was conducted using a gas filtration unit (Figure 3.5). The filtration unit comprises a circular stainless steel holder (Millipore) with an effective diameter of 2 cm, a handheld digital pressure meter (Omega Engineering Inc., England), and a highly accurate portable gas flow calibrator (Mesa labs, Dry Cal Technology, Definer 220). The utilization of the pressure meter allowed a full control of the applied pressure (10-2500 Pa) to obtain a very accurate result. A perforated stainless steel screen was used to support the membrane. The samples were cut to fit the holder size and then tightly screwed. Nitrogen gas was employed as the gas source, and a regulator controlled its flow. The pressure was set to 2 kPa for each
experiment, where the nitrogen flow was recorded using the gas flow meter. Five measurements were taken for three different samples for each coded membranes, and the average was considered.

![Gas permeation test apparatus](image)

**Figure 3.5:** Gas permeation test apparatus

### 3.3.4 Membrane porosity, mean pore size, liquid entry pressure (LEP), and pore size distribution measurements

Membrane porosity was determined using a gravimetric method and was estimated using the following equation [13]:

\[
\varepsilon = \frac{V_{pore}}{V_{total}} = \frac{m_{IPA}}{\rho_{IPA}} = \frac{m_{IPA}}{m_{IPA} + m_{PVDF}} \rho_{IPA} \rho_{PVDF} \quad (3.1)
\]

Where, \(m_{IPA}\) is the mass of a PVDF membrane wetted with 2-propanol (IPA), \(\rho_{IPA}\) is the density of the IPA, \(m_{PVDF}\) is the mass of the dried PVDF membrane, and \(\rho_{PVDF}\) is the density of PVDF material. The density of PVDF, and IPA is 1.78 g/ cm\(^3\), and 0.786 g/ cm\(^3\), respectively which were used during the calculation [13]. Each PVDF membrane samples was peeled off from the polyester support before measurement. A dried PVDF sample was weighted in an accurate balance and then immersed in a 25 ml container filled with IPA and left for 20 minutes. The wetted samples were
taken out and excess IPA was removed before weighing again. The test was performed four times and the average was determined.

The mean pore size, liquid entry pressure (LEP), and pore size distribution were measured using a Capillary Flow Porometer (CFP), (Porolux 1000 IB-FT GmbH, Germany). The fabricated membranes were cut in a circular shape with a diameter of 2 cm and then immersed in Porefil® wetting liquid (surface tension=16 mN/m) for 10 minutes. The wetted membranes were then put in the Porolux chamber and then the chamber was sealed tightly. The experiment started by running a pure gas nitrogen gradually into the chamber until the bubble point was determined by overcoming the capillary flow of the fluid through the largest pore size in which the LEP was estimated. Afterward, the nitrogen pressure was increased, and the flow rate was measured until all pores became dry, non-filled with the Porefil liquid in which the pore size distribution was measured. All measurements and readings were controlled through a computer software.

**3.3.5 Membrane Performance Evaluation by DCMD**

Direct contact membrane distillation (DCMD) process was utilized to evaluate the performance of the prepared membranes. Both steamed and un-steamed membranes were tested by commercial DCMD process (Aqua-still Company) that is described schematically in Figure 3.6. The hot feed tank was filled with 1 M NaCl solution, whereas the cold stream was filled with DI water. The temperature of both streams was monitored by temperature sensors located at different locations, and the hot feed side temperature was varied between 50 and 80 °C. The temperature of the permeate side was fixed to 20 °C. Both streams were also fixed at a flow rate of 520 L/hr.
Figure 3.6: Schematics of the experimental setup for DCMD testing.

The DCMD operation was a continuous process where the temperature started at 50 °C, then increased by increment of 10 °C till 80 °C. At beginning, the DCMD experiments were allowed to run for 1 hour to reach steady state before the permeate volume were collected externally from the permeate tank and 1 hour was considered between each an increment increase in temperature for steady state. The concentration of salt in the permeate side was monitored using an electric-conductivity meter (Cond 3310, WTW, Xylem Inc).
Figure 3.7: Flat Sheet Module design used in the experiment that comprises of 13 channels. The channel has a semi-circular pipe like shape with radius, length and width of 3 mm, 500 mm, and 6 mm, respectively.

The module design used in the experiments presented in Figure 3.7 was a plate and frame comprising of two compartments, one for the hot feed side, and the other for the cold distillate side. The module design contains 13 flow channels, and each channel consists of a semi-circular pipe like channel. The membranes were placed between these compartments in which the fluids were allowed to pass in countercurrent mode within these 13 flow paths. The effective membrane area was measured using Eq. (3.2):
\[ A_{\text{eff}} = N \times \left[ L \times Y + 2 \times \frac{\pi r^2}{2} \right] \] (3.2)

Where \( A_{\text{eff}} \) is the membrane effective area (m\(^2\)), \( N \) is the number of channels in the module design used, \( L \) is the length (mm) of one channel excluding the last two ends of the semi-circles, \( Y \) (mm) is the width of a one channel, \( r \) is the radius of the semi-circle located at the end of each channel as shown in Figure 3.7. Since there are two semi-circles, we multiply by two and it is necessary to multiply by 13 to consider all the channels covering membrane surface. Applying the dimensions in Eq. (2), the effective membrane area was found to be 394 cm\(^2\) or 0.0394 m\(^2\).

The permeate flux was measured using the following equation:

\[ J_w = \frac{V}{t \times A_{\text{eff}}} \] (3.3)

Where \( J_w \) is the permeate flux (L/h m\(^2\)), \( V \) is the permeate volume (L), \( A \) is the effective area (m\(^2\)) and \( t \) is the time (h). The electric conductivity for each membrane in the permeate tank was recorded and used as an induction of the membrane performance in terms of salt rejection.

### 3.4 Results and discussion

#### 3.4.1 Membrane structure and surface analysis

Top and bottom surfaces of the fabricated membranes were investigated using SEM as shown in Figure 3.8. The effect of exposing the casting solution to steam during membrane fabrication process can be recognized in the SEM surface images. The bottom surface of the M3 membrane showed a different surface morphology in terms of pore size compared to M1 and M2. The both-sided steamed membrane (M3) exhibited a more porous bottom surface with the absence of the dense layers compared to M1, and M2, which was one of the main factors, that significantly
contributed to obtaining the highest permeate flux (~ 40 L/h m$^2$ at 60 °C and 20 °C, hot side, and cold side temperatures, respectively).

Moreover, M1 and M2 membranes as shown in Figure 3.8 exhibited a very alike bottom structure as they both have a dense layer covering most of their bottom surfaces. This indicates that steaming the top side of M2 had no influence on its pore size at the bottom surface. On the other hand, steaming the top surface of M2 and M3 had no significant effect on their pore size as the mean pore size was found in the range of 191-245 nm. This might be attributed to the procedure of steaming the top side of membrane as the mouth of steamer was tilted 45°. It should be obvious that the structure (i.e. top and bottom surfaces, and cross-sections) of M3C is identical to M3 because sheets taken from M3 was only coated with Teflon AF2400.

Furthermore, the addition of LiCl in the PVDF casting solution can generally have two main structural effects depending on the LiCl concentration. It was reported that at high LiCl concentrations (7.5 wt% LiCl) in PVDF/DMAc system, the macrovoid formation was suppressed because high amounts of LiCl slows the exchange rate between the solvent in the coagulation bath and the non-solvents in the membrane film, but at a low LiCl concentration (2.5 wt% LiCl), it acts as a permeate flux enhancer [9, 14]. Therefore, from the SEM cross-sectional images, the presence of macrovoids confirms that the LiCl concentration did not exceed the limit for which it only enhanced the permeate flux by making the membrane more open.

All fabricated PVDF membranes with/without steam exhibited a porous, spongy structure with large macrovoids within the range of 50 µm ≥ macrovoids size >10 µm in their cross-sections (Figure 3.9). The top-sided steamed membrane (M2) exhibited fewer macrovoids in its cross-section compared to M1 and M3. It should be noted that the macrovoids formation is considered undesirable for pressure driven processes since they create weak spots in which the membrane
might collapse at high pressure [15]. However, this is not the case for low pressure membrane processes such as membrane distillation process; the macrovoids create more space for water vapor transfer [8]. Consequently, the presence of macrovoids and sponge-like structure enhanced the

Figure 3.8: SEM top and bottom surface images of fabricated PVDF membrane with/without 5 s of steaming. The SEM micrographs: (M1, Non-steamed membrane), (M2, top-sided steamed membrane), and (M3, Both-sided steamed membrane).
permeate flux because the macrovoids could assist in reducing the transport distance for vapor water to move across the membrane, whereas the presence of the sponge-like structure favored a high permeate flux by providing more available spaces for mass transport.

Several parameters can be used to explain the obtained PVDF membrane structure by phase inversion process, but the resulting structure mainly depends on precipitation rate of the polymer in the non-solvent coagulation bath. As PVDF is a semi-crystalline polymer, it can exhibit both liquid-liquid demixing, and solid-liquid demixing. However, the solubility parameter difference between the PVDF and the non-solvent (i.e. water) is high, so, the liquid-liquid demixing is the dominating process over the solid-liquid demixing process. The difference in solubility parameters

![Figure 3.9](image_url): Different magnifications of SEM cross-sectional images of PVDF membranes fabricated by phase inversion using 8 wt% PVDF (Kynar, HSV 900) in dimethylacetamide (DMAc), 4wt% lithium chloride as additive, and a coagulation bath of water. The SEM micrographs: (M1, Non-steamed membrane), (M2, top-sided steamed membrane), and (M3, Both-sided steamed membrane).
between the PVDF polymer, and the non-solvent is large which facilitated a rapid precipitation rate and there is little time for crystallization [16].

Therefore, macrovoid formation could be attributed to the fast precipitation of the PVDF during the casting process as well as to the high mutual affinity between the DMAc and the non-solvents (i.e. water, and LiCl) [17].

The liquid-liquid demixing process can have two different demixing speeds (i.e. instantaneous, and delayed demixing), which can generate two different kinds of membrane morphology. In general, instantaneous demixing process favors the formation of a finger-like structure whereas the delayed demixing produces membranes with a sponge-like structure [18]. The presence of the sponge-like structure in the prepared membranes’ cross-sections is related to kinetic aspects. An increase in the casting solution viscosity by the use of the high molecular weight polymer (Kynar HSV 900) and the addition of LiCl decreases the solvent/non-solvent exchange rate, which stimulated the delayed liquid-liquid demixing resulting in a sponge-like structure [14].

### 3.4.2 Thickness and supporting material analysis

The thickness, average contact angle, porosity, mean pore size, and liquid entry pressure (LEP) for each prepared membrane are summarized in Table 3.2 together with the standard deviation. The obtained thickness for all membranes did not change with steam exposure; all membranes have a thickness in the range of 32-36 µm. The thickness of the membrane is a crucial parameter for permeate flux. Increasing the membrane thickness decreases the permeate flux which is undesirable for the membrane distillation process. The permeate flux decreases when the membrane thickness is large because the mass transfer resistance gets higher [2, 5]. It was reported
that the optimum membrane thickness for membrane distillation application ranges between 30 and 60 µm [19].

Also, the polyester support plays an important role in the membrane distillation process. The support does not only provide mechanical strength and reduces the membrane shrinkage, but it also minimizes the heat loss by conduction. The used polyester support had a thickness of 150 µm in average, which creates a barrier between the hot and cold streams. Since the thickness of the support is relatively high, it can aid in minimizing the heat loss by conduction. For instance, if the total thickness of the membrane with the support between the hot and cold streams were very low, then hot water would heat the cold stream faster or increase its temperature more than 20 °C which in turn lowers the driving force.

Table 3.2: Membrane characteristic results of the prepared membranes

<table>
<thead>
<tr>
<th>Membrane Code</th>
<th>Membrane Thickness (µm)</th>
<th>Mean Pore size (nm)</th>
<th>LEPw (bar)</th>
<th>Contact Angle [°]</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>32.61</td>
<td>186 ±3.50</td>
<td>2.46±0.4</td>
<td>110.44±1.6</td>
<td>84.1±7.03</td>
</tr>
<tr>
<td>M2</td>
<td>31.88</td>
<td>191±8.10</td>
<td>1.43±0.15</td>
<td>132.80±1.2</td>
<td>82.6±2.63</td>
</tr>
<tr>
<td>M3</td>
<td>35.00</td>
<td>243±7.81</td>
<td>1.01±0.20</td>
<td>114.15±3.5</td>
<td>79.9±3.31</td>
</tr>
<tr>
<td>M3C</td>
<td>35.83</td>
<td>244±8.4</td>
<td>1.86±0.22</td>
<td>138.50±1.5</td>
<td>79.9±3.40</td>
</tr>
</tbody>
</table>

3.4.3 Contact angle analysis

The average contact angle of the prepared membranes with and without steaming and coating are also shown in Figure 3.10. Steaming the top surface of the fabricated membranes with tilting the steamer handle mouth during casting process enhances the contact angle for M2 (top-sided steamed PVDF membrane). The contact angle of M2 was found to be around 133° which was 21% higher than M1 (~110°). The increase of contact angle of M2 compared to M1 could be explained by the Cassie-Baxter theory in which the introduction of steam causes a rougher membrane surface, in which air could be trapped beneath the upper layer of the membrane surface.
Thus, the air trapped may have created a gaseous interface or phase between the liquid droplet and solid material leading to higher contact angles. However, the both-sided steamed PVDF (M3) showed a lower contact angle compared to M2, which was not expected. This unexpected reduction in the contact angle from ~133° to ~114° might be due to the bottom side steaming process since the air trapped in the top layer surface could be disturbed or diminished by the bottom side steaming compared to M2 where no steam exposure to its bottom surface was applied.

Figure 3.10: Results of the average contact angle of the prepared membranes.

The contact angle of the Teflon AF2400 coated membrane (M3C) was measured before, and after testing on DCMD to investigate its contact angle stability on the membrane surface. The contact angle for M3C before conducting the DCMD experiment was ~139°, but after testing it was reduced to ~ 118°. This reduction in contact angle indicates the coated Teflon layer was washed away during the DCMD testing which might limit its use for membrane distillation process. The confirmation of the instability of the Teflon coated layer was not only verified by
contact angle measurement but also using the DCMD process as almost identical values of the permeate flux were obtained for coated and uncoated Teflon PVDF membranes (i.e. M3C, and M3, respectively). Despite this limitation, M3 and M3C membrane still exhibited higher permeate flux compared to M1 and M2.

### 3.4.4 Nitrogen permeation test and porosity analysis

The nominal pore size of fabricated PVDF membranes with/without steaming and coating were measured using gas permeation tests. Figure 3.11 shows the results of the nitrogen permeation test, which shows that steaming the PVDF membranes leads to a significant increase in the nitrogen permeance from M1 to M3C, which was consistent with obtained permeate fluxes of the DCMD experiments. In particular, it was found M3 showed the highest nitrogen permeance (~4520 m³ h⁻¹ m⁻² bar⁻¹) compared to M1 (~2740 m³ h⁻¹ m⁻² bar⁻¹), and M2 (~4030 m³ h⁻¹ m⁻² bar⁻¹), whereas M3C was slightly reduced to about 4100 m³ h⁻¹ m⁻² bar⁻¹. The significant increase in nitrogen permeance of M3 could be explained from the resultant SEM membrane surface images, as the bottom surface was more open compared to M1, and M2. This was caused by the steaming of the bottom side. On the other hand, the reduction of nitrogen permeance of the M3C could be attributed to the presence of the Teflon coated layer, which created an additional resistance in the top surface of the membrane.
Membrane porosities of the prepared membranes with standard deviation are presented in Table 3.2. It can be clearly observed that membranes' porosity of all fabricated membranes are similar with no significant variations. The addition of lithium chloride (4 wt% LiCl), and the use of a low polymer concentration (8 wt% PVDF) played a major role in obtaining high porosities for all membranes since the pore forming additive LiCl increases porosity. It is already confirmed that decreasing the PVDF polymer concentration in the casting solution increases porosity, which was attributed to the fact that decreasing the polymer concentration increases the size of internal pores and voids or spaces within the membrane structure [21].

3.4.5 Mean Pore size, pore size distribution, and LEP analysis

The mean pore size and liquid entry pressure (LEP) for M1, M2, M3, and M3C are presented in Table 3.2 together with the standard deviation. The mean pore size was found to be in the range of 186±3.50 to 244±8.10 nm for all fabricated membranes. In addition, from Table 3.2 it can be noticed that the mean pore size increased gradually when the membranes were
steamed. In particular, the mean pore size of M3 and M3C membranes showed higher mean pore sizes with almost identical values. This was attributed to the surface structure at top and bottom sides being more porous compared to M1 and M2.

Furthermore, PVDF membranes exposed to steam at the top side of the membrane showed an increase in pore size compared to the control PVDF membrane (M1). This means that steaming the external part of the casting solution during the casting process enabled an improvement of the pore size which was confirmed using the Porolux 1000 machine. The pore size distribution for M1, M2, and M3 was found to be in the range of 100-260 nm, 130-450 nm, and 130-630 nm, respectively when using the Porolux 1000 with maximum pressure of 6 bar (Figure 3.12). To investigate smaller pore sizes than 100 nm, a pressure higher than 6 bar must be applied as it can be clearly seen from the SEM images smaller pore sizes than 100 nm are present.

![Pore size distribution](image)

**Figure 3.12:** Pore diameter or size distribution of the fabricated membranes

One of the main prerequisite for MD is that the membrane should not be wetted by the feed
solution. Liquid entry pressure (LEP) is an important parameter that can provide an indication of the membrane performance towards pore wetting issue. Pore wetting is a common problem in membrane distillation. In particular, pore wetting occurs when the applied pressure in the feed liquid is greater than the liquid entry pressure, so the LEP must be as high as possible [5].

In this study, the liquid entry pressure of each membrane was estimated using Porolux 1000 machine. Table 3.2 also displays the liquid entry pressure for all prepared membranes together with the standard deviation. In general, steaming the membranes reduced the liquid entry pressure because the mean pore size increased with steaming. This can be explained by the Young-Laplace equation which states, that as the pore size increases, the liquid entry pressure decreases. However, as shown in Table 3.2, the LEP of M1 was 2.46±0.40 bar whereas, the LEP of the M2, M3, and M3C membranes were found to have values of 1.43±0.15, 1.01±0.20, and 1.86±0.22 bar, respectively. The Teflon coated membrane (M3C) had a LEP higher than the uncoated membrane (M3), which was attributed to its higher contact angle. This also follows the Young-Laplace equation, in which the liquid entry pressure increases as the contact angle increases. Nevertheless, the obtained results of LEP allowed the use of M1, and M3C for long term experiment without exhibition of pore wetting issue.

3.4.6 DCMD Performance analysis

All fabricated membranes were examined for DCMD at different temperatures and their permeate flux and the permeate electric conductivity data are presented in Figure 3.13. It is worth mentioning that the permeate flux for all prepared membranes increases significantly as the feed temperature increases from 50 to 80 °C due to the increase of water vapor pressure with temperature. The effect of steaming on the membrane performance can be clearly realized in the obtained permeate fluxes. It can be seen that the membrane with both-sided steam,
with/without coating (M3, M3C) exhibited the highest permeate flux with no large variation on the electric conductivity compared to M1, and M2. It is also worth mentioning that the M3 and M3C exhibited almost identical permeate flux, but with slight increase in electric conductivity for M3 which indicates a slight passage of salt. However, when the M3 was coated with Teflon AF2400, the electric conductivity was not increased at operation of 8 hours from 50 to 80 °C. The slight increase in electric conductivity for M3 could be attributed to its low liquid entry pressure.

![Graph Image](image-url)

**Figure 3.13:** a) Result of the permeate flux of non-steamed membrane, M1, top sided steam membrane, M2, uncoated both sided steam membrane, M3, and coated both sided steamed membrane, M3C measured at different feed temperatures. b) Electric conductivity vs. operation time of all prepared membranes measured in the permeate tank at 20 °C while changing the feed temperature from 50 to 80 °C with operation time of 8 hours.
The permeate fluxes of M3 and M3C were 30.1% and 27% higher than the control membrane (M1) at a feed temperature of 60 °C. This higher permeate fluxes for M3 and M3C compared to M1 and M2 was mainly attributed to their larger pore size at the bottom surface generated by the steaming process as it was shown in the SEM images.

More than 6 hours of desalination experiments of 1 M NaCl feed solution was conducted for M1, M2, M3 and M3C as shown in Figure 3.13 (b). Electric conductivity measurements of salt in the permeate tank were used as an indication of salt passage through the pores of the membranes during the DCMD process. An increase in electric conductivity indicates an increased salt flux by liquid water permeation from the feed side to the permeate side. It should be noted that the electric conductivity in the permeate side was measured at 20 °C, while the feed temperature in feed tank was changed from 50 to 80 °C.

Furthermore, the large decrease in electric conductivity for M1, M2, and M3C (Fig. 15b) was attributed to the large amount of purified water transferred from the feed stream as the feed temperature was increased from 50 to 80 °C in a continuous operation mode. The initial electric conductivities of the used tap water in the permeate tank were measured for each membrane before running the DCMD experiments for M1, M2, M3, and M3C at room temperature; the initial conductivity was 0.400, 0.373, 0.360, 0.354 mS/cm, respectively. The electric conductivity for M1, M2, and M3C decreased with time when the temperature was varied from 50 to 80 °C, which implies that the salt flux was very low. However, M3 showed a slight increase in the electric conductivity with time in the permeate tank (i.e. 2.5% increase at feed temperature of 80°C). Overall, all prepared membranes exhibited a lower electric conductivity with no increase or
significant increase in salt flux or electric conductivity during the continuous DCMD operation of 8 hours.

3.5 Conclusion

Polyvinylidene fluoride (PVDF) membranes were prepared by non-solvent induced phase separation with DMAc as solvent and LiCl as additive with and without steaming process. The structure of the prepared PVDF membranes showed a sponge like structure in their cross sections with the presence of macorvoids. The thickness and porosity of the membranes were in the range of ~ 33-36 µm and ~ 80-84 %, respectively. The spongy structure and presence of macorvoids played a major role in providing more void spaces for vapor transport, and high porosity that contributed significantly to a high permeate flux. The properties of the top and bottom surfaces were highly dependent on the steaming process. The top and bottom surfaces of casting solution were steamed before immersing the membranes in the coagulation bath. The DCMD permeate flux increased significantly for steamed membranes compared when there was no steam applied. The decrease of the permeate conductivity with time indicated a very low salt permeation. No pore wetting could be observed under most experimental conditions. The obtained results suggest that PVDF membrane can be fabricated in a simple scalable technique using a non-solvent phase inversion combined with a steaming process. No toxic solvents were employed in the coagulation bath.
3.6 REFERENCES


CHAPTER 4: HEAT TRANSFER ANALYSIS OF TWO DIFFERENT MODULE DESIGNS USING AN IDENTICAL PVDF MEMBRANE

4.1 Introduction

Membrane distillation (MD) is a thermally driven technology that requires liquid water to evaporate across a hydrophobic membrane. Various MD configurations have been reported in the literature, and the most commonly used is the direct contact membrane distillation (DCMD) [1, 2]. In the DCMD, the hydrophobic membrane is placed in direct contact between hot and cold liquid phases flowing countercurrently. The hot liquid evaporates in contact with the membrane surface and then migrates through the membrane’s pores to the cold side of the membrane because of the temperature difference between the hot and cold streams. The cold liquid stream recovers the pure vapor water through condensation [1].

DCMD process requires a continuous flow of the hot and cold liquid streams, and as a result, its module design may exhibit either a turbulent or laminar flow. The former requires high flow rates while the latter does not need high pumping pressure [3]. Since the DCMD process is thermally driven process between hot and cold streams and requires the transport of vapor water through the membrane, both heat and mass transfer takes place simultaneously. Heat transfer depends on the nature of the flow, on the module design, and on the physical properties of the hot and cold streams. After a literature research, established empirical correlations for flat sheet module designs were identified for laminar and turbulent flow regimes. Various studies on heat and mass transfer in MD have been described in many publications [3, 4, 5, 6]. One purpose of performing heat and mass transport analysis is to find the membrane interfacial temperatures from the bulk temperatures by the use of heat energy balance for a membrane module design. This is important since the membrane surface interface temperatures ($T_{mf}$ & $T_{mp}$) cannot be determined experimentally (Figure 4.3) [4]. Therefore, in this study, heat transport analysis for two different
module designs was performed using identical PVDF membrane properties. Another goal is to evaluate the performance of each module design by finding the temperature polarization coefficients and evaporation efficiency. The heat energy balance using established empirical correlations obtained from the literature was carried out to find the convective heat transfer coefficients, which allows the calculation of the interfacial temperatures.

4.2 Materials and Experimental set-up

4.2.1 Materials
Poly (vinylidene fluoride) PVDF (Kynar HSV 900, powder, Arkema Inc.) was used as the polymer, dimethylacetamide (DMAc) was used as the solvent, (Sigma-Aldrich), and lithium chloride (LiCl) was used as an additive (Fisher Scientific, USA.) Distilled water was employed as the non-solvent in the coagulation bath. The non-woven fabric material was a polyester fabric with an average thickness of 150 µm which was purchased from Sojitz Europe, Germany.

4.2.2 Dope casting preparation and membrane fabrication method
The dope casting solution was prepared by mixing certain amounts of lithium chloride (4 wt. % LiCl) with DMAc solvent (i.e. 88 wt. %). The mixture of LiCl/DMAC was allowed to stir at 200 rpm and 80 °C until the Lithium chloride was completely dissolved. After dissolving lithium chloride, certain amounts of PVDF polymer (i.e. 8 wt. %) was added and stirred and heated at the same conditions of 200 rpm and 80 °C, respectively. To ensure dissolution of the polymer, the dope solution was allowed to stir overnight. The PVDF membranes were prepared using immersion precipitation in a large-scale production by Flat Sheet Membrane Casting Machine (See section 3.2 for more details). Table 4.1 lists the membrane properties used in this study. The characterization techniques for the membrane can be found in section 3.3.
Table 4.1: Membrane and support properties.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean pore size (µm)</th>
<th>Porosity</th>
<th>Thickness (µm)</th>
<th>Contact angle [°]</th>
<th>k (W/k m)</th>
<th>LEP (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>0.186</td>
<td>0.84</td>
<td>32.61</td>
<td>110.44</td>
<td>0.17</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Note: a is the reported thermal conductivity of the PVDF material [6].

4.2.3 Experimental setups

Two different direct contact membrane distillation (DCMD) set-ups with two different module designs were utilized to test the prepared membrane. For both set-ups, the hot feed tanks were filled with 1 M NaCl solution, whereas the cold stream was filled with DI water. The first DCMD set-up (Figure 4.1a) was a laboratory built equipment whereas, the second set-up was manufactured by Aqua still company, Netherlands.

![Figure 4.1: DCMD Setups: (a) Laboratory made DCMD setup and (b) Aqua still DCMD setup](image)

The prepared membrane was tested with operating temperatures in the hot feed side of 50, 60, and 70 °C, in the laboratory made DCMD set-up (Figure 4.1a) while the temperature of the permeate side was kept to 20 °C. For the Aqua still setup (Figure 4.1b), the hot feed side temperature was changed from 50 to 80 °C, with a permeate temperature of 20 °C.
Table 4.2 shows the module design specification and operation conditions. It should be mentioned that the flow rates were set to 9 L/hr for the laboratory made setup and 520 L/hr for the Aqua still setup in both feed and permeate sides. Also, the module design tested using Aqua still setup contained 13 semi-circular pipes like channels (Figure 4.5b), whereas, the laboratory DCMD set-up, the module design had a rectangular duct shape with two spacers (Figure 4.5a).

**Table 4.2: Module design specifications and operation conditions used for the two DCMD set-ups.**

<table>
<thead>
<tr>
<th>Module Specifications and operation conditions</th>
<th>Rectangular duct module design</th>
<th>Semi-circular pipe module design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Area (cm$^2$)</td>
<td>50</td>
<td>394</td>
</tr>
<tr>
<td>Number of Channels</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Flow rates (L/hr)</td>
<td>9</td>
<td>520</td>
</tr>
<tr>
<td>Feed Salt Concentration (M)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hot feed temperature range (°C)</td>
<td>50-70</td>
<td>50-80</td>
</tr>
<tr>
<td>Cold feed temperature (°C)</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

### 4.3 Heat Transfer Theory

Heat transfer occurring in direct contact membrane distillation (DCMD) can be divided into three regions, which include:

i) Convective heat transfer in the feed liquid boundary layer, $Q_{conv,f}$, and heat transfer due to vapour water transfer across the feed liquid boundary layer [4, 5].

ii) Conductive heat transfer across the membrane, $Q_{cond,m}$ and heat transfer due to vapour water transport through the membrane pores, $Q_{v,m}$ [4, 5].

iii) Convective heat transfer in the permeate liquid boundary layer, $Q_{conv,p}$ and heat transfer due to vapour transfer across the permeate liquid boundary layer [4, 5].
As results, the following electric circuit analogy of the approximated heat transfer module is presented in Figure 4.2.

\[ T_{bf} \rightarrow Q_{conv,f} \rightarrow T_{mf} \rightarrow T_{mp} \rightarrow T_{bp} \]

\[ Q_{v,m} \]

\[ Q_{conv,p} \]

\[ Q_{cond,m} \]

Figure 4.2: Electrical circuit analogy of the heat transfer model

The effect of vapour water transfer on heat transfer in the feed and permeate liquid boundary layers can be ignored because the mass transfer contribution to the overall heat flux of feed and permeate boundary layers is insignificant. In other words, the convective heat transfer on both feed and permeate boundary layers is dominant [4]. The actual driving force for water vapor transfer in the MD process is the temperature gradient between the temperature of the membrane surface in the feed side \( (T_{mf}) \), and the temperature of the membrane surface in the permeate side \( (T_{mp}) \) (Figure 4.3).
Since MD process exhibits heat losses, the bulk temperatures of the feed and permeate streams are different from membrane interface temperatures in the feed and permeate sides. This is called temperature polarization (TP) which is a common problem in the MD process. TP leads to a reduction in the driving force, which is unfavorable for MD processes. Temperature polarization coefficient (TPC) is a measure of the actual driving force over the theoretical driving force. TPC close to unity indicates that the module design exhibits a higher driving force, whereas a module design that is far away from unity indicates a poor module design [1, 2, 4]. TPC can be expressed as:

$$TPC = \frac{T_{mf} - T_{mp}}{T_{bf} - T_{bp}}$$ (4.1)
where $T_{mf}$ is the membrane surface temperature in the feed boundary layer, and $T_{mp}$ is the membrane surface temperature in the permeate boundary layer. $T_{bf}$ and $T_{bp}$ are the bulk temperatures for the feed and permeate sides, respectively.

TPC is an important parameter for evaluating the membrane module designs in MD applications. In order to determine the membrane surface boundary layer temperatures of the feed and permeate, a heat balance should be performed by relating them to the bulk temperatures. To solve for the heat balance, the convective and conductive heat transfer coefficients must be determined. In general, the convective heat coefficients can be calculated from the Nusselt number using empirical correlations available in the literature, whereas, the conductive heat transfer coefficients of the membrane can be measured from their thermal conductivities and thickness [4, 5]. Therefore, a heat transfer analysis of both module designs was performed to measure the temperature polarization coefficient (TPC).

In the first region (Figure 4.3), the convective heat transfer occurring in the feed side from the liquid feed to the membrane surface is based on Newton’s law of cooling [8] and can be expressed [1, 2, 4, 5]:

$$Q_{conv,f} = h_f (T_{bf} - T_{mf}) \quad (4.2)$$

where $Q_{conv,f}$ (W/m$^2$) is the convective heat transfer flux in the feed stream, $h_f$ is the convective heat transfer coefficient (W/m$^2$ K) in the feed side, $T_{bf}$ is the bulk temperature in the feed side, and $T_{mf}$ is the membrane surface temperature in the feed side.

In the second region, total heat transfer occurring in the membrane side can be calculated by the following equation [1, 2, 4, 5]:
\[ Q_m = Q_v + Q_{\text{cond},m} \]  \hspace{1cm} (4.3)

Where \( Q_v \) is the evaporative heat transfer caused by vapor transport which is determined by the product of vapor water flux \( (J_{w,v}) \) and enthalpy of vaporization \( (\Delta H_v) \) [1, 2, 4, 5]:

\[ Q_v = J_{w,v} \Delta H_v \]  \hspace{1cm} (4.4)

The enthalpy of vaporization of water (kJ/kg) can be estimated by the following equation [6, 8]:

\[ \Delta H_v = 1.750 \, T_{mf} + 2024.3 \]  \hspace{1cm} (4.5)

\( Q_{\text{cond},m} \) is the conductive heat transfer flux (W/m\(^2\)) through the membrane materials. It is measured using Fourier’s law of conduction by assuming a linear temperature distribution between \( T_{mf} \) and \( T_{mp} \) [4, 8, 9]:

\[ Q_{\text{cond},m} = -k_m \frac{dT}{dx} = \frac{k_m}{\delta_m} (T_{mf} - T_{mp}) \]  \hspace{1cm} (4.6)

Where \( k_m \) is the thermal conductivity in the membrane side (W/m K), and \( \delta_m \) is the membrane thickness (m). Thermal conductivity in the membrane side involves both polymer and gas conductivities [8, 9]:

\[ k_m = \left( \frac{\epsilon}{k_g} + \frac{1-\epsilon}{k_p} \right)^{-1} \]  \hspace{1cm} (4.7)

where \( \epsilon \) is the membrane porosity, which was determined in the previous chapter using the gravimetric method, \( k_p \) is the thermal conductivity of the membrane material, and \( k_p \) is the thermal
conductivity of the gas filling the membrane pores. Once the thermal conductivity in the membrane is evaluated, then the conductive heat transfer coefficient \( h_m \) of the membrane can be found by diving over the thickness of the membrane [9]:

\[
h_m = \frac{k_m}{\delta_m}
\] (4.8)

In the third or last region, the convective heat transfer occurring in the permeate side can be measured [1, 2, 4, 5]:

\[
Q_{conv,p} = h_p (T_{mp} - T_{bp})
\] (4.9)

where, \( h_p \) is the convective heat transfer coefficient \( \text{[W/m}^2\text{K]} \) in the permeate side.

At steady state condition [9]:

\[
Q_{conv,f} = Q_{conv,p} = Q_m
\] (4.10)

Substituting Eqs. (4.2), (4.3), and (4.9) into Eq. (4.10), the following can be obtained:

\[
h_f (T_{bf} - T_{mf}) = h_p (T_{mp} - T_{bp}) = \frac{k_m}{\delta_m} (T_{mf} - T_{mp}) + J_{w,v} \Delta H_v
\] (4.11)

From eq. (4.11), the interfacial temperatures of the membrane surface in the feed and permeate sides can be estimated as shown in Eqs. (4.12 &4.13) [3, 9]:
\[ T_{mf} = \frac{k_m \left( T_{bp} + \frac{h_f}{h_p} T_{bf} \right) + h_f T_{bf} - J_w \Delta H_v}{k_m \delta_m + h_f \left( 1 + \frac{k_m}{h_p \delta_m} \right)} \] (4.12)

The convective heat transfer coefficients, \( h_f \) and \( h_p \), can be estimated from empirical correlations depending on the flow mode whether it is turbulent or laminar, whereas, the conductive heat transfer coefficients of the membrane, \( k_m \) or \( h_m \), can be measured from equations (4.8). The permeate flux \( (J_w) \) was already measured experimentally using the DCMD process for the two module designs. The enthalpy of vaporization of water presented in Eq. (4.5) should be first converted into \((J/kg)\) and then substituted into equation (4.15) to solve for \( T_{mf} \):

\[ T_{mf} = \frac{k_m \left( T_{bp} + \frac{h_f}{h_p} T_{bf} \right) + h_f T_{bf} - 2024300 J_w}{k_m \delta_m + h_f \left( 1 + \frac{k_m}{h_p \delta_m} \right) + 1750 J_w} \] (4.13)

\[ T_{mp} = \frac{k_m \left( T_{bf} + \frac{h_p}{h_f} T_{bp} \right) + h_p T_{bp} + J_w \Delta H_v}{k_m \delta_m + h_p \left( 1 + \frac{k_m}{h_f \delta_m} \right)} \] (4.14)

It should be noted that the enthalpy of vaporization of water presented in Eq. (4.5) can be easily measured since the \( T_{mf} \) is solved as presented in equation (4.16) which can be then used in equation (4.14). Furthermore, it is worth mentioning that equations (4.12 or 13 and 4.14) cannot be directly applied because other parameters are still unknown such as convective heat transfer coefficients \( h_f \) and \( h_p \), which requires the use of empirical equations. In particular, these two convective heat coefficients in the feed and permeate sides can be determined from Nusselt number [3]:
\[ h_f = \frac{N_u f k_{fl}}{D_h} \]  \hspace{1cm} (4.15)

\[ h_p = \frac{N_u p k_{pl}}{D_h} \]  \hspace{1cm} (4.16)

where the subscripts, \( l \), \( f \) and \( p \) stand for liquid, feed and permeate, and \( D_h \) is the hydraulic diameter determined depending on the module design used in the experiment. \( k_{fl} \) and \( k_{pl} \) are the thermal conductivities of liquid in the feed and permeate sides. To solve for the convective heat transfer coefficients (i.e. in Eqs. (4.15) & (4.16)) in the feed and permeate sides, Nusselt numbers must be calculated. In the literature, there is a number of correlations that can be used to estimate the Nusselt number for a laminar or turbulent flow [2]. However, the type of the flow (laminar or turbulent regime) must be determined via Reynolds number. Once the Reynolds number is found, then it is easy to select the empirical correlation depending on the nature of the flow and the membrane module design. Reynolds number is expressed as [2, 5]:

\[ Re = \frac{v D_h \rho}{\mu} \]  \hspace{1cm} (4.17)

where \( v \) is the flow velocity (m/s), \( D_h \) is the hydraulic diameter (m), \( \rho \) is the liquid density (kg/m3), and \( \mu \) is the liquid viscosity (kg/m s).

Determination of the hydraulic diameter for the MD module design based on its geometry is the first step to measure Reynolds number in equation (4.17). The hydraulic diameter can be expressed as follows [4]:

\[ D_h = \frac{4 A_c}{Pe} \]  \hspace{1cm} (4.18)
where $A_c$ is the cross sectional area of the liquid flow channel ($m^2$), and $Pe$ is the wetted perimeter (m). The hydraulic diameter in equation (4.18) can be substituted in equation (4.17) giving a Reynolds number in terms of volumetric flow rate ($m^3/s$) [4]:

$$Re = \frac{4Q \rho}{Pe \mu} \quad (4.19)$$

where $Q$ is the volumetric flow rate ($m^3/s$) that is the product of velocity ($m/s$) and cross sectional area ($m^2$).

Figure 4.4 presents the two module designs geometry utilized when measuring the permeate DCMD flux. The first module design has a rectangular duct shape, whereas the second module design contains a semi-circular piped shape allowing the liquid feed or permeate flows between the surface of the module design and the membrane surface. In particular, the rectangular duct shape consists of a channel length, width, and channel height of 100 mm, 50 mm and 3.26 mm, respectively (Figure 4.4a). The semi-circular pipe module design consists of 13 channels, and each has a diameter, channel length, and width of 6 mm, 500 mm and 6 mm, respectively (Figure 4.4b). These values were used to measure the wetted perimeter and cross sectional area for each module design to determine their corresponding Reynolds numbers:

$$Pe_A = 2 (z + y) \quad and \quad A_{c,A} = z \ y \quad (4.20)$$

$$Pe_B = \left( \frac{\pi d}{2} + d \right) \quad and \quad A_{c,B} = 13 \times \left( \frac{\pi d^2}{4} \right) \quad (4.21)$$

From equation (4.20), $Pe_A$ and $A_{c,A}$ are the wetted perimeter and cross sectional area, respectively which was used for the rectangular duct module design. The height of the liquid flow channel or
thickness in one module compartment is $z$, and its width is $y$. In contrast, $Pe_B$ represents the wetted perimeter for the semi-circular pipe module design where $d$ and $A_{c,B}$ are its diameter and cross sectional area. It should be noted that the cross sectional area in Eq. (4.21) is multiplied by 13 to consider the number of channels and it is divided by 2 to consider the semi-circular geometry.

![Figure 4.4: A schematic diagram of the module designs with dimensions for the DCMD process (a) Rectangular duct module design, (b) Semi-circular pipe module design](image)

For a laminar flow of $(Re<2100)$ and best recommended equation for flat sheet membrane module to compute the Nusselt numbers in the feed and permeate streams [2, 6, 10, 11], the following can be used, respectively:

$$Nu_{fL} = 1.86 \left( Re_{fL} \ Pr_f \frac{D_h}{x} \right)^{0.33}$$

(4.22)

$$Nu_{pL} = 1.86 \left( Re_{pL} \ Pr_p \frac{D_h}{x} \right)^{0.33}$$

(4.23)
where $Re_f$, $Re_p$, $Pr_f$, and $Pr_p$ are laminar Reynolds and Prandtl numbers measured at the feed ($f$) and permeate sides ($p$), respectively. $x$ is the channel length in the module design presented in Figure 4.4(a), and $D_h$ is its hydraulic diameter. Equations (4.22 & 4.23) were used to measure the Nusselt numbers for the laminar flow of the rectangular duct module design.

Prandtl number ($Pr$) is a fluid property; dimensionless number ranges from 1 to 13 for water. $Pr$ is defined as the ratio of the momentum diffusivity and thermal diffusivity of the fluid [11]:

$$Pr = \frac{C_p \mu}{k}$$

(4.24)

where $C_p$, $\mu$, and $k$ are the heat capacity, the dynamic viscosity, and the thermal conductivity of the fluid. Saline water feed (i.e. 1 M NaCl solution) and pure water permeate properties used to determine the dimensionless numbers are presented in Table 4.3. In contrast, the reported range for turbulent regimes is in the range of $2100 < Re < 125000$ [2]. In the case of the semi-circular pipe module design or the turbulent flow system, the following equation was used which was proved to be the most suitable correlation in literature for turbulent flow modes [2, 6, 12]:

$$Nu_f = 0.023 \left(1 + \frac{6d_h}{L}\right) Re_f^{0.8} Pr_f^{\frac{1}{3}}$$

(4.25)

$$Nu_p = 0.023 \left(1 + \frac{6d_h}{L}\right) Re_p^{0.8} Pr_p^{\frac{1}{3}}$$

(4.26)

where $Re_f$ and $Re_p$ are the turbulent Reynolds numbers measured at the feed ($f$) and permeate sides ($p$), respectively. $L$ is the channel length in the module design presented in Figure 4.4(b), and $D_h$ is its hydraulic diameter. Equations (4.25 & 4.26) were used to measure the Nusselt numbers for the turbulent flow of the semi-circular pipe module design.
4.4 Results and discussion analysis

4.4.1 Effect of Temperature on permeate flux

Temperature is the main parameter that significantly affects the performance of the MD process. This is due to the dependence of the water vapor pressure on the temperature. Increasing the feed temperature results in an increase in water vapors leading to an enhancement of the permeate flux. The two modules designs (i.e. rectangular duct, and the semi-circular pipe module designs) tested in this study showed an increase in permeate flux when increasing the temperature. Although the PVDF membranes tested in the two different module designs were identical, the obtained permeate fluxes exhibited a large difference from each other (Figure 4.5). The semi-circular pipe module design showed higher permeate fluxes (~3 or 3.5 times higher at feed temperatures of 60 or 70 °C, respectively) than that of the rectangular duct module design. The large difference in the permeate fluxes was mainly attributed to the nature flow or design the module design. Therefore, it can be anticipated that the semi-circular pipe module has a higher driving force than that of the rectangular duct module.

Figure 4.5: DCMD Permeate flux against the bulk feed temperatures for the two module designs with identical PVDF membrane properties
4.4.2 Flow nature determination analysis

The nature of the flow whether a laminar or turbulent, depends mainly on the hydraulic diameter of the module design, dynamic viscosities and the operative flow rates of the feed and permeate sides. In particular, Reynolds number indicates whether the system is under the laminar or turbulent regime. As already mentioned, a module design that has a Reynolds number less than 2100 possesses a laminar regime while higher than 2100 is considered to be under the turbulent regime [2]. As it can be seen from equations (4.17) and (4.19), increasing the hydraulic diameter or the flow rate in the numerator part of these equations results in an increase in the Reynolds number which in turn favors a turbulent flow regime. Also, from equation (4.17), the denominator part contains the dynamic viscosity of the fluid, which increasing or decreasing the dynamic viscosity influences the Re number.

The data of the dynamic viscosities of pure and aqueous sodium chloride (NaCl, 1 M) solutions at different temperatures already measured by [13] were used during the measurement of Reynolds numbers (Table 4.3). It should be noted that increasing the temperature of the feed solution reduces its dynamic viscosity which leads to an increase in the Re number. Moreover, Table 4.3 shows the data of the liquid thermal conductivities and water heat capacity for the feed and permeate sides. These data aided in determining the convective heat transfer coefficients for both module designs. The water heat capacity was rounded to 4.20J/K g since there are no significant variations with temperature. It was tabulated in the range of 4.18-4.19 J/K g from 232.15 to 353.15 K.
Table 4.3: Data of the feed and permeate fluid properties at different temperatures

<table>
<thead>
<tr>
<th>( T_{bf} ) (K)</th>
<th>( T_{bp} ) (K)</th>
<th>( k_{wf} ) (W/m k) ( (10^{-3}) )</th>
<th>( k_{wp} ) (W/m k) ( (10^{-3}) )</th>
<th>( \mu_{wf} ) (Pa. s) ( (10^{-4}) )</th>
<th>( \mu_{wp} ) (Pa. s) ( (10^{-4}) )</th>
<th>( C_p ) (J/K kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>293.15</td>
<td>596</td>
<td>603</td>
<td>10.90</td>
<td>10.0</td>
<td>4200</td>
</tr>
<tr>
<td>323.15</td>
<td>293.15</td>
<td>636</td>
<td>603</td>
<td>6.06</td>
<td>10.0</td>
<td>4200</td>
</tr>
<tr>
<td>333.15</td>
<td>293.15</td>
<td>646</td>
<td>603</td>
<td>5.20</td>
<td>10.0</td>
<td>4200</td>
</tr>
<tr>
<td>343.15</td>
<td>293.15</td>
<td>655</td>
<td>603</td>
<td>4.53</td>
<td>10.0</td>
<td>4200</td>
</tr>
<tr>
<td>353.15</td>
<td>293.15</td>
<td>663</td>
<td>603</td>
<td>3.99</td>
<td>10.0</td>
<td>4200</td>
</tr>
<tr>
<td>Ref.</td>
<td>[13]</td>
<td>[13]</td>
<td>[14]</td>
<td>[14]</td>
<td>[13]</td>
<td></td>
</tr>
</tbody>
</table>

The hydraulic diameter of the duct rectangular module was calculated based on the module design specifications (i.e. cross-sectional area and the wetted perimeter) and has a value of 0.006 m. On the other hand, the hydraulic diameter of the semi-circular pipe module design was determined to have a value of 0.049 m, which is larger than that of the rectangular duct module. The operating flow rates on feed and permeate streams for the DCMD experiments were set to 520 L/h, and 9 L/h for the semi-circular duct pipe, and rectangular duct modules, respectively. The hydraulic diameter of the semi-circular pipe module design and the operating feed and permeate flow rates were larger or higher than that of the rectangular duct module, therefore; it exhibited a turbulent regime. This was confirmed by measuring the Reynolds numbers of the two module designs at different feed dynamic viscosities of 1 M NaCl solution measured at different bulk temperatures (Figure 4.6a).
Figure 4.6: Results of the Reynolds numbers for the DCMD module designs in a) the hot feed side at different dynamic viscosities with different feed temperatures b) the cold permeate side at constant permeate dynamic viscosity measured at 20 °C with feed temperatures.

Furthermore, it can also be noticed from Figure 4.6a, the rectangular duct module design has smaller values of the feed Reynolds number than 2100 which represents a laminar flow regime. Also, Figure 4.6a shows the feed Reynolds numbers for the semi-circular pipe module. The values of $Re_f$ were found to be in the reported range of $2100 < Re < 125000$ [2] referring to a turbulent regime. It is worth mentioning that the feed dynamic viscosity decreases as the feed temperature increases which increases the Reynolds number as it was explained in equation (4.17).
The permeate Reynolds number for the rectangular duct and semi-circular pipe module designs determined at a constant permeate dynamic viscosity at 20 °C are shown in Figure 4.6b. The Re numbers in the permeate side for both module designs showed a constant value because they were measured at constant permeate dynamic viscosity obtained at 20 °C as the operative permeate tank temperature was 20 °C. Re number in the permeate side \( (Re_p) \) for the rectangular duct module was \( \approx 94 \) which is also lower than 2100 (a laminar flow). In the case of the semi-circular pipe module, Re number in the permeate side \( (Re_p) \) was 15600 which is larger than 2100 (turbulent flow). The higher values of Re number or the presence of the turbulent regime in the semi-circular module design was due to the higher operative flow rates (520 L/h) and the larger hydraulic diameter (0.049 m). On the other hand, the presence of the laminar flow in the rectangular module design was associated with lower flow rates (9 L/h) during the DCMD testing and the smaller hydraulic diameter value (0.006 m).

As the nature of the flow was determined for each module design, it was possible to select the empirical correlation for each type of flow. Equations (22-23) were used for the laminar flow whereas, equations (25-26) were used for the turbulent flow to measure Nusselt number. It can be noticed from these equations Nu number is related to the Re and Pr numbers. The calculated Prandtl number determined at the feed and permeate fluid properties is shown in Figure 4.7. It can be clearly seen the values of the Pr number are within the reported range of 2-13 for liquid water [11]. Moreover, the Pr number for the feed aqueous NaCl solution decreases as the temperature decreases because of the dependence of the dynamic viscosity on temperature (Figure 4.7).
4.4.3 Analysis of convective heat transfer coefficients

Since the Reynolds and Prandtl numbers were evaluated for each module, the Nusselt numbers were determined. Calculation of the Nusselt number for each membrane module allowed the determination of the convective heat transfer coefficients in the feed and permeate sides as described by equations (4.15 & 4.16). Table 4.4 shows the estimated convective heat transfer coefficients on the feed and permeate sides for the rectangular duct (laminar) and semi-circular pipe (turbulent) module designs at different bulk feed temperatures (323.15-353.15 K or 50-80 °C) and at a constant permeate temperature (293.15 K or 20 °C). The rectangular module design shows low heat transfer coefficients in the feed and permeate streams compared to the semi-circular pipe module design which reflects the lower flow turbulence. This also demonstrates the presence of the laminar flow in the rectangular module design. On the contrary, the semi-circular pipe module design exhibited a substantially high feed and permeate heat transfer coefficients (i.e. more than
6-fold higher than that of the rectangular duct module design). The higher heat transfer coefficients for the semi-circular module reflects the appearance of the turbulent flow regime.

**Table 4.4:** Convective heat transfer coefficients in the feed and permeate sides for the laminar and turbulent flow measured using empirical correlations at identical feed and permeate flow rates of 9 L/h for the laminar regime and 520 L/h for the turbulent regime.

<table>
<thead>
<tr>
<th>Bulk Temperatures (K)</th>
<th>Convective heat transfer coefficients (W/m$^2$ K)</th>
<th>Laminar flow</th>
<th>Turbulent flow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$h_{fL}$</td>
<td>$h_{pL}$</td>
</tr>
<tr>
<td>Feed</td>
<td>323.15</td>
<td>658.34</td>
<td>619.12</td>
</tr>
<tr>
<td>Permeate</td>
<td>293.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>333.15</td>
<td>668.70</td>
<td>619.12</td>
</tr>
<tr>
<td></td>
<td>343.15</td>
<td>678.01</td>
<td>619.12</td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>686.30</td>
<td>619.12</td>
</tr>
</tbody>
</table>

Increasing the bulk feed temperature shows an increase in the feed heat transfer coefficients for both module designs (Table 4.4). The heat transfer coefficients for the feed laminar flow shows a little increase with bulk feed temperatures (e.g. 1.5% increase from 323.15 to 333.15 K), whereas the heat transfer coefficients for the turbulent regime increases by 9.1% when the temperature changed from 323.15 to 333.15 K. The increase of heat transfer coefficients with temperature is generally due to the dependence of temperature on water physical properties, and it is also due to the design specification of the module, and operating flow rates [4].

### 4.4.4 Temperature polarization analysis

Table 4.5 lists the estimated membrane interface temperatures measured using the energy heat balance between hot and cold streams for the laminar and turbulent module designs. It is well known that DCMD processes suffer from temperature polarization effect, which lowers the driving force [2]. In other words, the bulk temperatures are different from the actual interface temperatures.
Estimating \( T_{mf} \) and \( T_{mp} \) from equations (4.12 or 13 &4.14) and knowing the bulk feed and permeate temperatures allowed the calculation of the temperature polarization coefficient (TPC) from equation (4.1). The permeate fluxes for the tested module designs were far different from each other even though the membrane properties were identical. To explain this large variations in the permeate flux, the temperature polarizations coefficients (TPCs) for each module design were determined. The reported TPC values for a typical DCMD process has a range of 0.40-0.70 [1].

Table 4.5: Result of the membrane surface temperatures in the feed and permeate membrane surfaces with bulk temperatures for rectangular duct module (laminar), and semi-circular pipe module (turbulent).

<table>
<thead>
<tr>
<th>Bulk temperatures</th>
<th>Laminar module</th>
<th>Turbulent module</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>design</td>
<td>design</td>
</tr>
<tr>
<td>( T_{bf} )</td>
<td>(K)</td>
<td>(K)</td>
</tr>
<tr>
<td>( T_{bp} )</td>
<td>(K)</td>
<td>(K)</td>
</tr>
<tr>
<td>( T_{mf} )</td>
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<td>( T_{mp} )</td>
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<td>325.57</td>
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<td>353.15</td>
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Figure 4.8 depicts the result of the TPCs at different bulk feed temperatures for the module designs or in other words, for the flow regimes. The turbulent module design showed a considerably high increase in TPC compared to that of the laminar module design. For instance, the turbulent module design exhibited 22.4% increase in TPC at 323 K or 50 °C from that of the laminar module design. This demonstrates the higher permeate fluxes for the turbulent module design. The reported range of TPC for an acceptable DCMD module design is within the range of 0.40 to 0.70 [1] and the turbulent module design is within this range as depicted in Figure 8.
However, the rectangular module design were found to be less than 0.40 which indicates that it is a poor design.

Moreover, the larger values of TPC for the turbulent module design can also be attributed to the high values of the convective heat transfer coefficients (Table 4.4). Increasing the convective heat transfer coefficients minimizes the boundary layer resistance between the bulk temperature and the liquid-vapor interface, which causes the bulk temperatures to be close to the membrane surface temperatures (leads to a high TPC). To sum up, this study suggests that the performance of DCMD is not only dependent on the membrane properties but also to the module design or process conditions. Also, it suggests that the turbulent module design is better than the laminar module design particularly at higher flow rates and feed temperatures.

![Graph showing the effect of bulk feed temperatures on temperature polarization coefficient (TPC) for the DCMD module designs. The feed and permeate flow rates: 520 L/h for the semi-circular pipe module, and 9L/h for the rectangular module.](image)

**Figure 4.8:** Effect of bulk feed temperatures on temperature polarization coefficient (TPC) for the DCMD module designs. The feed and permeate flow rates: 520 L/h for the semi-circular pipe module, and 9L/h for the rectangular module.
4.5 Conclusion

Heat transfer analysis has been addressed for two different module designs (i.e. semi-circular pipe and rectangular duct module designs) exhibiting two different flow regimes. The semi-circular pipe module design showed higher Reynolds numbers (Turbulent flow) (65918-98721) at different dynamic viscosities. The obtained Re numbers for the semi-circular pipe module lie within the reported range for turbulent regimes. Re number values in the feed side were increased with increasing the bulk feed temperature whereas; the feed dynamic viscosity decreases with temperature. On the other hand, the rectangular duct module design displayed a lower Reynolds number in the range of (158-241) (laminar flow). The permeate fluxes for all module designs increased with increasing feed convective transfer coefficients. Therefore, semi-circular module design exhibited a more permeate flux, 3-fold higher than that of the duct rectangular module design at the feed temperature of 333.15 K or 60 °C due to its higher feed transfer coefficients.

The convective and conductive heat transfer coefficients for each module design increased with bulk feed temperatures. The effect of temperature on the feed side for the convective heat transfer coefficients was more significant than that of the permeate side. The membrane surface temperatures of the turbulent module design were close to that of the bulk temperatures indicating the effect of temperature polarization was not significant. In contrast, the effect of temperature polarization was significant for the laminar module design. In summary, this study suggests that working with turbulent module design exhibiting high flow rates and feed temperatures is recommended for high water productivity.
4.6 REFERENCES


