Membrane distillation : surface modification, module modeling and system optimization

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**MEMBRANE DISTILLATION: SURFACE
MODIFICATION, MODULE MODELING AND SYSTEM
OPTIMIZATION**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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ABSTRACT

Membrane distillation (MD) is an emerging membrane technology that can be applied for seawater desalination. Though boasting a promising future for industrial application, several technical challenges still need to be tackled, including membrane wetting and fouling, relatively low membrane permeability, concentration/temperature polarization effect, uncertainty of economic benefit, etc. Therefore, novel membrane development and improved module design will offer effective strategic solutions to these challenges.

This thesis provides a comprehensive review of previous studies on MD with a focus on the areas of membrane wetting and fouling, especially when seawater contains spilled oil. Moreover, membrane module modeling and system optimization in terms of energy and economic analysis were also investigated.

As the starting point, a preliminary study aimed to develop an effective strategy for modifying hydrophobic membranes. The modified polyvinylidene fluoride (PVDF) membrane shall be able to tolerate salty feed solution containing mineral oil. A novel approach was explored to obtain a highly hydrophilic membrane surface via plasma induced grafting of polyethylene glycol (PEG) and TiO_2 doping. A series of characterizations were conducted for the virgin and modified membranes. Scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) measurements confirmed the presence of PEG and TiO_2 particles on the PVDF

membrane substrate. The mechanism of oil affinity onto a membrane surface was quantitatively investigated by Extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory. Membrane distillation tests of synthetic oil-containing seawater were also performed to investigate the influences of membrane hydrophobicity, membrane surface structure, pH value of the feed solution and hydrodynamic conditions on oil fouling behavior. The hydrophilically modified PVDF-PT membrane exhibited a positive interfacial free energy with oil in the feed, indicating the TiO_2 deposition effectively improved the anti-fouling property of PVDF-P membrane and PVDF membrane. It also showed that the PVDF-PT membrane presents a stable water flux for over 24 h operation without fouling and wetting due to the combination effects of enhanced surface hydrophilicity and reduction of membrane pore sizes. In addition, the pH value of the feed solution plays an important role in oil fouling. More severe fouling can be observed at the pH, for which the membrane surface and oil droplets carry opposite charges. Moreover, a higher flow velocity enhanced the shear force exerted on the oil droplets, leading to the low level of oil present on the membrane surface and less oil fouling occurring on the membrane.

As a continuation, in order to have a better understanding of MD process, a two-dimensional (2D) numerical model was developed to provide the profiles of temperature, velocity and pressure in the vacuum membrane distillation (VMD) module. Unlike the conventional semi-empirical correlations, the novel model comprising energy conservation, momentum transport and continuity governing equations, together with the featured boundary conditions, was then solved by finite element method (FEM). The simulation results and the experimental results were in good agreement with each other, which confirmed the validity of the 2D model. Based

on the model, genetic algorithm (GA) was applied to optimization process by considering four design and operation variables related to the water production cost(WPC) which is defined as total cost over production, including feed temperature, hollow fiber length, feed volume flow rate and vacuum pressure. Furthermore, a case study was presented and the results indicated that optimized VMD process decreased WPC up to 38.1% compared with the non-optimized VMD process. In addition, sensitive analysis was performed to investigate the effects of design and operation parameters on WPC by a quadratic model. The guidance for reducing the WPC was provided as the following: the feed temperature should be adopted as high as possible; the hollow fiber length should be taken short; the flow rate should be opted for a lower bound value; and the degree of vacuum should be moderate. The objective of this study was to identify the optimal conditions for design and manage the MD process effectively, under a given MD production capacity and operation constraints.

Lastly, to modify the MD system, the optimization study based on commercial software package - Aspen plus platform has been conducted. The heat and mass transfer of the MD module were programmed using Matlab. The subsequent simulated module was then incorporated into the MD system on the Aspen plus platform. The MD system performance have been investigated by considering various operation variables and system arrangements, such as membrane area, feed velocity, permeate velocity, temperature difference in the heat exchanger. In addition, the energy and economy of existing MD systems have also been analyzed, followed by system optimization using a state-of-the-art software, Aspen plus. Simulation results revealed the existence of a critical membrane area, below which, a significant increases of water production and the gain output ratio (GOR) were observed with an increase of the membrane area. A significant drop in WPC can be expected. The

increase of feed temperature had a positive impact on the water flux, water production and the GOR value. Also, high feed and permeate velocities can help to increase the water flux, water production and the GOR value. However, by considering the WPC, the optimum fluid velocities were observed, beyond which, the penalty of energy input in the form of electricity consumption for pumping was increased significantly. It was also found that when the temperature difference of the heat exchanger exceeded 6 °C, the WPC can be reduced considerably by cutting down the heat exchanger cost.

Overall, it is expected that the study can help sought potential strategies to address the challenges for the practical application of MD process, such as reduction of membrane fouling by oil contamination, MD module modeling and system optimization, through better design and optimized operation conditions.

Keywords: membrane distillation, membrane surface modification, anti-oil fouling, module modeling, process simulation, system optimization, energy efficiency, economic analysis.

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LIST OF SYMBOLS

A_{MEM}	Membrane area, m^2
A_{HX}	Heat exchanger area, m^2
a, b, c	Depreciation rate of membrane module, heat exchanger and related installation components, respectively.
C	Membrane distillation coefficient, $kg \cdot m^{-2} \cdot h^{-1} \cdot kPa^{-1}$
d_h	Hydraulic diameter of the flowing channels, mm
d_i	Inner diameter of the hollow fiber, mm
F_c	Tube-row correction factor
h_f	Boundary heat transfer coefficients from feed side, $W \cdot m^{-2} \cdot K^{-1}$
h_m	Heat transfer coefficient of the membrane, $W \cdot m^{-2} \cdot K^{-1}$
h_p	Boundary heat transfer coefficients from permeate side, $W \cdot m^{-2} \cdot K^{-1}$
ΔH	Latent heat of evaporation, $kJ \cdot kg^{-1}$
k_m	Thermal conductivity of liquids, $W \cdot m^{-1} \cdot K^{-1}$
L	Effective fiber length, mm
M	Molecular weight of component, kg/mol

N	Vapor flux, $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$
Nu	Nusselt number
P	Partial pressure, kPa
Pr	Prandtl number
P	Price, \$
Q	Heat flux, $\text{W} \cdot \text{m}^{-2}$
Re	Reynolds number
T	Temperature, °C
ΔT	Temperature difference, °C
W	Electricity work, KW·H
u	Flow velocity of feed or permeate, m/s
Δx	Increment in x direction, mm
Δy	Increment in y direction, mm

Greek letters

ε	Membrane porosity, %
ϕ	Module packing density, %
τ	Membrane tortuosity
δ_m	Membrane thickness, μm
μ	Viscosity of the fluids, $\text{Pa}\cdot\text{s}^{-1}$
ρ	Liquid density, g/cm^3
η	Thermal efficiency of the DCMD module
γ	Surface tension, N/m
λ	Thermal conductivity of fluids, $\text{W}/\text{m}\cdot\text{K}$

Suffix

e	Electricity
i	Stream side, $i=f$ or p
f	Feed side
fm	Membrane surface at feed side
i	Inlet

<i>o</i>	Outlet
<i>m</i>	Membrane
<i>p</i>	Permeate side
<i>pm</i>	Membrane surface at feed side
<i>s</i>	Steam

CHAPTER 1 INTRODUCTION

1.1 Background

The past decades have witnessed several-folds increase in human population and industrial production, which thus lead to a tremendous demand for clean and potable water. Although water covers the majority of the earth surface, only a small portion is fresh water. To solve the problem of shortage of drinking water, several processes have been developed for the desalination of seawater. Compared to conventional desalination processes such as distillation-based multi-stage flash (MSF) and multiple-effect distillation (MED) technologies, and membrane-based processes, such as reverse osmosis (RO), membrane distillation (MD) is a relatively innovative approach that combines the features of membrane and distillation technologies. RO technology has been widely used for desalination, while MD technology is still under development as a promising alternative in the future. MD process utilizes the vapor pressure gradient across a hydrophobic microporous membrane as the driving force for mass transfer. Due to the hydrophobic characteristics, the liquid cannot pass through the membrane pores. In comparison with other separation technologies, MD possesses the following competitive advantages as a desalination technology:

- 1) It can produce water of high quality;
- 2) The process is at a moderate temperature and ambient pressure;
- 3) It can utilize low grade heat (i.e. solar power, waste heat from industry);

- 4) It does not require extensive pretreatment as other pressure-based membrane processes such as RO and nanofiltration (NF).

1.2 Challenges

Although MD has been investigated for decades, it is yet to be applied for large scale industrial applications, as several challenges still exist in MD technology. These challenges are summarized as the following:

- 1) MD process consumes a relatively high cost for water production in comparison with RO based desalination process if low grade or waste heat is not available;
- 2) MD exhibits a high tendency of membrane wetting due to the non-uniform pore size distribution and less hydrophobicity of the membrane surface;
- 3) It requires novel membranes with high water permeability and low heat conductivity;
- 4) It requires module and system design to enhance heat and mass transfer conditions(Lawson and Lloyd 1997).
- 5) In the case of seawater desalination, it may suffer serious fouling problem rendered by spilled or discharged oil since hydrophobic polymer materials of MD membrane are oil non-repellent.

1.3 Objective of the thesis

The objectives of the thesis are to shed light on some of these challenges. In general, four major aspects will be investigated to improve MD process:

- 1) Modification of the membrane surface to obtain anti-oil fouling property facilitated by plasma induced grafting;
- 2) 2D model development of the fluid flow in MD module for better performance prediction;
- 3) Systematic analysis of energy efficiency and economic benefits of the MD module and system;
- 4) Investigation of operation and investment strategies of MD process. Stream temperature, flow velocity, membrane area and heat exchanger area were all considered for the optimization of the MD system.

To achieve these objectives, novel membrane development via membrane modification is needed in order to obtain anti-wetting and low oil-fouling membrane for MD process. The inner pores for MD application should demonstrate hydrophobic character to prevent water wetting, while the modified outer surface layer shows hydrophilic character to avoid membrane fouling in seawater with the presence of oil droplets. The hydrophilic agent such as Polyethylene glycol (PEG) and TiO_2 will be grafted to the PVDF membrane surface via the state-of-the-art plasma technology. Hydrophobicity, pore size/pore size distribution, mass flux, etc. are taken into

consideration in comparing commercial flat sheet membranes with modified membranes. The factors influenced the oil fouling on membrane will be investigated including hydrophobicity, pH value, flow velocity and pore size/pore size distribution.

Additionally, the design and optimization of the MD module and system by means of modeling and simulation will be performed. The previous semi-empirical modeling needs to be improved for MD module, in order to achieve more accurate dynamic predication on temperature, pressure and velocity profiles. To simulate and optimize the integrated system, the modeled MD module will be incorporated into the MD system on Aspen plus platform. The guidance of design and operation conditions of MD, such as the fluid dynamic, feed temperature, the membrane usage and the heat exchanger usage, will be systematically investigated, which can be applied for developing more economic MD systems.

1.4 Thesis outline

The thesis includes six chapters, which are highlighted as the following:

Chapter 1: Introduction - Background, challenges, objectives and thesis outline are provided.

Chapter 2: Literature review – A comprehensive literature review is presented in chapter two, which contains the basic concept, mechanisms and configurations with

respect to membrane distillation, especially for direct contact membrane distillation (DCMD) and vacuum membrane distillation (VMD) process. It outlines two major strategies for the improvement of MD process, namely membrane modification and process optimization. Preliminary literature review on anti-oil fouling modification will shed light on next stage experiments. Various cutting edge technologies regarding the modification are carefully reviewed to provide guidance for future research. On the other hand, the semi-empirical and CFD methods are reviewed for developing more efficient MD modeling; previous studies for the improvement of MD process, especially on design and operation conditions have been summarized. The energy and economic analysis have also been reviewed.

Chapter 3: Novel membrane surface modification to enhance anti-oil fouling property for membrane distillation application—The commercial PVDF flat sheet membranes are modified by PEG and TiO_2 facilitated by helium plasma treatment to produce a hydrophilic membrane surface. The characterization of the modified membranes and the discussions on the influential factors including hydrophobicity, pH value, flow velocity, pore size/pore size distribution are presented.

Chapter 4: Numerical modeling and optimization of vacuum membrane distillation module for low-cost water production—Numerical modeling based on finite element method is conducted to provide the profiles of temperature, pressure and velocity. Four module design and operation conditions are investigated for MD system optimization by using genetic algorithm (GA). The comparison of optimized and non-optimized MD systems is performed in terms of water production cost (WPC)

and the guidance for module and system design is thus provided.

Chapter 5: Energy efficiency evaluation and economic analyses of direct contact membrane distillation system using Aspen Plus—It presents the optimization and simulation results of the MD system in this chapter. A comprehensive cross-flow model, in terms of heat and mass transfers, is programmed by using Matlab. Then, Aspen Plus platform is used to build up the flow diagram of the MD system for investigation of the system performance. Design and operation variables have been considered for the energy and economic analysis. Specifically, feed temperature, feed and permeate flow rate, membrane usage as well as temperature difference in a heat exchanger have been investigated. In the end, a comprehensive energy and economic analysis have been presented in the hope of providing a guideline for the future industrialization of MD process.

Chapter 6: Conclusions and recommendations – The important findings and conclusions of this thesis and recommendations for future work are presented in this chapter.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This review provides a comprehensive review of the membrane distillation (MD) process. Focuses are given on membrane surface modification for anti-oil fouling property, membrane module modeling, process simulation and system optimization. In membrane modification part, hydrophilic modification will be mainly reviewed. Later, previous membrane module modeling works including the conventional semi-empirical correlations and computational fluid dynamics (CFD) are to be summarized. Lastly, the optimization related topics, such as key design and operation conditions, analysis of energy and economic issues have also been reviewed systematically.

2.1.1 Membrane distillation history

In 1967, Weyl applied for a patent of a technique, which was considered as the prototype of MD. The process utilized temperature difference as the driving force for water recovery and multistage heat recovery. (Lawson and Lloyd 1997). Two years later, Findley carefully studied the MD process and proposed some important

characteristics, including high heat transfer resistance, thin membrane, hydrophobic material, high porosity and small tortuosity (Findley, Tanna et al. 1969). With the continuous development of polymer science and technology, the first wave of MD research emerged. In 1972, Rodger proposed several polymer materials that well suited MD process, including Polytetrafluoroethene (PTFE), Polyvinylidene fluoride (PVDF) and Polypropene (PP). It was also suggested the feasibility of hydrophobic surface modification to the hydrophilic membrane, which was later regarded as a great inspiration for the novel membrane development (Lonsdale 1982). Starting from 1980s, Gore pioneered the industrial application of MD and finished the pilot plant test of Gore-Tex membrane system (Gore, Gore et al. 1985). Hanbury believed that two requirement were necessary for industrial application of MD, including the reduction of membrane cost and improvement of heat recovery (Hanbury and Hodgkiess 1985). Later on, more work started to focus on optimization of operation parameters for flux enhancement (Schneider, Hölz et al. 1988). It was realized that the feed temperature, flow velocity and vacuum are among the key factors to improve the MD performance. During this period, temperature polarization and concentration polarization were recognized as the major barriers for flux enhancement (Schofield, Fane et al. 1990). Therefore, novel module design with baffle, spacer, bubbling, which can significantly minimize the polarization effect, has attracted much attention (Brewster, Chung et al. 1993, Lawson and Lloyd 1996, Teoh, Bonyadi et al. 2008). From the late 1990 s towards now, MD research has experienced another outbreak in the number of publications. Although, there is no important breakthrough in study on the mechanism, some progresses are still worth the attention. For example, Lawson applied the dusty gas model to unify the mass transfer process of MD from the statistical point of view (Lawson and Lloyd 1997). During this period, research started to pay more attention on the optimization of the system configuration and operation conditions, indicating the trend of progressive pilot or even industrial applications of

MD technology (Gilron, Song et al. 2007, Chang, Liao et al. 2009).

2.1.2 MD configurations

MD has four major configurations: (1) direct contact membrane distillation (DCMD), (2) air gap membrane distillation (AGMD), (3) vacuum membrane distillation (VMD) and (4) sweep gas membrane distillation (SGMD). The four configurations are introduced as follows:

(a)

(b)

(c)

(d)

Fig.2. 2 MD configurations (a) DCMD configuration; (b) VMD configuration; (c) AGMD configuration; (d) SGMD configuration

1. DCMD configuration has firstly been patented and is still attracting most of the attention in MD research. The schematic of DCMD is as shown in Fig. 2.1a. The process applies the hydrophobic membrane as the interface to separate hot feed stream from cool permeate stream. The water vapor is passes through the membrane pores at the driving force of pressure gradient caused by temperature difference. The major drawback of the configuration is that a large portion of the heat is lost by heat conduction via membrane matrix, due to the ‘direct contact’ of the streams of distinct temperature difference.

2. VMD is as shown in Fig. 2.1b. VMD concept has been developed to induce large pressure gradient across the membrane by applying high degree of vacuum in the downstream side. During the process, the pressure difference between the upstream feed side and the downstream vacuum side serve as the driving force for mass transfer; Due to no direct contact of hot and cool streams, heat loss by conduction can be significantly reduced.

3. VMD is shown as in Fig. 2.1c. The process works by introducing an extra air gap between the membrane and cool permeate stream, so that no direct contact of hot and cool streams inside the membrane module. This configuration is featured of relatively high energy efficiency. However, the major drawbacks are the increased resistance for

mass transfer and complicate membrane module, which make it a challenge for application.

4. SGMD is as shown in Fig. 2.1d. This configuration has been considered to be similar to AGMD. The difference is the application of sweeping gas for vapor transport and final condensation at a cooler. Therefore, the disadvantage is that extra gas source and pumping are required, making it not economic viable in comparison with other configurations and thus less favored.

According to the above discussion, DCMD has been recognized as the simplest configuration and is mostly used in the lab-scale MD study among the four configurations. In addition, VMD is featured of negligible conductive heat loss with a reduced mass transfer resistance and possesses a very high efficiency of energy consumption (Bandini, et al., 1997; Khayet et al., 2000). Therefore, in this thesis, DCMD and VMD configurations will be the major configurations to be discussed.

2.1.3 Limitations of MD

Based on the mechanism of MD process, the membrane materials are essentially hydrophobic to prevent liquid water from entering into the membrane pores, which might cause membrane wetting. Therefore, the materials in MD application are typically hydrophobic polymer including PTFE, PVDF, PP and etc. However, the

hydrophobic interaction between the membrane surface with low surface tension and the hydrophobic species such as organic compounds in seawater can potentially lead to more organic fouling on membrane surface due to the hydrophobic interaction. The attached organic compounds might block the surface pores of the membrane and lead to reduction of membrane permeability (Zuo, Wang et al. 2013). Even worse, the organic foulant can penetrate through the membrane pores and contaminate the permeate side, which is highly undesirable in MD.

Temperature polarization (TP) is another challenge to MD technology because it causes the energy inefficiency to the process. Intrinsically, TP can be explained as follows: the temperature difference ($T_{fm} - T_{pm}$) across the membrane is lower than the bulk temperature difference ($T_f - T_p$) because of the existence of the thermal boundary layer in both sides, which was shown in . The presence of temperature gradient within the boundary layer adjacent to the membrane surface leads to reduction of vapor pressure difference across the membrane, therefore resulting in lower permeate flux and thermal efficiency. It is acknowledged that the degree of TP is strongly dependent on the fluid dynamics conditions inside the membrane module and it can be effectively mitigated by the optimization of the operation conditions and proper design of membrane module.

Fig.2. 3 Principle of DCMD and the associated polarizations (Bui, Vu et al. 2010)

In addition, since phase conversion phenomenon (liquid-vapor-liquid) is involved in MD process, it is an energy-intensive process from the perspective of thermodynamics. When conventional energy such as electricity or fossil fuels is supplied as the heating source, water production cost can be too high to compete with other processes. To reduce the cost, cheap energy resource, such as low grade heat and solar energy shall be considered to apply to achieve a moderate operation cost. These novel MD systems have attracted the most attention and been explored tremendously in recent years (Hogan, Sudjito et al. 1991, Banat, Jumah et al. 2002, Koschikowski, Wieghaus et al. 2003, Ding, Liu et al. 2005, Banat and Jwaied 2008, Gomri 2009, Wang, Zhang et al. 2009, Chang, Wang et al. 2010). However, it is still resting on the investigation stage of lab-scale MD set up and leaving several challenges yet to be tackled, i.e. the fabrication and assembly of large number of membrane modules and potential deterioration of MD performance over time (Blanco Gálvez, García-Rodríguez et al. 2009). Therefore, no large-scale MD system, which is powered by low cost energy, has ever been built and it is difficult to estimate economic benefit of such systems.

Although, it has been decades since the MD process was patented in the 1960s, the interest within the academic community has never diminished, especially when novel high performance membranes became available. The benefits of MD process as a seawater desalination technique have been realized by more and more fellow scholars and researchers. In general, to economically implement MD technology in industry, the main barriers include (Burgoyne and Vahdati 2000): (1) Lack of specially designed and fabricated membranes for MD process; (2) Concentration and temperature polarizations, leading to the decrease of driving force for mass and heat transfer; (3) Pore wetting phenomenon caused by low liquid entry pressure and solute-membrane interactions; (4) Relatively low permeate flux; (5) Poor long-term performance without an attainable flux.

In order to overcome these challenges, attention should be paid to the following critical issues: (1) Developing novel high-performance membranes for MD process. From the beginning until recent years, the membrane used in MD application was ‘borrowed’ from Microfiltration (MF) and suffered from some severe drawbacks including non-homogeneous pore size distribution, which might cause the membrane pore wetting very easily. Novel MD membrane shall possess a relatively narrow pore size distribution. Moreover, membrane fouling in MD process shall not be underestimated, since seawater indeed contains a certain level of oil possibly discharged by the onshore industry or the oil spillage from the oil tank, which might severely foul the membrane surface, especially when the membrane materials are intrinsically hydrophobic PTFE, PVDF and PP materials. These low surface tension polymers can attach the organic species such as oil droplets easily due to the hydrophobic interaction, which will be elaborated in later sections;

(2) Optimization of the operation variables in the MD module and system. In order to optimize the MD module and system, a proper MD modeling is required. Previously, the MD modeling is based on the semi-empirical heat transfer model, which is very similar to the conventional heat exchanger. The basic difference between MD module and heat exchanger is the porous structure of the membrane and the rigid structure of the shell. MD process is an integrated process which combines heat and mass transfer across the porous structure of the membrane; while there is only heat transfer in heat exchanger. Therefore, to properly understand MD process, a more accurate model which integrates heat and mass transfer and represents the characteristics of the porous membrane structure is required. With the modeling and subsequent solution, a more accurate temperature field and flow field can thus be obtained, which can provide better guidance for MD module and system design and optimization.

In the following sections, the review will focus on the following topics: 1) membrane modification for anti-oil fouling surface via different state-of-the-art technologies; 2) the conventional semi-empirical and CFD module modeling; 3) the key factors of MD system that relate to the optimization, and 4) the analysis of energy consumption and economic benefits as well as the pilot MD system study.

2.2 Membrane modification

As previously introduced, membrane materials should be hydrophobic to prevent the liquid from entering into the membrane pores, which is known as membrane wetting.

Membrane wetting has always been a serious problem for MD process (Lawson and Lloyd 1997). In general, two major strategies of surface modification for MD membrane were proposed (Yang, Wang et al. 2011): one is to perform hydrophobic coating or grafting to reduce the maximum pore size and obtain a relatively even pore size distribution; the other is to perform hydrophilic coating or grafting to protect membrane pore mouth from liquid wetting. As one major objective of this thesis is to desalinate oil-containing seawater and hydrophilic modification can effectively minimize the attraction force between the oil species and the membrane material, therefore the following review will mainly focus on the hydrophilic surface modification methods for MD membranes. Generally speaking, there are several kinds of methods for membrane surface modification, including dip-coating, chemical treatment, UV treatment, and plasma treatment (Liu, Hashim et al. 2011). As dip-coating suffers the drawback of easily washing away by flowing liquid and will be excluded in the scope of the thesis. In addition, PVDF is very robust against most of the chemical agents, except for strong base such as sodium hydroxide. Immersing PVDF membranes in high concentrated sodium hydroxide followed by crosslinking has been reported in several published literature (Wongchitphimon, Wang et al. 2011).

However, it also has the weakness of reduced mechanical strength and discoloration, which are not desirable for the application. In the thesis, plasma treatment, as a state-of-art technique, will be mainly reviewed in the following section as it has been acknowledged to be an effective strategy for PVDF membrane modification (Zuo, Wang et al. 2013).

2.2.1 Plasma approach

Plasma technique was firstly introduced by Tonks and Langmuir in the work, referring to the electric gas in the vacuum tube (Tonks and Langmuir 1929). Plasma can be generated under certain severe conditions such as high temperature, combustion, laser, and nuclear reaction. Plasma modification is roughly categorized into plasma treatment, plasma polymerization and plasma-induced grafting (Yasuda 2005). The major differences among the three processes are the following aspects: the gas in plasma processing which includes simple molecular or complicate organic compounds and the reactive mechanisms.

Basically, plasma treatment involves the surface etching, where reactive atoms or ions (i.e. oxygen, chlorine, and fluorine) are produced in a low-pressure atmosphere. The reactive species is accelerated at the boundary region, which is located between the plasma and the substrate. The activated species is featured of high directivity and capability of creating deep grooves of steep walls. After the treatment, a considerable change in the surface structure can be observed because of the anisotropic etching in the surface layers. Plasma treatment can usually help to form hydrophilic groups on the surface to achieve hydrophilic modification.

Plasma polymerization refers to stimulated monomer polymerization under low pressure. And then, the formed polymer will deposit onto the membrane surface. The process is featured as the initial step to produce reactive sites on the surface, and then

the grafting of the polymerized monomer chain. Hydrophilic polymer thin films can be deposited on membrane surface by plasma polymerization so as to alter the surface tension of the membrane. Moreover, by selecting the monomer type and the energy density per monomer, the chemical composition and structure of the resulting thin film can be varied in a wide range (Yasuda 2005).

Plasma-induced grafting is a method to graft the functional monomers onto the membrane surface to form a layer of brush-like polymers. The advantages include the chemical bonding between the grafting layer and polymer surface, controllable surface coverage and high grafting yield. Unlike the other methods, the grafting layer can steadily anchor to the polymer surface by chemical bonding to prevent from being washed away by liquid flow. As mentioned in the previous section, it has been suggested that the hydrophobic interaction between the organic foulants such as the hydrophobic oil species and hydrophobic polymer surface might facilitate the membrane fouling during MD process. Therefore, hydrophilic grafting is usually employed to reduce the organic fouling.

Generally, the plasma-induced grafting process comprises two consecutive processes, including the surface activation by plasma ignition and the surface grafting. Its mechanism is shown in .

Fig.2. 4 Two mechanisms of plasma-induced grafting (Gancarz, Poźniak et al. 1999)

Plasma-induced grafting technique is an easy, stable and controllable method for membrane surface modification. Wavhal and Fisher modified Poly(ether sulfones) (PES) membranes by Argon plasma treatment and then grafted acrylamide (AAM). It was found that the treated membrane encountered less bovine serum albumin (BSA) fouling and greater flux recovery after cleaning (Wavhal and Fisher 2002). Besides, acrylic acid (AA) is also a popular monomers used in plasma-induced grafting because it is relatively cheap and can be easily polymerized to graft onto its polymer surface. For example, Toufik et al. used AAM and AA to graft poly (ethylene terephthalate) (PET) membrane after oxygen plasma treatment and it was found that flux was increased and the rejection rate of Dextrans were not affected (Toufik, Mas et al. 2002). Gancarz reported a very high grafting yield of $261 \mu\text{g}/\text{cm}^2$ of AA onto the polysulfone (PSF) membrane. The modified membrane possesses high surface tension and low fouling tendency. It was concluded that the brush-like structure is the key factor for anti-fouling performance (Gancarz, Poźniak et al. 1999).

Besides grafting in vapor phase, the plasma-induced grafting can also take place in liquid solution. For example, Tu et al. grafted PTFE membranes with AAM and sodium 4-styrenesulfonate by plasma and obtained high water flux and separation factor when treating several organic compound solutions. Ultrafiltration (UF) membranes were plasma-grafted with hydrophilic monomers to increase their surface hydrophilicity and hence improve the filtration of the protein (Tu, Liu et al. 2006). Chen and Belfort grafted N-vinyl-2-pyrrolidone (NVP) onto PES membranes after helium plasma treatment and observed the enhanced surface hydrophilicity. The investigation of grafting yield was made by adjusting plasma treatment time, grafting temperature and monomer concentration. It indicated that the plasma treatment roughened the membrane surface according to Atomic force microscopy (AFM) testing result. In addition, the modified membranes were less prone to BSA fouling comparing to the original PES membrane (Chen and Belfort 1999). Ulbricht and Belfort applied Helium plasma treatment followed by AA, methacrylic acid, and 2-hydroxyl-ethyl methacrylate (HEMA) grafting onto the membrane surface. And it was found that the contact angles of PAN and PSF were decreased from 48 ° to 34 ° and from 92 ° to 43 °, respectively. The dependency of water permeability of the membranes on grafting yield of the monomers was observed. The modified membrane demonstrated excellent performance in filtration of protein-containing solution in comparison with unmodified PSF membranes (Ulbricht and Belfort 1996).

In summary, since plasma-induced grafting is an effective method for modifying the very outmost layer of the polymer membrane surface, especially performing hydrophilic modification to achieve better anti-organic fouling property, it will be applied as the major strategy for membrane modification in the thesis.

2.3 Development of MD modeling

There are a lot of MD modeling works reported in recent years. The aim of the modeling is to predict the mass flux across the membrane. And also, according to the data from modeling solution, some key indicators of the MD performance can also be obtained, such as temperature polarization effect, energy efficiency driving force of mass transfer and etc. In MD modeling, both of the heat and mass transfer are simultaneously investigated by coupling the membrane structure characteristics and operation conditions. All of the important factors are incorporated into the complicated modeling in a step-by-step manner. However, there are still some challenges to overcome:

1. The application of empirical correlations of heat and mass transfer in MD flux prediction has been doubted since it was originally used for heat exchanger with non-porous and rigid boundary. The difference between heat exchanger and MD module is that heat exchanger comprises only heat transfer process, while MD process couples heat and mass transfer processes. Therefore, the traditional semi-empirical modeling is not good enough to simulate MD process. More comprehensive models are needed for a MD process.

2. Another issue to be addressed is the assumption of fully developed fluid flow from the very beginning of the membrane module in MD modeling. It lacks the consideration of the flow development at the entrance, which may provide an

inaccurate velocity distribution profile, thus a wrong temperature or pressure profile.

2.3.1 Semi-empirical models

- **Heat transfer in MD**

As the mechanisms are very similar for all the MD configurations, heat and mass transfer in DCMD is therefore used as the model configuration. The heat transfer from the feed side to the permeate side consists of two components: (a) latent heat associating with the water vapor across the membrane (Q_v), and (b) conduction heat by membrane matrix (Q_c). The heat transfer processes can be expressed for unit area as follows:

$$Q_f = h_f(T_f - T_{fm}) \quad (2.1)$$

$$Q_p = h_p(T_p - T_{pm}) \quad (2.2)$$

$$Q_m = Q_v + Q_c = N\Delta H + \frac{k_m}{\delta}(T_{fm} - T_{pm}) \quad (2.3)$$

where, Q_f , Q_p and Q_m are the heat flux transferred in the feed and permeate boundary layers and across the membrane, respectively; T_f and T_p are the bulk temperatures of the feed and permeate sides. T_{fm} and T_{pm} are the membrane surface temperatures in the feed and permeate sides, respectively. N is the mass flux ($\text{kg/m}^2\text{h}$); ΔH is the enthalpy of water evaporation (kJ/kg); k_m is the thermal conductivity of the porous membrane with the value of $631 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (Phattaranawik, Jiratananon et al.

2003). δ is the membrane thickness (m). At steady state, the heat balance guarantees that the three consecutive heat transfers satisfy the following equation:

$$Q_f = Q_m = Q_p \quad (2.4)$$

The heat transfer coefficients in the feed and permeate boundary layers, h_f and h_p can be calculated using a number of methods. The empirical equation which correlates the heat transfer coefficients and dimensionless Nusselt number are usually written as:

$$Nu = h d / k_L \quad (2.5)$$

where, h is the heat transfer coefficient in the thermal boundary layer; k_L is the thermal conductivity of liquid; d is the diameter of the flow channel. For the case of non-circular flow channel, the hydraulic diameter is given as:

$$d = 4A / L \quad (2.6)$$

where, A is the cross sectional area and L is the length of wetted perimeter of the flow channel. The empirical equation employed to correlate Nusselt number and two other hydrodynamic characteristic numbers: Reynolds number (Re) and Prandtl number (Pr) can be simply written in the following form:

$$Nu = a \cdot Re^b Pr^c \quad (2.7)$$

where, a , b , and c are characteristic constants of the membrane module and hydrodynamic conditions of the flow (Kreith, Manglik et al. 2010). In the following, some of the most useful correlation equations are to be summarized according to different hydrodynamic conditions, as shown in .

Table 2.1 Boundary layer heat transfer coefficients ratio using different correlations

Nu - equation	Condition	Reference
$0.023Re^{0.8}Pr^{0.33}$	$Re > 10^5, Pr > 0.5$	Bord, 1960
$0.34Re^{0.75}Pr^{0.33}$	$10^4 < Re < 10^5,$	Bord, 1960
$0.021Re^{0.8}Pr^{0.6}$	$Pr > 0.5$	Calderbank, 1961
$0.079Re^{0.5}Pr^{0.33}$	Gas-liquid flow	Churchill, 1977
$(f/2)Re \cdot Pr / (1 + 5(f/2)^{0.5}(Pr - 1))$	$Re > 10^4, Pr > 100$	Bord, 1960
$1.62(Re \cdot Pr \cdot d/L)^{0.33}$	$Re < 2100$	Bord, 1960
$4.36 + 0.036(Re \cdot L/d) / (1 + 0.011[Re/(L/d)]^{0.8})$	$Re < 2100$	Bord, 1960
$0.15Re^{0.33}Pr^{0.43}Gr^{0.1}$	$Re < 2100, L/d > 15$	Bord, 1960

- **Mass transfer in MD**

Mass transfer in MD occurs in two ways: convective transport of water molecular approaching the membrane surface and diffusive transport of water vapor across the micro porous membrane. The driving force for the mass transfer comes from the water vapor pressure difference on both sides of the membrane. Mass transfer resistance mainly comes from the membrane structure and the presence of air trapped in the membrane porous matrix. The mass transfer resistance generated by the

membrane structure (in the absence of air) can be depicted by either the Knudsen diffusion or the Poiseuille flow model, with the latter model being predominant in the case of the membrane pore size larger than the mean free molecular path of the gaseous water molecules (Schofield, Fane et al. 1987). The mass flux from the Knudsen diffusion model may be expressed as follows (Schofield, Fane et al. 1990):

$$N_K = \frac{2}{3} \frac{r \varepsilon}{\tau} \left(\frac{8RT}{\pi M} \right)^{0.5} \frac{M}{RT} \frac{\Delta P}{\delta} = K_K \frac{\Delta P}{\delta} \quad (2.8)$$

While, Poiseuille flow model can be expressed as the following form (Schofield, Fane et al. 1990):

$$N_P = \frac{1}{8} \frac{r^2 \varepsilon}{\tau} \frac{MP}{\mu} \frac{\Delta P}{\delta} = K_P \frac{\Delta P}{\delta} \quad (2.9)$$

Efforts have been tried to combine the above two equations to establish the mass transfer equation for the transition flow (Creutz and Zumwalt 1962). Here, a simple and effective method is to be described (Schofield, Fane et al. 1987). They proposed that the membrane permeate coefficient can be expressed by the following form:

$$\frac{K}{\delta} = a \zeta^b \quad (2.10)$$

Then, the mass flux through the membrane can be deduced by combining the Eq.2.8 and Eq.2.9 as the following:

$$N = a \zeta^b \Delta P \quad (2.11)$$

where, ζ is the dimensionless pressure (P/P_{refer}); a is the permeate constant that is closely linked to membrane structure. b indicates the type of mass transfer, that is zero

for Knudsen diffusion and one for Poiseuille flow. The value of a and b can be determined by experiment. The b value can clearly indicate the contribution of two mass transfer forms. They have tested the 0.1-0.45 μm membrane for gas permeation evaluation. b value is determined as 0.1-0.6, which means that Knudsen diffusion and Poiseuille flow play a comparably role in the MD process. ΔP is the trans-membrane water vapor pressure difference between the membrane surface of feed side and the permeate side.

In the DCMD process, the vapor pressure difference arising from the temperature difference between the two surfaces of the membrane is the driving force for water vapor transfer across the membrane. From Eqs. (2.8) to (2.11), the membrane surface temperatures can be derived as follows (Bui, Vu et al. 2010):

$$T_{fm} = T_f - (T_f - T_p) \frac{1/h_f * d_i / d_o}{1/h_f * d_i / d_o + 1/(N\Delta H / (T_{fm} - T_{pm}) + \frac{k_m}{\delta}) + 1/h_p} \quad (2.12)$$

$$T_{pm} = T_p + (T_f - T_p) \frac{1/h_p}{1/h_f * d_i / d_o + 1/(N\Delta H / (T_{fm} - T_{pm}) + \frac{k_m}{\delta}) + 1/h_p} \quad (2.13)$$

where, d_o is the outer diameter of the hollow fiber (d_i and d_o refer to the inner and outer diameter). Water vapor pressure (p) is correlated to temperature based on the Antoine equation:

$$p = \exp(23.20 - \frac{3816.44}{T + 226.87}) \quad (2.14)$$

where, T is the temperature of the membrane surface, with unit of $^{\circ}C$. Although

various mathematic models such as Knudsen, Poiseuille and molecular diffusion models have been developed for the predication of mass flux, it is generally accepted that the water flux across the membrane can be expressed empirically as the following (Fane, Schofield et al. 1987):

$$N = C(p_{fm} - p_{pm}) \quad (2.15)$$

where, C is the membrane distillation coefficient. Previous studies have suggested that C is only slightly dependent on temperature and can be considered as a relatively constant number in the calculation (Schofield, Fane et al. 1987, Song, Li et al. 2007, Bui, Vu et al. 2010).

2.3.2 CFD modeling

CFD applies numerical methods and algorithms to solve the problems that involve fluid flows. It presents the governing equation of Navier–Stokes equations into two dimensional (2D) or even three dimensional (3D) domains to solve and provide a very comprehensive and reliable information in the domain of our interest. For example, Yu and Yang applied CFD modeling for the three simultaneous heat transfer processes in the feed, permeate and membrane domain and analyze the heat transfer coefficients at different fluid conditions. Their research provided the insight of how mass flux and the thermal efficiency were affected by the operating conditions (Yu, Yang et al. 2011). Tang simulated the heat and mass transfer in VMD process. And the numerical solution of the 2D model has provided a series of visual image of distribution of volume fraction of vapor, pressure and velocity (Tang, Zhang et al. 2011). Further, 3D

modeling of DCMD module was also reported (Yang, Yu et al. 2012). In their study, wavy fiber design and gear-shaped fiber design were considered in 3D modeling. And it was found that the heat transfer coefficients have been increased by 4.5 - fold and 5.5 - fold, respectively. The improved hydrodynamics inside the module induced by the micro structured hollow fibers was carefully analyzed by the visualization of flow-field and temperature profiles in CFD.

However, to be noted, all of their studies have employed the commercial software FLUENT, which is one of the software specialized for computational fluid dynamics (CFD). And due to the complexity of the mesh and limited flexibility as a commercial software package, high performance of computer are required for the numerical solution, especially for the case with complex boundary conditions. To simplify the mesh processing and expand the flexibility of the modeling, self-coded packages for CFD application have been developed as well. Charfi et al. have applied CFD modeling to study the heat and mass transfer in the sweeping gas membrane distillation (AGMD) process (Charfi, Khayet et al. 2010). In their work, both numerical simulation and experiments have been performed for validation. The 2D model employed Navier-Stokes equations coupled with the Darcy-Brinkman-Forcheimer formulation in transient regime. Different operational parameters including the feed temperature, permeate temperature, feed concentration, feed velocity and the permeate velocity were investigated in the simulation. The simulation results were in good agreements with the experiment data. Chen et al. developed 2D model to predict the temperature polarization profile of direct contact membrane distillation (DCMD) processes (Chen, Ho et al. 2009). In the modeling, a fully developed flow field was assumed and finite difference method was applied to reduce the partial differential equations (PDE) into an ordinary differential equations system,

which was further solved by the fourth-order Runge-Kutta method. It was observed that the simulation results agreed well with the experimental data regarding water productivity in terms of operation conditions like temperature and volumetric flow rate.

To sum up, although semi-empirical modeling lacks accuracy and detailed information of the local temperature and flow field, it is still an easy and useful method to provide general information in the MD process. And in order to obtain a more comprehensive and reliable information, CFD modeling is required to investigate the distribution profiles of the key factors including the temperature, pressure, and velocity in the bulk and boundary layers of both sides as well as the membrane porous structure. Therefore, both of the semi-empirical and CFD modeling are to be employed in the thesis.

2.4 Optimization

2.4.1 The influence of key variables

- **Feed temperature**

Feed temperature is a very important factor that influences mass flux of the MD process. The feed temperature usually varies in a wide range from 30 °C to 90 °C, depending on the heating sources. According to the Antoine equation which correlates the temperature and the saturated vapor pressure, an exponential relationship between

the mass flux and the feed temperature can be expected. That is, a minor increase of the feed temperature can lead to a significant increase of the mass flux across the membrane. To be noted, this is also dependent on the range of the feed temperature. Therefore, it has been demonstrated that operating MD process at a relatively high feed temperature is greatly appreciable. Besides, it has been reported that high feed temperature can possess relatively high energy efficiency, which is defined as the ratio of the heat associated with mass flux and the total heat transferred from the feed to the permeate side. However, more severe temperature polarization, which indicates the extent of mass transfer driving force loss, is also expected with a relatively high feed temperature (Lawson and Lloyd 1996, Laganà, Barbieri et al. 2000, Martínez-Díez and Vázquez-González 2000, Khayet, Godino et al. 2002, Khayet, Godino et al. 2003, Phattaranawik, Jiratananon et al. 2003).

- **Flow velocity**

Mass flux also strongly depends on the hydrodynamic conditions, which can significantly influence the temperature profile in the membrane module. It has been proved that it is very effective to increase the heat transfer coefficient of the both sides and reduce the temperature polarization effect by increasing the flow velocity. And it is also observed that this kind of positive relationship between flow velocity and mass flux is limited by flow conditions; that is, the mass flux firstly increases with the increase of feed velocity, and then tends to reach an asymptotic value at even higher flow velocity when approaching the transition flow region ($Re \geq 2000$) (Banat and Simandl 1994, Banat and Simandl 1999, Khayet, Godino et al. 2003, Alklaibi and

Lior 2005). Therefore, in order to obtain high mass flux, it is advised to operate MD under turbulent flow condition, which can be realized by high mixing intensity and feed velocity. Since it is under turbulent flow condition that the membrane surface temperature can approach the bulk flow temperature, a large trans-membrane temperature difference can be obtained (Schofield, Fane et al. 1990, Lawson and Lloyd 1996, Lawson and Lloyd 1996). However, it should be noted that pressure drop inside the MD module (ΔP) is basically a function of the second power of the flow velocity, which indicates a delicate tradeoff has to be made in terms of the operation costs (OC).

- **Vacuum**

The relationship between vacuum and MD performance is relatively simple. When the vacuum pressure was increased at the shell side, the mass flux gradually decreased (Tang, Zhang et al. 2011). The increase of the vacuum resulted in the loss of the driving force across the membrane. Also, due to the relatively high vacuum that existed on the shell side of the membrane module, the conductive heat flux via the membrane matrix was minor in comparison with the latent heat associated with the water vapor. Therefore it can be neglected. It was worth noting that, although a higher vacuum can produce more mass flux with the same membrane area, the energy consumption should also be considered. The higher vacuum indicated that more work was required for the compression of the water vapor. Therefore, a tradeoff was also needed for the sake of low water production cost (WPC).

- **Membrane thickness**

Membrane thickness plays an important role in MD performance. It is closely related to the membrane permeability; that is the thinner the membrane thickness, the higher the membrane permeability. However, as the membrane directly contacts the hot feed side and cool permeate side, an inevitable heat loss in the form of sensible heat transfer is expected; therefore, a relatively thick membrane is preferred to reduce the conduction heat through the membrane matrix and achieve better energy efficiency of the system (Nigmatullin, Burban et al. 1993, Tomaszewska, Gryta et al. 1995, García-Payo, Rivier et al. 2002, Tang, Zhou et al. 2003, Khayet, Mengual et al. 2006). So it is acknowledged that a trade-off needs to be made when choosing a proper membrane thickness. However, to be noted, the optimum value of membrane thickness is probably case by case and is highly dependent on the membrane materials and the operating conditions (Nigmatullin, Burban et al. 1993).

- **Membrane porosity**

Membrane porosity is also an important factor in membrane characteristics because it can influence the mass flux and the mechanical strength of membrane. At the early age of membrane development, the porosity was as low as 30 % and the corresponding mass flux was also very low. Thanks to the development of polymer science and technology, the membrane porosity has increased to as high as 90 %, while still maintaining reasonable mechanical strength. Nowadays, those membranes

with high porosity are of relatively low conductive heat loss, because more air is trapped in the membrane pores and the its heat transfer coefficient is significantly smaller than that of the polymer matrix materials, such as PTFE, PP and PVDF(Tomaszewska, Gryta et al. 1995, García-Payo, Rivier et al. 2002, Khayet, Mengual et al. 2006).

- **Membrane pore size**

The pore size of membrane is very closely related to the membrane performance during MD process. On one hand, the mass flux increases with the increase of the membrane pore size; it is due to the enhancement of the mass transfer process whether by Knudsen diffusion mechanism (for small pore size), or by Knudsen-viscous transition mechanism (for larger pore size) (Curcio, Criscuoli et al. 2001). The enhanced mass flux also indicates better energy efficiency and lower water production cost. However, limitation also exists if the pore size is too big; as mentioned previously, membrane wetting is a serious challenge for MD application and needs to be carefully considered. Therefore, the maximum pore size shall be controlled and a narrow pore size distribution is preferred to avoid membrane pore wetting. In addition, it has been acknowledged that the optimum value of the pore size is related to the operation conditions, feed solution conditions and the membrane materials.

- **Membrane area**

Similar to the conventional heat exchanger, membrane area is related to the MD performance and economic gains. For hollow fiber membrane module, the membrane area is determined by hollow fiber length, number and dimension; while for flat sheet membrane module, the membrane area can simply be calculated by multiplying the length and width of the flat sheet sample (Khayet and Matsuura 2003). Generally speaking, membrane area is sensitive to the capital investment. It was reported that membrane cost account for around 19.7% of the total cost of water production for large solar-powered MD system (Banat and Jwaied 2008). In addition, larger membrane area indicates more water product can pass through the membrane. However, mass flux defined as the water production per unit membrane area, gradually decreases because of the gradual decrease of the driving force for mass transfer.

2.4.2 Energy consumption analysis

Energy consumption has always been a concern in MD application. High energy efficiency and reduction of energy consumption are hot topics in MD research. Basically, two concepts are worth introducing in MD system: one is energy efficiency, which is defined as the heat transfer associated with mass transfer over the total heat transferred from the hot side to the cold side; the other is gain and output ratio (GOR), which is defined as the ratio of heat associated with mass transfer to the energy input.

There are three major factors contribute to the energetic inefficiencies in MD process (Cath, Adams et al. 2004). The first is the TP effect inside the membrane module (Zakrzewska-Trznadel 1998, Zakrzewska-Trznadel, Harasimowicz et al. 1999, Zakrzewska-Trznadel, Harasimowicz et al. 2001, Feffera, van Keulen et al. 2002). Due to the existence of the thermal boundary layer, the temperatures at the membrane interface significantly differ from the bulk temperatures, leading to a reduction of the driving force for mass transfer. And it was reported that the practical driving forces for mass transfer employed in MD might be only 20 % to 70 % of the available thermal driving force (Lawson and Lloyd 1997). In addition, TP becomes more significant at higher operation feed temperatures, which are definitely associated with higher mass fluxes. It is also noted that the hydrodynamic condition has played an important role in TP effect by changing the heat transfer coefficients inside the thermal boundary layer. Therefore, it is favorable to operate MD under good mixing conditions by inducing turbulence flow and installing spacers/baffles.

The second factor is the mass transfer resistance to water vapor transfer through the membrane pores due to the presence of the trapped air within the membrane pores (Banat and Simandl 1996, Gryta, Karakulski et al. 2001, Drioli, Criscuoli et al. 2002). The trapped air inside the porous membrane barricades the diffusion of the water vapor across the membrane. The strategy for solving this problem is dependent on the pore size of the membrane. For small pore sizes, the Knudsen-Diffusion model is the dominant mechanism for mass transfer, the removal of air results in only a small increase in mass flux. While for the case of larger pore sizes, the Knudsen-Viscous transition is the dominant mechanism and thus substantial increases of mass flux can be achieved by deaeration (Schneider and Vangassel 1984).

The third factor is the conductive heat loss through the membrane material (Calabro, Pantano et al. 1990, Criscuoli and Drioli 1999, Wang, Zheng et al. 2001, Cath, Adams et al. 2005). In MD process, the latent heat of vaporization is provided at the membrane surface by the hot feed side and then the water vapor releases the latent heat of condensation at the membrane surface of the cool permeate side. In addition, the membrane material and the trapped air inside the membrane pores are also thermally conductive, especially when the membrane is thin and the operating temperature difference between feed and permeate sides is large. Of the total heat transfer in MD module Q , it is estimated that a portion of 50 % to 80 % is served as latent heat Q_v , while the remainder, Q_c is at loss as thermal conduction. Therefore, attempts of increasing the thickness of the membrane and/or reducing the conductive coefficient of heat transfer have been made to minimize the heat loss (Andersson, Kjellander et al. 1985). However, increasing the membrane thickness also increases the resistance to the mass transfer and temperature polarization coefficient. So it is clear that a trade-off has to be made between energy efficiency and mass flux. So, it is advised to employ moderate thickness of membranes in a deaerated system, which could offer significantly high mass fluxes to achieve high energy efficiency.

2.4.3 Economic analysis

In order to commercialize the MD technology, economic analysis is necessary to evaluate the water production cost. Among all of the components cost, heat exchanger was found to be the most costly items (Hogan, Sudjito et al. 1991). The capital cost of the unit is very sensitive to the extent to which heat is recovered, especially above a

heat recovery factor of about 0.8. The minimum capital cost requires heat recovery in the range of 60% to 80%. To obtain this level of energy conservation, the process conditions that need to use are generally those that result in fairly low mass flux, including the low flow velocity and large membrane areas. The exception is high feed temperatures which result in increased mass flux and proportionally less energy lost by heat conduction through the membrane matrix. To be noted, it is still difficult to give a detailed estimation of the MD system cost, simply because cost of some major components are still unknown and the MD system still has not been commercially applied in industry (Alklaibi and Lior 2005). Nevertheless, attempts have been made to provide a rough guidance of the cost estimation (Hogan, Sudjito et al. 1991, Gilron, Song et al. 2007, Al-Obaidani, Curcio et al. 2008, Banat and Jwaied 2008). Based on the economic analysis of the unit water production, valuable suggestions regarding cost reduction have been made for a more energy efficient and economic MD system. For example, it was reported that increasing the reliability and plant lifetime could reduce the cost of water production significantly (Banat, Jumah et al. 2002). The longer duration of MD system could lead to financing conditions equal to those of a conventional desalination system. Moreover, it is believed that water production cost can be competitive when the plant lifetime increases to 30 years and above. Beside, obtaining cheaper membrane materials that are suitable for membrane distillation, and achieving better heat transfer condition inside the membrane module were also proposed as the guideline for reduction of water production cost (Hanbury and Hodgkiess 1985). It was reported that the heat transfer coefficient in the thermal boundary layer of the membrane module can be enhanced by as high as 400% via using turbulence promoters, corrugated membrane surfaces, pulsatile flow and vortex generation (Imdakh and Matsuura 2005).

2.4.4 MD pilot system and optimization

After decades of development of MD technology, the innovative membrane material and fabrication technology, desirable MD performance can be expected within lab scale test. However, pilot and industrial scale of MD processes are still in scarcity. Some pioneers explored in this area with the aim of enlarging system scale for further industrial application. One example was as shown in . The preliminary pilot tests operate for consecutive months and the MD system performance was systematically investigated with various configurations (Song, Ma et al. 2008). The results are quite encouraging and a good water production capacity of $21\text{kg}/(\text{m}^2\text{h})$ along with a satisfactory rejection rate was obtained.

Fig.2.5 Schematic of DCMD pilot plants (Song, Ma et al. 2008)

Some novel alternative energies such as solar power are promising by integrating with MD system (Banat, Jumah et al. 2002, Banat and Jwaied 2008, Wang, Zhang et al. 2009). The solar powered MD system has been carefully designed and arranged as indicated in . It indicated that the flux of the system could be as high as 32.19 kg/(m²h) with solar energy collector area of 8m². The daily cumulated flux can be as high as 170kg/m² under sunny condition and still reached 50kg/m² when it was cloudy. The results were quite acceptable and it demonstrated the availability of a solar-heated MD system for pure water production. In addition, the system can even steadily operate in cloudy days, indicating the feasibility and flexibility of such large scale plants.

Fig.2. 6 Flow sheet of the solar-heated MD system for producing potable water (Wang, Zhang et al. 2009)

Optimization of the MD system is of special importance in large MD systems. Chang carefully analyzed the solar driven membrane distillation system by building up a dynamic model on the Aspen platform for the AGMD system. The water production was significantly optimized by their proposed PI control system (Chang, Wang et al.

2010, Chang, Liao et al. 2009). In the study, large scale MD module, together with heat recovery system for desalination was simulated in terms of various designs and operations. Then the optimal value of design and operation conditions was thus provided.

Fig.2. 7 MD module with heat recovery system (Chang, Wang et al. 2010, Chang, Liao et al. 2009)

Zuo et al. also investigated the DCMD system by applying Aspen Plus platform for the purpose of energy efficiency and economic analyses (Zuo, Wang et al. 2011). The study provides the understanding of the relationships of the water flux/production, the gain output ratio (GOR) and the water production cost (WPC) with respect to various design and operation parameters of the DCMD system. It suggested that a critical membrane area existed, below which, significant increases of water production and the GOR were observed with increasing membrane area, leading to a significant drop in the WPC. Increasing feed temperature imposes positive impacts on water flux and the GOR. For the higher feed and permeate velocities, there were increases in water flux, water production and the GOR. However for the WPC there were optimum fluid

velocities beyond which the penalty of more energy input in the form of electricity consumption for pumping was significant. It was also found that when the temperature difference in the heat exchanger was increased to 6 °C, the WPC can be reduced considerably by cutting down the heat exchanger cost. Al-Obaidani performed systematic analysis of direct contact membrane distillation (DCMD) system optimization (Al-Obaidani, Curcio et al. 2008). The optimized membrane properties included the thickness, porosity, and the operation temperature. In the study, DCMD with heat recovery via heat exchanger produced water at the cost of \$1.17 m⁻³, which is highly competitive with MED and MSF. Also, low-grade thermal energy was proposed as the heat source for MD application for further reducing the water production cost. Gilron also studied the energy issues in DCMD process and proposed that the energy efficiency of the processes is low unless the heat can be recovered from the hot permeate side to the cool feed side with a close temperatures approach in the heat exchanger (Gilron, Song et al. 2007). It was indicated that a high GOR value was obtained by applying cascade of cross flow membrane modules.

2.1 Summary

To apply MD processes for industrialization, the major challenges are the membrane wetting and energy consumption. Membrane modification has been proved to be an effective way to tackle the wetting problem. Surface modification can be applied to reduce maximum membrane pore size, narrow down its distribution or/and further enhance membrane hydrophobicity (Yang, Wang et al. 2011). However, membrane fouling is also a concern for a highly hydrophobic membrane surface when it is in

contact with an aqueous media containing hydrophobic organic species, as hydrophobic species tend to be absorbed on the hydrophobic membrane surface, resulting in the blockage of the membrane pores and membrane wetting (Liu, Hashim et al. 2011). For the feed water containing hydrophobic species such as oil species, hydrophilic modification, which can not only reduce membrane pore size, but also protect the pore mouth from fouling, seems to be more appropriate. Therefore, hydrophilic surface modification methods, especially plasma treatment were reviewed.

Although there are many reported 1D modeling work on MD process, they are mainly semi-empirical correlations inspired by conventional heat exchanger, which suffers the drawback of inaccuracy for MD process. Therefore, novel 2D modeling based on Navier–Stokes equations is needed to accommodate the MD features. And it is capable of providing more accurate and comprehensive information when simulating the module performance. It is anticipated that a better understanding of the heat and mass transfer inside the membrane module can help to simulate the MD process and provide the guidance for optimizing the MD performance.

Moreover, for industrial applications, many efforts have been made to optimize the MD pilot system design and operation conditions, aiming at maximizing the system performance and minimize the cost per unit of target product. Some existing design concepts were considered and adjusted to MD applications, such as the cross flow configuration and small membrane modules in series (Gilron, Song et al. 2007). It is anticipated that these strategies can be incorporated into novel MD design and may

provide significant enhancements. Though many researchers have worked on process modeling and employed various semi-empirical correlations to illustrate the mass/heat transport mechanisms, there is still no systematic MD process simulation for economic sensitivity analysis and optimization.

Chapter 3 NOVEL MEMBRANE SURFACE MODIFICATION TO ENHANCE ANTI-OIL FOULING PROPERTY FOR MEMBRANE DISTILLATION APPLICATION

3.1 Introduction

The chapter aims to explore a novel modification approach to obtain a highly hydrophilic membrane surface, and to investigate the impacts of membrane surface properties and operation conditions on the oil fouling during MD process for three different membranes, including one commercial PVDF membrane and two in-house modified membranes. To be noted, flat sheet membrane is used in this chapter as the substrate for surface modification for two reasons: (1) It is simpler and more repeatable to use the commercial flat sheet membrane for surface modification; (2) The contents in this chapter are associated with a MD project, which aims at using flat sheet membrane.

The two membranes were modified by PEG grafting and TiO_2 depositing onto the membrane surface. The interaction between mineral oil and membrane surface was quantitatively analyzed based on the interfacial free energy using the XDLVO theory.

In addition, since the membrane surface charge plays an important role in fouling behavior and the discharge of coastal petrochemical industry effluents probably alters the pH of the near shore seawater, MD tests were performed at varied pH values of the feed solution to approach the practical desalination condition. Meanwhile, the influence of hydrodynamic conditions was also investigated in order to identify the optimum operating parameters for desalinating seawater with oil. It is expected that this study can provide a deep insight on the oil-fouling mechanism and explore an effective way to develop novel anti-wetting and anti-fouling membranes for MD application.

3.2 Theory

3.2.1 Concept of surface tension

The wettability of a solid surface can be expressed by contact angle θ , which is governed by Young's equation:

$$\cos \theta = \frac{\gamma_s - \gamma_{sL}}{\gamma_L} \quad (3.1)$$

where, γ_s , γ_{sL} and γ_L refer to the surface tensions of solid in contact with air, solid in contact with liquid, and liquid in contact with air, respectively. The surface tension of a solid surface can be written as following when the Good-Van Oss model is applied (van Oss 1993):

$$\gamma_s = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (3.2)$$

where, γ_s^{LW} , γ_s^+ and γ_s^- are the dispersive component (indicating Lifshitz-Van Der Waals interactions), the electron-acceptor and electron-donor components (indicating acid-base interactions) of the solid surface tension, respectively. The relationship of the liquid surface tension (γ_L) with the contact angle (θ) can be written as the following equation (van Oss 1993):

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_s^{LW} \gamma_L^{LW}} + \sqrt{\gamma_s^+ \gamma_L^+} + \sqrt{\gamma_s^- \gamma_L^-} \quad (3.3)$$

where, γ_L^{LW} indicates the Lifshitz–Van der Waals interactions of the liquid; γ_L^+ and γ_L^- refer to the electron-acceptor and electron-donor components (indicating acid-base interactions) of the liquid surface tension, respectively.

The calculation of all components of the surface tension of a polymer (γ_s^{LW} , γ_s^+ , γ_s^-) is possible when Eq.(3.3) is applied for three liquids with known values of γ_L^{LW} , γ_L^+ , γ_L^- , which can be obtained from the database of goniometer OCA20, and thus the solid surface tension can then be computed using Eq. (3.2).

3.2.2 The XDLVO theory

The physicochemical interaction of the materials can be described by interfacial free

energy according to the XDLVO theory (Yotsumoto and Yoon 1993, Yotsumoto and Yoon 1993, Bhattacharjee, Sharma et al. 1994), which takes three types of forces, namely Van Der Waals, acid-base, and electrostatic double layer interactions, into consideration. The electrostatic double layer interaction is usually minor with respect to the interaction of oil and polymer and is thus ignored (Brant and Childress 2002). So the interfacial free energy can be written as the following:

$$\Delta G_{S-W-L} = \Delta G_{S-W}^{LW} + \Delta G_{S-L}^{AB} \quad (3.4)$$

The subscripts S , W and L denote solid, water and liquid, respectively. And the interfacial free energy for the interaction between solid and liquid immersed in an aquatic medium can be further expressed as following (van Oss 1993):

$$\Delta G_{S-W-L} = 2\sqrt{\gamma_S^{LW}\gamma_W^{LW}}\sqrt{\gamma_L^{LW}} + \sqrt{\gamma_S^{AB}\gamma_W^{AB}}\sqrt{\gamma_L^{AB}} + \sqrt{\gamma_S^{LW}}\sqrt{\gamma_W^{LW}}\sqrt{\gamma_L^{LW}} + \sqrt{\gamma_S^{AB}}\sqrt{\gamma_W^{AB}}\sqrt{\gamma_L^{AB}} \quad (3.5)$$

where the superscripts LW and AB stand for the Lifshitz–van der Waals interactions and acid-base interactions, respectively. According to the thermodynamic theory, the negative value of ΔG_{SWL} indicates the force of attraction. The lower the value, the stronger attraction between the liquid and the solid surface can be expected. In contrast, if the value is positive, there is a repulsive force between the solid and the liquid. For the situation that a membrane is in contact with oil-containing water, a higher negative value of ΔG_{SWL} would suggest a severe membrane fouling by oil, but a higher positive value would imply less membrane fouling tendency. In order to calculate ΔG_{SWL} , the Van Der Waals and acid-base interactions can be obtained from Eqs. (3.2) and (3.3) based on the contact angle measurements.

3.3 Experimental

3.3.1 Materials and chemicals

All solutions and reagents were prepared with analytical grade chemicals. Deionized (DI) water was from Millipore Water Purification System. Polyvinylidene fluoride (PVDF) membrane (GVHP), with an average pore size of 0.22 μ m and a thickness of 125 μ m was purchased from Millipore. Sodium hydroxide (Sigma–Aldrich) was used as the alkali solution for the post treatment. Polyethylene glycol (PEG Mw~1,000) used for plasma grafting was purchased from Sigma–Aldrich. Titanium tetraisopropoxide (TTIP) used for preparing titanium dioxide was purchased from Sigma-Aldrich (97%). The liquids used for contact angle measurements, including ethylene glycol and diiodomethane, were purchased from Sigma-Aldrich. Ethanol and nitric acid used for preparation of TiO₂ colloidal solution was purchased from Sigma-Aldrich. The synthetic seawater is prepared by dissolving 3.5 wt% NaCl into DI water. The mineral oil was taken from the petrochemical industry, the characteristics of the mineral oil is summarized in Table 3. 1 .

Table 3. 1 Characteristics of mineral oil taken from the petrochemical industry

Parameter	Property
Color	Brownish
pH	6.1
Turbidity (NTU)	180.5
TOC (mg/L)	120.2

3.3.2 Membrane plasma treatments

A PEG solution (5 wt%) was prepared by dissolving 15 g PEG into 300 g DI water. The top surface of a piece of PVDF membrane was dipped into the PEG solution for 10 min. Then it was taken out to dry in air. A coated PEG layer was only formed on the membrane surface without entering into the membrane pores due to its highly hydrophobic nature. The treated membrane was placed between the ground electrode and biased electrode in the plasma chamber, which was made by Changzhou Zhongke Changtai Plasma Technology Ltd, China. Then, helium (He) gas was subsequently allowed to flow into the chamber after the system pressure of 0 to 100 Pa was achieved. The glow discharge was initiated afterwards. The radio-frequency (RF) power of the He plasma was varied from 0 to 90 W, while the exposure time was from 0 to 120 s. After the plasma treatment, the grafted membrane was washed with 100 ml DI water for 2 h to remove the residual. The membrane sample designated as PVDF-P was dried in a vacuum oven at 50 °C for further characterizations and measurements.

The PVDF-PT membrane was prepared by the following steps. Firstly, a transparent TiO₂ colloidal solution was prepared as described in the literature (Bae, Kim et al. 2006). The preparation step is as follows: 10 ml of titanium tetraisopropoxide (TTIP) was firstly dissolved in 100 ml of ethanol. The mixture was then slowly added to 900 ml of deionized water under stirring for 12 h. The pH of the DI water was adjusted to 1.5 by using nitric acid. A piece of PVDF-P membrane sample was dipped into the TiO₂ colloidal solution for 10 min and then dried in air. Later, this membrane was treated by the plasma using helium gas with similar method described previously.

After the plasma treatment, the membrane was washed with 100 ml DI water for 2 h to remove the residual, and dried in a vacuum oven at 50°C for further characterizations and measurements.

3.3.3 Membrane characterizations

The mechanism of surface modification was examined by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectrum, which were collected at room temperature over a scanning range of 650–4000 cm^{-1} with a resolution of 4.0 cm^{-1} , by using an IR Presitige-21 FTIR (Shimadzu, Japan). Spectral analysis was performed using FTIR software (IR Solution, Shimadzu).

To observe the surface morphologies of the membranes, the flat sheet membrane samples were sputtered with a thin layer of gold using EMITECH SC7620 sputter coater. The outer surface of the membrane samples were examined using a Zeiss EVO 50 Scanning Electron Microscope (SEM). Images were obtained using an accelerating voltage 20 kV.

The pore size and pore size distribution were measured by a capillary flow porometer (model CFP 1500A, from Porous Material. Inc (PMI)). The membrane samples were stabilized in the sample holder and wetted by a low surface tension liquid of Galwick. Then, the nitrogen gas was allowed to pass through the saturated sample until the

applied pressure exceeded the capillary attraction of the liquid in the membrane pores. By comparing the gas flow rates of wet and dry samples at the same pressures, the pore size distribution of the membrane was obtained.

A goniometer (Dataphysics, Germany) was used to perform the static contact angle measurement for the three types of flat sheet membranes. The measurement is based on the sessile drop method, using an optical system to capture the profile of the tested liquids ($\sim 5 \mu\text{L}$) on a horizontal substrate membrane. To determine the isoelectric point, the membrane's zeta potential was measured using an eletro kinetic analyzer (EKA, SurPASS, Anton Paar GmbH, Austria) in a 3.5 wt% NaCl solution at various pH values at room temperature. The zeta-potential of the mineral oil emulsion was measured by a Zetasizer Nano ZS (Malvern, UK) in a 3.5 wt% NaCl solution at various pH values at room temperature.

3.3.4 MD performance tests

An oil/water (O/W) emulsion was prepared by dispersing mineral oil in water at the concentration of 0.01 wt%. The emulsion was made by mixing the oil and water via stirring with a high speed blender and heating at 60°C for 2 hours. The size distribution of the oil droplets was determined by using a Hydro 2000SM Mastersizer from Malvern Instruments and the result was shown in Fig. 3.1. By comparing the particle size distribution at various times, it was found that the particle sizes of oil emulsion do not change significantly during 24 hours of operation and the mean

diameter of the particle size is around $4.52\ \mu\text{m}$.

Fig. 3.1 Oil droplets size distribution in the feed

The three types of flat-sheet PVDF membranes were tested in a MD setup, shown in Fig.3.2. The flow channel of the MD cell is 3.7cm in width and 0.2cm in height. Both the feed and permeate solutions were cycled through the flat sheet membrane module in countercurrent mode. The feed water was prepared by dissolving sodium chloride in the prepared oil emulsion. The feed water has a conductivity of around $60\ \text{ms}\cdot\text{cm}^{-1}$, and was heated up to $60\ ^\circ\text{C}$ by a heater and circulated by a peristaltic pump. On the other side, the permeating pure water was cooled down to around $20\ ^\circ\text{C}$ by a cooling circulator and cycled by another peristaltic pump. The flow velocities of the feed and permeate streams were set in the range of 0.15 to 0.45 m/s, corresponding to the Reynolds number of 647 and 1941, respectively, so that the flows were controlled

within laminar flow region. The distillate was collected in an overflow tank sitting on a balance (± 0.01 g). In the current study, the pH values of the lab-synthesized seawater were set at 6.2 and 7.6 to investigate its influence on oil fouling behavior on the performance of the virgin and modified membranes during MD operation. This was because that the pH value of 6.2 was the isoelectric point of membrane PVDF-PT and membrane fouling is also affected by the surface charge; while the pH value of 7.6 was within the range of the normal pH value of seawater. The pH adjustment of the feed solution was performed by adding 0.1M HCl or NaOH, which might only lead to minor differences in the ionic strength of the solutions and was therefore neglected in this study.

Fig.3.2 Membrane distillation experimental set-up

3.4 Results and discussion

3.4.1 Confirmation of the surface modification mechanism

The chemical structures of commercial PVDF membrane, PVDF-PT membrane and PVDF-P membranes were examined by ATR-FTIR. Fig.3.3 provides the spectroscopy results in the wavenumber range of interest (650cm^{-1} - 4000cm^{-1}). As can be seen from Fig 3.3a the vibration bands at 1178cm^{-1} and 1275cm^{-1} correspond to the asymmetrical and symmetrical stretching of CF_2 , respectively, and the vibration of CH_2 groups appeared at the frequency of 1402cm^{-1} .

Fig.3.3 ATR-FTIR spectra of PVDF membrane, PVDF membrane grafted by PEG (PVDF-P) and PVDF membrane grafted by PEG and TiO_2 (PVDF-PT)

The change in the functional groups of PVDF-P membrane caused by PEG grafting is shown in curve b of Fig. 3.3. Compared with the spectrum of the virgin PVDF membrane, the asymmetrical and symmetrical stretching of CF_2 (1178cm^{-1} and 1275cm^{-1} , respectively) and the vibration of CH_2 (1402cm^{-1}) were reduced obviously after the modification, which might be due to the dehydrofluorination. The adsorption band at the frequency of around 3400cm^{-1} was assigned to the OH stretching, which only appeared after modification. This result confirmed successful PEG grafting onto the PVDF membrane surface. By comparing the curve b and c, it was observed that a new featured peak appeared in the TiO_2 deposited PVDF/PEG membrane. The new band at the frequency of around 660cm^{-1} , corresponding to the Ti-O-Ti, confirms that the TiO_2 particles were deposited onto the PVDF-P membrane surface. Similar result was also reported in literature (Shi, Ma et al. 2012).

Based on the ATR-FTIR results, possible mechanism for PVDF membrane surface modifications is proposed as illustrated in Fig. 3.4. The dehydrofluorination of PVDF and dehydrogenation of PEG under high-vacuum helium plasma environment produced radicals, which subsequently reacted to form OH- group on the PVDF membrane surface. Then, the presence of OH- functional group helped self-assembly of TiO_2 particles on the membrane surface. Therefore, it can be concluded that the self-assembly of TiO_2 particles on the surface of PVDF-P membrane is mainly determined by hydroxyl functional groups. Similar conclusion was also reported by the literature (Rahimpour, Jahanshahi et al. 2012).

Fig.3.4 Proposed reaction mechanism of TiO_2 depositing onto PVDF-P membrane

3.4.2 Membrane morphology observation

The surface morphologies of virgin and modified PVDF flat sheet membranes are displayed in Fig.3.5. By comparing the original PVDF membrane surface Fig. 3.5a with the PVDF membrane surface grafted by PEG Fig. 3.5b, it was observed that the pore sizes of PVDF-P membrane are smaller. This result is consistent with the results shown in Fig. 3.6, where the maximal pore size, mean pore size and pore size distribution of three membranes is presented. The reduction of the maximum pore size from $0.55\ \mu\text{m}$ for the virgin PVDF membrane to $0.27\ \mu\text{m}$ for the PVDF-P membrane can help reduce the membrane wetting tendency significantly, which was shown in Fig. 3.7. In Fig. 3.5c, micro-balloon shaped spheres can be observed on the surface after TiO_2 particles deposition (PVDF-PT membrane). Fig. 3.5d shows the

morphology of the membrane surface after the ultrasonic treatment, which intended to examine the attachment strength of the TiO_2 particles and PEG modified PVDF membrane surface (PVDF-P). As it was seen, some of the agglomerated TiO_2 particles were removed from the top surface. However, there were still plenty of fine-sized TiO_2 particles on the surface after the ultrasonic treatment, indicating that chemical bonding existed between the TiO_2 particles and the PVDF-P membrane.

Fig.3.5(a) surface of virgin PVDF membrane; (b) surface of PVDF-P membranes; (c) surface of PVDF-PT membrane (d) surface of PVDF-PT membrane after ultrasonic for 5 min

(a)

(b)

(c)

Fig.3.6 Pore size distribution of the original and modified membranes: (a) Original PVDF membrane; (b) PEG modified membrane (PVDF-P); (c) PEG and TiO_2 modified PVDF membrane (PVDF-PT)

3.4.3 Determination of interfacial free energy for three membranes

Three types of liquids (pure water, ethylene glycol and diiodomethane) were used for contact angle measurements and ten times were measured for each membrane. The averages and standard deviations of the data were given in Table 3.2. It can be seen that both the PVDF-P and PVDF-PT membrane surfaces exhibit highly hydrophilic property in comparison with the original PVDF membrane.

Table 3.2 Contact angles of three types of liquids* on the membranes

Membrane/oil	θ_e	θ_w	θ_d
PVDF	22.3±1.4	120.1±2.1	72.0±1.5
PVDF-P	20.7±0.7	40.9±0.8	35.2±1.6
PVDF-PT	15.1±0.8	25.2±0.7	20.5±1.1
Mineral oil	61.3±1.1	71.2±1.4	39.8±0.6

Table 3.3 shows the calculated surface tension parameters of each membrane. The data showed that the virgin PVDF membrane had a high electron acceptor component (γ^+) and a zero electron donor component (γ^-), resulting in non-polar component of surface tension, which was consistent with its molecular structure. Similar results were also reported in open literature (Liu, Hashim et al. 2011, Subhi, Verliefde et al. 2012). In contrast, the PVDF-PT membrane had a high electron donor component (γ^-) and a low electro acceptor component (γ^+), indicating that it was polar and likely to be ionized to donate electrons in an aqueous media. As for the PVDF-P membrane, its relatively high electron donor component (γ^-) and relatively low electron acceptor component (γ^+) suggests its polarity.

Table 3.3 Dispersive and acid-base components of surface tension

Membrane/oil	γ (mN/m)	γ^{LW} (mN/m)	γ^+ (mN/m)	γ^- (mN/m)
PVDF	21.71	21.71	16.28	0
PVDF-P	47.36	42.03	0.18	39.18
PVDF-PT	54.23	47.49	0.21	54.05
Mineral oil	37.31	37.31	0	15.22

With the surface tension data from Table 3.3, the interfacial free energy between membrane surface and oil droplet in an aqueous media can thus be determined according to the XDLVO theory. Table 3.4 shows the calculated results. The PVDF membrane exhibited a negative ΔG_{SWL} , suggesting the existence of an attraction force between the membrane surface and oil droplets. It was interesting to see that the PVDF-PT membrane possessed a positive value of ΔG_{SWL} , which implies a repulsion of oil droplets by the TiO_2 modified membrane surface. This result was believed to attribute to the most hydrophilic feature of the PVDF-PT membrane surface. A slightly negative value of ΔG_{SWL} was obtained for the PVDF-P membranes, which means that the interaction between the PEG modified membrane surface and oil droplets was weak. In addition, by comparing the interfacial free energy value of Van Der Waals (ΔG^{LW}) and polar interactions (ΔG^{AB}), it was observed that the acid-base force is dominant over the Van Der Waals force in the overall interaction for the PVDF membranes. Similar results were also reported in the literatures (Gourley, Britten et al. 1994, Meinders, van der Mei et al. 1995, Bhattacharjee, Sharma et al. 1996, Bouchard, Jolicoeur et al. 1997). However, it seemed the acid-base and Van Der Waals interactions are comparable for the PVDF-P and PVDF-PT membranes.

Table 3.4 Interfacial free energy of liquid and membrane surfaces in water

Membrane with oil	ΔG^{LW} (mJ/m ²)	ΔG^{AB} (mJ/m ²)	ΔG (mJ/m ²)
PVDF with oil	0.03	-53.33	-53.30
PVDF-P with oil	-5.22	1.59	-3.63
PVDF-PT with oil	-6.40	12.71	6.31
Mineral oil with oil	-4.14	-23.19	-27.34

3.4.4 Membrane performances in the MD process

- **Influences of the membrane hydrophobicity, pore sizes and pore size distribution**

Fig. 3.7a shows the water flux over time in the MD process using three different membranes. Although there was small reduction in water flux at the initial stage for the PVDF-P and PVDF-PT membranes in comparison with the virgin PVDF membrane, the water flux of the PVDF-PT membrane remained a stable value over 24h of operation, while there was a minor flux decline for the PVDF-P membrane over 24h of operation. No significant fluctuation in permeate conductivity can be observed for both the PVDF-P and PVDF-PT membranes. However, the water flux of the PVDF membrane decreased gradually over entire period of operation, which corresponds to the gradual increase of the permeate conductivity in the first 22 hours and a dramatic increase in the permeate conductivity (over $10 \mu\text{S/cm}$) afterward, as shown in Fig.3.7b.

Obviously, two distinctive phenomena occurred for the PVDF membrane in the MD process. It was hypothesized that the gradual reduction of the water flux was due to oil fouling on the PVDF membrane surface, while the dramatic increase in the permeate conductivity was attributed to the membrane wetting.

To validate this hypothesis, membrane hydrophobicity needs to be examined carefully, as the hydrophobicity of a membrane plays an important role in determining the

fouling tendency of oil droplets. As discussed in previous section, the virgin PVDF membrane was highly hydrophobic in comparison with hydrophilically modified PVDF-P and PVDF-PT membranes (Table 3.2), or in other words, the virgin PVDF membrane possessed a very low surface tension (Table 3.3). Table 3.4 also shows a large negative interfacial free energy for the PVDF membrane with oil in water, indicating a strong affinity of oil with the virgin PVDF membrane.

(a)

(b)

Fig.3.7 MD performance over operation time for original and modified membranes:

- (a) the mass flux over operation time; (b). the permeate conductivity over operation time (feed concentration: 3.5 wt%, PH: 7.6, feed temperature: 60 °C, permeate temperature: 25 °C, feed velocity: 0.15 m/s, permeate velocity: 0.15 m/s)

For the virgin PVDF membrane, there existed two major steps of membrane surface fouling by the oil droplets. At the beginning, the oil droplets may attach to the clean membrane surface spontaneously because of the large negative interfacial free energy, which was mainly contributed by the acid-base interaction (ΔG^{AB}). Thus only the interaction of oil and membrane should be considered. However, after a period of operation, when the oil droplets started to cover the membrane surface, the interaction between the oil droplets and fouled membrane should be taken into account. At this moment, according to Table 3.3, both the Van Der Waals interaction and the acid-base interaction contributed to the oil fouling. In contrast, for the PVDF-PT membrane, the negative ΔG^{LW} and positive ΔG^{AB} indicated that the Van Der Waals force imposed an attraction between the oil and the membrane and the acid-base force exerted a repulsive force. The combined effect was repulsive, resulting in less oil fouling and thus stabilized water flux, as shown in Fig. 3.7a. As for the PVDF-P membrane, the negative ΔG^{LW} played a slightly dominant role, hence causing a bit attraction between the oil and the membrane. The weak oil affinity to the PVDF-P membrane surface might probably be offset by the drag force exerted by the flow. On the other hand, membrane pore size and pore size distribution should also be taken into consideration. Referring back to Fig.3.6, the virgin PVDF membrane exhibits a maximum pore size of 0.55 μm and a wide pore size distribution. The grafting of PEG and deposition of TiO_2 on the membrane surface reduced the pore size and narrowed down the pores size distribution. Therefore, the virgin PVDF membrane was finally wetted due to combined effects of oil fouling and large pore sizes, while the

PVDF-PT and PVDF-P membranes remained almost constant performances.

- **Effect of pH value of feed solutions**

Fig. 3.8 shows the influence of the pH value of the feed solution on water flux for three membranes. It was observed that the pH value played an important role in the oil fouling during MD operation. Table 3.5 gives the isoelectric points of the three tested membranes. For virgin PVDF membrane, fouling was more severe at pH of 6.2 than at pH of 7.6. This can be explained by the dual influences of physicochemical interaction and surface charge interaction. At pH of 7.6, although both the membrane surface and the oil emulsion carried negative charges because of ionization, which caused a repulsive interaction force, the hydrophobic attraction was dominant. While at pH of 6.2, the membrane surface and oil emulsion carried opposite charges. The dual interactions tended to strengthen each other, thus resulting in more severe oil fouling and flux reduction. In addition, since the pH of 6.2 was close to the isoelectric point of the oil emulsion (6.5), which subsequently caused severe oil fouling to the already fouled membrane. This was because the minimum oil-oil repulsion may lead to an easier formation of multilayer oil attachment on the membrane surface. Similar observation was also reported in the literature(Loh, Beuscher et al. 2009).

However, for the PVDF-P membrane, no big difference was observed at both pH values except for normal mass flux fluctuation, because of the existence of low surface charges on the grafting layer which rendered surface charge effect

insignificantly. A similar effect was also reported previously (Tang, Kwon et al. 2007). For the PVDF-PT membrane, the fouling tendency at pH of 6.2 was a bit stronger than at pH of 7.6, causing a slight decrease of the mass flux with time. And it can be explained by the dual interactions of hydrophobicity and surface charge. At pH of 7.6, the PVDF-PT membrane surface and oil emulsion carried the same charges, which strengthened the repulsive force; while pH of 6.2 the membrane surface was neutral and oil emulsion was slightly positive, which contributed to the repulsive force insignificantly.

Fig.3.8 Water mass flux over operation time for original and modified membranes at different feed pH values (feed concentration: 3.5 wt%, feed temperature: 60 °C, permeate temperature: 25 °C, feed velocity: 0.15 m/s, permeate velocity: 0.15 m/s)

Table 3.5 Isoelectric points for the membranes and mineral oil emulsion

Membrane	Isoelectric point
PVDF	4.4
PVDF-P*	-
PVDF-PT	6.2
Mineral oil emulsion	6.5

* The PVDF-P surface is only slightly charged at tested pH, so the isoelectric point is neglected.

- **Impact of hydrodynamic conditions**

Fig. 3.9 depicts the impact of the flow velocities on water flux for three membranes over time. The flow velocities in the current study were set within the laminar flow region ($Re < 2000$). For the three membranes tested, the water flux increased significantly with the increase of the flow velocity. This was because a higher velocity can help mitigate the temperature polarization by reducing the thermal boundary layer, thus the driving force across the membrane was enhanced (Schofield, Fane et al. 1987).

By comparing the MD performance of the PVDF membrane at different velocities over time, an approximately 20% decline of mass flux were observed at flow velocity

of 0.45m/s (Re : 1941), in comparison with around 40% decline of mass flux at flow velocity of 0.15m/s (Re : 647). This was mainly because a higher flow velocity corresponded to a larger shear stress, making it much more difficult for the oil droplets to attach to the membrane surface, thus reducing the fouling tendency. In addition, the mass flux reductions over time for two modified PVDF-P and PVDF-PT membranes were comparatively insignificant. Since the physicochemical interaction between the hydrophilic modified membranes and oil droplets were almost neutral or repulsive, it was difficult for the oil droplets to firstly attach the membrane surface and allow for subsequent oil droplet interaction with the fouled membrane. Besides, it was observed that at a higher velocity (0.45m/s), flux decline is smaller than that at a lower velocity for all three membranes. The reason responsible for this result was that the exerted shear stress on oil droplets increased with increasing flow velocity, causing it more difficult for oil droplets to stay in the domain adjacent to the membrane surface.

To be noted, there is a sharp increase of the permeate conductivity for PVDF membrane (0.15m/s) after 22h run. This is due to the oil fouling and membrane wetting. At this stage, some oil-seawater emulsion droplets penetrated through the membrane and entered into the permeate side, the membrane pores got wetted and therefore the conductivity in permeate side increased significantly.

(a)

(b)

Fig.3.9 Water mass flux over operation time for original and modified membranes with different feed velocities: (a) the mass flux over operation time; (b). the permeate conductivity over operation time (feed concentration: 3.5wt%, PH: 7.6, feed temperature: 60 °C, permeate temperature: 25 °C)

3.5 Conclusions

In this chapter, a novel and effective way to modify hydrophobic PVDF flat sheet membrane to obtain hydrophilic surface property via plasma induced grafting of PEG and subsequent TiO_2 particles deposition onto the membrane surface has been reported. A series of characterizations were conducted for the virgin and modified membranes. Physicochemical interaction between oil droplets and membrane surface in an aqueous media was studied by evaluating the interfacial free energy based on contact angle measurement. The hydrophilically modified PVDF-PT membrane exhibits a positive interfacial free energy with oil in water, indicating the TiO_2 deposition effectively improve the anti-oil fouling property of PVDF-P membrane and PVDF membrane.

Membrane distillation tests were also performed to investigate the influences of membrane hydrophobicity, membrane surface structure, pH value of the feed solution and hydrodynamic conditions on oil fouling behavior. It was found that the pH value of the feed solution plays an important role in oil fouling. More severe fouling can be observed at the pH which made the membrane surface and oil droplets carry opposite charges. A higher flow velocity enhances the shear force exerted on the oil droplets, thus leading to less oil present on the membrane surface and less oil fouling of the membrane.

Chapter 4 NUMERICAL MODELING AND OPTIMIZATION OF VACUUM MEMBRANE DISTILLATION MODULE FOR LOW-COST WATER PRODUCTION

4.1 Introduction

Different from chapter 3, this chapter aims at achieving low-cost water production by numerical modeling and optimization of vacuum membrane distillation module. The reason of using vacuum membrane distillation (VMD) is mainly due to lower calculation load for a computational fluid dynamics (CFD) simulation. Less meshing is required for the PC capacity. In addition, according to the group's previous CFD simulation based on the commercial package (FLUENT), the fluid dynamics in permeate side has a similar distribution as that of feed side (Yu, Yang et al. 2011).. Therefore, simpler and more energy-efficient VMD is also investigated as for optimization of water production cost (WPC).

MD has not yet gained enough acceptance of industry despite many attractive advantages. One of the major challenges is the relatively high energy consumption and uncertain economic benefit(El-Bourawi, Ding et al. 2006).Among the four MD

configurations (DCMD, SGMD, AGMD and VMD), VMD has been reported to be the most energy efficient due to its insignificant temperature polarization effect, relatively high mass flux and energy efficiency (Lawson and Lloyd 1996, Li and Sirkar 2005). However, the disadvantage of VMD lies in the fact that it requires an external vacuum pump to facilitate the transfer of the permeate water vapor across the membrane, causing extra energy consumption (Mengual, Khayet et al. 2004). Thus, it suggests that more intensive efforts should be made with respect to the optimizations of the design and operating conditions of VMD process.

In order to make VMD process more economic for desalination, many investigations have been carried out in recent years (Lawson and Lloyd 1996, Bandini, Saavedra et al. 1997, Khayet and Matsuura 2004, Mengual, Khayet et al. 2004, Li and Sirkar 2005, Tang, Zhang et al. 2011). Among them, VMD using flat sheet membrane module was preferred because of its relatively easy fabrication (Bandini, Saavedra et al. 1997, Khayet and Matsuura 2004), while some studies also reported hollow fiber VMD modules, given its large specific membrane surface area in comparison with the flat sheet membrane module, as well as its easily scalable potentiality (Mengual, Khayet et al. 2004, Li and Sirkar 2005). However, to our best knowledge, there is no report on the economic analysis in terms of module design and the optimization of operating conditions for hollow fiber based VMD process, probably due to the fact that VMD requires external vacuum pump consumption in comparison with DCMD, making it unclear to estimate the overall energy cost.

To achieve the goal of VMD system optimization, appropriate modeling of VMD

process is required. As a conjugate heat transfer process, VMD essentially features two-dimensional (2D) heat and mass transfer in both the flow channel and membrane matrix. Therefore, the distributions of temperature, velocity and pressure along the longitudinal (z-axis) and transversal (r-axis) directions are of the concern, as a thorough understanding of the heat and mass transfer inside the VMD module cannot be attained until the profiles of these three parameters are determined. Nevertheless, at present, most of the modeling studies still adopts the approach of analytical one – dimensional (1D) modeling based on energy balance for the control volume by applying empirical heat and mass transfer equations, which were derived from non-porous and rigid heat exchangers (Lawson and Lloyd 1996, Bandini, Saavedra et al. 1997, Li and Sirkar 2005), whereas the 2D modeling employing Navier-Stokes equations as governing equations, which can provide more reliable and comprehensive information, are not commonly applied for investigation. To bridge the gap, some researches utilized commercial program packages such as FLUENT to simulate the flow condition and achieved satisfactory simulation results by comparing with the experimental data (Charfi, Khayet et al. 2010, Tang, Zhang et al. 2011). However, the computation speed of the commercial program packages is rather slow even with high performance computers. It is widely acknowledged that the numerical methods using scientific programming language (e.g. FORTRAN) or mathematical software systems (e.g. MATLAB) are superior to the commercial program packages (e.g. FLUENT, COMSOL) in terms of computation speed and efficiency (Chen, Ho et al. 2009). It seems the commercial program packages are more suitable for the cases which have very complex boundary geometry and require extremely high accuracy.

In addition, the conventional optimization strategy for a system was mainly single variable dependent, with other variables fixed (Mohamed 2011). This kind of

optimization procedures may require a large amount of experiment designs to correlate the object functions and decision variables, which can hardly reflect the interaction of the multi-variable dependent process. Intuitively, the most accurate way of the optimization is to try out all possible conditions and compare the target functions to ultimately identify the optimized match. However, this type of clumsy method is rather time consuming and extremely low efficient, especially for some complicated problems of multi-variables with a large value domain and the requirement of high accuracy.

Genetic algorithm is one of the advanced numerical methods that mimic the Darwin's natural selection and evolution, so that a better match (offspring) may probably be generated regarding to the requirement (object function). It is able to significantly scale down the choices of the match and facilitate the generation of the desired design and operating conditions from a series of combination of the match rather than from a huge number of the possibilities. Recently, Chen et al. used the genetic algorithm to perform the optimization of DCMD and AGMD systems with two and three variables based on their 1D modeling, respectively (Cheng, Wu et al. 2008, Cheng, Wu et al. 2009), but limited works on multi-variable optimization of VMD process based on 2D modeling have been reported.

In current study, we will optimize the module design and operating conditions of the VMD process. The aim objective of the study is to develop a VMD system with the lowest cost based on the economic analysis of the optimized system. Specifically, A 2D model was firstly built up for hollow fiber VMD membrane module and solved

using finite element method (FEM), which led to the acquirement of the distribution profiles of temperature, velocity and pressure in the membrane module. The objective function was established for targeting the lowest cost of water production by investigating four variables, including feed temperature, hollow fiber length, volume flow rate and vacuum pressure. The genetic algorithm was applied to seek the best design and operation conditions for VMD system. Finally, the optimization results were provided as the guidance for a VMD system with membrane area of 0.1m^2 .

4.2 Theory and methodology

4.2.1 VMD model development

- **Governing equations**

The schematic of a VMD hollow fiber module is shown in Fig. 4.1a, which represents the 2D model simulating the main configuration of the VMD module. The feed stream flowed into the lumen side, while the shell side was maintained vacuum. N represents water flux across the membrane; q_f is the volume flow rate of the feed stream. L is the length of the hollow fiber and membrane module. The r - and z -coordinates are perpendicular and parallel to the hollow fiber membrane surface, respectively.

Fig. 4. 1(a) Schematic of the VMD membrane module (b) The generated mesh in the flow and membrane domain

In principle, the steady state heat transfer in the MD module includes the convective and conductive heat transfer of the feed flow in the lumen side, the latent heat transfer associated with water vapor transport across the membrane pores, and the conductive heat transfer in the polymer membrane matrix. To define and simplify the model, some assumptions were made as follows: (1) the feed stream is a steady-state flow; (2) the flow pattern is within laminar flow region; (3) the feed stream has constant physical properties; (4) only z -axis velocity exists and r -axis velocity is assumed zero; (5) the temperature profile has no influence on the velocity profile; (6) there is no slip condition at the boundary. By considering these assumptions, the model equations of the feed flow can be expressed according to the Boussinesq approximation (Gray and Giorgini 1976):

$$\rho_f C_f u \cdot \nabla T = \nabla \cdot (k_f \nabla T) \quad (4.1)$$

$$\rho_f u \cdot \nabla u = -\nabla p + \nabla \cdot \left[\mu \left((\nabla u + (\nabla u)^T) - \frac{2}{3} \nabla \cdot u I \right) \right] + \rho_f g \quad (4.2)$$

$$\nabla \cdot u = 0 \quad (4.3)$$

where, ρ_f , C_f and k_f are the feed flow density, heat capacity and thermal conductivity, respectively; To be noted, the density of the fluid is constant in the model; T is the local temperature of the feed flow; u is the local velocity of the feed flow; p represents the local pressure; r is the local position in radial direction; μ is the viscosity of the feed flow.

If we take a piece of control volume of a HF, the feed stream flowed through the cross section area from z to $z+\Delta z$. Permeate was obtained through the cross section area. The continuity, momentum and energy balances were shown as following:

$$\frac{\pi}{4} d^2 e_z - \frac{\pi}{4} d^2 e_{z+\Delta z} - \pi d Q \Delta z = 0 \quad (4.4)$$

$$\frac{\pi}{4} d^2 \phi_z - \frac{\pi}{4} d^2 \phi_{z+\Delta z} = 0 \quad (4.5)$$

$$\frac{\pi}{4} d^2 (\rho u)_z - \frac{\pi}{4} d^2 (\rho u)_{z+\Delta z} - \pi d N \Delta z = 0 \quad (4.6)$$

where, ϕ and e were respectively the z-components of combined momentum-flux tensor and energy vector, and N and Q were the mass flux and the total heat flux.

Then, we can divide the equations by $(\frac{1}{4} \pi d^2 \Delta z)$, and the limit as Δz goes to zero,

the equations can be given as:

$$\frac{de}{dz} = \frac{4Q}{d} \quad (4.7)$$

$$\frac{d\phi}{dz} = 0 \quad (4.8)$$

$$\frac{d(\rho u)}{dz} = \frac{4N}{d} \quad (4.9)$$

When we substituted the definitions of ϕ and e , the momentum and energy equations for control volume can be given as:

$$\frac{d}{dz} \left(p - 2\mu \frac{du}{dz} + \rho v^2 \right) = 0 \quad (4.10)$$

$$\frac{d}{dz} \left(\frac{1}{2} \rho_f u^2 u + \rho_f C_f (T - T^\vartheta) u + (p - p^\vartheta) u - \mu u \frac{du}{dz} - k \frac{dT}{dz} \right) = \frac{4}{d} Q \quad (4.11)$$

The water permeate was relatively low in comparison with the feed stream. The diffusive heat transfer can also be neglected. Therefore, the above Eq. (4.11) could be simplified as:

$$\rho_f C_f u \frac{dT}{dz} + u \frac{dp}{dz} = \frac{4}{d} Q \quad (4.12)$$

The boundary conditions at the membrane surface are provided by following equations, including the heat transfer at the interface of membrane and fluid, inlet temperature and velocity and the intrinsic symmetry in terms of temperature and velocity distribution.

$$-k_f \frac{\partial T}{\partial r} \Big|_{(r=d_i/2)} = N \cdot \Delta H + \frac{k_m \cdot (T_{fm} - T_{pm})}{\delta} \quad (4.13)$$

$$T(r, 0) = T_0 \quad (4.14)$$

$$\frac{\partial T}{\partial r}(0, z) = 0 \quad (4.15)$$

$$u(r, 0) = u_0 \quad (4.16)$$

$$\frac{\partial u}{\partial r}(0, z) = 0 \quad (4.17)$$

By noting that a high degree of vacuum exists in the shell side of the VMD membrane module, the conductive heat flux across the membranes can be neglected for further simplification (Li and Sirkar 2005). Therefore, the Eq. (4.13) can be expressed by the following equation

$$-k_f \frac{\partial T}{\partial r} = N \cdot \Delta H \quad (4.18)$$

In order to solve the governing Eqs. (4.1) ~ (4.3) to determine the temperature distribution in the feed channel, the partial differential equations (PDE) need be solved by numerical methods.

- **Mass transfer in VMD process**

Although various mathematic models such as Knudsen, Poiseuille and molecular diffusion models have been developed for the predication of mass flux, it was

generally accepted that the water flux across the membrane can be expressed empirically as:

$$N = C(p_{fm} - p_{pm}) \quad (4.19)$$

where, C is the membrane distillation coefficient of the membrane and dependent on the membrane geometry and operating conditions (Schofield, Fane et al. 1990). The subscript f_m and p_m represent the membrane surface in the feed side and permeate side, respectively. It is believed that the three mechanisms of Knudsen diffusion, molecular diffusion and Poiseuille flow transition model are helpful in prediction of the MD mass flux (Fane, Schofield et al. 1987, Schofield, Fane et al. 1987, Schofield, Fane et al. 1990, Bui, Vu et al. 2010). In this study, the Knudsen model was to be applied as the molecule-pore collision mechanism was dominant in the mass transfer of VMD process (Dullien 1992). The membrane distillation coefficient C can be written as (Schofield, Fane et al. 1987, Mengual, Khayet et al. 2004):

$$C = 1.064 \frac{D\varepsilon}{\delta\tau} \left(\frac{M}{RT} \right)^{0.5} \quad (4.20)$$

where, r is the pore size; ε the porosity of the membrane, δ the membrane thickness; τ the membrane pore tortuosity; M the mass molecular of water and R the gas constant.

In the VMD process, the vapor pressure difference arisen from the temperature difference between the membrane surfaces was the driving force for water vapor transfer across the membrane. The partial pressure can be determined by correlating with the membrane surface temperature according to Antoine equation:

$$p = \exp\left(23.20 - \frac{3816.44}{T - 46.13}\right) \quad (4.21)$$

where, P and T are the water vapor pressure and membrane surface temperature at the feed side, respectively.

- **Finite element method for numerical solutions of VMD model**

In this study, Galerkin finite element method (FEM) as a standard strategy was applied to provide numerical solutions. To solve the 2D model of the flow in the lumen side, the domain of interest was heterogeneously divided by the free quad elements with the maximum element size of 5×10^{-3} m and minimum element size of 1.4×10^{-4} m. The number of the elements in the feed flow channel was set to be 4661, as it was found that no distinct higher accuracy can be achieved with more elements. The element distribution became reasonably denser towards the boundary in order to achieve a better computing accuracy due to more severe change approaching the membrane surface. A detailed distribution of the elements in the lumen side of the membrane module is shown in Fig. 4.1b.

After meshing the flow channel inside the hollow fiber, the PDE governing equations for energy, momentum and continuity were discretized and solved by Galerkin FEM. As the temperature profile did not significantly influence the hydrodynamic condition according to the model assumptions, it can be computed after the velocity profile was determined. The iteration procedure to solve the coupled equations in the governing equation is shown in Fig.4.2. The VMD module dimensions and the operating conditions were initially provided as the parameters. In addition, the boundary

conditions were also specified as introduced previously in Eqs. (4.13) ~ (4.17). The governing equations, together with the boundary were finally reduced to the algebraic equations for solution by standard Galerkin FEM using the FAESOR package. The MATLAB source codes were developed by Pkrysl from University of San Diego (http://hogwarts.ucsd.edu/~pkrysl/faesor/faesor_publish.html).

Fig. 4.2 The schematic of the calculation algorithm

4.2.2 Optimization strategy for low-cost water production

- **Economic analysis of the VMD system**

The total cost (TC) of the VMD system comprises two major parts: (1) the membrane material cost (MC); (2) the operation cost (OC). To make a valid economic analysis, several assumptions were also made in the following: (1) the membrane life time was 5 years; (2) the system availability was 90%; (3) the maintenance cost was not considered; (4) the interest rate was 5%. Therefore, the MC and OC would be formulated by the following equations (Banat and Jwaied 2008):

$$MC = P_m A \frac{i(1+i)^n}{(1+i)^n - 1} \quad (4.22)$$

$$OC = P_e W_e t + P_s W_s t \quad (4.23)$$

where, A , i and n are the membrane area, the interest rate and life expectancy of the membrane, respectively. P_m , P_e and P_s refer to the costs of unit membrane area, electricity and steam respectively. W_e , W_s and t indicate the work of electricity and waste steam heat. t is the system operating time. The OC here mainly comprises two parts: the pump energy consumption (vacuum creation and flow circulation) and the heating of feed solution by waste heat steam. The individual cost of all the items used in the VMD system for the TC calculation is listed in Table 4.1.

Table 4.1 Costs of the items used for water production cost calculation (Zuo, Wang et al. 2011)

Membrane	Electricity	Interest	Plant availability	Waste steam
\$ 36/m ²	\$ 0.06/KWH	5%	90%	\$ 0.73/t

- **Objective function for optimization**

In the study, two constraints were considered to ensure that a certain scale of VMD membrane module was maintained for water production, and the pressure drop in the tube side of the hollow fiber module did not go beyond a reasonable value. Therefore, either the membrane area smaller than the process requirement or the pressure drop in the tube side over the maximum allowable value would be eliminated during the optimization process. As such, the water production cost (WPC) was set as the objective function with two constraints for optimization:

$$\text{Min. } WPC = TC / N \cdot A \cdot t \quad (4.24)$$

$$\text{Subject to } A \geq A_{\text{required}}$$

$$\Delta P_t \leq \Delta P_{tp} \quad (4.25)$$

where, the TC is the total cost of the VMD system; N and A are the mass flux per unit membrane area and membrane area, respectively; P_t and ΔP_{tp} are the real pressure drop and permitted pressure drop in the tube side of the hollow fiber.

The TC and N are associated with the module design and operating variables of the VMD systems. Four key parameters, including the feed temperature, hollow fiber length, vacuum pressure and the feed flow rate with certain boundaries, were taken into consideration, and the ranges of these parameters are listed below:

- 1) The feed temperature was ranging from 50 °C to 90°C.
- 2) The length of the hollow fiber was from 0.25 m to 0.50 m.

- 3) The flow rate of the feed stream varied from 1.2 LPM to 6.0LPM.
- 4) The vacuum pressure was taken from 4 kPa to 10 kPa.

- **The genetic algorithm for optimization**

The optimization was conducted using the genetic algorithm. With four design and operation variables in consideration, millions of combinations were possible options. For a large-scale discrete optimization problem, the genetic algorithm is able to determine the optimal designs. A detailed description of the genetic algorithm could be found in literature(Sivanandam and Deepa 2010).

Fig.4.3 presents the schematic diagram of the genetic algorithm optimization procedure. To be noted, since the genetic algorithm was a numeric search method based on the theory of stochastic probability, it was difficult to set a criterion of convergence as the traditional search methods. Here, the genetic algorithm procedure was terminated after 300 consecutive generations if no improvement of the best design occurred.

Fig. 4.3 The schematic diagram of the genetic algorithm (GA) optimization procedure

- **Sensitivity analysis**

In order to further elucidate the optimization results, sensitivity analysis involving the investigation of the impacts of selected design variables (feed temperature (x_1), hollow fiber length (x_2), flow rate (x_3) and vacuum (x_4)) and their second-orders as well as their interaction terms on the objective function of WPC was also provided. The quadratic model for the VMD system can be formulated as the following equation (Chang, Liao et al. 2009):

$$WPC = C_0 + \sum_{i=1}^4 C_i x_i + \sum_{i=1}^4 C_{ii} x_{ii}^2 + \sum_{i=1}^4 \sum_{j=1}^4 C_{ij} x_{ij} + \omega \quad (4.26)$$

where, C_i , C_{ij} and ω are the first-order coefficient, symmetrical interaction coefficient and random error respectively. To determine the coefficients in Eq. (4.26), a multiple linear regression (MLR) was applied, and then the least square method was used to determine the coefficients. Analysis of variance was performed by applying Minitab software package.

4.3 Results and discussion

4.3.1 Verification of cross-flow VMD model

Fig.4.4 depicts the mass flux as a function of the feed temperature ranging from 35 °C to 65°C with the feed flow velocity of 0.6 m/s in a cross-flow MD module obtained by the 2D modeling in the present work and the experiment reported in the literature

(Mengual, Khayet et al. 2004). Basic characteristics of the membrane module used for the simulation are listed in Table 4.2. It can be seen that the simulated results were in good agreement with the experimental data under the same conditions. This suggested that the 2D model was valid to predicate the performance of VMD modules in the cross-flow configuration. And therefore, the proved modeling will be used in the following sections.

Fig. 4.4 Comparison between simulation results and experiment results (Mengual, Khayet et al. 2004) (Feed temperature: 35-65 °C, feed velocity: 0.6 m/s, Vacuum: 4k Pa)

Table 4.2 Basic characteristics of the membrane module used for simulation (Mengual, Khayet et al. 2004)

Length (mm)	470
Inside diameter (mm)	1.8
Outside diameter (mm)	2.6
Pore size (μm)	0.2
Membrane material	Polypropylene
Thickness (μm)	400
Porosity	70%
Number of fibers	40

4.3.2 Temperature, pressure and velocity profiles in the flow channel

For a 2D process, the variation in parameters was featured in both axis direction (z -) and radial direction (r -). Fig. 4.5a shows the temperature profile in the flow channel. To make it clearer in both directions, Fig. 4.5b shows the temperature profiles in the radial direction at different locations of the flow channel, while Fig. 5c depicts the temperature distributions of the lumen center and membrane surface along flowing direction. From Fig. 4.5b, it was observed that along the radial direction from the center of the hollow fiber ($r=0$) to the wall ($r=d_i/2$), the temperature gradually decreased because of the heat transfer through the membrane, which was associated

with the mass transfer of the water vapor. In addition, the temperature gradient was relatively small near the center of the flow channel and increased significantly nearby the membrane surface due to the existence of the thermal boundary layer near the membrane surface.

(a)

From Fig. 4.5c, it can be seen that both of the temperatures decreased along the flow direction due to the loss of the latent heat associated with the water vapor across the membrane. Similar results were also found in the literature (Chen, Ho et al. 2009). The decrease of membrane surface temperature along flow direction suggests that the membrane length should be optimized as the mass flux across the membrane would decrease gradually along the membrane module due to reduced driving force for mass transfer. A long membrane module may not be efficient for water production.

(b)

(c)

Fig. 4.5(a) Temperature distribution in 2D domain of the flow channel; (b) Temperature profiles in radial direction at different locations of the flow channel; (c) Temperature distributions of the lumen center and membrane surface along flowing direction ($T_{fo}=60\text{ }^{\circ}\text{C}$, $v_f=0.6\text{ m/s}$, $P_{vacuum}=4\text{ kPa}$)

Fig. 4.6 and Fig. 4.7 illustrate the pressure and velocity profiles in the lumen side of the membrane fiber. Since it was assumed that only the z -direction velocity existed, the pressure gradient in the r -direction was zero. From Fig. 4.6, it can be seen that the pressure gradient in the z -direction was linear-like, corresponding to the empirical relationship of pressure drop and the length of flow channel (Bird, Stewart et al. 2006). Along with the flow direction, the pressure gradually drops mainly due to the shear stress existence between the fluid and the membrane surface. From Fig. 4.7, it is observed that the feed flow enter into the hollow fiber with a uniform velocity in the cross section of the flow channel. And when the feed flow develops along the hollow fiber, the boundary layer starts to form when approaching to the membrane surface. That is simply due to the flow adjacent to the membrane surface has zero velocity when the non-slip boundary is to be respected. Based on the profiles shown in Figs. 4.5 to 4.7, the VMD performance and related parameters can thus be determined.

Fig. 4.6 Pressure distribution in 2D domain of the flow channel ($T_{fo}=60\text{ }^{\circ}\text{C}$, $v_0=0.6\text{ m/s}$, vacuum pressure =4k Pa)

Fig. 4.7 Velocity distribution in 2D domain of the flow channel ($T_{fo}=60\text{ }^{\circ}\text{C}$, $v_0=0.6\text{ m/s}$, vacuum pressure =4k Pa)

4.3.3 Optimization of module design and operating conditions

To elaborate the optimization process, one case study was performed by taking the basic data from literature (Mengual, Khayet et al. 2004). Table 4.3 showcases suitable constraints regarding to feasible ranges of input parameters were also defined for the process. Table 4.4 presents optimized design variables and the corresponding values of the objective function of WPC for VMD membrane module. The variation ranges of the design and operation parameters were also listed in the table. In comparison with the non-optimized VMD configuration (experiment conditions) (Mengual, Khayet et al. 2004), the optimized VMD tended to adopt a high feed temperature, as it can significantly enhance the water production, but the lower boundary of the hollow

fiber length was chosen to effectively reduce the increase of the operation cost caused by the pressure drop. The flow rate was at the lower bound of the domain from 1.2LPM to 6.0LPM, indicating that the pressure loss induced operation cost was significant, while the benefit of a larger volumetric flow rate was not enough to offset the increase of the pump energy cost. The vacuum pressure was adopted a moderate value of the domain from 2kPa to 10kPa, suggesting the benefit of high vacuum-induced water production not overwhelming the electric cost of the vacuum creation by isothermal compression work.

Table 4.3 Process requirements for case study of VMD process (operation period =7884 h/year, electricity cost= 0.06 \$/KWH, $n=20$, $i=5\%$, $\eta=80\%$)

Parameter	Tube side
Fluid	3.5 wt% NaCl in water
Flow rate (LPM)	0.8 -6.0
Temperature (°C)	50-90
Operating pressure (kPa)	100
Allowable pressure drop (kPa)	10

Table 4.4 Optimized design variables from genetic algorithm (GA) for VMD
membrane module

Parameter	Optimized	Non-optimized	Variation range
Feed temperature (°C)	90	60	50-90
Fiber length (m)	0.25	0.47	0.25-0.50
Volume flow rate (LPM)	1.2	3.6	1.2-6.0
Vacuum pressure (kPa)	6.8	4.0	2-10
Total membrane area (m ²)	0.1	0.1	
Mass product (kg/h)	5.4	2.3	
Pressure drop (kPa)	0.55	2.7	
Operating cost (\$/year)	4.70	2.98	
Membrane cost ((\$/year)	0.83	0.83	
Total cost ((\$/year)	5.53	3.81	
Water production cost (\$/t)	0.13	0.21	
Decrease by (%)	38.1		

Fig. 4.8 shows the convergence of the objective function of WPC with the number of generation. It was observed that the average value of the WPC was higher than the optimum value before 200 generations and then remained the same after 200 generations. It indicated that the better gene was gradually shared by the community and ultimately the solutions approached to the same value.

Fig. 4.8 The minimization of the water production cost with optimized solution and average solution by GA

4.3.4 Sensitivity of four variables

One hundred sets of data points were selected to determine the coefficients of Eq. (4.25) used for the sensitivity analysis of four variables to WPC. The coefficients and analysis of variance for the quadratic model with 95% of confidence level are listed in Table 4.5. The F value, which tests the homogeneity of variance, was used to evaluate whether the regression model was adequate to describe the obtained simulation data (Peck, Olsen et al. 2011). And it was observed that the overall F-test for the quadratic regression model was significant with probability less than 0.05, which suggested that WPC was closely related to the four selected design variables, including feed temperature (x_1), hollow fiber length (x_2), flow rate (x_3) and vacuum (x_4). To verify the model, residuals analysis was also performed. Fig. 4.9a and

Fig.4.9b present normal probability plot of the studentized residuals and the plot of studentized residuals versus predicted values for the WPC, respectively. It was observed that the majority of the residuals fell around the straight line, indicating that the predicting model was fairly valid. Based on the results listed in Table 4.5, some of the coefficients are negligible due to lack of close correlation (probability larger than 0.05).

Table 4.5 Coefficients and analysis of variance for quadratic model with 95% of confidence level

Term	Coefficient	Standard error	F value	Probability
model	-	-	28.84	<0.0001*
x ₁	-1.31E-3	2.95E-4	23.78	<0.0001*
x ₂	-2.11E-1	4.98E-2	56.69	<0.0001*
x ₃	-4.82E-2	6.67E-3	32.81	<0.0001*
x ₄	-6.98E-5	3.03E-6	25.71	<0.0001*
x ₁ x ₁	6.00E-7	5.00E-8	17.96	0.0036*
x ₂ x ₂	6.74E-0	4.60E-1	17.28	0.0035*
x ₃ x ₃	1.27E-2	1.24E-3	18.64	0.0038*
x ₄ x ₄	5.80E-9	2.31E-10	27.68	<0.0001*
x ₁ x ₂	-1.50E-4	5.23E-5	13.09	0.0077*
x ₁ x ₃	-7.10E-5	6.85E-6	8.78	0.0229*
x ₁ x ₄	-7.00E-8	5.00E-9	1.13	0.5243
x ₂ x ₃	6.10E-2	8.04E-3	2.44	0.1172
x ₂ x ₄	-1.30E-4	3.88E-5	1.87	0.1968
x ₃ x ₄	8.00E-8	3.70E-9	4.42	0.0421*
R ² = 98.7% * indicates significant term

(a)

(b)

Fig. 4.9 (a) Normal probability plot of the studentized residuals for water production cost; (b) Plot of studentized residuals versus predicted values for water production cost.

Fig. 4.10a shows the response surface plot of the effects of feed temperature and fiber length on water production cost, while Fig. 4.10b illustrates the effects of vacuum and flow rate on water production cost. The decrease in feed temperature significantly increased the WPC. This result was in agreement with the general acknowledgement that a high feed temperature can enhance water flux significantly because of the exponential relationship between the vapor pressure and temperature, as shown in Eq. (4.12). Obviously, the VMD module should operate at a feed temperature as high as possible provided that the heating sources are available (Zuo, Wang et al. 2011).

As can be seen in the surface plots shown in Fig.4.10, the decrease in feed temperature significantly increased the WPC. It is well understood that, a high feed temperature has a positive effect on water production rate. This result was in agreement with the general acknowledgement that a high feed temperature can enhance water flux significantly because of the exponential relationship between the vapor pressure and temperature. Based on the simulation result, it is recommended that the VMD module should operate at a feed temperature as high as possible, though low-grade waste heat as the heating source may be expected (Zuo, Wang et al. 2011).

(a)

(b)

Fig. 4.10(a) Response surface plot of the effect of fiber number and fiber length on water production cost (b) Response surface plot of the effect of vacuum and flow rate on water production cost

Hollow fiber length also played an important role in WPC of the VMD system based on two aspects. On one hand, the driving force was gradually lost because of the development of the thermal boundary layer along the fiber length, as shown in Fig. 4.5a, leading to a lower average mass flux for a longer fiber. On the other hand, a longer hollow fiber would cause a higher pressure drop as shown in Fig. 4.5c. Similar finding was also reported in the literature (Yang, Wang et al. 2011). Therefore, it was necessary to use a shorter fiber in an attempt to reduce the WPC.

With the increase of the feed flow rate, the mass flux across the membrane increased accordingly. The dependence of the mass flux on Reynolds number was due to the heat transfer in the thermal boundary layer in the lumen side. With a higher flow rate, which corresponds to a larger Reynolds number, the heat transfer coefficient was enhanced, leading to the suppression of the temperature polarization, which was one of the most important factors adversely affecting the MD process (Yang, Wang et al. 2011). Nevertheless, a higher Reynolds number, which benefited the heat transfer within the thermal boundary layer, was actually at the penalty of higher energy consumption. With the increase of the circulation velocity (larger Re), the pressure drop in the lumen side of the fiber was significantly increased. Thus, it was required to balance the benefit of the more mass flux and the penalty of the energy usage.

When the vacuum pressure was increased at the shell side, the mass flux gradually decreased because of the loss of the driving force across the membrane, as indicated by Eq. (4.10). It was worth noting that although a higher degree of vacuum can produce more mass flux with the same membrane area, the energy consumption

should also be considered due to more work required to maintain the vacuum for water production. In the current study, it seemed the benefit of high water production did not significantly outweighed the electrical cost stemming from the high vacuum, resulting in the choice of a moderate degree of vacuum for the sake of low WPC.

4.4 Conclusions

In this study, a 2D heat and mass transfer model for the VMD system was developed and numerically solved. The modeling has been proved to be valid for the prediction of the VMD performance. With the temperature, velocity and pressure profiles obtained from the modeling, four variables, including feed temperature, fiber length, volume flow rate and vacuum pressure as the key design and operating conditions, were optimized for low-cost water production using genetic algorithm.

It was found that the water production cost per ton decreased by 38.1% for an optimized system. It is preferable to adopt a higher feed temperature to produce more water. While for a given membrane area used, a shorter fiber length is favored in order to decrease the pressure-drop induced operation cost. The volume flow rate should be low as a significant pressure drop is expected, leading to relatively high operation cost. The vacuum pressure should be kept moderate because the increase of water production does not overwhelm the electric cost in the current stud

Chapter 5 ENERGY EFFICIENCY EVALUATION AND ECONOMIC ANALYSES OF DIRECT CONTACT MEMBRANE DISTILLATION SYSTEM USING ASPEN PLUS

5.1 Introduction

As discussed in Chapter 4, to improve MD performance, studies have focused on strategies to optimize the single lab-scale MD module through module modeling, design and operation parameters. However, to make MD an industrial technology, the scale-up of MD module and system are required. Therefore, this chapter aims at evaluating the energy efficiency and economics of large-scale DCMD system on Aspen Plus platform, which was also a part of a collaborated project of Singapore Membrane Technological Center (SMTC). Further comparison study of DCMD and VMD system, based on Aspen Plus platform has been ongoing now in order to provide a comprehensive investigation of the energy consumption of both configurations.

At present, the main challenge for large-scale MD desalination is energy consumption, which leads to a relatively high cost for water production as compared with reverse

osmosis (RO), one of the most important desalination technologies (Martínez-Díez, Florido-Díaz et al. 1999, Khayet, Godino et al. 2003). However, MD only requires moderate temperature to generate a thermal driving force across the membrane. It can be economically competitive when low-grade waste heat or renewable energy resources such as solar energy are available for use (Lawson and Lloyd 1997, Banat, Jumah et al. 2002, Alklaibi and Lior 2005). In addition, many efforts have been made to improve the hydrodynamic conditions in MD modules (Schofield, Fane et al. 1987, Zhongwei, Liying et al. 2003, El-Bourawi, Ding et al. 2006, Cheng, Wu et al. 2008, Teoh, Bonyadi et al. 2008), as the hydrodynamics are closely associated with the thermal condition for water transfer. It was reported that temperature polarization in a DCMD module can be minimized through hydrodynamic improvement (Schofield, Fane et al. 1987, Schneider, Hölz et al. 1988, Hogan, Sudjito et al. 1991). Moreover, system optimization, by incorporating a heat exchanger in the MD system for heat recovery, can further reduce the energy requirement (Fane, Schofield et al. 1987, Schneider, Hölz et al. 1988, Ding, Liu et al. 2005, Al-Obaidani, Curcio et al. 2008). The concept of gain to output ratio (GOR), which is defined as the ratio of heat associated with mass transfer to the energy input, has been applied to reflect the energy efficiency of the MD process decades ago. Nevertheless, little research has been focused on the influence of the design and operating parameters on the GOR value (Fane, Schofield et al. 1987, Gilron, Song et al. 2007). The economic analyses on MD process have been performed mainly for the situations where all the design and operation variables are fixed (Hogan, Sudjito et al. 1991, Banat, Jumah et al. 2002, Al-Obaidani, Curcio et al. 2008, Banat and Jwaied 2008). There is a scarcity of economic analysis in terms of the influences of the key design and operating parameters (Gilron, Song et al. 2007).

In order to achieve system optimization, simulation of the MD process has to be carried out. The membrane module, which is the core element of the MD system, has been modeled extensively (Bouguecha, Chouikh et al. 2003, Ding, Ma et al. 2003, Imdakm and Matsuura 2004, Imdakm and Matsuura 2005, Cheng, Wu et al. 2008, Khayet, Imdakm et al. 2010). Several researchers have applied Matlab to simulate the heat and mass transfer in the MD module and the results were compared with the experimental data (Gilron, Song et al. 2007, Qtaishat, Matsuura et al. 2008, Bui, Vu et al. 2010). In contrast, limited reports are available for system design and optimization (Gilron, Song et al. 2007, Al-Obaidani, Curcio et al. 2008). The commercial software, Aspen Plus, which is a widely used simulation platform in chemical engineering processes, has been applied recently to study the MD system (Chang, Liao et al. 2009, Chang, Wang et al. 2010). In these studies, a customized membrane module was programmed by FORTRAN, and then incorporated as a user-defined unit into the system. The mass fluxes based on different operating conditions were predicted for a small membrane unit (membrane area: 0.286m^2), but no direct linkage of operation and design parameters with economic analysis was provided, though this is very important for practical MD applications. In the present study, a DCMD system was simulated using the process simulation platform, Aspen Plus, for the purpose of energy efficiency and economic analyses. A cross-flow membrane module, which is not available in the Aspen Plus, was firstly defined and modeled, and then incorporated into the flow sheet for system simulation. Detailed investigations have been conducted to understand the relationships between the water flux/production and design & operation parameters, including membrane area, feed temperature, feed and permeate velocities, etc. Moreover, this study examined the variation of the GOR with the design and operation parameters. With the assumption of using an alternative energy such as waste heat in the MD system, economic analysis was also performed. It is expected that based on this study, a guideline for

optimal design and operation of DCMD system in terms of energy efficiency and water production cost can be attained, which will benefit practical applications of DCMD for desalination.

5.2 Theory and methodology

5.2.1 Heat and mass transfer in DCMD

- Heat transfer in DCMD

Fig. 5.1 Schematic of DCMD module

The heat transfer from the feed side to the permeate side consists of two components: (a) latent heat associating with the water vapor across the membrane (Q_v), and (b) conduction heat by membrane matrix (Q_c). Fig. 5.1 illustrates the heat transfer processes, which can be expressed for unit area as follows:

$$Q_f = h_f(T_f - T_{fm}) \quad (5.1)$$

$$Q_p = h_p(T_p - T_{pm}) \quad (5.2)$$

$$Q_m = Q_v + Q_c = N\Delta H + \frac{k_m}{\delta}(T_{fm} - T_{pm}) \quad (5.3)$$

where, Q_f , Q_p and Q_m are the heat flux transferred in the feed and permeate boundary layers and across the membrane, respectively; T_f and T_p are the bulk temperatures of the feed and permeate sides. T_{fm} and T_{pm} are the membrane surface temperatures in the feed and permeate sides, respectively. N is the mass flux ($\text{kg/m}^2\text{h}$); ΔH is the enthalpy of water evaporation (kJ/kg); k_m is the thermal conductivity of the porous membrane with the value of $631 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ (Phattaranawik, Jiraratananon et al. 2003). δ is the membrane thickness (m). At steady state, the heat balance guarantees that the three consecutive heat transfers satisfy the following equation:

$$Q_f = Q_m = Q_p \quad (5.4)$$

The heat transfer coefficients in the feed and permeate boundary layers, h_f and h_p can be calculated using a number of methods (Qtaishat, Matsuura et al. 2008). Here, one simple and effective form, which has been proved to be valid in the cross-flow configuration of MD module, was taken from the literature (Li and Sirkar 2004, Song, Li et al. 2007):

$$Nu_p = \frac{h_p d_i}{k_p} = 1.86 \left(\frac{d_i}{L} \right) 0.33 (\text{Re}_p \text{Pr}_p)^{0.33} \left(\frac{\mu_p}{\mu_{pm}} \right)^{0.14}$$

$$\text{Re}_p = \frac{d_i u_p \rho_p}{\mu_p}; \quad \text{Pr}_p = \frac{C_p \mu_p}{k_p} \quad (5.5)$$

$$Nu_f = \frac{h_f d_o}{k_f} = 0.71 Re_f^{0.5} Pr_f^{0.36} \left(\frac{Pr_f}{Pr_{fm}} \right)^{0.25} F_c$$

$$Re_f = \frac{d_o u_f \rho_f}{\mu_f}; \quad Pr_f = \frac{C_f \mu_f}{k_f}; \quad Pr_{fm} = \frac{C_{fm} \mu_{fm}}{k_{fm}} \quad (5.6)$$

where, Nusselt number (Nu) is correlated with Reynolds number (Re) and Prandtl number (Pr), the former is related to hydrodynamic conditions, while the latter is only temperature dependent. L is the fiber length. d_i is the inner diameter of the hollow fiber, d_h is the hydraulic diameter of the flow channel when the feed stream flows in the shell side. μ is the fluid dynamic viscosity. k is the liquid thermal conductivity, and F_c is the tube-row correction factor. The definitions of other symbols can be found in the nomenclature.

- **Mass transfer in DCMD**

In the DCMD process, the vapor pressure difference arising from the temperature difference between the two surfaces of the membrane is the driving force for water vapor transfer across the membrane. From Eqs.(5.1) ~ (5.4), the membrane surface temperatures can be derived as follows (Bui, Vu et al. 2010):

$$T_{fm} = T_f - (T_f - T_p) \frac{1/h_f * d_i / d_o}{1/h_f * d_i / d_o + 1/(N\Delta H / (T_{fm} - T_{pm}) + \frac{k_m}{\delta}) + 1/h_p} \quad (5.7)$$

$$T_{pm} = T_p + (T_f - T_p) \frac{1/h_p}{1/h_f * d_i / d_o + 1/(N\Delta H / (T_{fm} - T_{pm}) + \frac{k_m}{\delta}) + 1/h_p} \quad (5.8)$$

where, d_o is the outer diameter of the hollow fiber. Water vapor pressure (p) is correlated to temperature based on the Antoine equation:

$$p = \exp\left(23.20 - \frac{3816.44}{T + 226.87}\right) \quad (5.9)$$

where, T is the temperature of the membrane surface. Although various mathematic models such as Knudsen, Poiseuille and molecular diffusion models have been developed for the predication of mass flux, it is generally accepted that the water flux across the membrane can be expressed empirically as (Fane, Schofield et al. 1987)

$$N = C(P_{fm} - P_{pm}) \quad (5.10)$$

where, C is the membrane distillation coefficient. Previous studies have suggested that C is only slightly dependent on temperature and can be considered as a relatively constant number in the calculation (Schofield, Fane et al. 1987, Song, Li et al. 2007, Bui, Vu et al. 2010). Here, the C value was taken as $8.6 \times 10^{-7} \text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{kPa}^{-1}$ as recommended in the literature (Song, Li et al. 2007).

5.2.2 Modeling of cross-flow DCMD module

A cross-flow membrane module as shown in Fig. 5.2a, was selected as a model DCMD unit for simulation. Several studies on this type of configuration suggested that it has less temperature polarization effect and the mass transport coefficient can be enhanced significantly for Reynolds numbers that are not very high (Wickramasinghe, Semmens et al. 1992, Gilron, Song et al. 2007).

Fig. 5.2(a) Cross-flow configuration of MD module

(b) Division of MD module into small regions ($N \times N$) for modeling

Fig. 5.2b shows the simulation strategy. The DCMD module was divided into many small regions ($N \times N$). The heat and mass transfer models discussed in Section 5.1 were applied to each region and programmed in Matlab, and the differential equations for each region were solved using the *fsolve* function in Matlab.

The detailed algorithm is illustrated in Fig. 5.3, which involved initial assumptions, calculation, comparison and iteration. The results, including the outlet temperature and flow rate at both the feed and permeate sides in the MD module, served as the input parameters in the subsequent system simulation on the Aspen Plus platform. The experimental data reported in the literature (Chang, Liao et al. 2009) for the same MD configuration were used to verify the modeling results. The basic characteristics of the membrane module used for modeling are listed in Table 5.1.

Table 5.1 Basic characteristics of the membrane and module
(Chang, Liao et al. 2009)

Length (mm)	254
Inside diameter (mm)	0.33
Outside diameter (mm)	0.043
Packing factor	0.22
Membrane material	Polypropylene
Thickness (μm)	150
Porosity	0.04

Fig. 5.3 Calculation procedures in MD module

5.2.3 Simulation of DCMD system

A DCMD system, which includes a cross-flow membrane module, one heat exchanger, two centrifugal pumps, one heater, one cooler, four valves and two tanks, was designed to simulate an entire DCMD system using Aspen Plus. Fig. 5.4 shows the flow sheet of the system. A feed solution (model seawater: 3.0 wt% sodium chloride) was heated to an initial temperature in the range 60°C-90 °C, and then circulated through the shell side of the membrane module a velocity between 0.022 and 0.055 m/s, followed by heat exchange to recover heat from the hot permeate side. Meanwhile, the permeate side (pure water) was maintained at 25 °C and circulated through the lumen of the membrane fibers at a velocity in the range 0.25-0.83 m/s, and then flowed into the heat exchanger for energy recovery.

Fig. 5.4 The schematic flow chart of the MD system

To run the system, the self-defined cross-flow DCMD module was connected with

Aspen Plus as a user modular through four parameters of outlet temperature and flow rate at the feed and permeate sides. Other units such as the heat exchanger are built-in modules in Aspen Plus. Since the feed stream is seawater (3.0 wt%), the electrolyte NRTL, which is a thermodynamic fluid package in Aspen Plus, was selected for the simulation.

5.2.4 Energy efficiency based on the GOR

Based on the system simulation in Aspen Plus platform, the GOR, expressed in terms of the water produced per steam equivalent, as a function of various design and operating parameters can be found. The following equation was used for the GOR calculation (Gilron, Song et al. 2007):

$$GOR = \eta \frac{\Delta T_{axmd}}{\Delta T_{md} + \Delta T_{HX}} \quad (5.11)$$

where, η is the thermal efficiency of the DCMD module, which is defined as the ratio of heat associated with mass flux across the membrane to the total heat transferred from the hot feed side to the cold permeate side. ΔT_{axmd} is the temperature drop on the feed side; ΔT_{md} is the temperature difference across the membrane module; and ΔT_{HX} is the temperature difference in the heat exchanger.

5.2.5 Economic analysis of water production

Several assumptions were made for the economic analysis (Banat and Jwaied 2008): (1) the system life is expected to be 20 years; (2) the membrane usage time is 5 years; (3) the system availability is 90%; (4) operation and maintenance costs are not considered; (5) the interest rate is 5%. To be noted, the omission of (4) is balanced by the relatively low value in (3).

It was also assumed that water production cost (WPC) (\$/m³) involves five main components, namely membrane module, heat exchanger, electricity consumption for pumping, waste steam and installation of the system. Similar considerations can be found in the literature (Hogan, Sudjito et al. 1991, Banat, Jumah et al. 2002, Al-Obaidani, Curcio et al. 2008, Banat and Jwaied 2008). The replacements of membrane and heat exchanger were considered by estimating the depreciation rates. The pumping cost was caused by the pressure drop in the circulation loop, which can be calculated in Aspen Plus. Table 5.2 lists the estimated costs of the above mentioned items in the MD system. The detailed calculation of WPC is based on following equation:

$$WPC(\$/m^3) = \frac{a \times A_m \times P_m + b \times A_{HX} \times P_{HX} + c \times W \times P + c_e \times IF \times (A_m \times P_m + A_{HX} \times P_{HX})}{M_{wp}} + P_s / GOR \quad (5.12)$$

where, a , b , c are depreciation rates of membrane module, heat exchanger and related installation components, respectively. A_{MEM} and A_{HX} are the areas of the membrane and heat exchanger, respectively. P_m , P_{HX} , P_e and P_s refer to the costs of unit

membrane area, heat exchanger area, electricity consumption and waste steam respectively, which are listed in Table 5.2. M_{wp} is the annual water production (kg/year). IF is the installation factor and GOR is the gain output ratio of the DCMD system.

Table 5.2 Costs of the items used for WPC calculation

Membrane	Heat exchanger	Electricity	Waste steam	Installation factor
\$ 36/m ²	\$ 92.3/m ²	\$ 0.06/kwh	\$ 0.73/t	1.67

5.3 Results and discussion

5.3.1 Verification of cross-flow DCMD model

Fig. 5.5 depicts the water flux as a function of feed temperature ranging from 50°C to 90 °C in a cross-flow DCMD module obtained by modeling in the present work and the experiment reported in the literature (Song, Li et al. 2007). It can be seen that the simulated results were in good agreement with the experimental data under the same conditions. This suggests that the MD model can be used to predict the performance of MD modules in the cross-flow configuration. Thus, with simulated results under various operating conditions, the cross-flow DCMD module was incorporated into the flowsheet of the designed MD system for further energy efficiency and economic analyses.

Fig. 5.5 Comparison of modeling results with experimental data in a cross-flow DCMD module (feed temperature: 50°C -90 °C, feed velocity: 0.04 m/s, feed concentration: 3.0 wt%, permeate temperature: 25 °C, permeate velocity: 0.48 m/s, membrane area: 0.286 m²)

5.3.2 Effects of membrane area and feed temperature on water flux and production

The DCMD module performance was studied as a function of membrane area, feed temperature, feed velocity and permeate velocity. Since permeate temperature is usually maintained at a relatively constant level of room temperature (25 °C), it is not considered as an operational variable in the simulation. As shown in Fig. 5.6a and b, an increasing feed temperature had a positive effect on the water flux and production

rate (mass flux multiplied by membrane area). This result is, of course, in agreement with the general acknowledgement that a high feed temperature can enhance water flux significantly because of the exponential relationship between vapor pressure and temperature, as shown in Eq. (5.9). Whilst it is recommended that the DCMD module should operate at a feed temperature as high as possible, it is recognized that when utilizing low-grade waste heat as the heating source, a moderate feed temperature may be expected.

From Fig. 5.6, it can also be observed that with an increase of membrane area, the water flux gradually decreased, and then approached to an asymptotic value. In contrast, the water production presented a different trend of a gradual increase followed by a tendency towards an asymptotic value. This arises because there was a loss in the driving force with increasing membrane area, which was less exploited for mass and heat transfers. With an increase in fiber length, T_{fm} eventually approaches T_{pm} resulting in an extremely low temperature gradient across the membrane at the end of the fiber, which would make a negligible differential contribution to the flux (Cheng, Wu et al. 2008). However, the water production is proportional to the membrane area. For the given layout and parameters a critical point corresponding to the membrane area of about 4m^2 was identified in the present study. When the membrane area was beyond this critical point, the changes in water flux and production were not so significant. Obviously, more water production in a larger membrane module is at the penalty of more capital investment, which will be discussed in Section 5.5. Therefore, it is desirable to operate a DCMD system with moderate membrane area, which is consistent with the finding of Gilron et al. (Gilron, Song et al. 2007).

(a)

(b)

Fig. 5.6(a) Effects of membrane area and feed temperature on water mass flux; (b) Effects of membrane area and feed temperature on water production (feed velocity: 0.04m/s, feed concentration: 3.0wt%, permeate velocity: 0.48m/s, permeate temperature: 25 °C)

5.3.3 Effects of feed and permeate velocities on water flux and production

Fig. 5.7 presents the effects of feed and permeate velocities on water production for a membrane module with fixed membrane area. In this case, the trend of water flux over the feed and permeate velocities is similar to the water production curve. It was observed that a quasi-linear increase of water production as a function of feed and permeate velocities occurred when the permeate velocity was below 0.48 m/s and feed velocity was below 0.04 m/s, but the slopes of the curve gradually flattened when the velocities were further increased.

It has been widely reported that higher feed and permeate velocities can help to reduce the thickness of the boundary layer adjacent to the membrane surface, thus the concentration and temperature polarizations can be mitigated, leading to a higher driving force between the feed and permeate sides. However, when the flows of the feed and permeate streams have reached a certain level, the heat transfer in the boundary layer is no longer the controlling step and so the mass flux/water production is not as sensitive as before to increases in feed and permeate velocities. One thing worth noting is that, for the cross-flow MD process, the heat transfer coefficients can approach an asymptotic value before the fluids reached turbulence ($Re > 2000$) (Li and Sirkar 2004, Li and Sirkar 2005, Song, Li et al. 2007). Thus moderate permeate velocity (0.48 m/s) and feed velocity (0.04 m/s) in this study are preferred for maintaining a reasonable water production with less pumping energy, as further increase in fluid velocities would not benefit the mass transfer significantly.

Fig. 5.7 Effects of permeate velocity and feed velocity on water production (feed temperature: 60 °C, feed concentration: 3.0 wt%, permeate temperature: 25 °C, membrane area: 4 m²)

5.3.4 The GOR analysis

The effects of membrane area and feed temperature on the GOR value based on the system simulation using Aspen Plus are shown in Fig. 5.8. As discussed in the section 5.2, the feed temperature has a significant influence on the water flux and production. To operate a DCMD system at a high feed temperature, high energy efficiency is anticipated. This is in accordance with the finding from Fane *et al.* (Fane, Schofield et al. 1987). However, the energy source is of concern if DCMD systems are to be economically viable. In the present study, waste heat was assumed to be used in the MD system, which would limit the feed temperature to a moderate level.

A higher GOR value can also be attained with an increase in membrane area, and a similar result was found in the literature (Gilron, Song et al. 2007). However, more capital costs are required for providing more membranes and making larger membrane modules, which will be further discussed in section 5.5. It was also observed that the increase of the GOR was slowed down with increasing membrane area over 4m^2 . This result implies that an optimal membrane area does exist.

Fig. 5.8 Effects of membrane area and feed temperature on the GOR (feed velocity: 0.04m/s, feed concentration: 3.0wt%, permeate velocity: 0.48m/s, permeate temperature: 25 °C)

Fig. 5.9 depicts the relationships of the GOR with the feed and permeates velocities. It can be seen that the GOR increased with the increase of both velocities, and finally reached a stable value. The permeate velocity of around 0.48 m/s seems to be a critical value, beyond which, no significant improvement in the GOR can be observed,

whilst the change in the GOR caused by the feed velocity was relatively steady. These results corresponded to the impacts of fluid velocities on the water production, shown in Fig. 5.7. It is recommended that a DCMD system be operated at the feed velocity as high as possible from the concern of the GOR enhancement. However, the GOR only reflects how well the energy is utilized for the water production. For economic analysis, operation and capital costs associated with the design and operation strategy should be taken into account.

Fig. 5.9 Effects of permeate velocity and feed velocity on the GOR (feed temperature: 60 °C, feed concentration: 3.0 wt%, permeate temperature: 25 °C, membrane area: 4 m²)

5.3.5 Water production cost (WPC)

Fig. 5.10 illustrates the effects of temperature difference (ΔT_{HX}) in the heat exchanger and membrane area on the WPC. The estimated WPCs are within the range reported in the literature (Gilron, Song et al. 2007). Although ΔT_{HX} was not included in the Eq.(5.12) directly, the higher ΔT_{HX} is, the less heat exchanger area is required for heat recovery based on the results provided by Aspen Plus. Thus, the WPC decreased significantly with an increase in ΔT_{HX} because of cost saving in reducing the heat exchanger size. However, the reduction of the heat exchanger area is limited when ΔT_{HX} is over a certain value. In addition, according to Eq. (5.11), a high ΔT_{HX} will render a high energy cost. Hence, it is not surprising to see that WPC tended to be stabilized when ΔT_{HX} was larger than 6 °C.

Fig. 5.10 Effects of temperature difference in heat exchanger and membrane area on WPC (Feed velocity: 0.04 m/s, feed concentration: 3.0 wt%, permeate velocity: 0.48 m/s, permeate temperature: 25 °C)

From Fig. 5.10, it was also found that there was a minimum point of \$1.1/m³ for the WPC when the membrane area was around 4 m². When the membrane area was smaller than 4m², the WPC dropped considerably with increasing membrane area because of significant increases of water production (Fig. 5.6b) and the GOR value (Fig. 5.8), though the membrane cost was also increased. On the other hand, when the membrane area was further increased over 4m², the increase in the water production (Fig. 5.5b) and the GOR value (Fig. 5.8) was slowed down. Consequently, the gain from higher water production and higher energy efficiency was not sufficient to surpass the expense of extra membrane area, leading to the increase in the WPC.

The relationship of the WPC with both feed and permeate velocities is illustrated in Fig. 5.11. The WPC reduced gradually and reached a plateau with increasing fluid velocities. It seems the power consumption for pumping the fluids played a minor role in total WPC at low feed and permeates velocities. Referring back to Figs (5.7) and (5.9), the water production and the GOR increased remarkably as the feed and permeate velocities increased from a low level, and this dominates the GOR result. At high velocities, however, the feed and permeate velocities have limited impacts on the water production and the GOR. The WPC would not decrease any more as the penalty of more energy input in the form of pump electricity consumption will not be off-set. Thus, it is favorable to operate the DCMD system at the feed velocity of 0.04 m/s and permeate velocity of 0.48m/s for the benefit of the lowest WPC, when membrane area and ΔT_{HX} are fixed.

Fig. 5.11 Effects of feed velocity and permeate velocity on WPC (feed temperature: 60 °C, feed concentration: 3.0 wt%, permeate temperature: 25 °C, temperature difference in heat exchanger (ΔT_{HX}): 10 °C, membrane area: 4 m²)

5.4 Conclusions

In this chapter, energy efficiency and economic analyses of a direct contact membrane distillation system have been performed by using Aspen Plus in combination with the modeling of a cross-flow membrane module, which was incorporated into the flow sheet as a user module for system simulation. Detailed investigations have been conducted to understand the relationships of the water flux/production, the GOR value and the WPC with the design and operation parameters, including the membrane area, the size and operating temperature of the heat exchanger, feed temperature and feed/permeate velocity, etc. The size of membrane module/membrane area has been investigated. There was a critical value of membrane area, below which, significant

increases of water production and the GOR were observed with increasing membrane area, leading to a significant drop in the WPC. However beyond this point extra membrane area had a limited impact on water production and the GOR value, and the increase in the membrane cost became the dominant factor causing the WPC to increase.

Increasing feed temperature gave positive impacts on the water flux, water production and the GOR value, which is well in agreement with previous studies in the literature. However, when utilizing low-grade waste heat as the heating source, a moderate feed temperature may be expected. Feed and permeate velocities played an important role in water flux and production. The higher the feed and permeate velocities, the higher the resulting water flux, water production and GOR. However, when the flows of the feed and permeate streams reached a certain level, the water flux/water production/the GOR is not so sensitive to further increases in the feed and permeate velocities. Also the WPC does not decrease any more as the penalty of more energy input in the form of electricity consumption for pumping become important. It is favorable to operate the DCMD system at moderate feed and permeate velocities for the benefit of the lowest WPC. Energy recovery is very important for the operation of DCMD system. When the temperature difference (ΔT_{HX}) in the heat exchanger was increased to 6 °C, the WPC was reduced considerably by cutting down the heat exchanger cost. The range 2 to 10 °C was investigated and as the heat exchanger area does not change much at a higher ΔT_{HX} of 6 °C is recommended for the conditions studied.

CHAPTER 6 CONCLUSIONS AND RECOMENDATIONS

6.1 Overall conclusions

The thesis focuses on novel membrane development, MD module modeling and system optimization so as to make MD a more technically and economically viable process for further industrial application. Attempts have been made in modifying membrane surface via plasma treatment, running a 2D numerical modeling and optimizing a MD system facilitated by simulation platform ASPEN PLUS.

To start with, modified membranes based on commercial PVDF flat sheet membranes coating with PEG and TiO_2 were formed through helium plasma treatment to generate the hydrophilic membrane surface. The characterization of the modified membranes and the impact of the influential factors including hydrophobicity, pH value, flow velocity and pore size/pore size distribution were identified. Then, 2D numerical modeling based on finite element method (FEM) was presented to attain the profiles of temperature, pressure and velocity. Four module design and operation conditions were investigated for MD system optimization by using genetic algorithm. The performance of optimized and non-optimized MD systems was compared in terms of water production cost (WPC), which provided the guidance for module and system design. For better understanding the energy consumption in MD process, the energy and economic analysis of membrane distillation system for seawater desalination was

conducted. Finally, to simulate and optimize the MD system, a comprehensive flow model, considering heat and mass transfers, was simulated using Matlab. Then, Aspen Plus platform was applied to investigate the performance of the MD system by drawing the flow diagram. With this model, factors affecting the energy and economic analysis were studied including design and operation variables. Specifically, the effect of four factors in a heat exchanger, such as feed temperature, feed and permeate flow rate, membrane usage as well as temperature difference, have been investigated. A comprehensive energy and economic analysis have been presented for establishing a guideline for future industrialization of MD process. To sum up, the major findings and conclusions are listed as the following:

- Physicochemical interaction between oil droplets and membrane surface in an aqueous media was studied by evaluating the interfacial free energy based on contact angle measurement. The hydrophilically modified PVDF-PT membrane exhibits a positive interfacial free energy with oil in water, indicating the TiO_2 deposition effectively improve the anti-oil fouling property of the PVDF-P membrane and the PVDF membrane.
- Membrane distillation tests were performed for the three membranes over time. The PVDF-PT membrane presents a stable water flux over 24h of operation without oil fouling and wetting due to combined effects of enhanced surface hydrophilicity and reduced membrane pore sizes. A longer period of operation will be tested in the further study.
- The pH value of the feed solution plays an important role in oil fouling. For virgin PVDF membrane, fouling was more severe at pH of 6.2 than at pH of 7.6. For the

PVDF-P membrane, no big difference was observed at both pH values because of the existence of low surface charges on the grafting layer which rendered surface charge effect insignificantly. For the PVDF-PT membrane, the fouling tendency at pH of 6.2 was a bit stronger than at pH of 7.6, causing a slight decrease of the mass flux with time. To sum up, more severe fouling can be observed at the pH which made the membrane surface and oil droplets carry opposite charges.

- A higher flow velocity enhances the shear force exerted on the oil droplets, thus leading to less oil present on the membrane surface and less oil fouling of the membrane.
- A 2D heat and mass transfer model for the VMD system was developed and the temperature, velocity and pressure profiles were thus obtained. By comparing with the experimental results under the same conditions from the literature, the modeling has been proved to be valid for the prediction of the VMD performance. The useful information was applied for subsequent optimization based on genetic algorithm. By comparing optimized and non-optimized VMD membrane modules, the water production cost per ton decreased by 38.1% for optimized system.
- It was preferable to adopt higher feed temperature to produce more water; when using the same membrane area, shorter fiber length was favored in order to decrease the pressure-drop induced operation cost. The volume flow rate should be low since significant pressure drop was expected for high flow rate. The vacuum pressure should be moderate because the increase of water production is comparable to the electric cost incurred by vacuum creation in the study.
- The size of membrane module/membrane area has been investigated. There was a critical value of membrane area, below which, significant increases of water

production and the GOR were observed with increasing membrane area, leading to a significant drop in the WPC. However beyond this point extra membrane area had a limited impact on water production and the GOR value, and the increase in the membrane cost became the dominant factor causing the WPC to increase.

- Increasing feed temperature gave positive impacts on the water flux, water production and the GOR value, which is well in agreement with previous studies in the literature. However, when utilizing low-grade waste heat as the heating source, a moderate feed temperature may be expected.
- Feed and permeate velocities played important roles in water flux and production. The higher the feed and permeate velocities, the higher the resulting water flux, water production and GOR. However, when the flows of the feed and permeate streams reached a certain level, the water flux/water production/the GOR is not so sensitive to further increases in the feed and permeate velocities. Also the WPC does not decrease any more as the penalty of more energy input in the form of electricity consumption for pumping become important. It is favorable to operate the DCMD system at moderate feed and permeate velocities for the benefit of the lowest WPC.
- Energy recovery is very important for the operation of DCMD system. When the temperature difference (ΔT_{HX}) in the heat exchanger was increased to 6 °C, the WPC was reduced considerably by cutting down the heat exchanger cost. The range 2 to 10 °C was investigated and as the heat exchanger area does not change much at a higher ΔT_{HX} of 6 °C is recommended for the conditions studied.

6.2 Recommendation for future research

As discussed in Chapter 3, hydrophilic modification of the membrane surface can impart anti-oil fouling property to the membrane surface. It has been reported that, besides chemistry nature (hydrophilicity/hydrophobicity), the roughness of the membrane surface can also develop anti-oil fouling property (Koch and Barthlott 2009). Various surface engineering technologies are available, including acid etching and plasma treatment. Strong rusty acids including H_2SO_4 or HF can be used to fabricate a rough surface to prevent the attachment of oil droplet to the membrane surface so that the fouling problem can be solved. Plasma treatment can etch the membrane surface and change the surface structure significantly. In addition, the acceptable and tolerant oil concentration in seawater (or the range of oil concentration) for a long time operation of modified membrane can be identified. The mechanism of oil absorption on membrane surface will be also investigated to provide guidance for the anti-oil fouling membrane modification.

In addition, present energy consumption studies of MD system are mostly based on the principle of conservation of energy, which employs the first law of thermodynamics and calculated the energy efficiency based on undistinguished energy. While, the irreversible thermodynamics is relatively new applied to analysis MD process and is still developing. The core part of irreversible thermodynamics is the entropy production and exergy loss, which has been reported to be significant in MD process (Criscuoli and Drioli 1999, Banat and Jwaied 2008, Gomri 2009). However, the previous studies focused more on the calculation of exergy balance, but lacked the

investigation of the influence of the operation conditions. In future study, the influence of the operation conditions on exergy loss can be investigated by identifying the energy loss distribution in each component of the MD system. It aims at identifying the lion's share, which is held accountable for the exergy loss in MD system by varying the operating temperatures and flow rates, so that guidance for optimization of MD system can be provided.

Last but by no means least, novel MD system design can be explored by optimizing the MD system, especially for those scaled up systems with multiple flow streams. In Chapter 5, the performance of large-scale MD module has been investigated with enormous number (over 1000) of hollow fibers by system integration and simulation. However, since the individual MD module is limited in production capacity and energy efficiency, a bunch of modules in various combinations should be explored for the industrial application. It has been reported that the highest gained output ratio(GOR) for equal flows of feed and permeate stream should lower than 2.2(Gilron, Song et al. 2007). However, by adding the number of internal stages of membrane modules and shortening the difference of temperature between the hot feed stream and cool permeate stream, the GOR increases up to 5.4. Therefore, the MD system can be optimized by re-arranging the modules to couple hot feed stream and cool permeate stream in every single module based on pinch analysis. In addition, it is interesting to compare cascades of MD modules of the same membrane area. The impact of temperature approach in MD module, internal module arrangement, pressure drop and mass flux on energy efficiency can therefore be investigated.

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APPENDIX

Genetic algorithm for VMD

Main

```
function []=main(N,pcro,pmut,A0)

tic;

di=0.0018;

low=0;

up=1;

perk=0.0001;

n=100;

length=ceil(log2((up-low)/perk+1));

pop=encode(length,n);

gen=0;

while(gen<=N)

fval=zeros(1,n);
```

```
fit=zeros(1,n);

for i=1:n

[N0,L,q,P]=decode(pop(i,:),low,up,length);

end

fsum=sum(fval);

fmax=max(fval);

fs=n*fmax-fsum;

fit=(fmax-fval)/fs;

q(1)=fit(1);

for i=2:n

q(i)=q(i-1)+fit(i);

end

pop=select(pop,q,n);

pop=crossover(pop,pcro,n,length);

pop=mutation(pop,pmut,n,length);

gen=gen+1;

end
```

```
minf=inf;

for i=1:n

[N0,L,q,P]=decode(pop(i,:),low,up,length);

if fval<minf

minf=fval;

x0=[N0,L,q,P];

end

end

minf,x0

toc;
```

Cross over

```
function popnew=crossover(pop,pcro,n,length)

k=1;

i=0;

while (k<=n)

rk=rand();
```



```
if rk<pcro

b(i+1)=k;

i=i+1;

end

k=k+1;

if i==2

pos=fix(rand()*16)+1;

for i=pos:4*length

c=pop(b(1),i);

pop(b(1),i)=pop(b(2),i);

pop(b(2),i)=c;

end

i=0;

end

end

popnew=pop;
```

Decode

```
function [N0,L,q,P]=decode(a,low,up,length)

str1=0;

str2=0;

str3=0;

str4=0;

for i=1:length

if a(length+1-i)

str1=str1+2^(i-1);

end

end

N0=low+str1*(up-low)/(2^length-1);

for i=1:length

if a(2*length+1-i)

str2=str2+2^(i-1);

end

end

end
```

```
L=low+str2*(up-low)/(2^length-1);
```

```
for i=1:length
```

```
if a(3*length+1-i)
```

```
str3=str3+2^(i-1);
```

```
end
```

```
end
```

```
q=low+str3*(up-low)/(2^length-1);
```

```
for i=1:length
```

```
if a(4*length+1-i)
```

```
str4=str4+2^(i-1);
```

```
end
```

```
end
```

```
P=low+str4*(up-low)/(2^length-1);
```

Encode

```
function pop=encode(length,n)
```

```
pop=randint(n,4*length);
```

Mutation

```
function popnew=mutation(pop,pmut,n,length)
```

```
k=1;
```

```
while k<=n
```

```
rk=rand();
```

```
if rk<pmut
```

```
pos=fix(rand()*4*length)+1;
```

```
pop(k,pos)=~pop(k,pos);
```

```
end
```

```
k=k+1;
```

```
end
```

```
popnew=pop;
```

Select

```
function popnew=mutation(pop,pmut,n,length)
```

```
k=1;
```

```
while k<=n
```

```
rk=rand();

if rk<pmut

pos=fix(rand()*4*length)+1;

pop(k,pos)=~pop(k,pos);

end

k=k+1;

end

popnew=pop;
```

Aspen Unit Operation Model Subroutine for Excel Models (Based on Aspen plus manual)

```
#include "dms_errout.cmn"
```

```
#include "ppexec_user.cmn"
```

```
#include "dms_ncomp.cmn"
```

```
#include "dms_plex.cmn"
```

```
REAL*8 B(1)
```

```
EQUIVALENCE (B(1),IB(1))
```

```
INTEGER DMS_IRRCHK, DMS_IFCMNC
```

```
INTEGER OFFSET, NUM_COLS, NUM_ROWS, RETCODE, LID,
```

```
+ IBLANK(2), KREAL(3), KINT(3), KINPUT(2), KOUTPUT(2),
```

```
+ LDATA, I,J,K, LEN, KDIAG, IDX(10),
```

```
+ LIDSC, NCD, C_OFF, ERRNUMBER, NUM_LINES,
```

```
+ SOURCE(16), HOL_STRLEN, SOR_LENGTH, SSID(2), IPROG(2),
```

```
+ DESC_LENGTH,KOUTSOL(3), EXCEL_NAME_LEN,
```

```
+ EXCEL_NAME(16), KINPSOL(3),
```

```
+ DESCRIPTION(128)
```

Integer LABELS(2,10), ROWNAMES(2,NCOMP_NCC+10)

Integer REALROWS(2,NTOT+1) !Hollerith Realparam row ID's. (2)

Integer LMW, NCP

Real*8 FLOW, XMW, X(10)

Character*8 RealLabels(13)

REAL*8 INSTREAM(NTOT*NMATI),OUTSTREAM(NTOT*NMATO)

DATA KINPUT /4HINPU, 4HT /

DATA KOUTPUT /4HOUTP, 4HUT /

DATA KREAL /4HREAL, 4HPARA, 4HMS /

DATA KINT /4HINTP, 4HARAM, 4HS /

DATA KINPSOL /4HINP_, 4H , 4H /

DATA KOUTSOL /4HOUT_, 4H , 4H /

DATA IPROG /4HUSRX, 4HLS /

DATA IBLANK /4HIMIS, 4HS /

DATA LABELS /4HTOTF, 4HLOW ,

+ 4HTEMP, 4H ,

+ 4HPRES, 4H ,

+ 4HENTH, 4HALPY,

+ 4HVAP , 4HFRAC,

+ 4HLIQ , 4HFRAC,

+ 4HENTR, 4HOPY ,

+ 4HDENS, 4HITY ,

+ 4HMOLE, 4H WT ,

+ 4HMUMX, 4H / !MUMX is viscosity label. (6)

DATA RealLabels /'x ',

+ 'L ', !(each total eight chars). (7)

+ 'Dab ',

+ 'Cg ',

+ 'R ',

+ 'C1 ',

+ 'C2 ',

+ 'C3 ',

+ 'C4 ',

+ 'Pperm ',

+ 'DeltaP ',

+ 'Cp ',

+ 'Cr ' /

CALL USRUTL_GETEXCEL(EXCEL_NAME, EXCEL_NAME_LEN)

CALL StartIteration(RETCODE, EXCEL_NAME, 64, IDS(1,1), 8)

IF(RETCODE .NE. 0) GOTO 1000

OFFSET = DMS_IFCMNC('IDSCC')

DO J=1, NCOMP_NCC

I = OFFSET + 2*(J-1) + 1

ROWNAMES(1,J) = IB(I)

ROWNAMES(2,J) = IB(I+1)

END DO

DO K=1, 10

J = K + NCOMP_NCC

ROWNAMES(1,J) = LABELS(1,K)

ROWNAMES(2,J) = LABELS(2,K)

END DO

```
NUM_ROWS = NCOMP_NCC + 10

LMW = DMS_IFCMNC('MW')

NUM_COLS = NMATI

DO J=1, NUM_COLS

  OFFSET = (J-1)*(NCOMP_NCC+10)

  DO I=1, NUM_ROWS

    IF (I.EQ. NUM_ROWS) THEN

      Call SHS_CPACK(MSIN(1,J), NCP, IDX, X, FLOW)

      KDIAG = 4 !then get

      K = NCOMP_NCC !viscosity. (11)

      Call PPMON_VISCL(MSIN(K+2,J), MSIN(K+3,J), X, NCP,

        + IDX, NBOPST, KDIAG,

        + INSTREAM(OFFSET+I), RETCODE)

    ELSE

      XMW = 1

      IF(I.LE. NCOMP_NCC) XMW = B(LMW + I)

      INSTREAM(OFFSET + I) = MSIN(I,J)*XMW
```

END IF

IF (I.EQ. NCOMP_NCC+1) INSTREAM(OFFSET+I) =

+ INSTREAM(OFFSET+I)*MSIN(I+8,J) !Convert total mole flow

END DO

END DO

LDATA = 8*NUM_ROWS*NUM_COLS

CALL WRITETABLE(RETCODE , KINPUT, 8 , NUM_ROWS,

+ ROWNAMES, 8 , NUM_COLS, IDSMI ,

+ 8 , 2 , INSTREAM, LDATA)

IF (RETCODE .NE. 0) GO TO 1000

LDATA = 8*NINT

CALL WRITETABLE(RETCODE, KINT, 12 , NINT ,

+ IBLANK , 0 , 1 , IBLANK,

+ 0 , 1 , INTV, LDATA)

IF (RETCODE .NE. 0) GO TO 1000

DO I = 1, 13 !Make the 13 labels into Holleriths. (14)

CALL USRUTL_CHARTOH(RealLabels(I), RealRows(1,I), 8)

END DO

LDATA = 8*NREAL

CALL WRITETABLE(RETCODE, KREAL, 12 , NREAL,

+ RealRows, 8 , 1 , IBLANK,

+ 0 , 2 , REALV, LDATA)

IF (RETCODE .NE. 0) GO TO 1000

NUM_ROWS = NCOMP_NCC + 9

DO J=1, NMATO

OFFSET = (J-1)*(NCOMP_NCC+9)

DO I=1, NUM_ROWS

OUTSTREAM(OFFSET+I) = 0.D0

END DO

END DO

NUM_COLS = NMATO

LDATA = 8*NUM_ROWS*NUM_COLS

CALL WRITETABLE(RETCODE , KOUTPUT, 8 , NUM_ROWS,

+ ROWNAMES, 8 , NUM_COLS , IDSMO ,

+ 8 , 2 , OUTSTREAM, LDATA)

IF (RETCODE .NE. 0) GO TO 1000

IF (NSUBS .GT. 1) Then

DO K=2,NSUBS

IF (ITYPE(K) .EQ. 3) THEN

LIDSC = DMS_IFCMNC('IDSNCC')

NCD = NCOMP_NNCC

ELSE

LIDSC = DMS_IFCMNC('IDSCC')

NCD = NCOMP_NCC

ENDIF

DO J=1, NCD

LID = LIDSC + 2*(J-1)

ROWNAMES(1,J) = IB(LID+1)

ROWNAMES(2,J) = IB(LID+2)

END DO

DO J=1, 9

I=NCD+J

ROWNAMES(1,I) = LABELS(1,J)

ROWNAMES(2,I) = LABELS(2,J)

END DO

NUM_ROWS = NCD+9

CALL SHS_PID(LD, K, SSID)

KINPSOL(2) = SSID(1)

KINPSOL(3) = SSID(2)

KOUTSOL(2) = SSID(1)

KOUTSOL(3) = SSID(2)

NUM_COLS = NMATI

DO J=1, NUM_COLS

OFFSET = (J-1)*(NCD+9)

DO I=1, NCD+9

INSTREAM(OFFSET+I) = MSIN(IDXSUB(K)+I-1,J)

END DO

END DO

LDATA = 8*NUM_ROWS*NUM_COLS

CALL WriteTable(RETCODE , KINPSOL, 12 , NUM_ROWS,

+ ROWNAMES, 8 , NUM_COLS, IDSMI ,

+ 8 , 2 , INSTREAM, LDATA)

IF (RETCODE .NE. 0) GO TO 1000

NUM_COLS = NMATO

DO J=1, NUM_COLS

OFFSET = (J-1)*(NCD+9)

DO I=1, NCD+9

OUTSTREAM(OFFSET+I) = 0.D0

END DO

END DO

NUM_ROWS = NCD+9

LDATA = 8*NUM_ROWS*NUM_COLS

CALL WriteTable(RETCODE , KOUTSOL, 12 , NUM_ROWS,

+ ROWNAMES, 8 , NUM_COLS , IDSMO ,

+ 8 , 2 , OUTSTREAM, LDATA)

IF (RETCODE .NE. 0) GO TO 1000

END DO

End If

CALL CalculateData(RETCODE)

IF (RETCODE .NE. 0) GOTO 1000

LDATA = 8*NINT

CALL READTABLE(RETCODE, KINT, 12 , NINT ,

+ 1 , 1 , INTV, LDATA)

IF (RETCODE .NE. 0) GOTO 1000

LDATA = 8*NREAL

CALL READTABLE(RETCODE, KREAL, 12 , NREAL,

+ 1 , 2 , REALV, LDATA)

IF (RETCODE .NE. 0) GOTO 1000

NUM_ROWS = NCOMP_NCC + 3

NUM_COLS = NMATO

LDATA = 8*NUM_ROWS*NUM_COLS

CALL READTABLE(RETCODE , KOUTPUT, 8 , NUM_ROWS,


```
+ NUM_COLS, 2 , OUTSTREAM, LDATA )

IF (RETCODE .NE. 0) GOTO 1000

DO J = 1, NMATO

FLOW = 0

OFFSET = (J-1)*NUM_ROWS

DO I = 1, NUM_ROWS

IF(I .LE. NCOMP_NCC) THEN

SOUT(I, J) = OUTSTREAM(OFFSET+I)/B(LMW+I)

FLOW = FLOW + SOUT(I,J) !Store total. (17)

ELSE IF(I .EQ. NCOMP_NCC+1) THEN

SOUT(I,J) = FLOW !Total flow to SOUT (3rd row). (17)

ELSE

SOUT(I,J) = OUTSTREAM(OFFSET + I)

END IF

END DO

END DO

END DO

IF (NSUBS .GT. 1) Then
```

```
DO K = 2, NSUBS

IF (ITYPE(K) .EQ. 3) THEN

NCD = NCOMP_NNCC

ELSE

NCD = NCOMP_NCC

ENDIF

CALL SHS_PID(LD, K, SSID)

KOUTSOL(2) = SSID(1)

KOUTSOL(3) = SSID(2)

NUM_ROWS = NCD+9

NUM_COLS = NMATO

LDATA = 8*NUM_ROWS*NUM_COLS

CALL ReadTable(RETCODE , KOUTSOL, 12 , NUM_ROWS,

+ NUM_COLS, 2 , OUTSTREAM, LDATA )

IF(RETCODE .NE. 0) GO TO 1000

DO J=1, NMATO

OFFSET= (J-1)*(NCD+9)
```

DO I=1, NCD+9

SOUT(IDXSUB(K)+I-1, J) = OUTSTREAM(OFFSET+I)

END DO

END DO

END DO

End If

CALL EndIteration(RETCODE)

RETURN

CALL EndIteration(RETCODE)

RETURN

1000 CONTINUE

HOL_STRLEN = 64

DESC_LENGTH= 512

SOR_LENGTH = 64

CALL GetLastTableDataErr(RETCODE, ERRNUMBER, DESCRIPTION,

+ DESC_LENGTH, HOL_STRLEN, SOURCE,

+ SOR_LENGTH)

```
USER_ICONVG = -3

IF (DMS_IRRCHK(IPROG, 1, 4, 4, USER_IUMISS,
+ 0, 0, 2) .NE. 0) THEN

NUM_LINES = ( (DESC_LENGTH+HOL_STRLEN-1) /HOL_STRLEN)

IF (NUM_LINES .GT. 8 ) NUM_LINES = 8

WRITE(ERROUT_IEROUT(1), 10)

WRITE(ERROUT_IEROUT(2), 11)(SOURCE(I), I=1,(SOR_LENGTH+3)/4)

DO 111 J=1,NUM_LINES

C_OFF = (J-1) * HOL_STRLEN/4

WRITE(ERROUT_IEROUT(J+2), 11)

+ ( DESCRIPTION(I+C_OFF), I=1,(HOL_STRLEN+3)/4 )

111 CONTINUE

CALL DMS_ERRPRT(NUM_LINES+2)

ENDIF

2000 CONTINUE

999 CONTINUE

10 FORMAT(' MS EXCEL Interface Reports:')
```

11 FORMAT(' ',16A4)

END