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POSTDOCTORAL STUDIES**

Chaoyang Feng

AUTEUR DE LA THÈSE / AUTHOR OF THESIS

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Desalination by Air Gap Membrane Distillation**

TITRE DE LA THÈSE / TITLE OF THESIS

Takeshi Matsuura

DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

EXAMINATEURS (EXAMINATRICES) DE LA THÈSE / THESIS EXAMINERS

Christopher Lan

André Tremblay

Arturo Macchi

Rémi Lebrun

Gary W. Slater

Le Doyen de la Faculté des études supérieures et postdoctorales / Dean of the Faculty of Graduate and Postdoctoral Studies

DEVELOPMENT OF NOVEL NANOFIBER MEMBRANES FOR SEAWATER DESALINATION BY AIR GAP MEMBRANE DISTILLATION

By
Chaoyang Feng
Ph.D. Thesis

A thesis submitted to the Faculty of Graduate and Postdoctoral Studies in
partial fulfillment of the requirements for the degree of

Ph.D. in Chemical and Biological Engineering

Under the Supervision of:
Professor Takeshi Matsuura of University of Ottawa, Canada

Department of Chemical and Biological Engineering
University of Ottawa
Ottawa, ON
Canada, K1N 6N5



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Abstract

Our world is facing water and energy shortage. As a relatively new process, membrane distillation (MD) is being investigated as a low cost and energy saving alternative to conventional separation processes such as distillation and reverse osmosis since 1990s. As a result of material limit, the development of membrane distillation has not yet come to the commercial scale. But, it has become a hopeful technology of the future. The objective of this research is to develop novel nanofiber membranes for seawater desalination by air gap membrane distillation (AGMD).

The concept of novel nanofiber membranes is based on the electro-spinning technology. By using electro-spinning method, a highly hydrophobic material (PVDF, poly vinylidene fluoride) was spun to filaments with diameters in nanometer range. The PVDF nanofibers turn into a nanofiber non-woven mat or web and bring high hydrophobicity and a highly open pore structure. This further fulfils the requirements for the MD membranes with reduced mass transport resistance and temperature polarization. Thus, membranes with high MD fluxes are expected.

In Part I of the current research, hydrophilic and hydrophobic polymers and a polymer blend (PVDF, PVDF/PVP, PS, PES, PEI, PVC, PC, PAN, Nomex (PA), PVA and Collagen) were used for electro-spinning to generate nanofibers and nanofiber membranes. The electro-spinning parameters that affect the structure and other properties of the membrane and the MD membrane performance were identified. They include spinning dope concentration, solution feed rate, spinning voltage and nanofiber collect distance. The electro-spinning parameters were then optimized for obtaining the best performance data.

The PVDF nanofiber membranes were characterized by SEM, AFM, DSC, measurement of LEPw (liquid entry pressure of water), equilibrium contact angle and particle separation. It was found that the pore size of the PVDF nanofiber membrane was around 1.5 μm . The equilibrium contact angle of some nanofiber membranes were above 120°. It

shows that the novel membranes have a very open pore structure and are highly hydrophobic. Those characteristics are exactly what are needed for MD membranes.

In Part II of the current research work, a novel PVDF nanofiber membrane was tested for saline water desalination by AGMD (air gap membrane distillation). Desalination by AGMD was carried out for various sodium chloride concentrations in feed (1 to 22 wt%) at the feed solution and cooling water temperature difference of 60 °C. Above 99% salt rejection and above 8 kg/m² h flux was obtained. As well, ethanol/water separation was investigated by using 5 and 10 wt % aqueous ethanol solution.

Two theoretical models were developed to simulate the AGMD process; the first model was developed to describe the AGMD process based on the mass and heat transfer through the membrane, while the second model deals with the transfer of volatile component through the air gap. The experimental flux value fits the second model very well. It shows that the air gap is the dominating stage for the heat transfer of the AGMD process.

In an early stage of this work, polypropylene (PP) was chosen to prepare membranes of high hydrophobicity and high porosity for membrane distillation by a solution casting method. The results are reported in Appendix I. This method, even though novel, was not quite appropriate to fabricate membranes with hydrophobicity and porosity high enough for MD application. However, the microporous PP membranes so prepared seem to have a great potential for other separation applications than MD.

Résumé

Pour palier à la pénurie d'eau et d'énergie, la distillation membranaire (MD), processus relativement nouveau, est l'objet de nombreuses études visant à remplacer des processus traditionnels et plus coûteux tels que la distillation et l'osmose inversée. Malheureusement, les contraintes imposées par les matériaux empêchent toutes applications commerciales à grande échelle. Cependant, les récentes percées technologiques permettent d'envisager un avenir viable pour la distillation membranaire. L'objectif de ce projet de recherche est de développer une membrane novatrice composée de nanofibres permettant la désalinisation de l'eau de mer en utilisant la distillation membranaire avec espacement intermembranaire (AGMD).

Le concept des nouvelles membranes fabriquées à partir de nanofibres est basé sur la technologie d'électrofilage. L'électrofilage permet d'obtenir des filaments ayant un diamètre de l'ordre du nanomètre à partir de matériaux hautement hydrophobes tel que le polyfluorure de vinyldiène (PVDF) avec lequel on génère un tapis ou une toile non-tissée. Cette technologie permet d'obtenir une membrane hautement poreuse et hydrophobe résultant en une diminution significative de la résistance au transport de masse ainsi que l'effet de polarisation de la température.

Lors de la première partie du projet de recherche, des nanofibres et des membranes de nanofibres furent conçues par électrofilage à partir de polymères et de mélanges polymériques tant hydrophiles qu'hydrophobes (PVDF, PVDF/PVP, PS, PES, PEI, PVC, PC, PAN, Nomex (PA), PVA et collagène). Les facteurs influençant l'électrofilage du PVDF pour la préparation de membranes tels que l'enrichissement de la concentration et le débit de la solution de filage, le voltage utilisé lors du filage ainsi que la hauteur relative de la buse furent investigués et leurs effets sur la structure des nanofibres fut clairement compris. Suite à ces observations, les facteurs pour l'électrofilage du PVDF furent optimisés.

Les membranes de nanofibres furent caractérisées par MEB, AFM, DSC, LEPw (liquid entry pressure of water), contact angulaire à l'équilibre et séparation particulaire. Il fut

déterminé que le diamètre des pores des membranes de nanofibres de PVDF était approximativement de $1,5\ \mu\text{m}$ et que l'angle de contact à l'équilibre est supérieur à 120° . La nouvelle membrane exhibe une structure plus poreuse et plus hydrophobe, caractéristiques recherchées pour un procédé de distillation membranaire.

Lors de la seconde partie du projet de recherche, la nouvelle membrane de nanofibres de PVDF fut installée en configuration AGMD afin de caractériser les performances de celle-ci. Afin d'évaluer les performances de désalinisation, des solutions contenant diverses concentrations de chlorure de sodium furent traitées par AGMD. Des solutions de chlorure de sodium (1 %, 3,5 %, 6% et 22 %) furent utilisées pour évaluer les nouvelles membranes de nanofibres et le procédé AGMD. Avec une différence de température de $60\ ^\circ\text{C}$, 99% du sel fut retiré et un flux de $11\ \text{kg} / \text{m}^2\ \text{h}$ fut obtenu. De plus, la séparation de mélanges eau-éthanol (5 % p/p et 10 % p/p) fut investiguée.

Deux modèles théoriques ont été développés pour simuler le processus d'AGMD ; le premier modèle a été développé pour décrire l'AGMD traitant basé sur la masse et le transfert thermique par la membrane, alors que le deuxième modèle traite le transfert du composant volatil par l'espace d'air. La valeur expérimentale de flux adapte le deuxième modèle très bien. Il prouve que l'espace d'air est l'étape de domination pour le transfert thermique du processus d'AGMD.

Au début de ce projet, polypropylène (PP) fut choisie pour préparer des membranes avec de haute porosité et haute hydrophobicité pour la distillation avec membrane utilisant une méthode de formation en solution. Les résultats se trouvent dans l'Appendix 1. Cette méthode qui est très nouvelle n'était pas appropriée pour fabriquer des membranes avec une hydrophobicité et une porosité adéquate pour être utilisé dans la distillation avec membrane. Par contre, les membranes PP fabriquées avec cette méthode démontrent beaucoup de potentielle pour d'autres applications de séparation.

To my dearest parents, brothers, sister and;
My wife, my beloved son and daughter (Qiyun and Angela)

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List of Publications and Presentations related with PhD study
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2. C. Feng, K.C. Khulbe, T. Matsuura, R. Gopal, S. Kaur, S. Ramakrishna, M. Khayet "Production of drinking water from saline water by air-gap membrane distillation using polyvinylidene fluoride nanofiber membrane" Journal of Membrane Science, Volume 311, Issues 1-2, 20 March 2008, Pages 1-6.
3. Renuga Gopal, Satinderpal Kaur, Chao Yang Feng, Casey Chan, Seeram Ramakrishna, Shahram Tabe, Takeshi Matsuura "Electrospun nanofibrous polysulfone membranes as pre-filters: Particulate removal" Journal of Membrane Science, Volume 289, Issues 1-2, 15 February 2007, Pages 210-219.

Conference Papers:

1. C.Y. Feng, K.C. Khulbe, T. Matsuura "The Study of Preparation and Characterization of Micro-Porous Polypropylene Flat Sheet Membranes" Oral presentation at 54th Canadian Chemical Engineering Conference, Oct 3-6 2004, Calgary Marriott Hotel and Telus Convention Centre, Calgary, Alberta, Canada.
2. Chaoyang Feng, K.C. Khulbe, Takeshi Matsuura, Renuga Gopal, Satinderpal Kaur, Seeram Ramakrishna "Preparation and Characterization of PVDF Electrospun Nanofiber Membranes" Poster presentation at North American Membrane Society (NAMS) 2006 Annual Meeting, Chicago, Illinois, May 12-17, 2006.
3. C.Y. Feng, K.C. Khulbe, T. Matsuura, O. Younes-Metzler, J.B. Giorgi, M. Khayet "Study of surface properties and morphology of nano-fiber membrane

made by different polymers” Oral presentation at North American Membrane Society (NAMS) 2007 Annual Meeting, Orlando, Florida USA, May 12-16, 2007.

4. Chaoyang Feng, K.C. Khulbe, Takeshi Matsuura, R. Gopal, S. Kaur, S. Ramakrishna, M. Khayet “ PVDF Nano-Fiber Membrane: New Approach To Produce Potable Water From Sea-Water Via Air Gap Membrane Distillation (Agmd) ” Poster presentation at 2008 International Congress on Membranes and Membrane Processes (ICOM 2008) July 12-18, 2008, Honolulu, Hawaii USA.
5. Chaoyang Feng, K.C. Khulbe, Takeshi Matsuura “ Production of drinking water from saline water by air-gap membrane-distillation (AGMD) using poly(vinylidene fluoride) (PVDF) nanofiber membrane” 11th GSAÉD Interdisciplinary Conference, University of Ottawa, February 5-7, 2008.
6. Chaoyang Feng, K.C. Khulbe, Takeshi Matsuura " New Achievement in Desalination by Membrane Distillation Using Nanofiber Membrane" 58th Canadian Chemical Engineering Conference (*CSCChE 2008*) October 19–22, 2008
Ottawa

Book:

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GENERAL INTRODUCTION

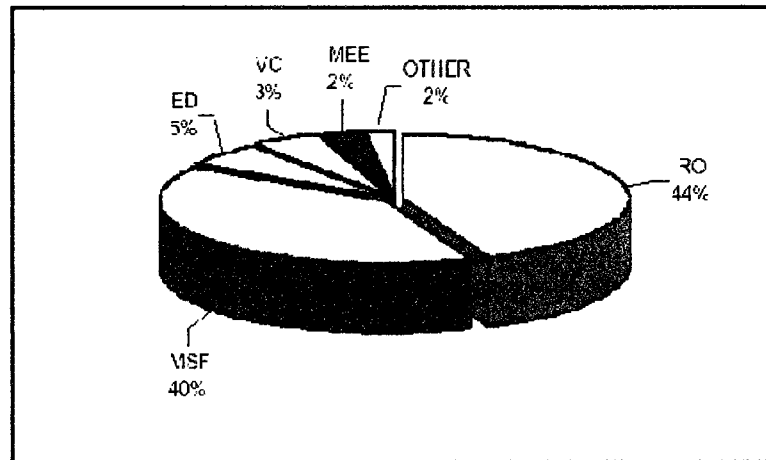
1. RESEARCH BACKGROUND

Water covers about two-thirds of the Earth's surface, admittedly. But most is too salty for use. Only 2.5% of the world's water is not salty, and two-thirds of that is locked up in the icecaps and glaciers. Only 0.3% can be used for human activity.

Unfortunately, the world is running out of water. Human are polluting, depleting, and diverting its finite freshwater supplies so quickly, creating massive new deserts and generating global warming. In many parts of the world, surface waters are too polluted for human using. Ninety per cent of wastewater in the Third World is discharged untreated. Eighty percent of China's and 75 percent of India's surface waters are too polluted for drinking, fishing, or even bathing. The story is the same in most of Africa, Middle East and Latin America [1-3]. To produce fresh water from saline water (Desalination), wastewater treatment and recycle became more and more important for human life.

In search of new sources of water supply, saline water desalination is increasingly recognized as a viable option. Costs of desalination have declined substantially throughout recent decades. In terms of cost competitiveness, desalination is catching up fast to alternative options for boosting water supply, namely water reclamation and water transport.

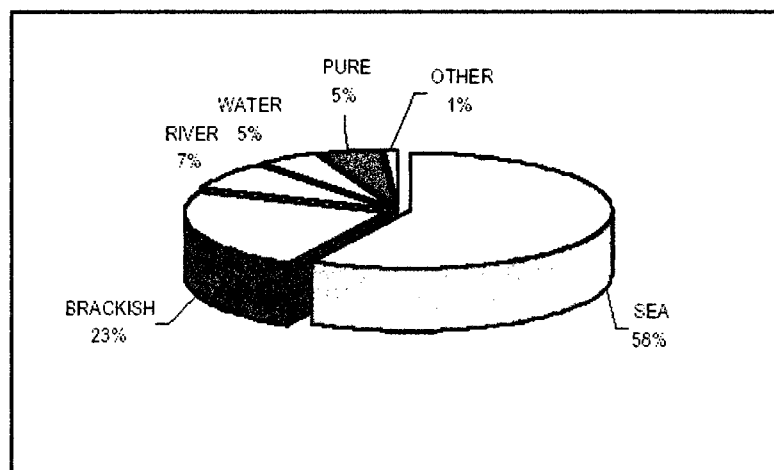
Desalination produces fresh water by desalinating seawater or brackish groundwater [4-5]. Both seawater and brackish groundwater are desalted by using two different approaches: i) distillation or thermal processes through evaporation, and ii) membrane processes through reverse osmosis (RO). As judged by installed capacity, the membrane desalination process leads with 44 percent of total capacity, closely followed by a thermal process called multi stage flash (MSF) with 40 percent of total capacity. The remaining 16 percent are divided between other processes, such as electro dialysis (ED, 5%), vapour compression (VC, 3%), a process called multiple effect evaporation (MEE, 2%), and other partially new concept (Figure 1) [6].



Source: IDA, 2002.

Figure 1: Installed desalination capacity divided by different processes [6].

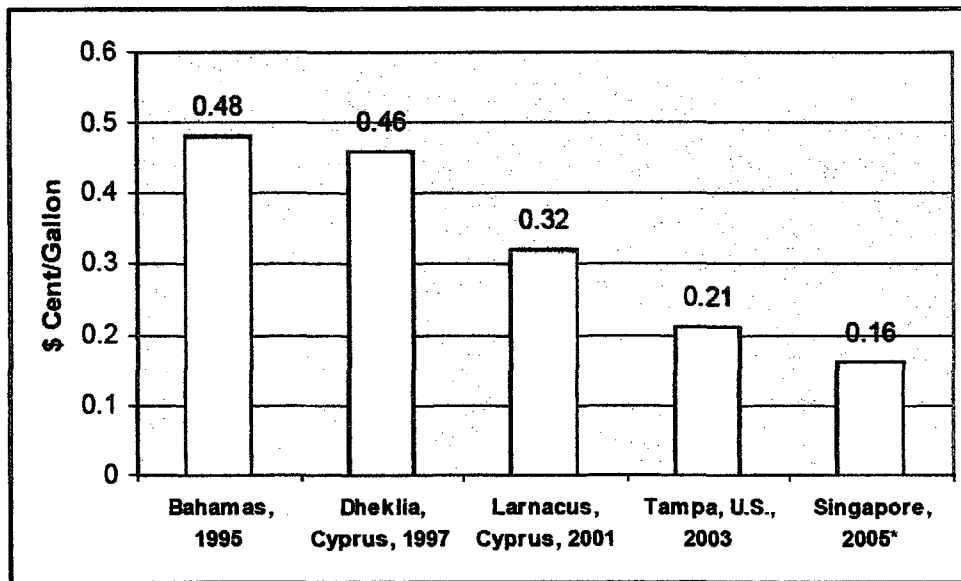
The main sources of feed water for desalination are seawater at 58 percent and brackish ground water, which accounts for 23 percent (Fig. 2).



Source: IDA, 2002.

Figure 2: Installed capacity divided by raw water quality [6].

With the development of membrane technology, the cost of obtaining fresh water by using membrane desalination processes has substantially decreased and consistently fast annual rate throughout recent decades (Fig. 3). But there is an obstacle for membrane application. Desalination by reverse osmosis needs high pressure and the membrane fouling is serious. The cost of desalination is still at a high level. Innovative technologies are expected.



Source: Estimates prepared from various sources by CRWPPC

* Projected estimate

Figure 3: Change of RO product unit cost over time [7].

2. TECHNOLOGY OF DESALINATION PROCESSES

There are several methods to desalt salty water. The following are the different methods for desalination processes:

2.1. Desalination by Reverse Osmosis Membrane

The fastest growing desalination process is a membrane process called reverse osmosis (RO). RO employs dynamic pressure to overcome the osmotic pressure of the salty

solution, hence causing water-selective permeation from the saline side of a membrane to the freshwater side [8-10]. Salts are rejected at the membrane barrier. RO membranes are usually made of cellulose acetates or polyamides [8, 11].

2.2. Desalination by Thermal Process

There are three main thermal processes for desalination, which are as follows [12-27]:

1. MSF (Multistage Flash).
2. MEE (Multiple Effect Evaporate).
3. VC (Vapour Compression).

In MSF process, the incoming seawater passes through the heating stage(s) and is heated further in the heat recovery sections of each subsequent stage. After passing through the last heat recovery section, and before entering the first stage where flash boiling (or flashing) occurs, the feed water is further heated in the brine heater using externally supplied steam. This raises the feed water to its highest temperature, after which it is passed through the various stages where flashing takes place. The vapour pressure in each of these stages is controlled so that the heated brine enters each chamber at the proper temperature and pressure (each lower than the preceding stage) to cause instantaneous and violent boiling/evaporation. The freshwater is formed by condensation of the water vapour, which is collected at each stage and passed on from stage to stage-in parallel with the brine. At each stage, the product water is also flash-boiled so that it can be cooled and the surplus heat recovered for preheating the feed water. In multiple-effect evaporate (MEE) steam is condensed on one side of a tube wall while saline water is evaporated on the other side. The energy used for evaporation is the heat of condensation of the steam. The saline water is usually applied to the tubes in the form of a thin film so that it will evaporate easily. Although this is an older technology than the MSF process described above, it has not been extensively utilized for water production. The vapour-compression process (VC) uses mechanical energy rather than direct heat as a source of thermal energy. Water vapour is drawn from the evaporation chamber by a compressor and except in the first stage is condensed on the outsides of tubes in the same chambers.

2.3. Desalination by Membrane Distillation

Membrane distillation (MD) is a relatively novel membrane separation process. It is based on the phenomenon that pure water can be extracted from aqueous solutions by evaporation, with the vapour passing through a hydrophobic micro-porous membrane when a temperature difference is established across the membrane. In MD process, the temperature difference leads to a vapour pressure difference across the membrane. Due to the hydrophobic nature of the membrane, only vapour can pass through the membrane. By this method, saline water can be desalted and polluted water can be purified. Temperature sensitive industrial stream can be concentrated or separated. It should be pointed out that the temperature difference across the membrane is the driving force in MD process, which is quite different from other well-known membrane separation processes such as reverse osmosis (RO) driven by hydraulic pressure difference [28-31].

MD concept was introduced in the late 1960s [32, 33]. However, it has not been established as a desalination process on a commercial level, partly because membranes with the properties that are mostly suitable for this process were not available. These properties include a negligible permeability to the liquids and non-volatile components, high porosity for the vapour phase, a high resistance to heat flow by conduction, a sufficient but not excessive thickness, low moisture adsorptivity [34-36], and a commercially long life with the saline solutions under the operating conditions. Furthermore, the halt in development was partially caused by some negative opinions about economics of the process [33, 37, 38], which, was however performed long ago and on a far-from-optimal membrane and model. For instant, using typical data, the temperature polarization coefficient for their membrane distillation system was roughly estimated to be 0.4-0.7 by Martinez-Diez et al. [39], for this system, when the temperature difference between centers of the hot and cold channels is 10 °C, the actual temperature difference across the membrane is only 3 °C.

However, membrane distillation process not only can be used for desalination, but also can be used for specific industrial separation process. Basically, if a solution or stream which contains one or more volatile components contacts with the membrane as feed, the

solution does not wet or pass through the membrane. The volatile components can be separated by membrane distillation process. That means membrane distillation process can also be used for food juice concentration, fermentation stream separation, heavy metal ion wastewater treatment and so on.

Comparing with other membrane desalination processes, MD (Membrane distillation) has many advantages: First, membrane distillation system is simple and easy to maintain. Second, membrane distillation system does not consume too much energy (It is not necessary to heat the feed stream up to its boiling point). Third, the quality of permeate from membrane distillation is high and stable. Fourth, the membrane fouling is not as serious as other membrane processes.

MD systems can be classified into four types, according to the configuration of the cold side of the membrane:

- i) Direct Contact Membrane Distillation (DCMD), in which the membrane is directly contacted only with liquid phases; e.g. saline water on one side and fresh water on the other.
- ii) Air Gap Membrane Distillation (AGMD), in which an air gap is interposed between the membrane and the condensation surface.
- iii) Sweeping Gas Membrane Distillation (SGMD), in which a stripping gas is used as a carrier for the produced vapour, instead of vacuum as in VMD.
- iv) Vacuum Membrane Distillation (VMD), in which the cold side of membrane is kept under vacuum and the generated vapour is drawn to a separate condenser.

Membrane materials that are suitable for membrane distillation and have been used by many researchers are polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene (PE) and polypropylene (PP) [40-41]. PP and PE polymer are more economical for membrane distillation for they have very good solvent resistance, chemical resistance and highly hydrophobic property. It is widely used in membrane

contactor and blood separation. Normally, PP has good mechanical strength, low surface energy and high hydrophobicity and is one of the important polymers for membrane distillation. But, the flux of membrane distillation for PP membrane is still not as high as expected. PVDF also has very good solvent resistance, chemical resistance and high hydrophobic property. It is widely used in making ultrafiltration membranes. Because it contains fluorine group, PVDF has lower surface energy and high hydrophobicity. PVDF is another important polymer for membrane distillation [42-45]. Theoretically, membranes used in membrane distillation should have the following properties:

- a) Reasonable thickness, since the permeate flux is inversely proportional to the membrane thickness.
- b) Reasonable pore size, since the entry pressure of water is inversely proportional to the pore size.
- c) High hydrophobicity.

3. PROBLEM DEFINITION

In 1960s, Loeb and Sourirajan developed cellulose acetate membrane for seawater desalination. Based on the idea of Loeb and Sourirajan [46-48], Cadotte [49-53] in 1980s, was able to prepare a composite membrane that consisted of a thin layer of polyamide which was formed by in-situ interfacial poly-condensation of branched polyethyleneimine and 2, 4-diisocyanate on a porous polysulfone membrane. Since then, the focus has been placed to the development of composite membranes with a thin skin layer, mostly made of aromatic polyamide material. Interfacially polymerized aromatic polyamide has become the major polymer to be used in the present RO desalination process. Compared with cellulose acetate RO membrane, high permeation flux can be achieved by the interfacially polymerized aromatic polyamide membranes [52, 53]. However, membrane fouling and membrane deterioration in the presence of chlorine are two major drawbacks of the aromatic polyamide membrane. Although the removal efficiency of non-ionized organic molecules by the aromatic polyamide membranes is much greater than cellulose acetate membranes, currently available RO membranes

cannot remove small molecules such as methanol and chloroform effectively.

Membrane Distillation is a new, rapidly increasing membrane research direction for desalination technology characterized by the possibility of overcoming some limits of other membrane processes, such as reverse osmosis. As compared with traditional evaporation, membrane distillation offers the basic advantages as a new membrane separation process: easy scaling up, simplicity of operations, possibility of high quality of product and high membrane surface/volume ratio, etc. Moreover, there exists the possibility of treating solutions with thermo sensitive compounds and high level of suspended solids, at a temperature much lower than the boiling point and at the atmospheric pressure. Theoretically, for membrane distillation, 100% rejections might be predicted for all electrolyte and non-volatile or non-electrolyte solutes. The possibility to reach a high solute concentration in the feed solution is of particular interest, considering the limits of RO due to the osmotic pressure increase with concentration.

In order to achieve good membrane distillation performance, a strong and stable hydrophobic character, good thermal and chemical resistance, low thermal conductivity and high mechanical properties are some of the basic requirements for the polymer membrane of potential interest for membrane distillation.

Methodologically, the above set of problems and approaches is closely related to find new membrane material and to fabricate novel membranes for membrane distillation process, and also to develop a membrane system for membrane distillation. In particular, to enhance the rejection of organic contaminants by polymeric membranes, understanding of membrane structure, permeant-membrane interactions, and their effects on membrane transport is important.

Nanofibers are an exciting new class of material used for several valuable applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, and energy storage. Special properties of nanofibers make them suitable for a wide range of applications from medical to consumer products and industrial to high-tech

applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, energy storage, fuel cells, and information technology [54-61].

Generally, electrospinning process can produce polymeric nanofibers. Electrospinning is a process that spins fibers of diameters ranging from 10nm to several hundred nanometers. Another technique for producing nanofibers is spinning bi-component fibers such as Islands-In-The-Sea fibers. Dissolving the polymer leaves the matrix of nanofibers, which can be further separated by stretching or mechanical agitation. Compared to electrospinning, nanofibers produced by this technique will have a very narrow diameter range but they are thicker and special equipment is required.

A membrane made of nanofibers has high porosity, high hydrophobicity and good strength. Hence, it has a potential to be a suitable material for membrane distillation. But until now, no research and investigation have been reported on the application of nanofiber membranes for membrane distillation.

4. RESEARCH OBJECTIVES

The major objective of this research is to develop a novel membrane with high desalination performance for membrane distillation process; more specifically, with high rejection capacity for non-volatile molecules. The research is further extended to the separation of ethanol/water mixtures by membrane distillation. The research work is divided into the following two parts.

Part I focuses on the nanofiber and nanofiber membrane preparation and membrane characterization. More specifically, it is concerned with the membrane preparation method based on electrospinning. The main target of this part is to develop a new membrane with high hydrophobicity, high porosity and high mechanical strength for membrane distillation. Conditions of nanofiber and nanofiber membrane preparation, nanofiber membrane characterization are carefully discussed in this part.

Development of novel nanofiber membranes for membrane distillation is one of main tasks of the current research.

Part II focuses on the applications of the novel nanofiber membrane for using membrane distillation process. Attempts are made to desalinate aqueous sodium chloride solution as a model of seawater desalination and also to separate ethanol/water mixtures. Air gap membrane distillation (AGMD) was chosen for this purpose for its product has higher quality and its operation needs less energy.

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PART I

NANOFIBER AND NANOFIBER MEMBRANE

PREPARATION AND CHARACTERIZATION

Chapter 1 INTRODUCTION

1. INTRODUCTION

Nanofibers are solid state linear nano-materials characterized by flexibility and an aspect ratio greater than 1000:1. If the size of material reaches this range, it will have different properties compared with the same material which has a normal size. The thermal, magnetic, photonic, electric and mechanical properties will also dramatically change. Nanomaterial can be classified to:

- (1) nano particle ----- (Zero dimension)
- (2) nanowire (nanofiber, nanotube) ---- (One dimension)
- (3) nano membrane (nano film)----- (Two dimension)
- (4) nano block (cube)----- (Three Dimension)
- (5) nano structure
- (6) nano composite

According to the National Science Foundation (NSF), nano-materials are matters that have at least one dimension equal to or less than 100 nm [1]. Therefore, nanofibers are fibers that have diameters equal to or less than 100 nm. With the development of research, the definition of nanofiber, especially, that of electrospun nanofiber has changed. The upper limit of the fiber diameter was enlarged to 1000 nm. If the fiber diameter is smaller than 1000 nm, it can be called nanofiber. The reason is when the fiber diameter is smaller than 1000 nm; the fiber already has a very high surface area and a very high surface/volume (mass) ratio. Many fiber properties change significantly as the fiber diameter decreases. In the present work, the latter definition of nanofibers is followed.

With the fiber diameter decreasing, the surface area of material will significantly increase. When the length/mass ratio of fiber is 0.3 dtex, ($5.54 \mu\text{m}$, $1 \text{ dtex} = 9000 \text{ m/g}$ for textile fiber measurement), dramatically changes in membrane properties can occur. Even when the diameter is 1000 nm ($= 1.0 \mu\text{m}$), significant changes in fiber properties are

expected. It is obvious that the ratio of surface area to volume (mass) will increase significantly with the decrease in fiber diameter. Table 1.1 shows the examples for polyester fibers [2].

Table1.1. Relationship of fiber diameter to length/mass and surface area/mass ratio of polyester fiber.

Fiber diameter (μm)	Length/mass ratio		Surface area/mass ratio(m^2/g)
	(dex)	(m/g)	
10.12	1	9000	0.2863
5.54	0.3	30000	0.5211
1.01	0.01	900000	2.863
0.1	0.001	9000000	9.051

Table 1.1 shows that as fiber diameter decreases from 10 μm to 0.1 μm , the surface area/mass ratio increases more than 30 times. Even if the fiber diameter is 1 μm , the surface area/mass ratio is still 10 time higher than that of 10 μm ($\cong 1\text{dtex}$) fiber.

Materials in nanofibrous form are of great practical and fundamental importance. The combination of high surface area, flexibility and superior directional strength makes fiber a preferred material form for many applications ranging from clothing to reinforcement, for aerospace structures and other industrial applications.

Furthermore, fibrous materials in nanometer scale are the fundamental building blocks of living systems. From the 1.5 nm double helix strand of DNA molecules, including cytoskeleton filaments with diameters around 30 nm, sensory cells such as hair cells and rod cells of the eyes are formed. Nano-scale fibers form the extra-cellular matrices or the multifunctional structural backbone for tissues and organs. Specific junctions between these cells conduct electrical and chemical signals that result from various kinds of stimulation. The signals direct normal functions of the cells such as energy storage, information storage, retrieval, tissue regeneration and sensing.

Considering the potential opportunities provided by nanofibers, there is an increasing interest in nanofiber technology. There are many methods that can be employed to fabricate nanofiber. The technology includes the template method [3], vapour grown [4], phase separation [5] and electrospinning [6-23]. For example, bi-component or multiple-component polymer is spun first by melt-blowing to fabricate fibers whose diameters are over the micrometer range. The mechanism of micro or nanofiber by melt spinning is described in Figure 1.1, where each of white and black portions indicates a polymer component.

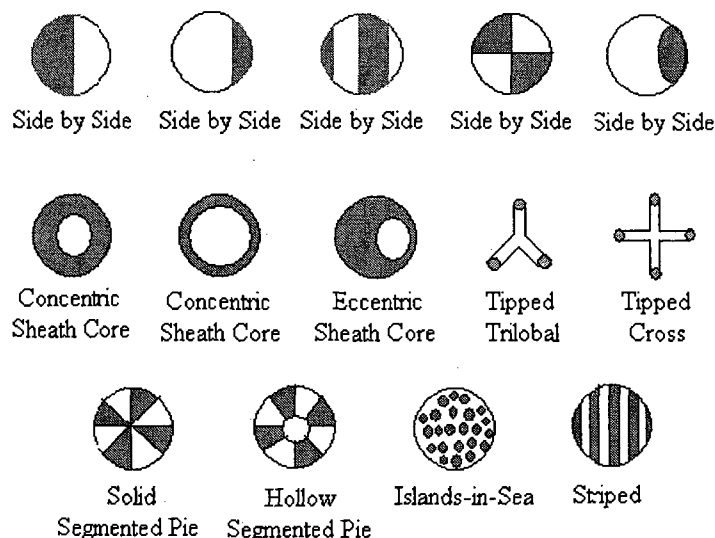
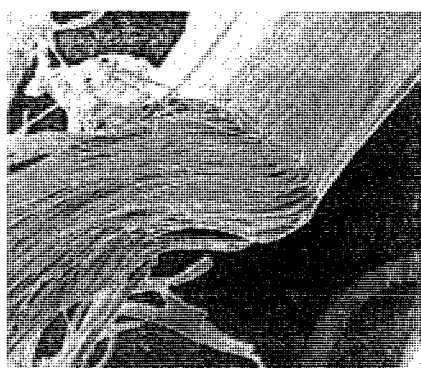


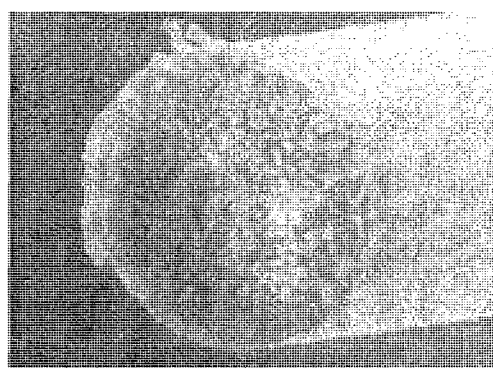
Figure 1.1 Bi-component Fiber Cross-sections

As shown in Figure 1.1, bi-components or multiple-components fibers can be made by extruding two or more polymers of different chemical compositions and/or physical properties simultaneously from the same spinneret with the polymers contained in the same filament [24]. After the precursor of the nanofiber is spun, one component of the fiber is leached out by the post treatment or the fibers are split by mechanical or chemical methods. Recently, Hills Inc. (USA) reported that they had developed nanofibers with a diameter of several hundred nanometers by islands-in-sea technology. This company also developed melt-blowing technology to make nanofiber. The diameter of nanofiber made

by melt-blowing can reach 250 nm. However, melt-blowing technology is more complex and expensive [23]. The nanofibers made polymer blends after and before post-treatment are shown in Figure 1.2. As shown in the images, the dimension of fiber is 6.44 mm × 6.44 mm before the splitting of the fiber components. After splitting, the diameter of a single fine fiber becomes 0.5 μm. This technology also needs a very complex system and extremely accurate control.



600 Islands-In-Sea (1500X Magnification)
Polypropylene: Islands
PVA: Sea
PVA SEA 0.5μm (after dissolving sea)



900 Islands-In-Sea
Polyester: Islands
Polyethylene: Sea
6.4mm x 6.4mm on centers

Figure 1.2 Islands-In-Sea micro or nanofibers

Although there are many methods to fabricate nanofibres, electrospinning is the most simple and effective method to fabricate nanofiber. Materials such as polymer, composites, ceramic and metal have been used to fabricate nanofibres by electrospinning directly or indirectly through post-treatment. However, what makes electrospinning different from other nanofiber fabrication processes is its ability to form various fibre assemblies. This will certainly enhance the performance of products made from nanofibres and allow specific application of nanofiber product.

Generally, electrospinning technology enables production of continuous polymer nanofibers from polymer solutions or melts by using a highly electric field. When the electric force on induced charges of the polymer liquid overcomes surface tension, a fine

polymer jet is ejected. The charged jet is elongated and accelerated by the electric field force, undergoes a variety of instabilities, dries, and is deposited on a substrate as a random nanofiber mat or web. If a well designed take-up is used, the nanofiber may also be arranged in order.

The first patent on the process was reported in 1934 [13]; however, outside of the filter industry, there was little interest in the electrospinning or electrospun nanofibers, until the middle of 1990s [6]. Since that time, the process attracted rapidly growing interest triggered by potential applications of nanofibers in nanotechnology. The publication rate has nearly doubled annually. Over a hundred synthetic and natural polymers were electrospun into fibers with diameters ranging from a few nanometers to micrometers. Uses of nanofibers in composites, protective clothing, catalysis, electronics, biomedicine (including tissue engineering, implants, membranes, and drug delivery), filtration, agriculture, and other areas are presently being developed. Here, it needs to be pointed out that using of nanofiber membranes for membrane distillation is the creative contribution of present research work.

The main advantage of electrospinning process is its relatively low cost compared to that of other methods. The resulting nanofiber samples are uniform and do not require expensive equipment and accurate control technology. Unlike sub micrometer diameter whiskers, inorganic nanorods, carbon nanotubes, and nanowires, the electrospun nanofibers can be continuous. Beyond this, nanofibers are expected to possess high axial strength combined with extreme flexibility. The nanofiber assemblies may feature very high open porosity coupled with remarkable high surface area. Yet, these assemblies would possess excellent structural mechanical properties. Using the electrospinning process, Reneker and co-workers [9] demonstrated the ability to fabricate nanofibers of organic polymers with diameters as small as 3 nm. These molecular bundles, self-assembled by electrospinning, have only 6 or 7 molecules across the diameter of the fiber! That means half of 40 parallel molecules in the fiber are on the surface. Collaborative research in MacDiarmid and Ko's laboratory [7, 10] demonstrated that blends of nonconductive polymers with conductive polyaniline polymers and pure

conductive polymers can be electrospun. Additionally, in situ methods can be used to deposit 25 nm thick films of other conducting polymers, such as polypyrrole or polyaniline, on preformed insulating nanofibers. Carbon nanotubes, nanoplatelets and ceramic nanoparticles may also be dispersed in polymer solutions, which are then electrospun to form composites in the form of continuous nanofibers and nanofibrous assemblies [8]. Specifically, the role of fiber size has been recognized in significant increase in surface area; in bio-activity; electronic properties; and in mechanical properties.

1.1. Effect of Fiber Size on Surface Area

One of the most significant characteristics of nanofibers is the enormous availability of surface area for per unit volume or per unit mass (Table 1.1.). When fibers have diameters from 0.005 to 0.5 μm , as shown in Fig. 1.3, the surface area per unit mass of fiber is around 10 to 1,000 square meters per gram. When nanofibers are three nanometers in diameter, which corresponds to only about 40 molecules; about half of the molecules are on the surface. As seen in Fig. 1.3, the high surface area of nanofibers provides a remarkable capacity for the attachment or release of functional groups, absorbed molecules, ions, catalytic moieties and nanometer scale particles of many kinds.

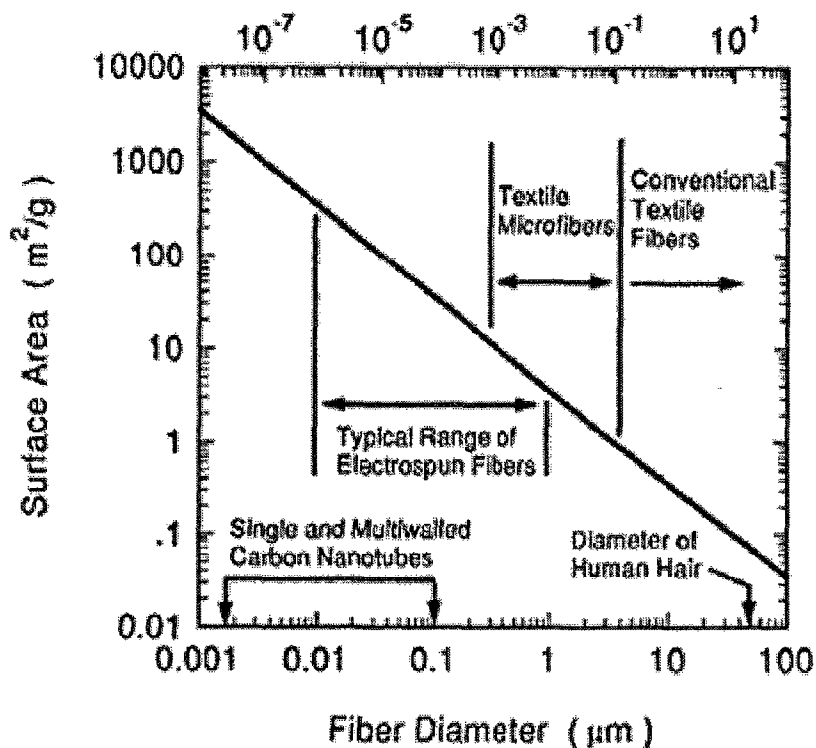


Figure 1.3 Effect of fiber diameter on surface area [8]

1.2. Effect of Fiber Size on Hydrophobicity

Another significant characteristic of nanofibers is that such kind of material is highly hydrophobic. With the enormous surface area per unit volume or per unit mass, nanofiber material will trap air in the void of the nanofiber mat. As the result, most nanofiber material will have a highly hydrophobic surface, especially for those polymers which are called hydrophobic polymers. Hydrophobic surfaces with a water contact angle higher than 100° play an important role in many applications such as biocompatibility, contamination prevention, enhanced lubricity and durability of materials [25-28].

It is well known that the hydrophobicity of a material depends on both the surface chemical composition and surface geometrical microstructure [29, 30]. Hydrophobic

surfaces can also be observed in nature; for example, lotus leaves have a self-cleaning ability, which removes dust particles and contaminants by rain drops [31-33]. The super-hydrophobicity of the lotus leaf is believed to be a result of the hydrophobic wax layer present on the leaf surface, as well as the complicated leaf surface structures. Micrometer-scale bumps as well as nanometre-scale hair-like structures are found covering the surface of the lotus leaf, allowing air to be trapped under the water droplets that fall on the leaf.

Recently, the fabrication of fibres with diameters from tens of nanometres to several micrometres by an electrospinning technique has been widely reported [6, 34, 35]. Jiang et al.[36], Singh et al. [37], and Acatay et al. [38] reported the mimicry of the lotus-leaf-like structure by electrospinning a dilute PS solution, a dilute poly[bis(2,2-trifluoroethoxy)phosphazene] solution, and a dilute solution of poly(acrylonitrile-co- α,α -dimethyl-isopropenylbenzyl isocyanate) with a perfluorinated linear diol, respectively. They prepared super-hydrophobic surfaces consisting of a lotus-leaf-like porous microsphere/nanofibre composite mat. However, electrospun fibrous mats of the same materials without the existence of microspheres do not show super-hydrophobicity. Additionally, an electrospun mat surface composed of fibres with diameters below 1 μm has also been reported as a super-hydrophobic surface by other researchers [39-45].

Generally, with the decreasing of fiber diameter, the hydrophobicity of material will increase. The real mechanism of this phenomenon is not very clearly understood.

1.3. Effect of Fiber Size on Bioactivity

Considering the importance of surfaces for cell adhesion and migration, experiments were carried out in the Fibrous Materials Laboratory at Drexel University using osteoblasts isolated from neonatal rat calvarias and grown to confluence in Ham's F-12 medium (GIBCO). These experiments were supplemented with 12% Sigma fetal bovine on PLAGA sintered spheres, 3-D braided filament bundles and nanofibrils [9]. Four matrices were fabricated for the cell culture experiments. These matrices included 1) 150 - 300 μm PLAGA sintered spheres 2) unidirectional bundles of 20 μm filaments 3) 3-D

to the greater available surfaces for cell adhesion as a result of the small fiber diameter which facilitates cell attachment.

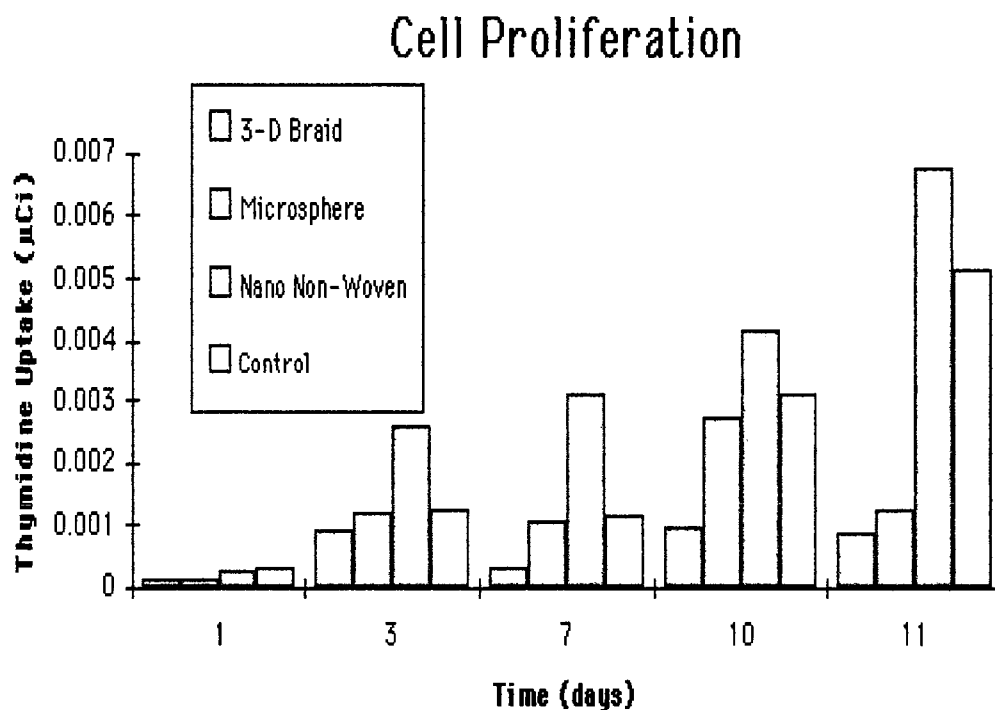


Figure 1.4 Fibroblast cell proliferations as indicated by the Thymidine uptake of cell as a function of time showing that polylactic-glycolic acid nanofiber scaffold is most favourable for cell growth [9]

1.4. Effect of Fiber Size on Strength

Materials in fiber form are unique in that they are stronger than bulk materials. As fiber diameter decreases, it has been well established in glass fiber science that the strength of the fiber increases exponentially, as shown in Figure 1.5, due to the reduction of the probability of including flaws. The diameter of material gets even smaller, as shown for the case of nanotubes in Fig. 1.6, the strain energy per atom increases exponentially, contributing to the enormous strength of over 30 GPa for carbon nanotube.

the case of nanotubes in Fig. 1.6, the strain energy per atom increases exponentially, contributing to the enormous strength of over 30 GPa for carbon nanotube.

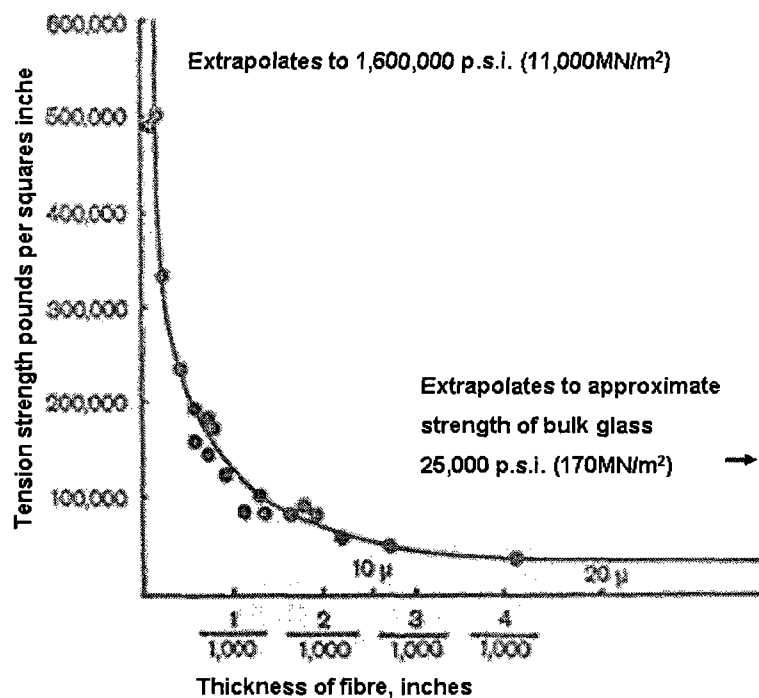


Figure 1.5 Dependence of glass fiber strength on fiber diameter [46]

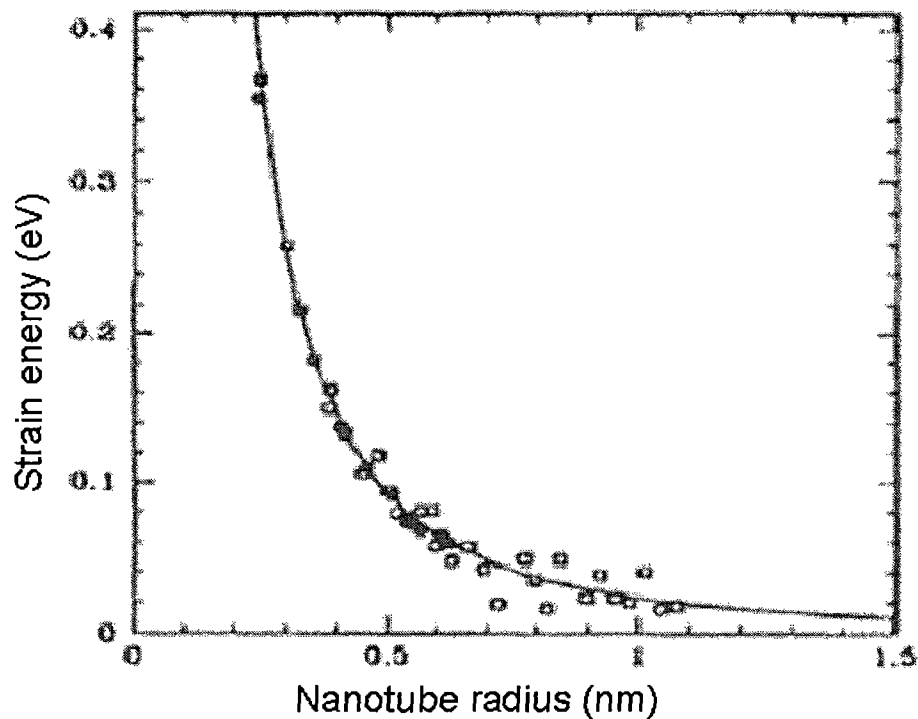


Figure 1.6 Strain energy as a function of nanotube diameter [47]

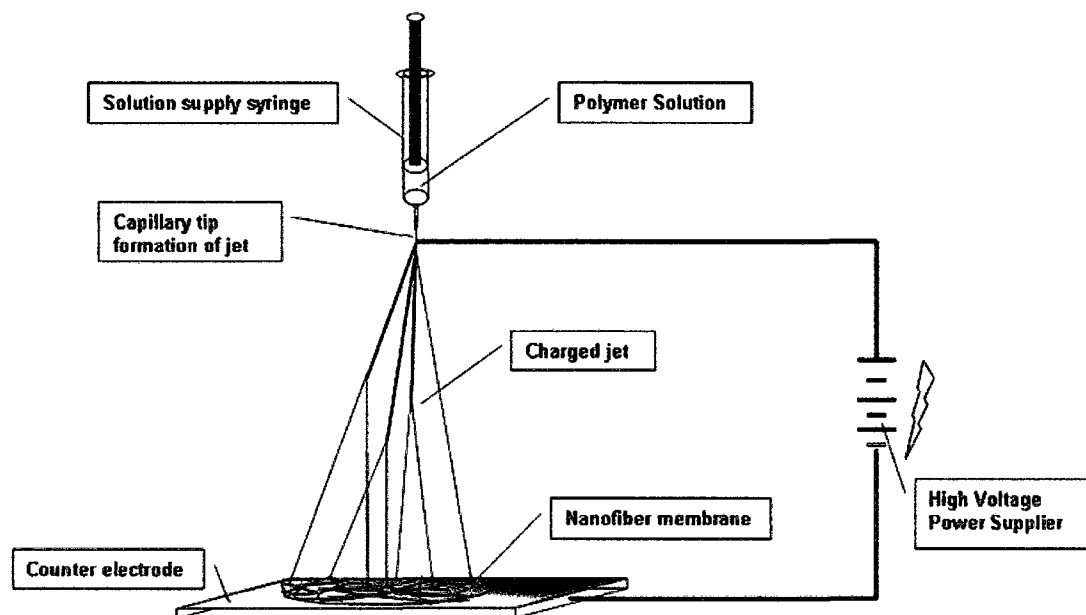
Although the effect of fiber diameter on the performance and possibility of fibrous structures has long been recognized, the practical generation of fibers down to the nanometer scale was not realized until the rediscovery and popularization of the electrospinning technology by Professor Reneker almost a decade ago [11]. The ability to create nanoscale fibers from a broad range of polymeric materials in a relatively simple manner using the electrospinning process coupled with the rapid growth of nanotechnology in the recent years has greatly accelerated the growth of nanofiber technology. Although there are several alternate methods for generating fibers in nanometer scale, none matches the popularity of the electrospinning technology due largely to the great simplicity of the electrospinning process.

2. LITERATURE REVIEW: ELECTROSPINNING OF NANOFIBERS

The technology of electrostatic spinning or electrospinning may be traced back to 1745. Bose created an aerosol spray by applying a high potential to a liquid at the end of a glass capillary tube. The principle behind what is now known as electrospinning was furthered when Lord Rayleigh calculated the maximum amount of charge which a drop of liquid can hold before the electrical force overcomes the surface tension of the drop [14].

In 1934, Formhals [13] issued a patent for a process capable of producing micron level monofilament fibers using the electrostatic forces generated in an electrical field for a variety of polymer solutions. The patent describes how the solutions are passed through an electrical field formed between electrodes in a thin stream or in the form of droplets in order to separate them into groups of filaments. This process, later to become known as a variant of electrospinning, allows the threads, which are repelling each other when placed in the electric field, to pile up parallel to each other on the filament collector in such a way that they can be unwound continuously in skeins or ropes of any desired length. The operational principle of electrospinning is quite simple. In this non-mechanical, electrostatic technique, a high electric field is generated between a polymer fluid contained in a spinning dope reservoir with a capillary tip or a spinneret and a metallic fiber collection ground surface. When the voltage reaches a critical value, the electrical force overcomes the surface tension of the deformed drop of the suspended polymer solution formed on the tip of the spinneret, and a jet is produced. The electrically charged jet undergoes a series of electrically induced bending instabilities during its passage to the collection surface that results in the hyper-stretching of the jet. This stretching process is accompanied by the rapid evaporation of the solvent molecules that reduces the diameter of the jet, in a cone-shaped volume called the “envelope cone”. The dry fibers are accumulated on the surface of the collection plate resulting in a non-woven mesh of nano to micron diameter fibers. The process can be adjusted to control the fiber diameter by varying the electric field intensity, collect distance and polymer solution concentration, whereas the duration of electrospinning controls the thickness of fiber deposition [13]. A schematic drawing of the electrospinning process is shown in Figure 1.7.

and temperature of spinning space, all of these factors will have serious effects on nanofiber structure and diameter. Further, it will affect the performance of nanofiber material.



Schematic diagram of the apparatus of electrospinning

Figure 1.7 Schematic drawing of the electrospinning process showing the formation of nanofibers under the influence of an electric field

Numerous polymers have been electrospun by an increasing number of researchers around the world. Examples of some of the polymers that have been successfully spun are shown in Table 1.2. Solvents and polymers with molecular weights ranging from 10,000 to 300,000 and higher had been electrospun.

Table 1.2 Examples of polymers that have been electrospun

Polymer	Solvent	Concentration	Reference
Nylon 6,6	96 %Formic acid	12.1 wt%	[48]
Polyacrylic acid	Ethanol	6 wt%	[49]

Table 1.2 Examples of polymers that have been electrospun

Polymer	Solvent	Concentration	Reference
Nylon 6,6	96 %Formic acid	12.1 wt%	[48]
Polyacrylic acid	Ethanol	6 wt%	[49]
Polyamide-6	85 % v/v formic acid	34 wt%	[50]
Poly (benzimidazol)	Dimethyl acetamide, 185 °C	20 wt%	[51]
Polycarbonate	Dichloromethane	15 wt%	[52]
Polyetherimide	1,1,2-Trichloroethane	14%	[53]
Poly(ethylene oxide) Mw=400K	Water	10 wt%	[54]
Poly(ethylene terephthalate)	Trifluoroacetic acid	0.2g/ml	[55]
Polystyrene	Chloroform	30% (w/v)	[56]
Poly(vinyl alcohol)	Water	25 wt%	[57]
Poly (vinyl chloride)	Tetrahydrofuran: Dimethylformamide = 6:4	13 wt%	[58]
Poly(vinyl pyrrolidone)	Ethanol	4 wt%	[59]
Poly(vinylidene fluoride)	Dimethylacetamide	25 wt%	[60]
Cellulose acetate	DMA:Acetone=1:2	15 wt%	[61]
Collagen Type I	Hexafluoropropanol	0.083g/ml	[62]
Gelatine type A	2,2,2-Trifluoroethanol	10-12.5 wt%	[63]
Poly(urethane)	Tetrahydrofuran: Dimethylformamide=6:4	13 wt%	[64]

In addition to the polymers on Table 1.2, many other polymers also have been spun by electrospinning, including natural biopolymers and inorganic polymers. Polymers were blended with inorganic compounds to prepare inorganic nanofibers [65]. Hollow nanofibers were also developed [66].

Electrospinning technology has many advantages such as simple, cheap, and stable. But it still has many limits: (1) Very low out profits. Typically, its spinning rate is (1mg-1g)/h. (2) Nanofiber made by electrospinning has a fix structure. It is difficult to spin a single separated nanofiber. Mostly the product is like non-woven web or mat. (3) There is no further stretching process. Orientation of macromolecules in the polymer can not be completed so that nanofibers may not reach expected higher mechanical strength. (4) Even if numerous papers about nanofiber electrospinning had been published, systematic research on electrospinning mechanism is still required.

3. RESEARCH OBJECTIVES

Recently, notable research activities in the field of new membranes for membrane distillation (MD) are evident in the increased number of patents [67-69] and publications [70-73]. Generally, research activities are aimed at developing highly hydrophobic or hydrophobic/hydrophilic composites, and chemically stable membranes. The main results include the reduction of membrane wetting out, maintaining feasible water fluxes at the same time. In case of MD for desalination, the selection of membranes has been rather limited because of the demand for chemical and temperature resistance. As the MD process for desalination will be operated at a temperature about 80°C, hydrophobic micro-porous membranes made of polyolefin are not very suitable for such application.

Fluoropolymer materials remain the main group that possesses the required properties to produce membranes which are suitable for desalination by MD. The most well-known property for which fluoropolymers are employed in high-demanding applications is their outstanding thermal and chemical resistance. However, there are yet many challenges to overcome, which are associated with the use of these materials for membrane manufacture. The cost of membranes, especially of those that will be used on a large industrial scale, is a very important issue to be considered as well.

As mentioned, electrospinning technology is suitable to fabricate fibers of high area/volume ratio and high hydrophobicity. Hence, PVDF, when it is electrospun into nanofiber, offers a material which is desirable for MD. Even though PVDF is the polymer of the first choice, other polymers may also be useful to fabricate nanofiber membranes for membrane distillation.

In the present work, PVDF nanofiber membrane is prepared by electrospinning technology. The electrospinning conditions are investigated. The PVDF nanofiber membrane is characterized by SEM, AFM DSC, LEPw, Contact angle analyzer and mass transfer method. Nanofibers made from other polymers are also investigated. But the major research work is focused on PVDF nanofiber and PVDF nanofiber membrane fabrication for desalination by membrane distillation.

Chapter 2 FABRICATION AND CHARACTERIZATION OF PVDF NANOFIBER AND NANOFIBER MEMBRANE

1. INTRODUCTION

Poly (vinylidene fluoride) is a semi-crystalline polymer that is produced commercially by a free-radical emulsion or suspension polymerization of vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) in water [74-76]. PVDF polymer exhibits a unique combination of mechanical and electrical properties due to the alternating spatial arrangement of CH_2 and CF_2 groups along the polymer backbone. PVDF is the fluoropolymer consumed in the greatest quantities aside from PTFE [77], because of its i) high mechanical and impact strength, ii) resistance to environmental stress, iii) ease of melt-process ability, and iv) low cost compared to other fluoropolymers. PVDF is used in architectural coatings (~40%), semiconductor manufacture and chemical processing (~40%), and wire and cable insulation (~20%) [78]. A small, but increasing amount of PVDF is used as electrodes in lithium batteries [79]. Anti-oxygenic property and antipollution property are the most important advantages of PVDF. Recently, PVDF has been becoming more and more popular material for membrane fabrication. Its chemical stability is better than other groovy material, especially for the ability of endurance of washing with oxidizer, since washing by oxidizer is a main method to solve the fouling problem that ultrafiltration (UF) membrane may be plugged up by organic matter. Thus, UF membrane made from PVDF will be more durable, stable and more everlasting. Membranes made from PVDF are generally chemically inert and, as such, are useful for filtration of a wide variety of fluids. However, they are not inherently wettable by water. The natural hydrophobicity of PVDF membranes limits their usefulness in the filtration of aqueous solutions. Different wetting properties are required for different applications of membranes. Some applications require wettability by liquids of extremely high surface tensions, while membrane distillation requires non-wettability by water. In practice, this limitation is a very important property for membrane distillation. Numbers of researches on membrane distillation have adopted PVDF membrane [80-85]. PVDF membrane made by phase inversion or casting and stretching method already has relatively high hydrophobicity. Its contact angle is higher than 80° , but lower than 90° . Among polymers that have been

tested for MD, PVDF is considered the best, because of the above mentioned properties. However, high hydrophobicity would be preferred for desalination by membrane distillation. Electrospinning nanofiber enhances the hydrophobicity of membrane. Hence in the present work, it is attempted to use electrospun PVDF nanofiber membranes for membrane distillation.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

Polymers used for electrospinning are as follows:

- PVDF, Poly (vinylidene fluoride), (Kynar 761, Elf Atochem)
- PES, Polyethersulphone, (ICI, Victrex-4100P)
- PS, Polysulphone, (Ultrason®-S, BASF)
- PVA, Poly (vinyl alcohol), ($M_w \sim 127,000$, Sigma-Aldrich)
- PEI, Polyetherimide, (Ultem, GE)
- PAN, Polyacrylonitrile (M_w 86,200, Sigma-Aldrich)
- PC, Polycarbonate, ($M_w \sim 20200$, Sigma-Aldrich)
- PVC, Poly (vinyl chloride), ($M_w \sim 62,000$, Sigma-Aldrich)
- PVP, Poly (vinylpyrrolidone), (K90, Sigma-Aldrich)
- Nomex, Polyamide (Dupont)
- Collagen-I, (Supplied by Eye Institute of University of Ottawa)

Solvents used for nanofiber electrospinning are as follows:

- Chloroform, (CR grade, Sigma-Aldrich)
- DMF, Dimethylformamide, (AR grade, Sigma-Aldrich)
- DMAc, Dimethylacetamide, (CR grade, Sigma-Aldrich)
- HFP: Hexafluoro-2-propanol (Sigma-Aldrich)
- IPA: Isopropyl alcohol (Sigma-Aldrich)
- Water, Deionized water, (Self-made at lab)

Polystyrene latex: Micro-particles of 0.1, 0.5, 1, 2, 3, 7, 8 and 10 μm in diameter were

purchased from Sigma–Aldrich (Missouri, USA).

2.2. Nanofiber Preparation by Electrospinning

2.2.1. Preparation of spinning dope

Polymers and solvents used for the preparation of the spinning dopes and the polymer concentrations are listed in Table 2.1. The polymers cover a wide range of hydrophilicity/hydrophobicity and the criteria for the choice of the solvent is the high miscibility of polymer with solvent.

Table 2.1 Polymer, solvent and polymer concentration of the spinning dope

Polymer	Solvent	Concentration wt%
PVDF	DMF	20
PVDF+PVP	DMF	18+6
PS	DMF	18
PES	DMF	20
PEI	DMAc	18
PVC	DMF	10
PC	Chloroform	10
PAN	DMF	15
Nomex (PA)	DMF	15
PVA	Water	8
Collagen	HFP	0.12

A 150 mL glass bottle was loaded with polymer and solvent, before it was placed on a rolling mixer. The mixer was rolled until the polymer was completely dissolved. For the preparation of the PVA solution, the bottle which contained the polymer and water was placed in an oven at 90°C and the bottle was shaken manually from time to time until polymer was completely dissolved and a clear PVA solution was prepared. Even though various polymers were involved in electrospinning, the major focus material in present work is PVDF.

It should be emphasized that nanofiber membrane made from polymers other than PVDF may also be very useful. Nanofiber membranes made of different materials have potential

for special applications. For example, Silk fibroin and collagen nanofiber membranes can be used as a bio scaffold. It may be used for nerve guiding growing, drug release control or wound dressing [86, 87]. Nanofiber web has already been successfully commercialized for gas filtration by Donaldson [88]. The filtrate efficiency could reach 99.99% and a long life was achieved compared with the normal fiber filter. Some new applications have also been attempted [89]. The use of nanofiber membranes for desalination by membrane distillation can be considered as one of such exploration of novel applications.

2.2.2. Electrospinning

Electrospinning was conducted by the laboratory made setup illustrated in Figure 1.7. The polymer solution was supplied by a syringe pump (74900 series, Cole-Parmer). The volume of the syringe was 10 mL and the flow rate could be adjusted in a range from 0.001 $\mu\text{L/h}$ to 147 mL/min. A needle (27G1/2, BD Pharmingen, San Diego, USA) was attached to the syringe to be used as the spinneret. The top of the needle was tailored evenly and was connected to the positive electrode (+) of the high voltage digital power supply (DW-P503-1C, Tianjin, China) with adjustable voltage (0 to 50 KV) and the current below 1mA. Aluminium foil used as nanofiber collector was connected to the negative electrode (-) of the high voltage power supplier. The distance between the top of the spinneret and the aluminium foil is adjustable within a range of 0 cm to 30 cm. While electrospinning was conducted, a high voltage electric field was formed in the space between the spinneret (needle) and the foil. Once the electric force overcame the surface tension of the polymer solution, nanofiber was spun continuously, until the solution in the syringe pump was consumed. A membrane is obtained on the aluminium foil in a form of nonwoven web or mat.

2.3. Membrane Characterization

2.3.1. Optical microscope

Electrospinning process was monitored by an Optical microscope (BH2-UMA, Olympus). Nanofibers were spun on a glass slide. Under the optical microscope, the fiber structure was observed. The magnification is adjustable from 20 times to 200 times. The

microscopic image gave the information of the nanofiber such as the approximate diameter size of nanofiber and the shape of nanofiber. Based on the information, concentration, voltage and collect distance were adjusted. A more accurate measurement of the nanofiber diameter was carried out by an Optical microscope (BX40, Olympus) that could display a digital image of the nanofiber. The measurement of the diameter was enabled by a scale attached to the digital image. However, due to the limited resolution, the measurement was not as accurate as the SEM method. Further diameter measurement was conducted by SEM.

2.3.2. Scanning Electron Microscope (SEM)

Nanofiber samples made from different polymer were prepared by the electrospinning method described above. The nanofiber was collected on the aluminium foil, before being cut together with the aluminium foil to 3×10 mm without peeling. Then, the aluminium side of the sample was pasted on a SEM sample holder with a double side carbon adhesive tape. The sample was put into a sputter-coating chamber to coat with Pt, gold or carbon. In the present work, the sample was coated with carbon. After sputter-coating the membrane with a thin carbon film, the sample was mounted on another sample holder and put into SEM instrument. The morphology was observed by using a Scanning electron microscope (SEM) (JEOL JMS-6400, Japan).

2.3.3. Contact Angle Measurement

The VCA Optima Surface Analysis System (AST Products, Inc., Billerica, MA) is shown in Fig. 2.1. It was used for measuring the equilibrium contact angle of nanofiber membrane made by the above method.

Nanofiber membrane samples were prepared by electrospinning under different conditions. As for the dense film, it was prepared by using the same polymer solution as the nanofiber spinning dope. The polymer solution was evenly spread on a glass plate and placed in a fume hood for 72 hours until solvent was evaporated and a dense film was formed.

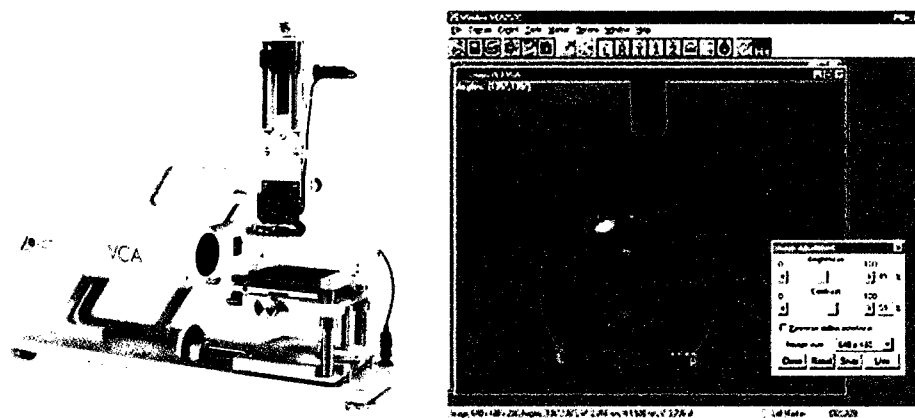


Figure 2.1 VCA Optima Surface Analysis System

Samples prepared for contact angle measurement were evenly placed on a glass slide and fixed by plastic tape. The sample slide was mounted on the plate holder shown in Fig. 2.1. The plate can be adjusted by forward or backward, and by left or right movement. Water drops come from a syringe needle mounted on the top of the sample. The amount of the water drop can be controlled by a computer system. In the current research, 1 μL water was fed to form a water droplet. The water droplet was placed on the surface of sample. Then, the equilibrium contact angle was measured by a digital picture made by a computer system as shown in Figure 2.1. The equilibrium contact angles were measured both for the nanofiber membrane and for the dense film.

It should be noted that the collagen nanofiber membrane was cross-linked by glutaraldehyde. Otherwise, collagen nanofiber membrane dissolves when it comes into contact with water. Vapour phase cross-linking of collagen nanofiber membrane was conducted as shown in Figure 2.2. Aqueous glutaraldehyde solution (25 wt% in H_2O)

was loaded in a 50 ml beaker. The beaker with the aqueous glutaraldehyde solution and the collagen nanofiber membrane were placed in a closed chamber at room temperature for 48 hours. The size of the chamber is 25×25×30 cm. For safety reason, the chamber should be kept in a fume hood.

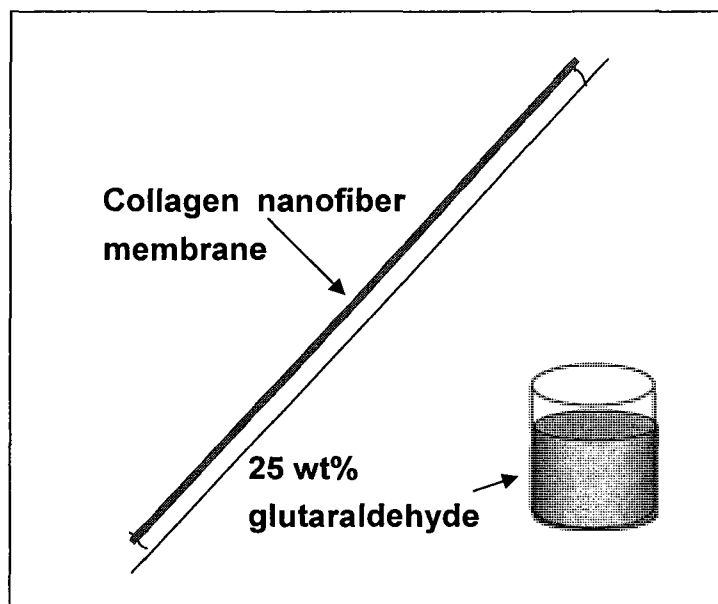


Figure 2.2 Vapour crosslinking treatment of Collagen nanofiber membrane

2.3.4. Atomic Force Microscope (AFM)

AFM is a relatively new technology to observe the material structure. It has been extensively applied on material research and other fields. Compared with SEM, the sample preparation of AFM is very simple. AFM samples do not need coating or other pre-treatment. Also AFM images can be obtained at room temperature. It does not need high voltage and low temperature. The risk of sample damage in the measurement processing is less than with other methods. The mechanism of AFM is shown in Figure 2.3. A cantilever with a probe is moved under computer control on the top of a sample. When the probe is close to the sample surface, a repellent force will push the probe away

from the surface. At the same time, the mechanical spring force of the cantilever will bring it back to the surface of the sample. As a result, a vibration movement of the cantilever will occur. The movement is captured by a laser beam, transformed to an electrical signal which is further transmitted to the detector. Based on the signal, the computer will give the image of sample surface. In most cases, the sample of AFM is not coated or treated by pre-treatment. Also the probe will not touch the sample surface. Therefore, the AFM can bring about more information close to the nature of material.

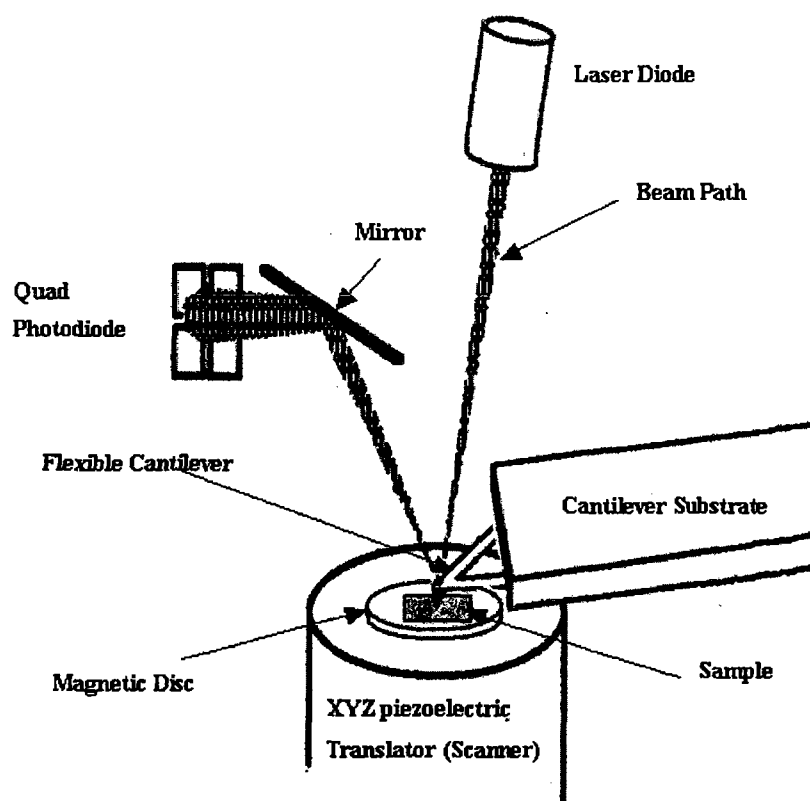


Figure 2.3 Mechanism of AFM [90]

Therefore, a nanofiber membrane sample was taped by a double side adhesive tape on a magnetic metal plate. Then, the plate was mounted on a sample holder. The holder is controlled by computer to move on 3D axis directions until a clear image was obtained. As the probe tip of AFM is very fine and sensitive, if membrane has a loose surface, a particle may come up and stick on the tip of probe. In this case, clear images, or even no

images can be obtained.

In the present work, two AFM instruments made by different companies were used. One AFM system is Nanoscope Digital IIIa from Digital Instruments Inc., Santa Barbara, USA. The other one is Agilent 5100 AFM/SPM Microscope from Agilent Technologies, Inc. USA. All AFM images were obtained at room temperature.

2.3.5. Differential Scanning Calorimetry (DSC)

By differential scanning calorimetry (DSC), the thermal properties of a sample are compared against a standard reference material which has no phase transition in temperature range of interest, such as powdered alumina. Sample and reference are contained in a small holder within an adiabatic enclosure as illustrated below (Figure 2.4).

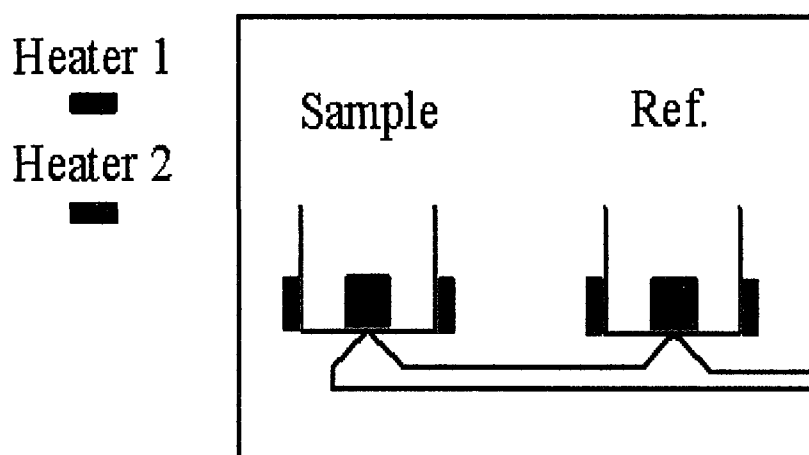


Figure 2.4 Schematic diagram of DSC sample holder

The temperature of each holder is monitored by a thermocouple and heat can be supplied electrically to each holder to keep the temperature of the two equal. A plot of the difference in energy supplied to the sample against the average temperature, as the latter

difference in energy supplied to the sample against the average temperature, as the latter is slowly increased through one or more thermal transitions of the sample, yields important information about the thermal transition. DSC can be used to determine glass transition temperature (T_g); melt temperature (T_m) and crystallinity of a polymer.

In this research, DSC model QA-1000 (TA Instrument, New Castle, DE, USA) was used. A nanofiber membrane sample was placed in one of the holders after being weighed. The sample was then heated from room temperature to 250°C at a heating rate of 10°C/min, before it was cooled back to -30°C. Another cycle of heating and cooling was then started from -30°C to 250°C. Two samples were prepared for this experiment. One is a nanofiber membrane. Another is a dense film cast from the same polymer solution as the spinning dope. For polymer film preparation, polymer solution was spread evenly on a glass plate and dried in a fume hood at room temperature for 72 hours until the solvent is completely evaporated. A small piece of the film was weighed and put in an aluminum case; the aluminum case was mounted into the DSC-QA 1000 instrument to measure the thermal behavior of nanofiber membrane and the polymer film.

2.3.6. Liquid Entry Pressure of Water (LEPw)

LEPw is the pressure that must be applied to pure water before it penetrates into dried membrane pores. This pressure depends on the pore size and the hydrophobicity of the membrane. The apparatus used for this measurement is shown in Figure 2.5. The membrane was placed in a static stainless steel cell between the upper chamber (600mL), the feed side which was filled with pure water, and the lower chamber, the permeate side which was connected to a digital capillary flow meter (Varian Optiflow 420). First, a relatively low pressure (3 psi) was applied to the system for at least 10 min; then, the pressure was increased stepwise with an increment of 0.1 psi. The pressure at which a continuous flow was observed in the permeate side is the LEPw. This method has been described extensively by Smolders and Franken [91].

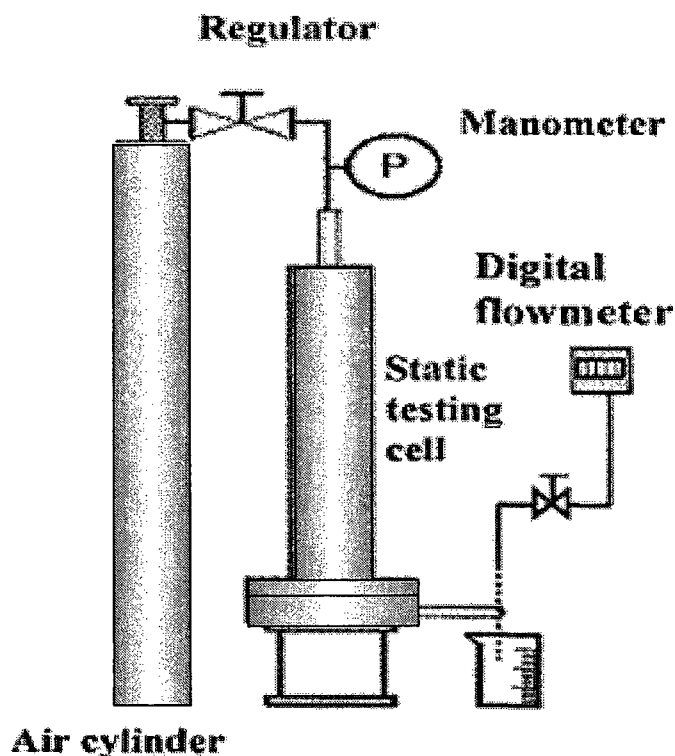


Figure 2.5 Schematics of the experimental system used for membrane liquid entry pressure of water (LEPw) measurement

2.3.7. Porosity

Porosity is defined as the volume of the pores divided by the total volume of the membrane. It can be determined by measuring the density of the polymer material using isopropyl alcohol (IPA), which penetrates inside the pores of the membrane, and the density of the membrane using pure water, which does not enter the pores. In this method, a pycnometer and a balance were employed. The following equation can be used to determine the porosity as suggested by Smolders and Franken [91].

$$\varepsilon = 1 - \frac{\rho_m}{\rho_{pol}} \dots \dots \dots (2-1)$$

Where, ρ_m is the density of the membrane and ρ_{pol} is the density of the polymer

material.

2.3.8. Pore size distribution measurement

Molecular-weight cut off (MWCO) of a membrane is defined by IUPAC as the molecular weight of a solute that gives 90% rejection coefficient [92]. The rejection coefficient is measured by a filtration experiment and is equal to one minus the ratio of the concentrations of a component on the downstream side and the upstream side of a membrane:

$$\text{Rejection coefficient} = \left(1 - \frac{\text{Concentration of downstream}}{\text{Concentration of upstream}}\right) \times 100\% \dots (2-2)$$

Usually, polyethylene glycol and polyethylene oxide, dextran, cow blood cell and other molecules are used to measure the MWCO. If the solute molecule had a spherical shape and the diameter of the spherical molecule could be measured, the diameter of solute molecule corresponding to the molecular weight cut-off (MWCO) could be used as the membrane pore size. But in reality, most of the molecular probes to measure the MWCO are non-spherical, and other methods have to be used.

In the present work, polystyrene latex micro-particles of 0.1, 0.5, 1, 2, 3, 7, 8 and 10 μm in diameter (Sigma–Aldrich) were used instead of the above mentioned molecular probes. The latex suspension was reconstituted in distilled water to prepare a 100 ppm suspension for each particle size. Using these suspensions as feed, separation experiments were carried out at a pre-set pressure (30 psi) with the wetted PVDF nanofiber membrane. Two hundred mL of feed was loaded to the feed chamber of the separation cell and the pressure was applied. The first 5 mL of permeate was discarded to ensure that the steady state was reached. 30 mL of permeate was collected before the separation experiment was terminated and the permeation rate was calculated by knowing the time required to collect 30 mL of permeate. Polystyrene micro-particles concentration in permeate was determined using the calibration curve. The separation experiment was terminated after

30 mL of permeate was collected. The remaining Polystyrene suspension in the feed chamber was removed and the cell rinsed three times with distilled water, without removing the PVDF nanofiber membrane. The solute separation was determined using the formula below:

$$f = (1 - \frac{C_p}{C_f}) \times 100 \dots \dots \dots (2-3)$$

Where C_p and C_f are the polystyrene latex suspension concentrations in permeate collected and the original feed, respectively, which were determined via TOC Analyzer (Appollo-9000, TELEDYNE Tekmar, Mason, Ohio, USA). f is the solute rejection. It should be noted that f is basically the same as rejection coefficient defined by equation (2-2). When solute separation (%) of a membrane is plotted vs. the solute diameter on a log-normal probability paper, a straight line is yielded [93, 94], which ensures that the solute separation correlates with the particle diameter according to the log-normal probability function. Then this relationship can be expressed as:

$$f = erf(z) = \frac{1}{2\pi} \int_{-\infty}^z e^{-\frac{\mu^2}{2}} d\mu \dots \dots \dots (2-4)$$

Where,

$$z = \frac{\ln d_s - \ln \mu_s}{\ln \sigma_g} \dots \dots \dots (2-5)$$

And d_s is the particle diameter, μ_s is the geometric mean diameter of the particle and σ_g is the geometric standard deviation about the mean diameter. According to equations (2-4) and (2-5), a straight line in the form of

$$F(f) = A_0 + A_1(\ln d_s) \dots \dots \dots (2-6)$$

will yield between f and d_s on a log-normal probability paper. A_0 and A_1 are the intercept and the slope, respectively. From this log-normal plot, mean particle diameter (μ_s) can be calculated as d_s corresponding to $f = 50\%$. σ_g can be determined from the ratio of d_s at $f = 84.13\%$ and $f = 50\%$. By ignoring the dependence of solute separation on the steric and hydrodynamic interaction between the particle and the pore [93, 94], the mean pore diameter (μ_p) and the geometric standard deviation (σ_p) around the mean pore diameter of the membrane can be considered to be the same as those of the mean particle size (μ_s) and its geometric standard deviation (σ_s). From μ_p and σ_p the pore size distribution of a membrane can be expressed by the following probability density function [95].

$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \dots (2-7)$$

where d_p is the pore size.

Chapter 3 RESULTS AND DISCUSSIONS

As mentioned before, electrospinning technology is a simple and effective method to fabricate nanometer scale filament material. Within the electrospinning process, concentration of the spinning dope, flow rate of the spinning dope, spinning voltage, fiber collect distance and other factors will affect the diameter of the nanofiber. The effects of these factors were investigated and the results given below:

1. MORPHOLOGY AND DIAMETER OF NANOFIBER FABRICATED FROM DIFFERENT POLYMERS

The details of the electrospinning conditions are shown in Table 3.1. Spinning was carried out at room temperature without exception. The optical microscopic and SEM images of nanofibers spun from different polymers are shown in Fig. 3.1 and Fig. 3.2, respectively. The images show that fibrous structures were indeed obtained from all the polymers studied in present research work. However, the nanofiber diameters are quite different from polymer to polymer, depending on the used polymer and the spinning conditions. The diameters of nanofiber are based on measuring of images analysis. 25 spots were chosen to calculate an average value of diameter. The standard deviation also was calculated. The average diameters of the nanofibers are summarized in Table 3.2.

Table 3.1 Electrospinning conditions of nanofibers spun from different polymers

Polymer	Nanofiber collect distance (cm)	Spinning voltage (kV)	Solution feed rate (ml/h)
PVDF	18	18	2
PVDF+PVP (80:20)	18	18	1
PS	18	18	2
PES	18	18	2
PEI	18	18	2
PVC	18	18	1
PC	18	18	1
PAN	18	18	2
Nomex (PA)	18	18	2
PVA	18	18	1
Collagen	18	18	1

Looking into Fig. 3.2 closely, PES, PS and PEI nanofibers have solid beads. PVC and Nomex have beads that consist of several smaller beads or nanofibers. Nanofibers made of PVA and collagen is attached to each other tightly. The shape and morphology of the nanofiber membrane therefore largely depend on the polymeric material. However, it also depends on the electrospinning conditions as will be shown for PVDF nanofiber membranes. More investigations are necessary for the precise control of the nanofiber morphology.

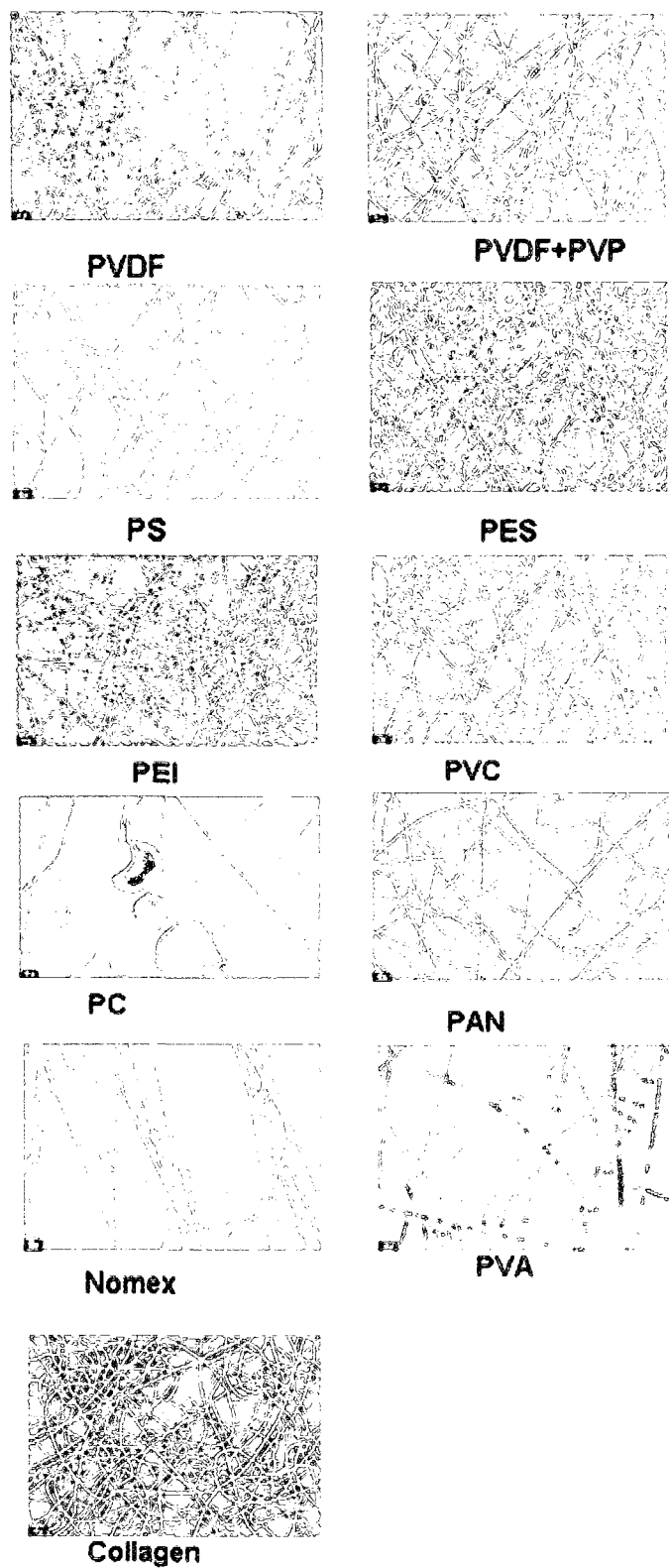


Figure 3.1 Optical microscopic-images of the nanofibers (200 times)

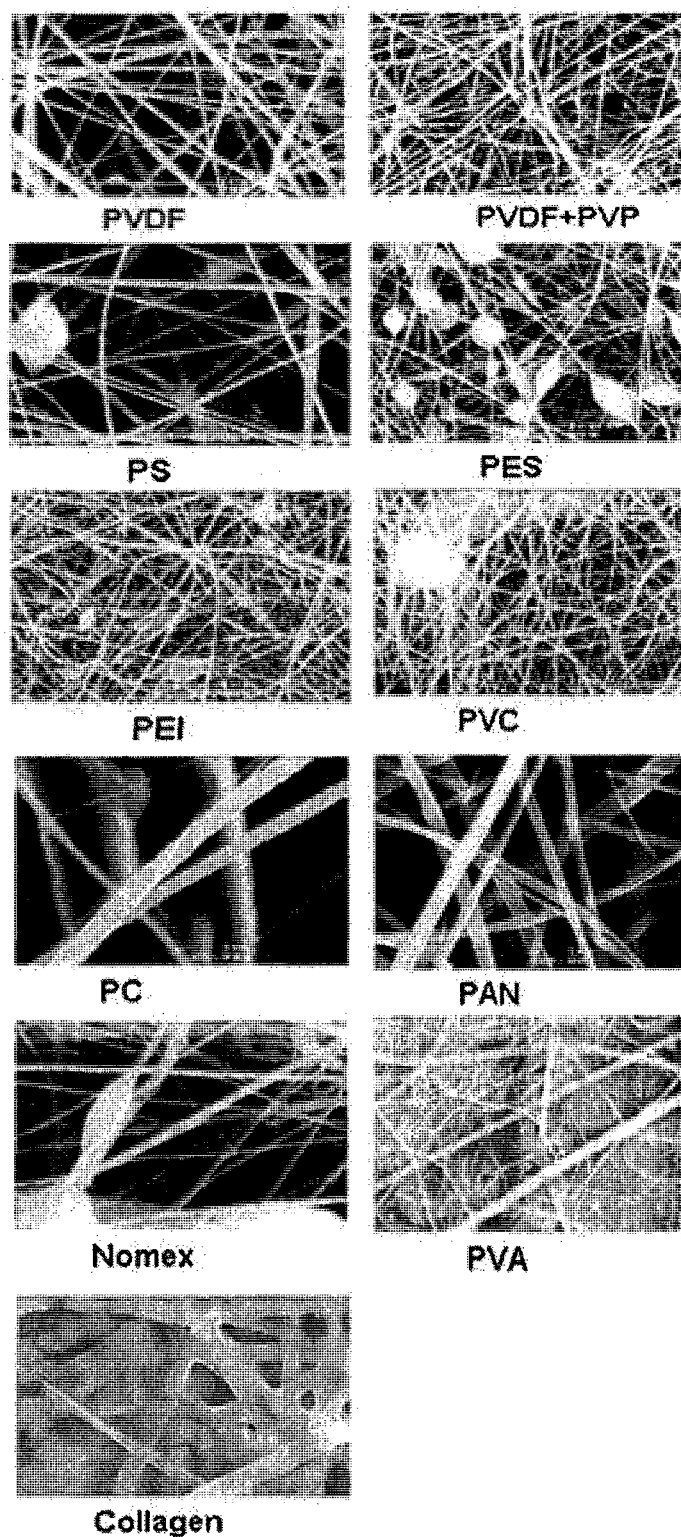


Figure 3.2 SEM images of the nanofibers (5000 times)

Table 3.2 Average diameter of the nanofibers obtained by image analysis

Polymer	Nanofiber diameter from optical image (nm)	Nanofiber diameter from SEM image (nm)
PVDF	535±50	403±32
PVDF+PVP	433±37	326±46
PS	385±32	290±63
PES	267±43	201±52
PEI	250±53	188±77
PVC	307±61	231±48
PC	1396±23	1050±37
PAN	735±45	553±55
Nomex (PA)	396±36	298±67
PVA	325±57	245±59
Collagen	2006±25	1509±66

Note: The average values are based on observations of at least 25 spots.

Although many researchers have reported to fabricate nanofibers by using various polymers by electrospinning as described in the literature section, investigations were made on few specific polymers by each researcher. In the present study, 10 polymers and 1 polymer blend are used, covering a wide range of hydrophilicity to hydrophobicity. The result shows that both hydrophilic and hydrophobic polymer can be electrospun to nanometer scale filament. But the morphology of nano filament depends on the properties of polymer, solvent and the spinning condition.

Among others, the diameter of PVDF ranges from 400 to 600 nm. Optical images and SEM images clearly show that PVDF nanofiber membrane has a fibrous structure.

2. EFFECTS OF ELECTROSPINNING CONDITIONS ON NANOFIBER DIAMETER

Further investigations were focused on specific polymer (PVDF) nanofiber spinning; the reason is that PVDF polymer is one of the most hydrophobic polymers among those

investigated in the present study. As discussed before, the high hydrophobicity is the most important property required for the membrane to be used in membrane distillation process.

2.1. Effect of Spinning Voltage

In the present research, the PVDF concentration in DMF solvent and the collect distance (vertical distance between the top of the syringe needle to the fiber collection plate) were maintained at 20 wt% and 18 cm, respectively. The dope flow rate was 2 mL/h while the spinning voltage was changed.

Figure 3.3 shows the optical images of the nanofiber at different spinning voltages, from which the average nanofiber diameters were obtained. 25 spots were chosen randomly from the image to measure the diameter of nanofiber. The images show that the fiber shape depends on the spinning voltage. At low spinning voltage, some beads are observed and as the voltage increases the beads gradually disappear. However, as the spinning voltage continues to increase, beads start to appear again.

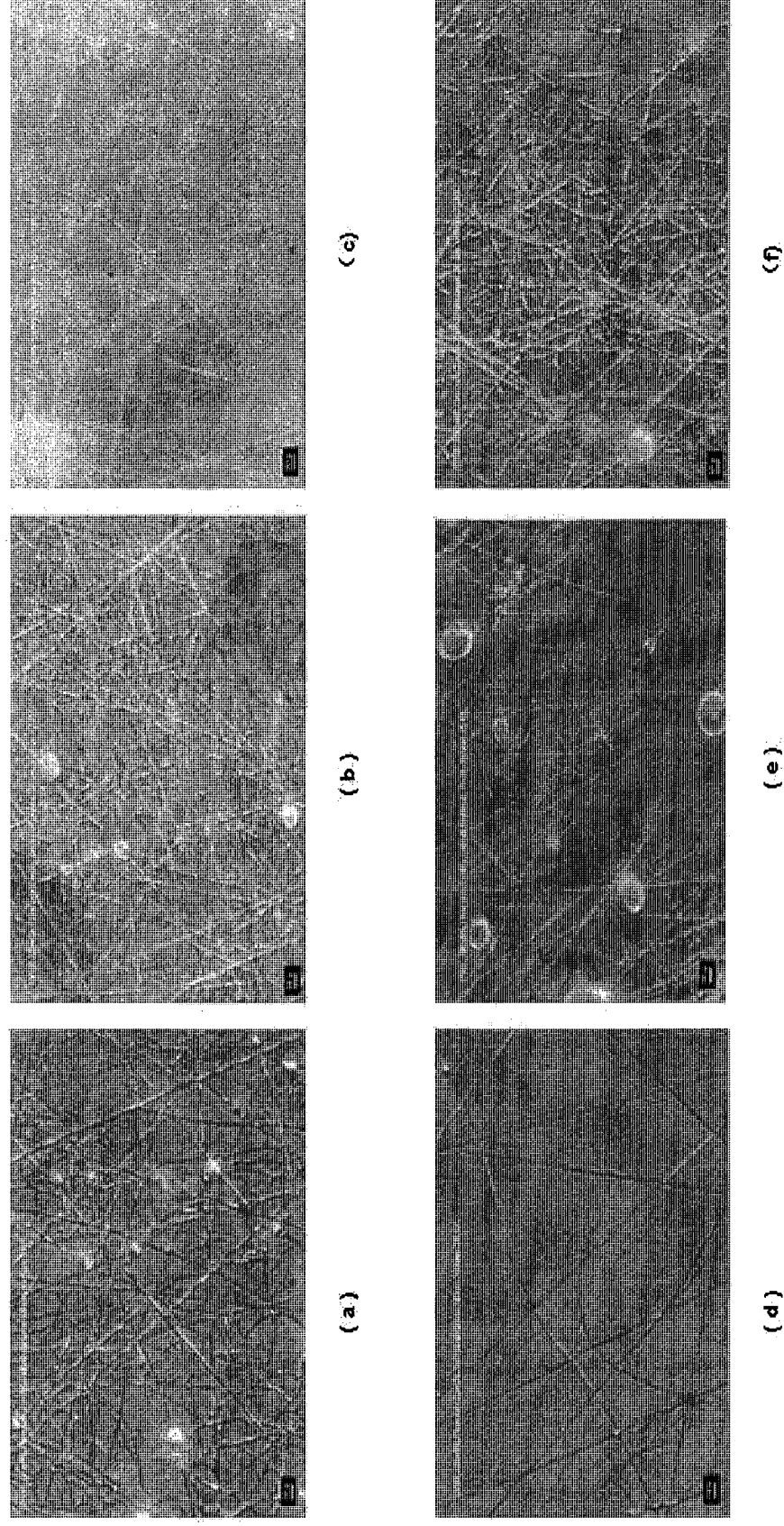


Figure 3.3. Optical images of nanofibers prepared at different spinning voltages. PVDF concentration: 20 wt%, Collect distance: 18 cm, Flow rate: 2 ml/h, Spinning voltage: (a) 9 kV, (b) 12 kV, (c) 15 kV, (d) 18 kV, (e) 25 kV, (f) 35 kV.

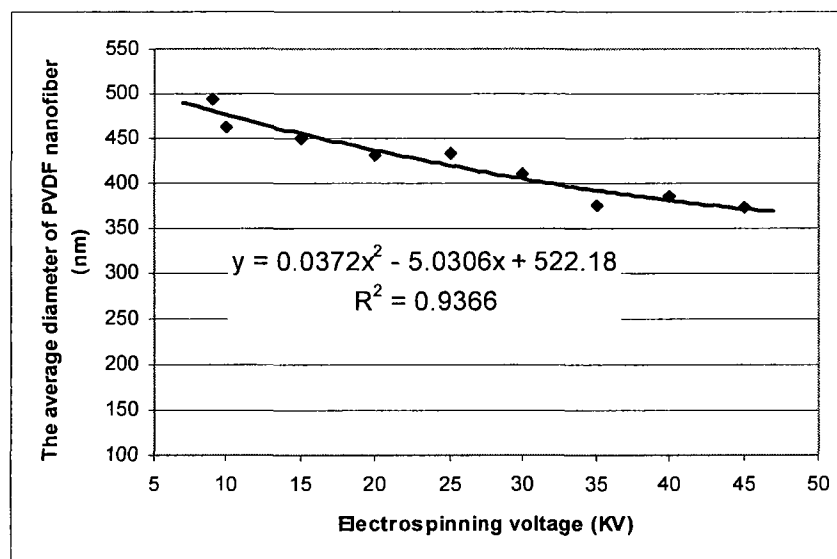


Figure 3.4 Effect of spinning voltage on nanofiber diameter.

The diameter of PVDF nanofiber is plotted in Fig. 3.4. The diameter decreased with an increase in spinning voltage. As the spinning voltage increases, the spinning dope that is extruded in a form of a droplet from the needle (spinneret) tip will have a higher surface charge density. As a result the electrical potential on the polymer solution droplet will increase and the electrical force will split the polymer droplet and draw it from the needle to the low electrical potential side (Aluminium foil: nanofiber collector). If the applied voltage and the concentration (viscosity) of polymer are high enough, and the solvent evaporates fast enough, a nanofiber is formed. On the other hand, if the concentration (viscosity) of the polymer is low, polymer droplets are sprayed on the collector surface. The later phenomenon has been commercially used for a long time and is called electro-spray or electrostatic spray. The processing of electrostatic spray process can be used as an analogy for electrospinning since the mechanism of both processes are very similar.

For electrostatic spray, there is a following relationship between the size of the droplet and the applied voltage [96].

$$E\sqrt{\frac{d}{2\sigma}} = C \dots\dots\dots (3-1)$$

Where, E is the strength of electrical potential, d is the droplet diameter, σ is the surface tension of spraying liquid, and C is a constant.

From Equation (3-1), d will be proportional to E^{-2} , hence

$$d \propto E^{-2} \dots\dots\dots (3-2)$$

Strength of electrical potential, E , and voltage, V , are in a linear relationship, as far as the collect distance is kept constant. Then, the relationship between d and V^{-2} can also be in a proportional relationship. Hence,

$$d \propto V^{-2} \dots\dots\dots (3-3)$$

Where, V is voltage of electrical field.

Figure 3.4 indicates that diameter of nanofiber decreases with an increase in electrospinning voltage. However, diameter of nanofiber did not necessarily decrease with an increase of spinning voltage according to the relationship shown by Equation (3-3). This shows the limitation of applying the relationship established for the

electrostatic spray to the electrospinning.

Interestingly, however, Nasir et al. [97] showed that diameter of nanofiber was indeed proportional to V^2 . In any case, the mechanism of electrospinning has not yet been established even as much as for the electrospraying process.

2.2. Effect of Spinning Dope Concentration

Electrospinning voltage and collect distance were maintained at 18 kV and 18 cm, respectively. PVDF concentration in the spinning dope was in a range from 4 to 20 wt%. The flow rate of polymer solution was kept at 2 mL/h. When the PVDF concentrations were as low as 4 and 6 wt%, nanofibers were very hard to be obtained. The reason is when the viscosity of the solution is very low. Since the liquid fibers travel through the collect distance very fast, the solvent is not removed completely when they reach the collect plate. The fibers merge on the collect plate without producing any solid fibers.

Fig. 3.5 shows the optical images of the electrospun nanofibers. Even though good nanofibers were obtained when the PVDF concentration was equal to or above 8 wt%, with few or no beads found on the formed nanofibers, the diameter of the nanofiber filament is un-even along the fiber axis, when the concentration of PVDF in the spinning dope was lower than 16%.

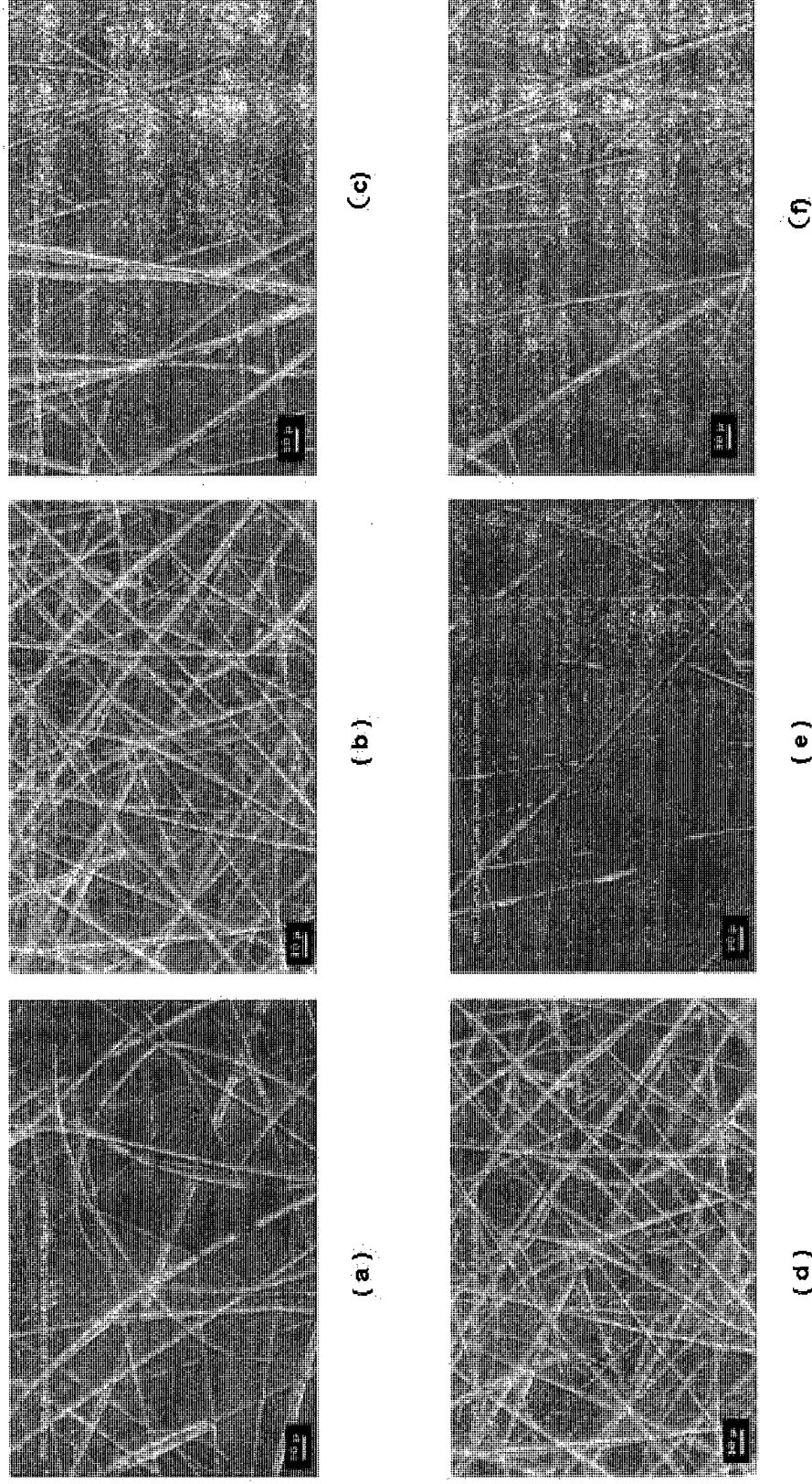


Figure 3.5 The optical images of nanofiber prepared from different polymer concentration., Flow rate: 2 ml/h, Collect distance: 18 cm, Spinning voltage: 18 KV PVDF concentration: (a) 8 wt%, (b) 12 wt%, (c) 14 wt%, (d) 16 wt%, (e) 18 wt%, (f) 20 wt%.

The relationship between the concentration of PVDF in the spinning dope and the diameter of PVDF nanofiber is shown in Figure 3.6. Similar trends were also observed by Nasir et al. [97]. With an increase of PVDF concentration in the spinning dope, the diameter of PVDF nanofiber increases. As the polymer concentration of the spinning dope increases, the viscosity of the dope will increase and the surface tension of the spinning dope will also increase. A higher force is required to draw the polymer solution out from the spinneret (needle) and the spray stream will also have less chance to split.

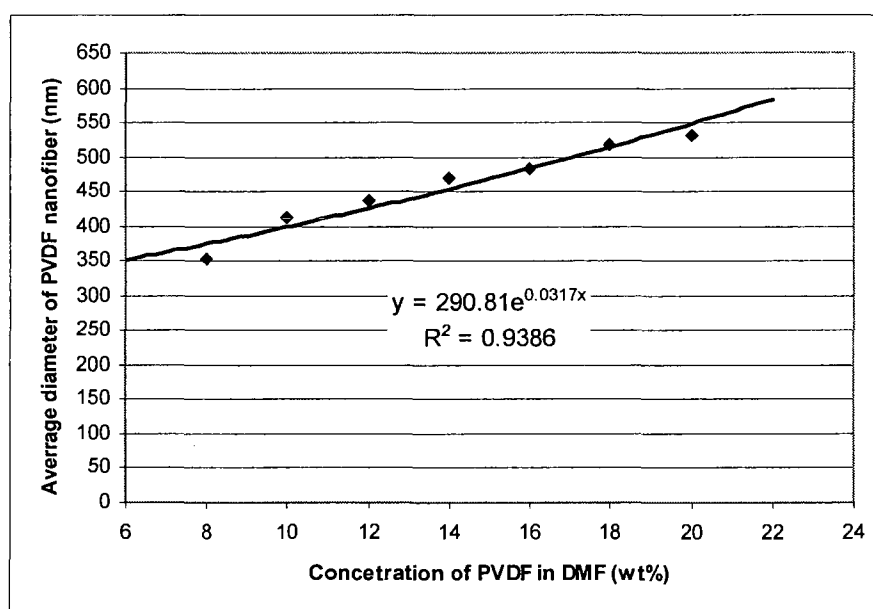


Figure 3.6 Effect of spinning dope concentration on nanofiber diameter.

Deitzel et al. studied the electrospinning of polyethylene oxide (PEO)/H₂O solutions and found the following relationship between the diameter of PEO nanofiber and the PEO concentration of spinning [22].

$$d \propto c^{0.5} \dots\dots\dots(3-4)$$

Where, d is the diameter of the PEO nanofiber and c is the PEO concentration of the

spinning dopes.

Baumgarten used the PAN/DMAc solutions to electrospin PAN nanofibers [98]. He found that the diameter of PAN nanofiber and the viscosity of the spinning were related to each other by the following equation.

$$d \propto \eta^{0.5} \dots\dots\dots(3-5)$$

Where, d is the diameter of the PAN nanofiber and η is the viscosity of the spinning dope.

For both equations, increasing in nanofiber diameter with an increase in the concentration of polymer solution can be predicted. Indeed, the results shown in Fig. 3.6 exhibited the predicted trend, but the fiber diameter was not necessarily proportional to either the square root of the concentration or the square root of the dope solution viscosity. Because Equations (3-4) and (3-5) are empirical equations for a specific polymer and electro-spray condition, they are not universal equations for nanofiber spinning. The theoretical research of nanofiber spinning by electrospinning technology is still at the initial stage.

For fiber spinning, the viscosity of spinning dope is more important than the concentration since viscosity is related to rheological behaviour of solution. For the polymer solution, viscosity is related to concentration, and in most cases the relationship is not linear.

The following equation is one of such relationships.

$$\left(\frac{\eta}{\eta_0}\right)^{(1-2k)} = 1 + (1 - 2k) \times c \times [\eta] \dots \dots \dots (3 - 6)$$

Where, k is the Huggins--Martin constant, $[\eta]$ is the intrinsic viscosity, c is the concentration of polymer solution, η_0 is the viscosity of the solvent [99].

Another interesting thing to be studied is the effect of temperature on the nanofiber diameter. In a limited range the relationship between the viscosity of the polymer solution and the temperature is given by Andrade's viscosity equation [99]:

$$\eta = De^{BT} \dots \dots \dots (3 - 7)$$

Where η denotes the viscosity, T the temperature and D and B denote empirical coefficients that can be determined by experiments.

Usually B has a negative value and the viscosity decreases with an increase in the temperature. Combining equations (3-5) and (3-7), a decrease in the nanofiber diameter is predicted with an increase in the temperature. This however was not confirmed by the experiment due to the limitation in available equipment.

Optical images in Fig. 3.5 shows that fine nanofibers can be obtained at PVDF concentrations equal to or above 8 wt%. It is difficult to conclude from Fig. 3.5 alone which dope concentration is the best. For the present research, 20 wt% was chosen arbitrarily for nanofiber membrane fabrication.

2.3. Effect of Collect Distance on Nanofiber Diameter

The electrospinning voltage and the PVDF concentration of the dope solution were maintained at 18 kV and 20 wt%, respectively. The flow rate of polymer solution was

maintained at 2 mL/h. Only the nanofiber collect distance was changed. The optical images are shown in Fig. 3.7, and experiment results are summarized in Fig. 3.8.

In Fig. 3.7, the optical images indicate that with the collect distance increasing, the nanofiber shape changed from without beads to with beads.

The electric field surrounding a point charge is given by Coulomb's law:

$$E = \frac{1}{4\pi\epsilon_0} \frac{Q}{r^2} \hat{r} \dots\dots\dots (3-8)$$

Where, Q is the charge of the particle creating the electric field, r is the distance from the particle with charge Q to the electric field evaluation point, $\hat{r}$ is the Unit vector pointing from the particle with charge Q to the electric field evaluation point, ϵ_0 is the vacuum permittivity.

Coulomb's law is actually a special case of Gauss's law, a more fundamental description of the relationship between the distribution of electric charge in the space and the resulting electric field.

According to Equation (3-8), as the collect distance increases, the intensity of electrical field will decrease; i.e. the electrical force decreases. As the force for electrospinning decreases, more beads are formed.

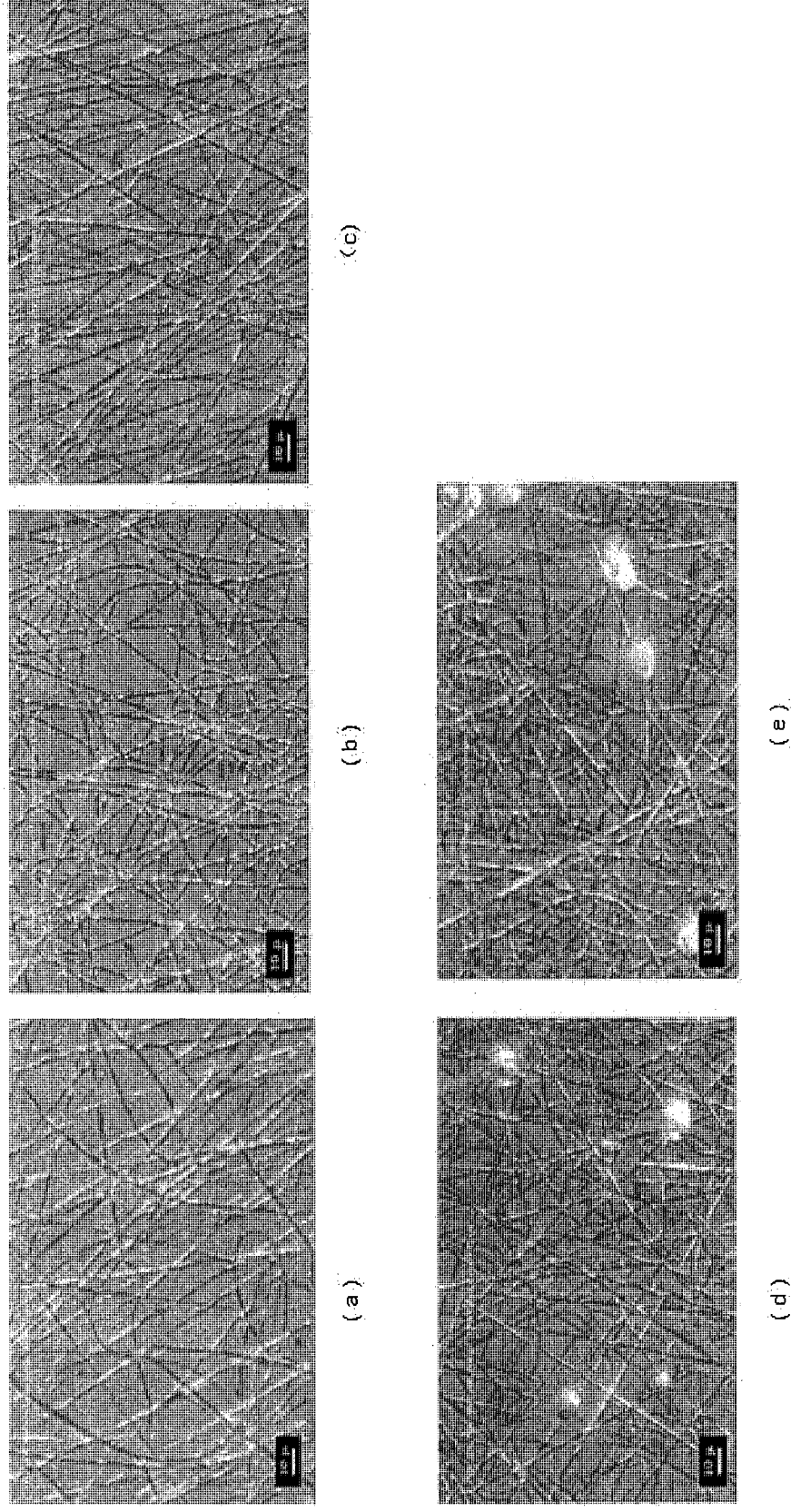


Figure 3.7 The optical images of nanofiber prepared with different collect distances
PVDF concentration: 20 wt%, Spinning voltage: 18 KV, Flow rate: 2 ml/h, Collect distance: (a) 12 cm, (b) 15
cm, (c) 18 cm, (d) 21 cm, (e) 24 cm.

According to Fig. 3.8 the diameter of the PVDF nanofiber slightly decreases as the collect distance increases. Thus, the increase in collect distance will help to obtain finer nanofibers.

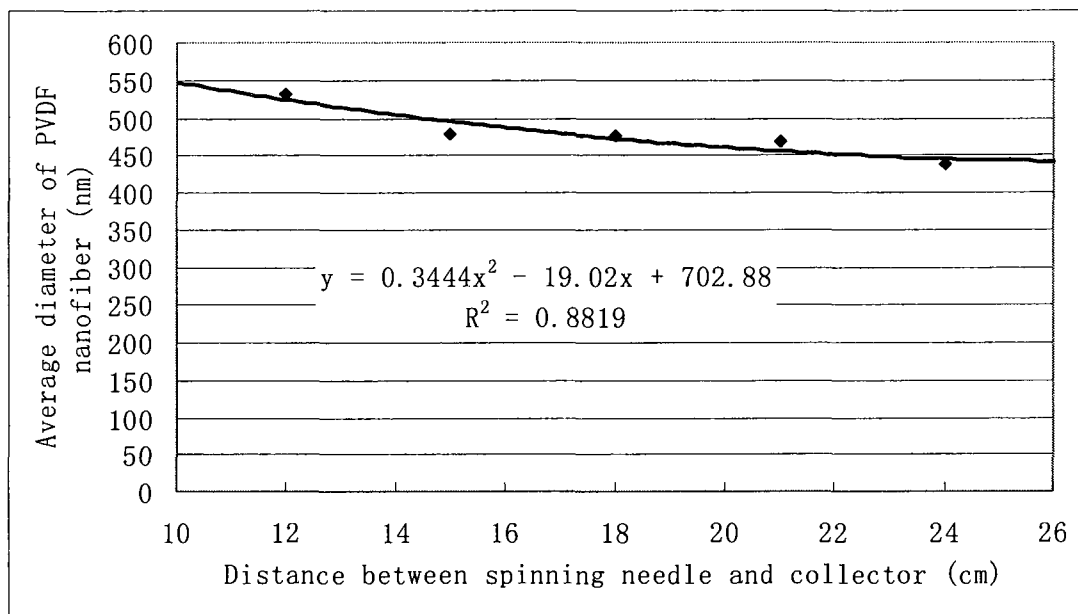


Figure 3.8 Effect of collect distance on nanofiber diameter

The collect distance is an important parameter for nanofiber electrospinning and it also needs to be properly controlled. A long collect distance enhances solvent evaporation along the way from the spinneret to the collect plate and the polymer solidification becomes more complete. This means that nanofibers do not stick to each other. Nanofiber membrane structure becomes loose.

To fabricate individual nanofibers is another very important research direction for nanofiber and nanofiber membrane. For example, nano-carbon tube is a filament structure material with diameter less than 100nm. By Template, Vapour Grown, Molecular Assembly and other methods, single carbon nanotube can be prepared. But the length of carbon nanotube is limited when prepared by the above methods. By improving the collect method for electrospinning, single or individual polyacrylonitrile

(PAN) nanofibers can be prepared and they can be used as the precursor of carbon nanofibers. According to the definition of nanotube, if the diameter of carbon nanofiber is less than 100nm, it is exactly carbon nanotube. This kind of carbon nanotube is very useful for hydrogen storage, super large capacitor, fuel cell and electron device. Hence, electrospinning is a new and practical approach for many potential applications.

Even though for other applications of nanofibers, the separation of each fiber is more favourable, for membrane applications, nanofibers should stick to each other to some extent, to maintain the membrane integrity and to enhance the mechanical strength of the membrane. Since the nanofiber attachment depends on the collect distance for the above mentioned reasons, the collect distance needs to be properly controlled. If the collect distance is too short, the attachment will be excessive, while, if the distance is too long, the fibers will be separated. For this reason, an intermediate value of 18 cm was chosen to be used hereafter. However, it should be admitted that this is a quite arbitrary choice.

2.4. Effect of Polymer Solution Flow Rate

In the present research, the spinning voltage and PVDF concentration in the spinning dope were maintained at 18 kV and 20 wt%, respectively. Collect distance was set equal to 18 cm. The only parameter changed was the flow rate of the dope solution.

Optical images (Fig. 3.9) show the change of the diameter of PVDF nanofibers with the change of the dope flow rate. With the increasing in dope flow rate, the diameter of the PVDF nanofiber seems to increase slightly. In order to enable continuous nanofiber spinning, the dope flow rate should be above a limiting value that allows a sufficient amount of the spinning dope to be extruded.

It should be noted that 6 mL of the spinning dope was required for spinning,

particularly to obtain a sufficient membrane area and thickness on the aluminum foil. The mat together with the aluminum foil was dried in a fume hood for 48 hours. Then, the nanofiber membrane was carefully peeled off from the aluminium foil prior to its use as a nanofiber membrane for characterization study and for membrane distillation study.

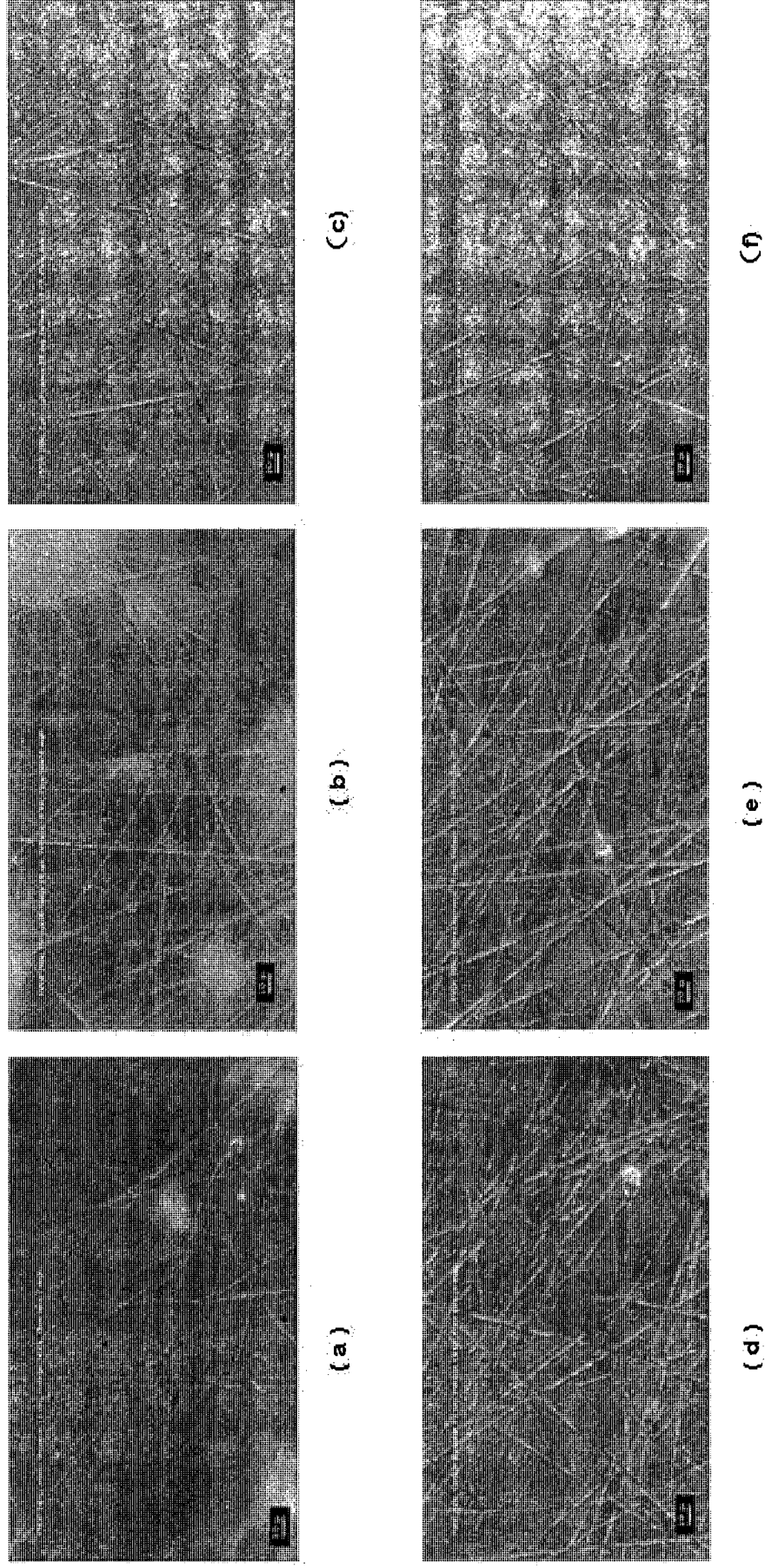


Figure 3.9 The optical images of PVDF nanofibers prepared with different flow rates. Spinning voltage: 18 kV, PVDF concentration: 20 wt%, Collect distance 18 cm, Flow rate: (a) 2 ml/h, (b) 4 ml/h, (c) 8 ml/h, (d) 16 ml/h, (e) 32 ml/h, (f) 64 ml/h.

The effect of polymer solution flow rate on the average diameter is summarized in Fig. 3.10.

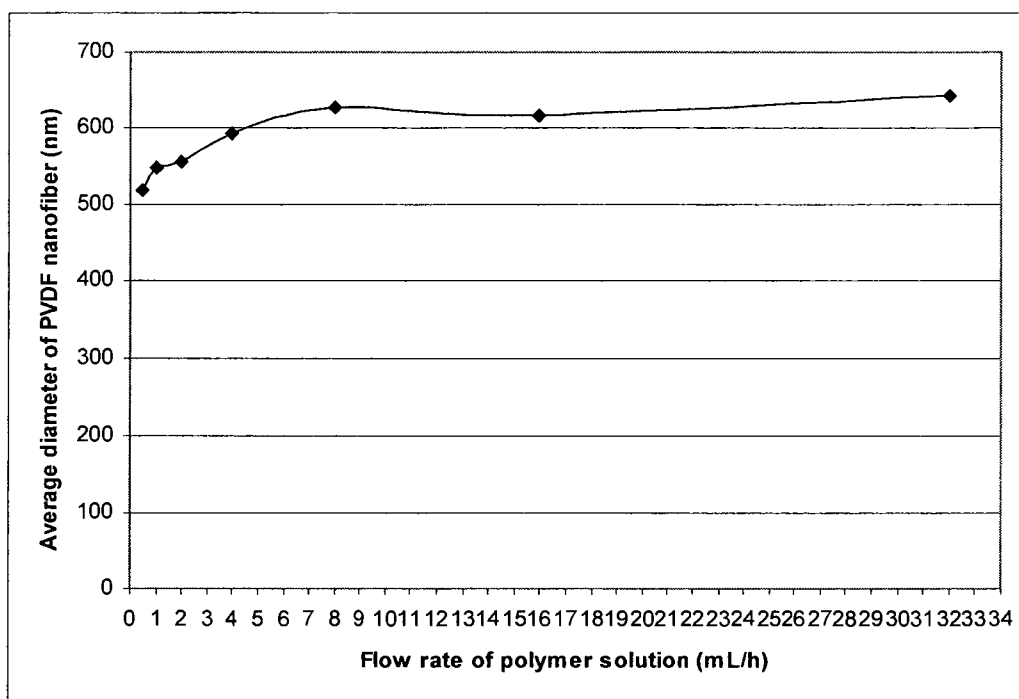


Figure 3.10 Effect of polymer solution flow rate on nanofiber diameter

Figure 3.10 shows that the diameter of PVDF nanofiber slightly increases with increasing spinning dope flow rate. Polymer solution comes out from the spinning needle with an electric charge. When the spinning dope flow rate increases, the amount of the electric charge increases, hence the electric field intensity also increases. But the increase in the charge amount eventually levels off; dope flow rate can continue to increase. Due to the decrease in charge density, there is less chance for nanofiber to split. This is the reason for the slight increase of fiber diameter with an increase in flow rate of polymer solution. The process is shown as in Fig. 3.11.

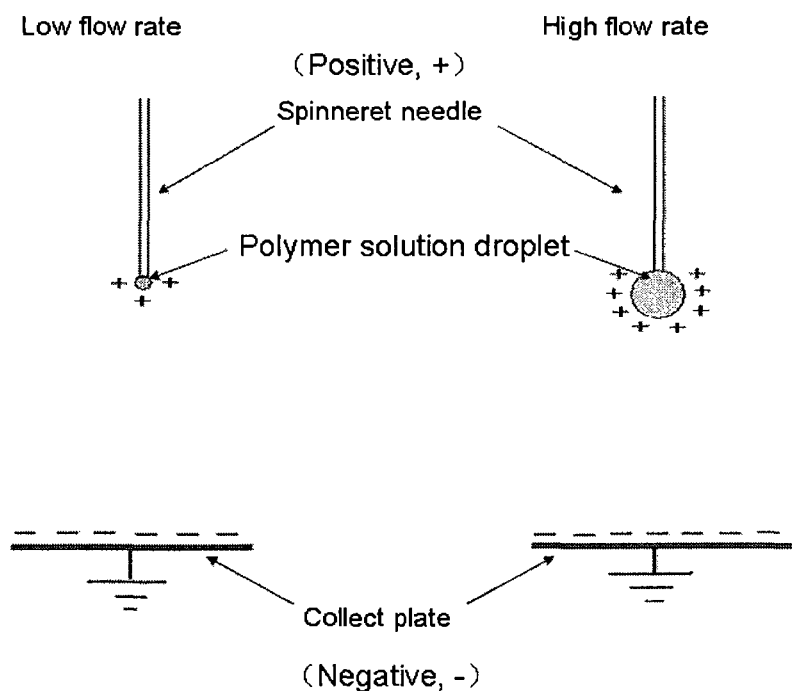


Figure 3.11 Effect of polymer solution flow rate on nanofiber spinning

3. PVDF NANOFIBER MEMBRANE CHARACTERIZATION

3.1. Scanning Electron Microscope (SEM)

Figure 3.12 shows the SEM images of PVDF nanofiber membranes obtained under the following conditions; spinning voltage 18 kV, polymer concentration in the dope 20 wt%, collect distance 18 cm and polymer solution flow rate 2 mL/h.

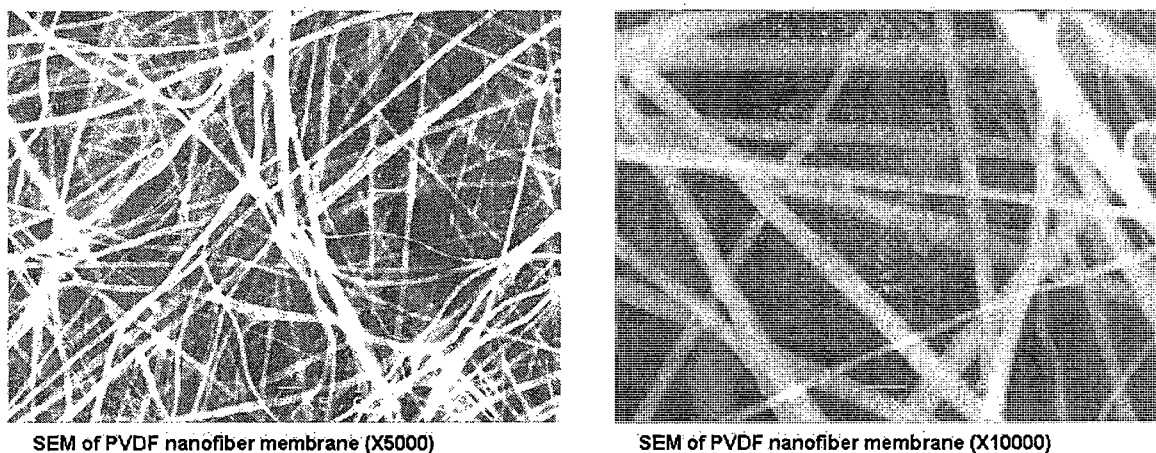
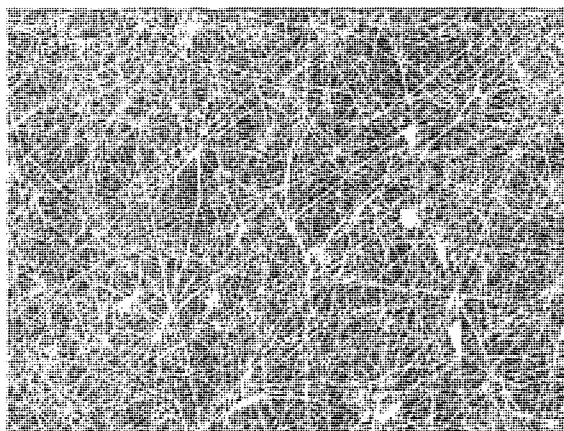


Figure 3.12 SEM of nanofiber membranes

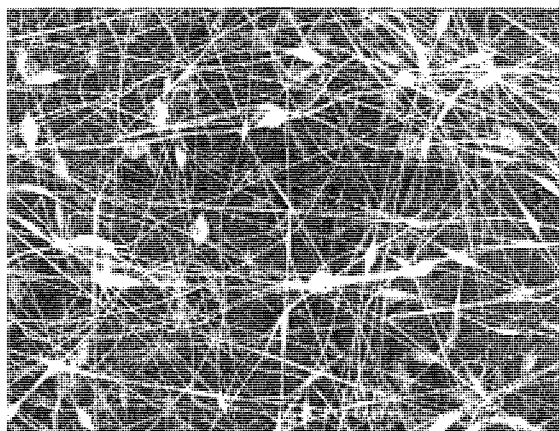
According to the SEM images shown in Fig. 3.12, the membrane was formed by random arrangement of nanofibers. Considering the spaces between the nanofibers as pores, the size of the pores of this membrane are several micrometers. The pore size, together with the high hydrophobicity of the PVDF membrane, makes the PVDF membrane appropriate to be used for membrane distillation.

It should be noted that unlike many membranes made by the phase inversion or other methods, the PVDF nanofiber membrane consists of open pores, which means the pores are interconnected. It is expected therefore that the vapour can easily and freely pass through the nanofiber membrane in membrane distillation. Further detailed analysis of accurate pore size and pore size distribution was conducted by particle separation experiments. However, the SEM images give a clear idea that nanofiber membrane has a completely different structure when compared with membranes fabricated by the phase inversion and other methods.

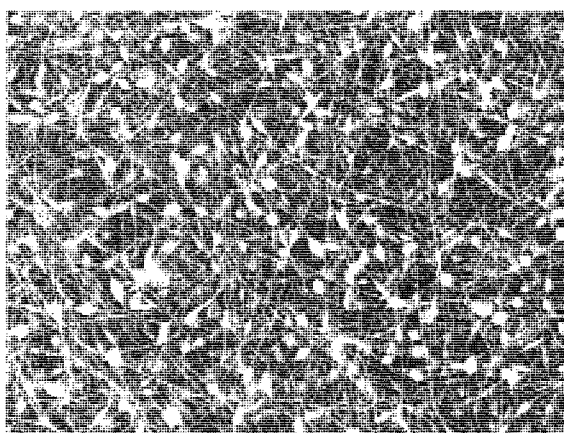
Figure 3.13 shows the SEM of nanofiber made from different polymers, spun under the conditions reported in Table 3.1. Although nanofibers could be spun under the given conditions the morphology of nanofiber is different, depending on the polymer. Similar trends are observed as those discussed in section 1 of this chapter.



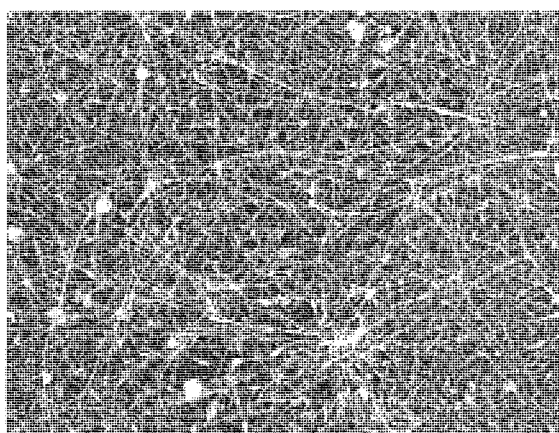
PVDF+PVP



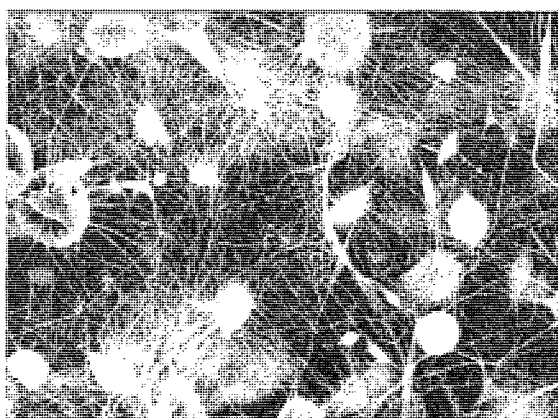
PS



PES



PEI



PVC



PC

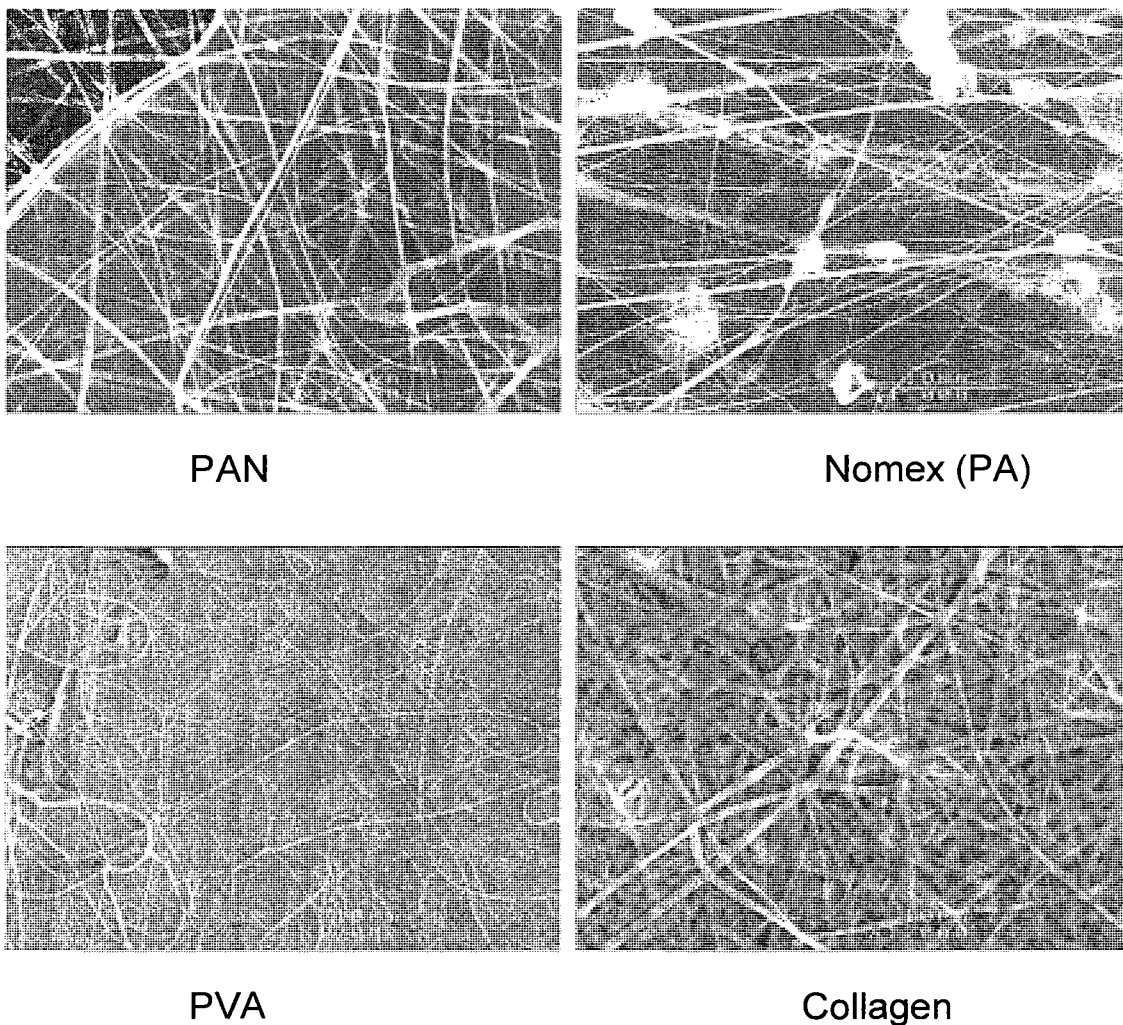


Figure 3.13 SEM images of nanofiber membrane made from different polymers

3.2. Atomic Force Microscopy (AFM)

AFM is a relatively new technology to observe the material structure. It has been extensively applied in material research and other fields. AFM has also been extensively used to observe the membrane surface morphology [90]. Compared with SEM, preparation of the AFM sample is simple, since sample coating or other sample pre-treatments are not necessary. For this reason, AFM image will release more information close to the nature of materials. Also it does not need high voltage and low temperature. The risk of sample damage is therefore less than other methods such as SEM. However, to observe nanofiber membranes by using AFM needs a special skill. Since the

nanofibers are only randomly and loosely attached to each other, a fibre can be adhered to the cantilever tip and move together with the cantilever tip, which makes the response of the cantilever tip to the surface structure inaccurate. In this case, the image becomes either unclear or even no image is obtained.

AFM images are shown in Figs. 3.14 to 3.16 for PVDF and PES nanofiber membranes.

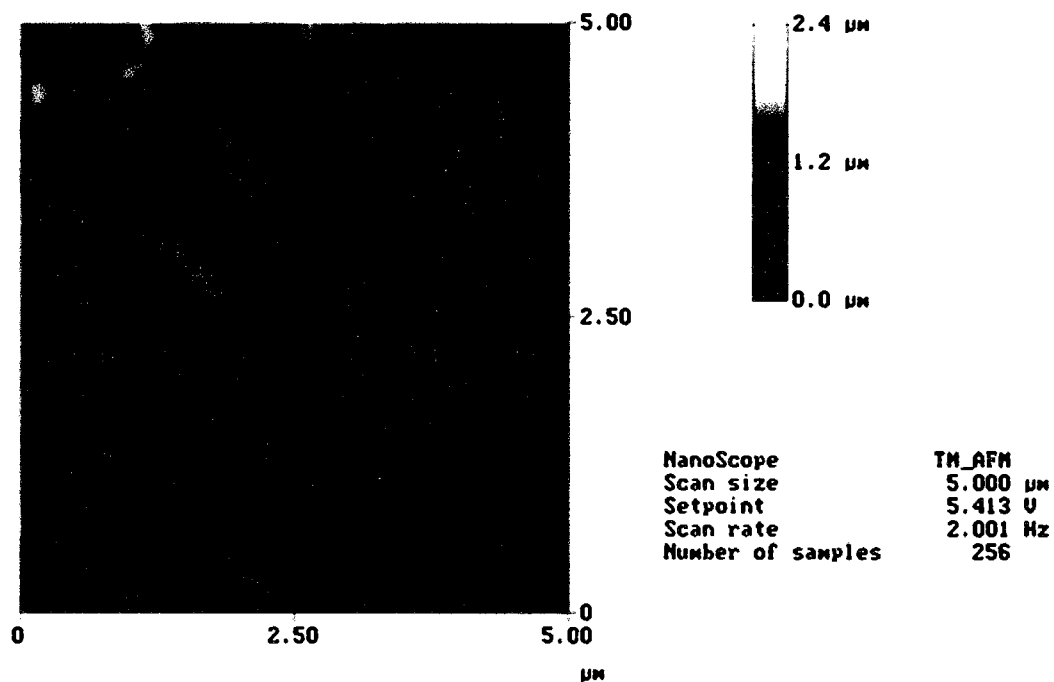


Figure 3.14 AFM image of PVDF nanofiber membrane (Digital III)

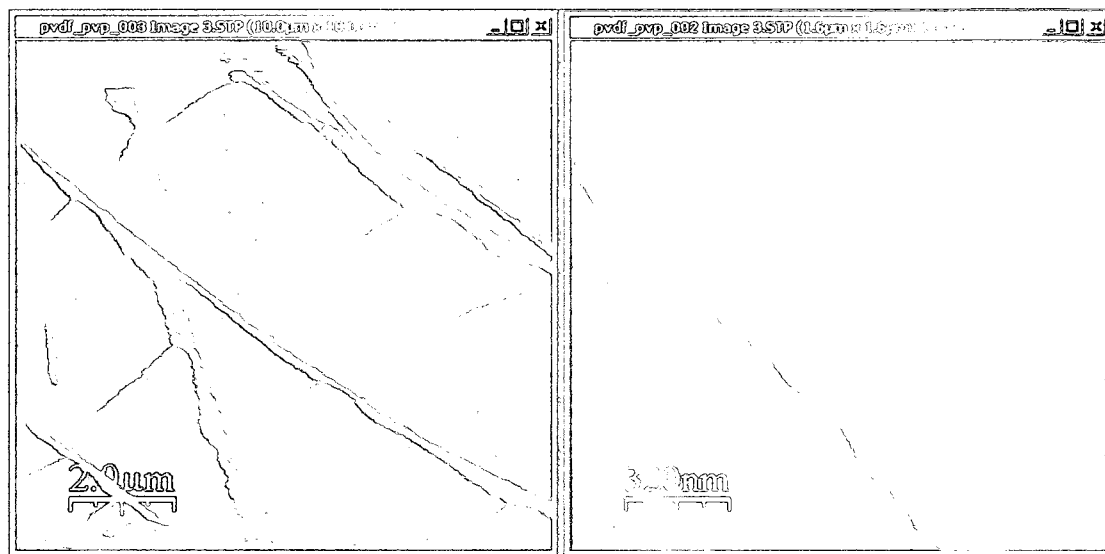


Figure 3.15 AFM images of PVDF nanofiber membrane (Molecular Image)

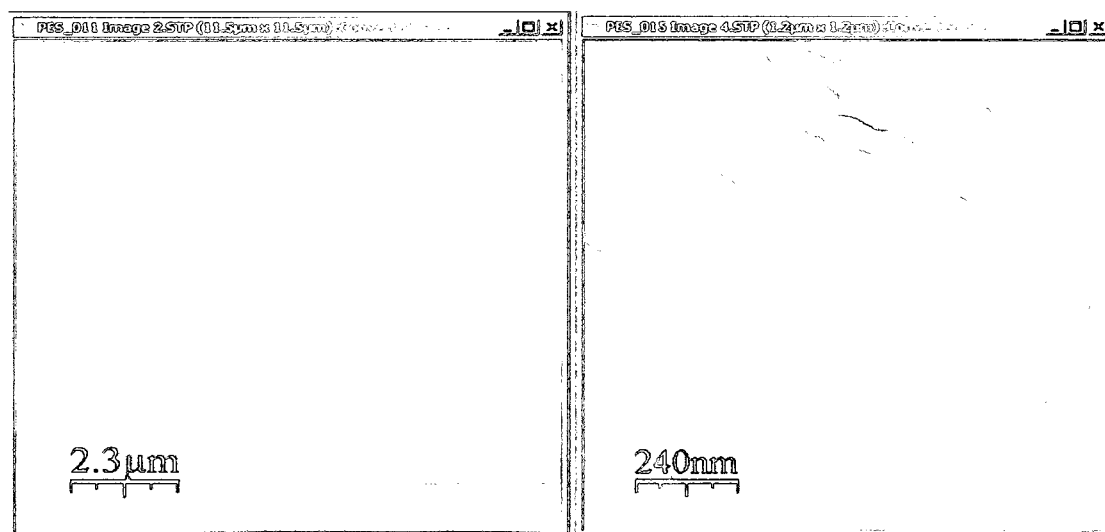


Figure 3.16 AFM images of PES nanofiber membrane (Molecular Image)

Similar to the SEM images, the AFM images also show the random arrangement of nanofibers. However, more details of the fibre surfaces can be observed by AFM. Interestingly, even though the images shown in Figs. 3.15 and 3.16 are for the nanofiber membranes made of different polymeric materials, the essential feature of the surface morphology is similar; i.e. aggregates of macromolecules are aligned vertically to the axial direction of the fiber. This surface morphology was observed for the first time by the present work.

The formation of the observed nanofiber morphology is explained in the following way. As a dope droplet is extruded from the spinneret, it is split into a very fine polymer solution stream by the electrical force. Along the way from the spinneret to the collector, solvent evaporates and the polymer solidifies. The polymer aggregates are packed closely due to the capillary force working between the aggregates as the solvent evaporates very fast from the surface. It is well known that the polymer aggregates are closely packed at the top surface of the dense membrane. As the distance from the surface increases, the packing density decreases. It is interesting to note that only the densely packed layer is observed in the nanofiber because the diameter of the fiber is in the nanometer range. This structure suggests an extremely high mechanical strength of a single nanofiber since there is hardly any defects observed in the densely packed layers of polymer aggregates. Indirect evidence is found in the literature [46], where it is reported that the strength of glass fiber increases dramatically, with a decrease in the diameter.

It is also speculated that if a two dimensional film of a similar structure (a single layer of closely packed polymer aggregates) obtained instead of one dimensional nanofibers, it could be used as air filter of extremely high selectivity, and also permeability. The company named Donaldson had used nanofiber nonwoven mat as air filter and it reached 99.99% separation. [88]

The AFM of the PES nanofiber membrane also shows clearly that many nanofibers are in contact with other fibers, while in the PVDF naofiber membrane, the nanofibers are more separate from each other. It seems that the degree of contact of the fibers depends on how

completely the solvent is removed while the nanofiber is travelling from the spinneret to the collector. The more the residual solvent remains in the nanofibers, the more contact points are formed among the nanofibers. This is favourable for having strong mechanical strength for the nanofiber membrane. On the other hand, as the degree of contacts decreases the porosity becomes higher; the membrane becomes looser, resulting in an increase in the membrane's permeability.

3.3. DSC of Nanofiber Membrane

Differential scanning calorimetry is a widely used technique to study the thermal properties of polymer. In particular, the technique is applied to study the thermal transitions of a polymer. Thermal transitions are defined as the changes that take place in a polymer when the polymer is heated.

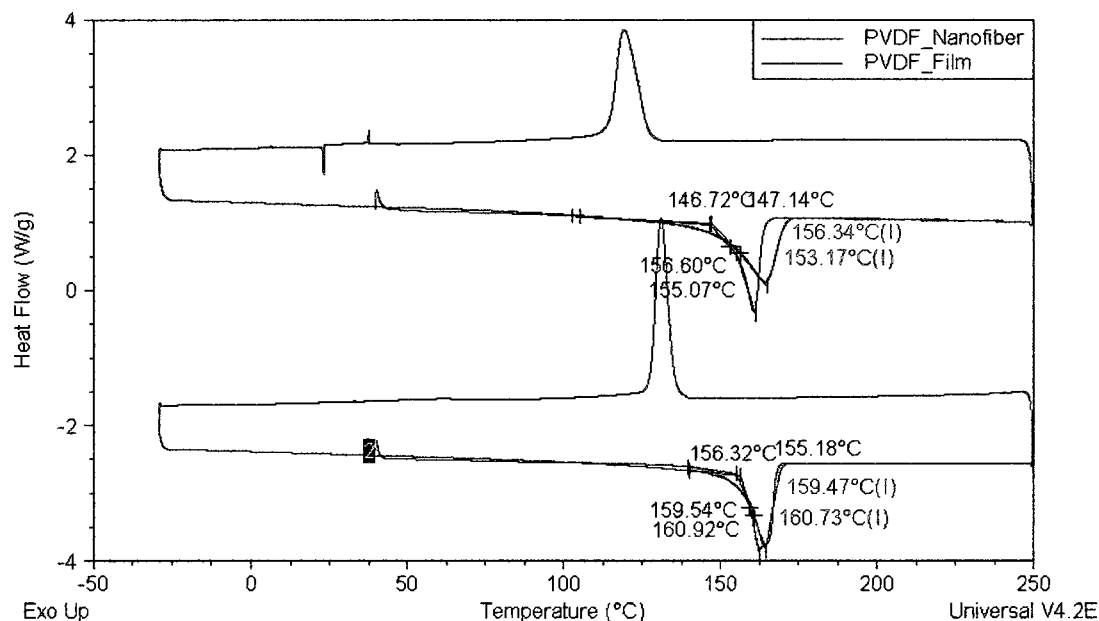


Figure 3.17 DSC results of PVDF nanofiber membrane and dense PVDF film

PVDF has a glass transition temperature (T_g) of about -35°C and melt temperature (T_m) of about 168°C (Elf AutoChem). Since the temperature range of this experiment was

from -30 °C to 250 °C, the glass transition of PVDF could not be detected. Therefore, only T_m results are shown in Fig. 3.17.

In Fig. 3.17, for the PVDF film, the T_m was 159.47 °C and 160.73 °C for first heating and second heating, respectively. But for the PVDF nanofiber membrane, the T_m was 153.17 °C and 156.34 °C for the first heating and second heating, respectively. It reflects the structural change of the polymer after electrospinning. As the size of materials goes down to the nanometer range, each independent part of the materials becomes aggregates of few molecules to few hundred molecules. The affinity between the separate parts will be less than affinity between molecules themselves. Therefore, the T_m of PVDF polymer decreases from the film to the nanofiber. It is another evidence for the nanonization of PVDF material by electrospinning. Similar results were reported by Choi and co-workers [100].

Similar DSC results have been obtained from the PES polymer. But in PES, the glass transition temperature (T_g) was obtained instead of the polymer melting point. For PES the glass transition temperature (T_g) is reported to be 230 °C [101].

Figure 3.18 shows that T_g values of the PES film were 213.76 °C and 214.07 °C, respectively, for the first and second heating. On the other hand, those of the PES nanofiber were 199.27 °C and 206.74 °C, respectively. After nanonization of PES, the T_g of the polymer decreased. This also indicates the change in the degree of crystallinity.

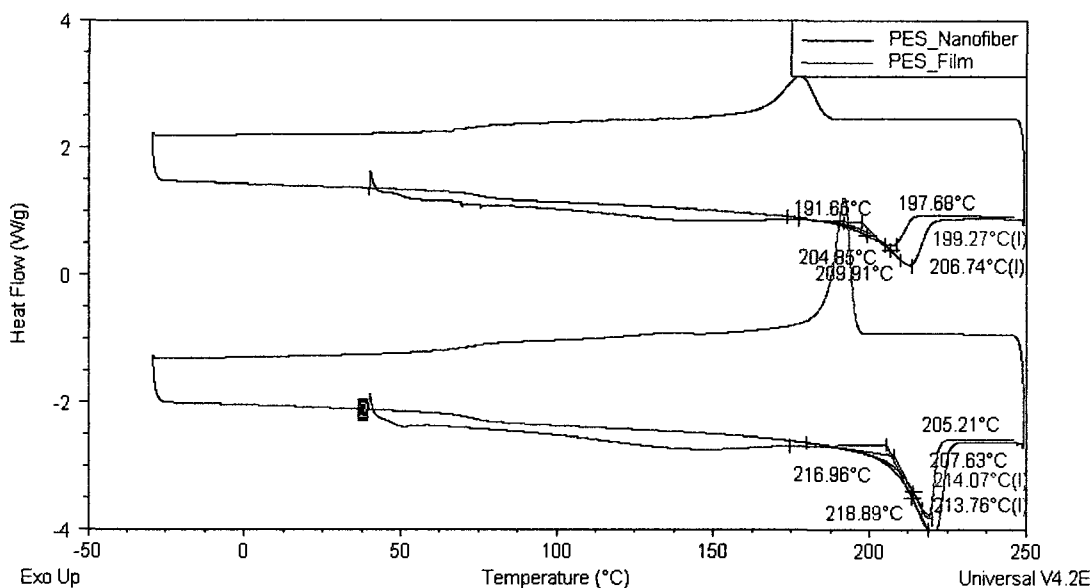


Figure 3.18 DSC of PES nanofiber membrane and PES dense film

3.4. Contact Angle of Nanofiber Membrane

The contact angle is the **angle** at which a **liquid/vapour** interface meets the solid surface (Fig. 3.19). The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the following **Young-Laplace equation** [102]. Contact angle is measured using a contact angle **goniometry**.

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \dots \dots \dots (3-9)$$

Where, γ_{LV} , γ_{SV} and γ_{SL} refer to the interfacial tension of the liquid/vapour, solid/vapour and solid/liquid interfaces, θ is the contact angle.

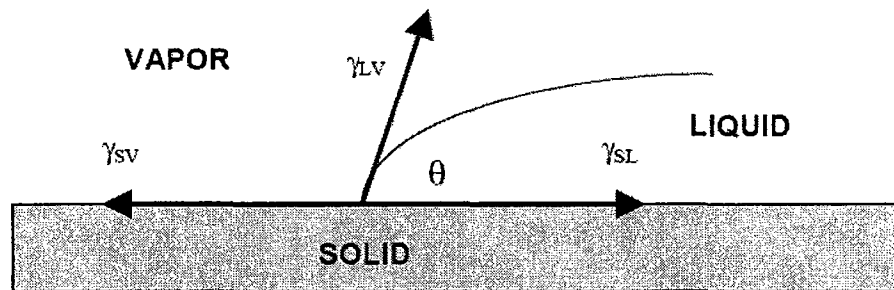


Figure 3.19 Contact angle of solid material

Consider a liquid droplet on a solid surface. If the liquid is very strongly attracted to the solid surface (for example water on a strongly hydrophilic solid) the droplet will completely spread out on the solid surface and the contact angle will be close to 0° . Less strongly hydrophilic solid surface will have a contact angle up to 90° . If the solid surface is hydrophobic, the contact angle will be larger than 90° . On highly **hydrophobic** surfaces, the surfaces have water contact angles as high as 150° or even nearly equal to 180° . On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent. These surfaces are termed **superhydrophobic** and can be obtained on **fluorinated** surfaces (**Teflon**-like coatings) that have been appropriately micro patterned. This is called the **Lotus effect**, as these new surfaces are based on lotus plants' surface (which has little protuberances) and would be super hydrophobic. The contact angle thus directly provides information on the interaction energy between the surface and the liquid.

As discussed earlier, a membrane suitable for desalination by membrane distillation is required to have high hydrophobicity. Hence, the contact angle is an important property of the membrane and it needs to be carefully investigated.

Figure 3.20 shows the digital picture of water droplet on PVDF nanofiber membrane, and Fig 3.20 (A) shows the method of contact angle measurement. Fig. 3.20 (B) shows the digital picture of water rest on the surface of a PVDF nanofiber membrane.

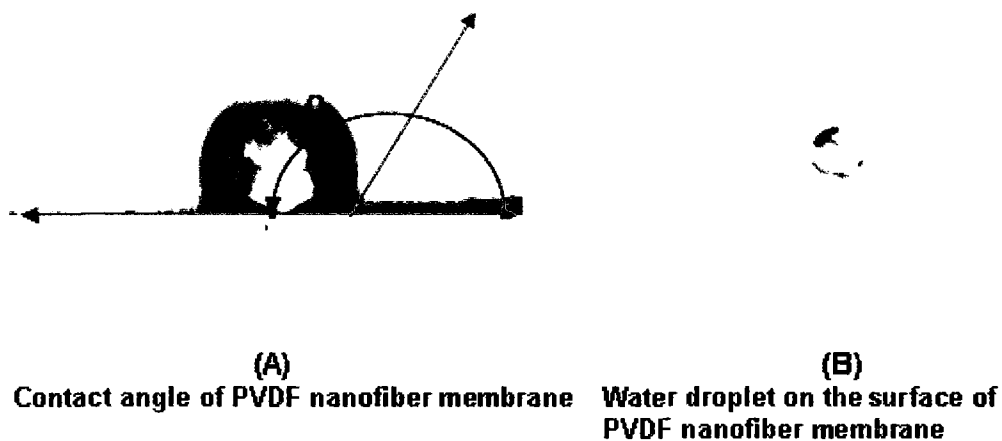


Figure 3.20 Contact angle measurement

Table 3.3 summarizes the equilibrium contact angles of PVDF nanofiber membranes which were made at different spinning conditions.

Table 3.3 Contact angles of PVDF nanofiber membranes

Nanofiber membranes	Electrospinning conditions		Equilibrium Contact angle (°)
PVDF in DMF	Distance (cm)	12	118 ±3
		15	123 ±5
		18	119 ±2
		21	115 ±4
		24	122 ±5
	Voltage (kV)	15	124 ±3
		20	116 ±5
		25	123 ±3
		30	119 ±4
		35	118 ±5
	Flow Rate (ml/h)	2	119 ±2
		4	118 ±4
		8	122 ±2
		16	116 ±3
		32	119 ±3

Note: PVDF polymer solution concentration: 20 wt%

It shows that the average equilibrium contact angles of PVDF nanofiber membranes were distributed randomly around a value of 119° . It can be concluded that the electrospinning condition has less effect on contact angle of PVDF nanofiber membrane. Together with the data shown in chapter 3 section 3.2, it can also be concluded that when the diameter of nanofiber reaches nanometer range, the fiber diameter does not affect the contact angle of nanofiber membrane.

The equilibrium contact angles for the nanofiber membranes made from different polymers under the conditions specified in Table 3.1 were also measured and the results shown in Fig. 3.21.

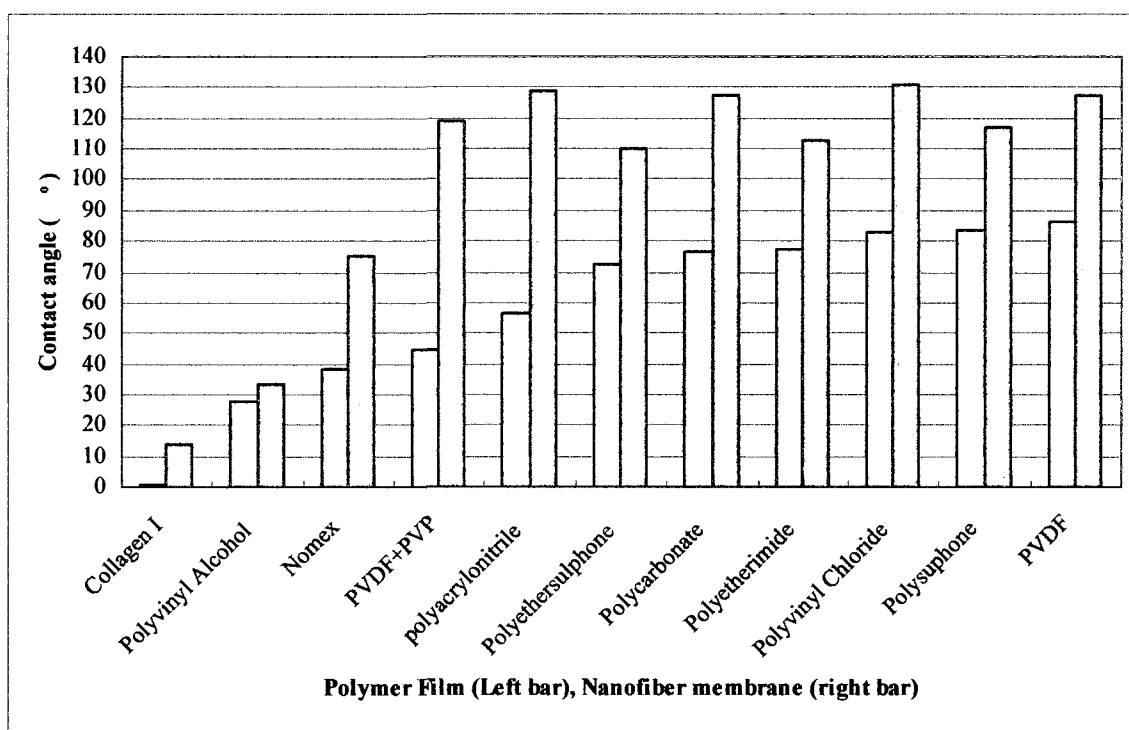


Figure 3.21 Equilibrium contact angle of nanofiber membranes and dense films made from different polymers. 1) Blue bar: contact angle of polymer film. 2) Brown bar: contact angle of nanofiber membrane

Figure 3.21 shows the equilibrium contact angle of nanofiber membranes made from PVDF, PVDF blended with PVP, PS, PES, PEI, PVC, PC and PAN increased dramatically from the contact angle of the dense film up to above 119° . However, contact angles of the nanofiber membranes made from hydrophilic polymers such as PVA and collagen did not increase very much.

From Fig. 3.21, there seems to be a threshold value of 35° of the dense film. Below the threshold value the contact angle of the nanofiber membrane does not increase very much, although some increase is noticed. Above the threshold value, a sharp increase in the contact angle is observed. Therefore, it can be concluded that the contact angle depends not only on the chemical property but also on the physical structure of the sample. Recognizing the effect of the physical structure of the sample, some researchers developed a superhydrophobic surface of nanofiber structure from hydrophilic polymer by template method. According to this report, the contact angle even reached 173° [32].

It has been known that contact angle is seriously affected by the porous structure of the material. The reason for these phenomena could possibly be obtained from the lotus effect and from Cassie's law [103]. Cassie's law describes the effective **contact angle** θ_c for a liquid on a **composite surface**. The law explains how the increase in roughness of a surface increases the apparent contact angle. The law is stated as:

$$\cos \theta_c = \gamma_1 \cos \theta_1 + \gamma_2 \cos \theta_2 \dots \dots \dots (3-10)$$

Where θ_1 is the contact angle for component 1 with a fraction γ_1 and θ_2 is the contact angle for component 2 with a fraction γ_2 present in the composite materials. This equation takes on special meaning when in a 2-component system one component is **air** with a **contact angle** of 180°. As $\cos(180) = -1$, the equation reduces to:

$$\cos \theta_c = \gamma_1 (\cos \theta_1 + 1) - 1 \dots \dots \dots (3-11)$$

Since $\gamma_1 + \gamma_2 = 1$. Equation (3-11) implies that with a small γ_1 and a large θ_1 , it is possible to create surfaces with a very large contact angle. For example, the above equation points out that the water repelling quality of **ducks** is due to the very nature of the composite formed between air and feather and not by other causes such as the presence of exceptional proofing agents like oils. **Water striders** also exploit this phenomenon.

Artificial **superhydrophobic materials** such as **nanopin film** in the laboratory also make use of this law. The lotus effect in **material science** is the observed self-cleaning property found with **lotus** leaves. Their microscopic structure and surface chemistry of lotus leaves mean that the leaves never get wet. Rather, water droplets roll off a leaf's surface like **mercury**.

In the present work, most nanofiber membranes made from different polymeric materials exhibited very high contact angles. These results could be explained by the images of AFM, SEM and from Cassie's law. The nanofiber membranes have composite structures where single nanofibers are laid down in random way. The spaces among nanofibers are filled with air. The difference between the structure of the nanofiber membrane and that of the lotus leaf is possibly in the fact that nanofibers in the nanofiber membrane are arranged horizontal to the surface, while in the lotus leave they are vertical to the surface. That means a water droplet has a chance to contact with a larger area of nanofibers. This may be the reason why the contact angle of the nanofiber membrane is smaller than that of the lotus leaf. The super-hydrophobic surface developed from a hydrophilic polymer provides another evidence for this theory [32].

For many different polymers, their nanofiber membranes have large contact angles. Theoretically, they may have the potential to be used for membrane distillation for desalination. But the MD membrane requires permanent hydrophobicity. Therefore, in this study, PVDF was chosen as the target material for further investigation for MD.

Figure 3.22 is digital pictures of equilibrium contact angle of those nanofiber membranes measured by VCA Optima Surface Analysis System. It clearly shows the PVDF nanofiber membrane has a high contact angle. Nanofiber membranes made from PS, PES, PEI, PC and PVC polymers also have very high contact angles. Compared with other polymers used in this study, PVDF seems to have one of the highest intrinsic hydrophobicities. For this reason, PVDF nanofiber membrane was chosen for further study.

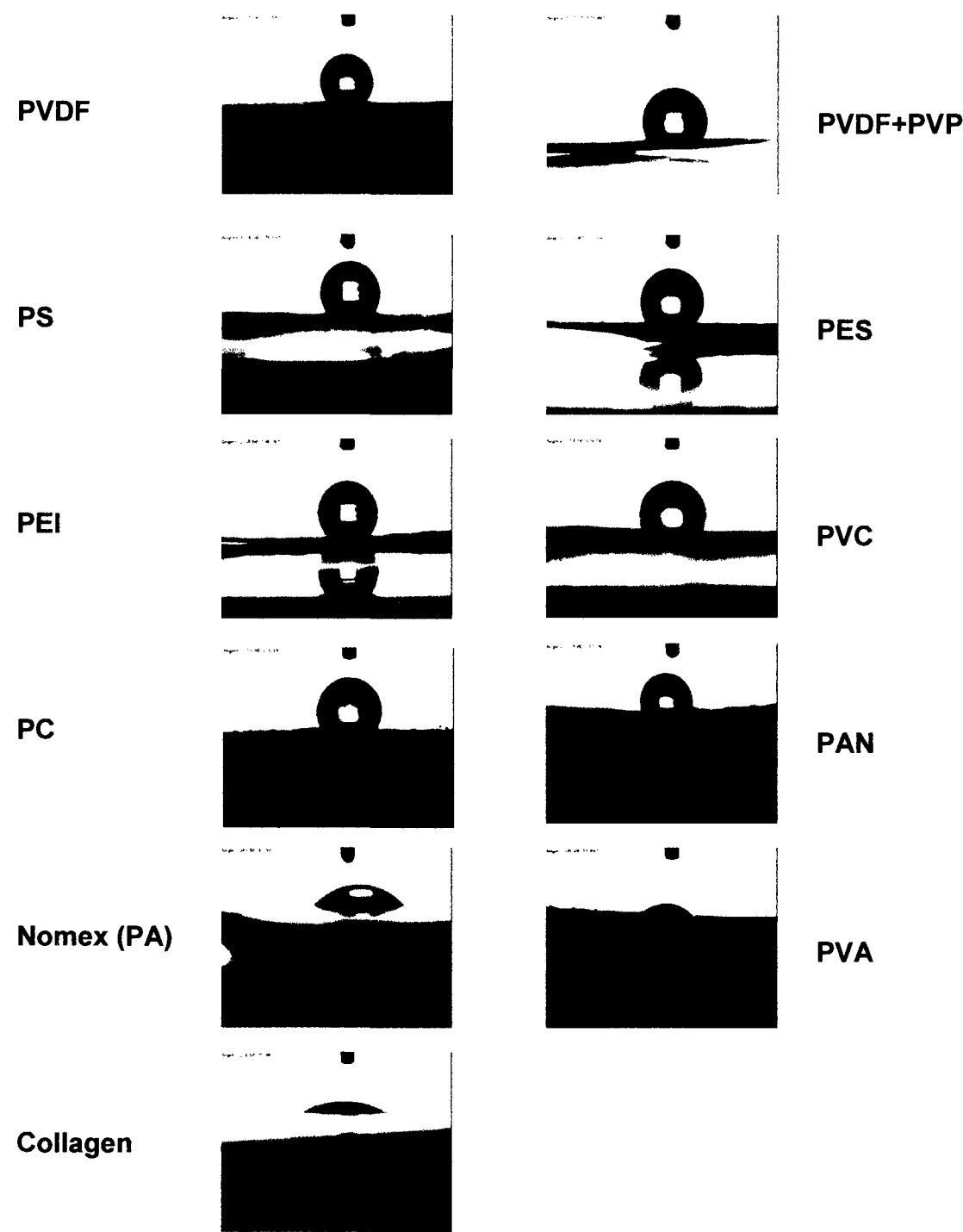


Figure 3.22 Digital pictures of contact angle measurement

3.5 Porosity of Nanofiber Membrane

The porosity of a **porous medium** describes the fraction of void space in the material, where the void may contain, for example, air or water. It is defined by the **ratio**:

$$\varepsilon = \frac{V_v}{V_T} \dots \dots \dots (3-12)$$

Where, ε is the porosity of material, V_v is the volume of void-space (such as fluids) and V_T is the total or bulk volume of material, including the solid and void components. Porosity is a fraction between 0 and 1, typically ranging from less than 0.01 for solid **granite** to more than 0.5 for **peat** and **clay**.

The porosity of membrane is an important parameter to describe the membrane property particularly when the membrane is applied for membrane distillation, since it will decide the transport of the vapour through membrane. Porosities obtained by experiments are summarized in Table 3.4.

Table 3.4 Porosity of nanofiber membranes made from different polymers

Nanofiber membrane	Membrane porosity (%)
PVDF	76±5
PS	72±6
PES	78±2
PEI	69±4
PVC	66±3
PC	58±5
PAN	67±7
Nomex (PA)	63±4
PVA	51±3
Collagen	46±2

Table 3.4 indicates that the porosity decreases as the hydrophobicity of the polymer decreases. This may also be the reason why the contact angles of the nanofiber membranes were not significantly higher than those of the dense films for the hydrophilic polymeric materials. The amount of air contained in the nanofiber membranes made of polymers of low hydrophobicity was not as high as in the nanofiber membranes made of highly hydrophobic material.

Porosities reported in Table 3.4 are not necessarily higher than the commercially available microfiltration membranes that are currently used for membrane distillation. In most cases, the porosity of commercially available membranes used for membrane distillation is in a range 0.7-0.8 [104]. Only the membranes made from the three highest hydrophobic polymers (PVDF, PS and PES) reached the range of commercial membranes. However, as mentioned earlier, the nanofiber membrane has, unlike the membranes made by the phase inversion and stretching technique, an open pore structure, which enables the vapour transport from one pore to the other. This will enhance the vapour permeability through the membrane. PVDF nanofiber membranes have the highest porosity and open pore structure, which is also the reason why PVDF was chosen for membrane distillation experiments.

3.6. Liquid Entry Pressure of Water (LEPw)

The separation process known as membrane distillation (MD) usually refers to the thermally driven transport of vapour through micro pores of hydrophobic membranes. The liquid feed is always in contact with the membrane and can not penetrate into dry membrane pores unless a transmembrane hydrostatic pressure that exceeds the so-called liquid entry pressure of water (LEPw) is applied [104-110]. When, the hydrostatic pressure is lower than the LEPw, the feed liquid does not enter the pores, and a liquid-vapour interface is formed at the entrance of each membrane pore. LEPw above 3 psi is normally considered as sufficient to hold the liquid outside of the membrane pore. This value is required since the pressure at the feed inlet is not necessarily atmospheric pressure, even when the feed outlet is kept at atmospheric pressure due to the pressure drop from the inlet to the outlet of the feed. Hence, to hold the feed liquid outside of the membrane pore, a certain LEPw is required.

The LEPw values of nonofiber membranes made of different polymeric materials are summarized in Table 3.5.

Interestingly, the data shown in Table 3.5 do not show any trend between LEPw and hydrophobicity/hydrophilicity. The reason may be that the LEPw is determined by the interplay of hydrophobicity and pore size.

Table 3.5 LEPw of nonofiber membranes made from different polymeric materials

Nanofiber membrane	LEPw (psi)
PVDF	17.6±2
PS	23.2±1
PES	18.6±3
PEI	21.4±1
PVC	27.0±2
PC	19.2±4
PAN	27.6±1

3.7. Pore Size and Pore Size Distribution of Nanofiber Membrane

Figure 3.23 shows the solute separation versus Polystyrene latex particle diameter for the PVDF nanofiber membrane and for the PVDF/PVP blend membrane. The electrospinning conditions are specified in the caption.

From Fig. 3.23 and the definition of MWCO [92], the MWCO of the PVDF and the PVDF/PVP blend nanofiber membranes are 1.38 μm and 2.51 μm , respectively, in terms of particle size (not molecular weight).

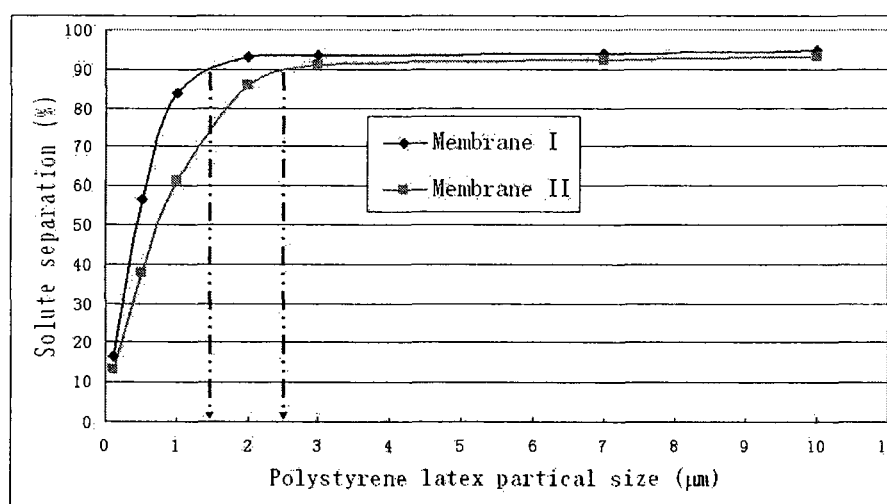


Figure 3.23 Solute separation vs. Polystyrene particle diameter obtained by filtration experiments

I) PVDF concentration 20%, spinning voltage 18kV, collect distance 18cm, dope flow rate 2mL/h. II) PVDF+PVP concentration 20%, spinning voltage 18kV, collect distance 18cm, dope flow rate 2mL/h.

Filtration experiments were performed at 30 psig and latex concentration of 100 ppm.

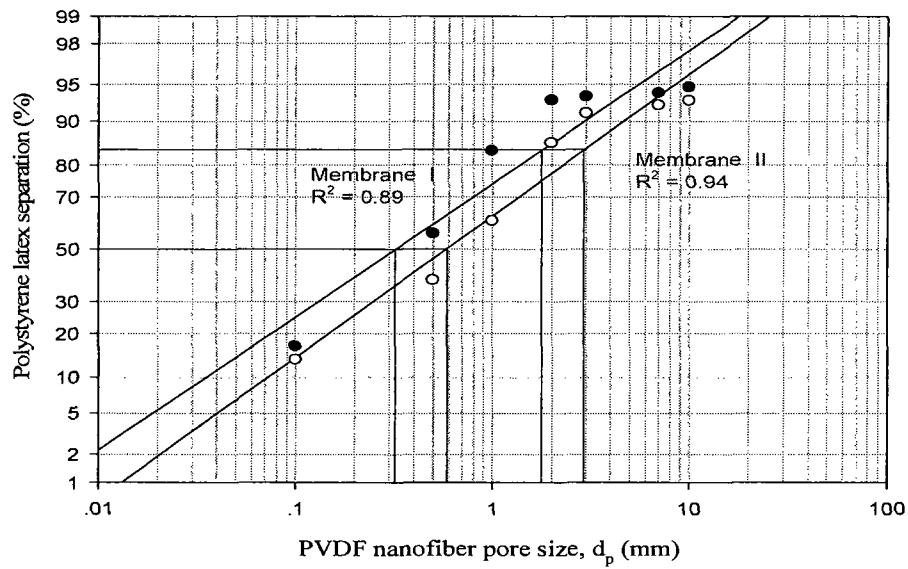


Figure 3.24 Log-normal probability plot of solute separation vs. Polystyrene particle size
Membrane preparation and filtration experimental conditions, same as Fig. 3.23

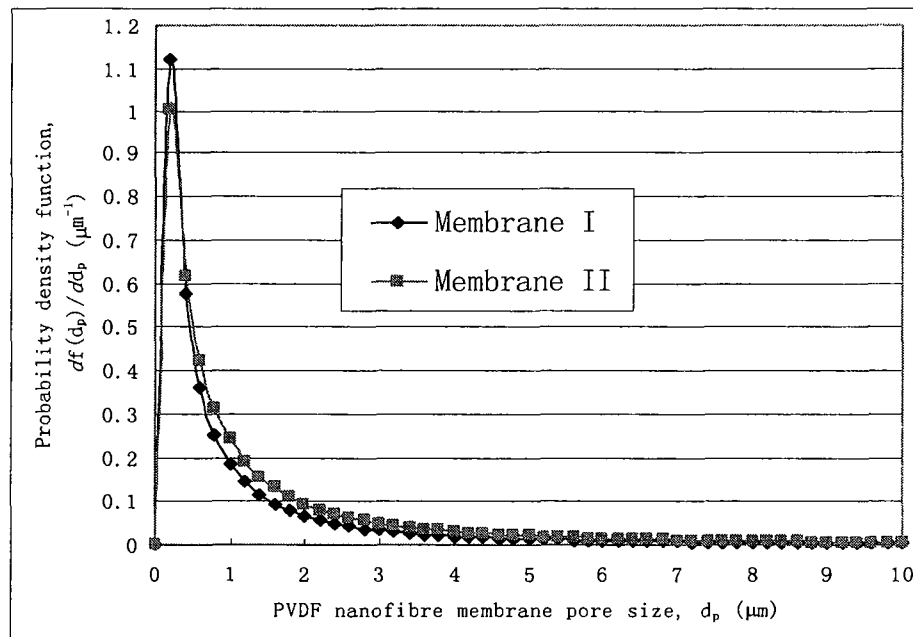


Figure 3.25 Probability density function curve
Membrane preparation and filtration experimental conditions, same as Fig. 3.23

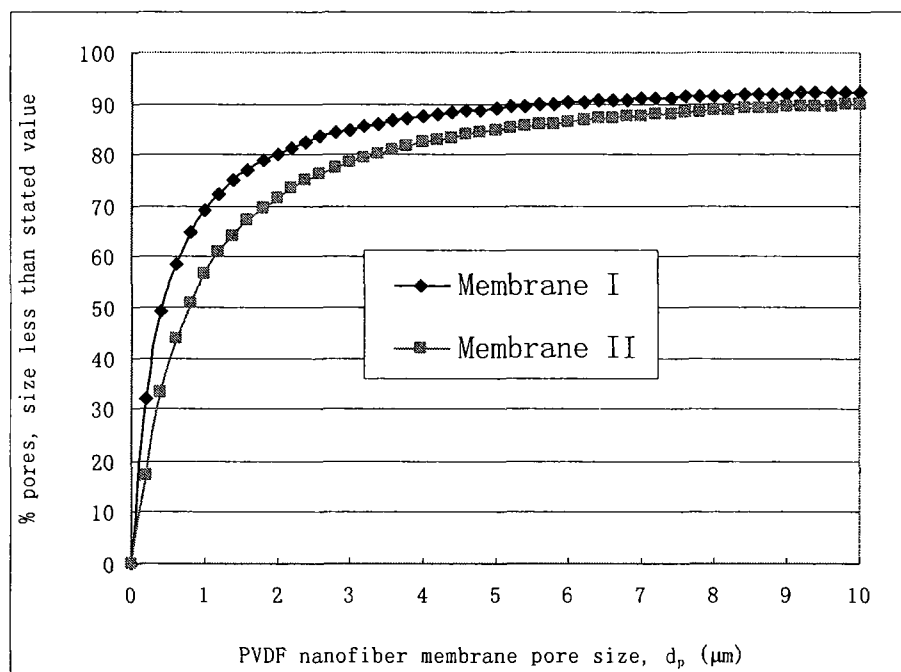


Figure 3.26 Cumulative pore size distribution

Membrane preparation and filtration experimental conditions, same as Fig. 3.23

In Fig. 3.24, the probability-lognormal plot of separation vs. particle size does not necessarily fit straight line, since all of large particles showed separations close to 95%. By forcing the straight line fit to the data, the obtained mean pore sizes (diameters) of the PVDF and the PVDF/PVP membranes were 0.32 and 0.62 μm , respectively, and geometric standard deviation 2.58 and 2.73. These mean pore sizes are much smaller than the pore diameters obtained from the image analysis. The reason may be two-fold; one, that the membrane pores were partially plugged by the latex particles and the path for the particle transport was narrowed and two, that some particles were trapped in the membrane temporarily before being leased eventually. In other words, the steady state has not been achieved.

Figures 3.25 and 3.26 show the pore size distribution of PVDF nanofiber membrane [93].

Chapter 4 CONCLUSIONS AND FUTURE WORK

As discussed earlier, the main objective of the present work is to use electrospinning technology to fabricate nanofiber membranes with high porosity and high surface hydrophobicity. The newly developed nanofiber membrane in the current research will eventually be applied for membrane distillation. Before its application for membrane distillation, the effects of the electrospinning conditions on membrane properties were carefully studied and nanofiber membrane characterization methods were firmly established so that all the material conditions required for membrane distillation application could be achieved. A large amount of research had been carried out for this purpose and discussions were made based on the research results. The following conclusions were drawn as a result of the experimental work.

1. CONCLUSIONS

1.1 Conclusions From Nanofiber Electrospinning

- 1) Electrospinning technology is a simple and effective method to fabricate nanofibers and nanofiber membranes.
- 2) Under appropriate electrospinning conditions (Including solvent, polymer concentration, spinning voltage, collect distance, feed flow rate and so on.), PVDF, PVDF+PVP, PS, PES, PEI, PVC, PC, PAN, Nomex (PA), PVA, and Collagen could be successfully electrospun. The nanofibers made from different polymers by electrospinning have different structures and diameters at the spinning conditions adopted in the current research. The diameter of nanofiber is in a range from 200 nm to 2 μ m.
- 3) The average diameter of PVDF nanofiber changes by changing a spinning parameter, while other parameters are fixed, in the following way.
 - a) With an increase in the spinning voltage, the average diameter of PVDF nanofiber decreases.

- b) With an increase in polymer concentration in the casting dope, the average diameter of PVDF nanofiber increases.
 - c) With an increase in the collect distance, the average diameter of PVDF nanofiber decreases.
 - d) With an increase in the dope flow rate, the average diameter of PVDF nanofiber slightly increases.
- 4) SEM shows PVDF nanofibers precipitate on the collector surface randomly, loosely in contact with each other. Nanofibers made of different polymers have different structures.
- 5) AFM images show structures similar to those observed in SEM images: i.e. nanofibers are of fibrous structure and their diameters are in nanometer-range. In particular, AFM of PVDF and PES nanofibers show that the polymer aggregates are arranged in layer by layer formation along the nanofiber axis.
- 6) DSC results show, after nanonization, the T_m of the PVDF nanofiber is lower than that of the dense PVDF film. The T_g of the PES nanofiber is lower than that of the dense PES film.

1.2. Conclusions From Nanofiber Membrane Characterization

- 1) Compared with the dense film made from the same polymer, nanofiber membranes exhibit much higher contact angles. For the studied PVDF nanofiber membrane, the equilibrium contact angle was above 120° . Compared with 82.3° obtained by Khayet [111], and 82° reported by Huang [112], the above value is extremely high.
- 2) The contact angle of the studied nanofiber membranes made from PVDF+PVP, PS, PES, PEI, PVC, PC, PAN are also above 110° . If the contact angle of the dense film is lower than 35° , the contact angle of the nanofiber membrane made from the same polymer exhibits only a slight increase.

- 3) The porosity of the studied PVDF nanofiber membrane is $76 \pm 5\%$. Porosity of the studied nanofiber membranes made of other polymers vary from 46 ± 2 to $78 \pm 2\%$.
- 4) The Liquid entry pressure of water (LEPw) of the studied PVDF nanofiber membrane is 17.6 ± 2 psi. The LEPw of the studied nanofiber membranes made of PS, PES, PEI, PVC, PC, PAN and Nomex (PA) vary in a range from 13.7 ± 3 to 27.6 ± 1 psi.
- 5) Regarding the MWCO in terms of the latex particle size, the pore size of the studied PVDF and PVDF/PVP blend nanofiber membranes are 1.38 and 2.51 μm , respectively.
- 6) The PVDF nanofiber membrane has a wide range of pore size distribution.

2. GENERAL CONCLUSIONS

Electrospinning technology is a simple and effective method to generate nanofibers and fabricate nanofiber membranes from different polymers. Nanofiber membranes have high porosity and high hydrophobic character. Moreover, observations by SEM and AFM revealed that the studied PVDF nanofiber membranes had more open pores compared with membranes made by other conventional methods. The LEPw of a studied PVDF membrane was 17.6 psi that is high enough for membrane distillation application.

All of these properties of the PVDF nanofiber membrane are exactly what is required for the membrane material for membrane distillation. Nanofiber membranes made of some other polymers also demonstrated similar properties. Examples are the nanofiber membranes fabricated from PES and from PVDF/PVP blend. However, considering the possibility of long term operation without MD performance deterioration, probably, polymeric materials with intrinsically high hydrophobicity are desirable. Hence, PVDF polymer is the ultimate choice for membrane distillation application conducted in the

latter part of this work. With its low surface tension and fluorine content, PVDF has the most desirable properties for membrane distillation.

Another nanofiber membrane of potential usefulness is the nanofiber membrane made of collagen. It can be developed for bio-scaffold, wound dressing, nerve guiding growing material and other bio-medical applications. However, it is out of the scope of the current research.

3. FUTURE WORKS

As mentioned earlier, main focus of this work was on PVDF nanofibers and nanofiber membranes. Nanofibers and nanofiber membranes made from other polymeric materials were not investigated in detail. However, nanofiber membranes made of different polymers may also be used in various industrial sectors. Collagen in biomedical applications is one of such examples. In particular, combined with chemical and physical post treatments, it seems that nanofibers and nanofiber membranes can be used for various separation processes if appropriate chemical and physical post treatment is applied. Grafting, plasma etching, interfacial polymerization, coating, PVD, CVD and other surface modification technologies shall be employed to develop nanofibers and nanofiber membranes with new properties and new applications. New fiber collect technology can also be developed to obtain regular orientation and highly ordered arrangement in nanofibers and nanofiber membranes. By this way, the control of pore size and pore size distribution may become possible. Thus, the future applications of nanofibers and nanofiber membranes seem unlimited.

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PART II

SEAWATER DESALINATION AND
ETHANOL/WATER MIXTURE SEPARATION BY
PVDF NANOFIBER MEMBRANE

Chapter 1 INTRODUCTION

1. INTRODUCTION

Fresh water is an essential commodity. As human population grows and industry develops, water shortage becomes one of the major problems in many places nationally and internationally. At the same time, the human population has already crossed 6 billion. It is expected to reach 8.3 billion in 2025, and 10 to 12 billion in 2050 [1]. However, the global fresh water supply is limited; 97.5 % of the total global water is saline and only 2.5% is fresh water. In the 2.5 %, only one third can be used for human life, even though fresh water is seriously polluted by human activity. Over next 50 years, water supply per capita will be reduced to approximately one third due to the population increase [2]. Therefore, alternative source of fresh water is necessary. Desalination is a major technology to produce fresh water. So, desalination will be required to meet the rising demand for fresh water. Indeed, desalination technologies have been developing rapidly during the past decades for desalting a variety of water (seawater, brackish water and industrial wastewater). Desalination has made a major contribution to improve quality of life in the most arid region of the world and to provide safe drinking water in the regions where the water pollution is more serious. Desalination is a very important technology of augmenting and sustaining the world's fresh water supplies.

2. DESALINATION TECHNOLOGIES

Desalination can be defined as a process that removes dissolved minerals (including NaCl) from seawater, brackish water, or treated wastewater. A number of technologies have been developed for desalination. Current commercially available desalination technologies can be divided in: a) thermal processes, which evaporate water to separate it from the salt solution that remains in the brine and b) membrane processes, which make use of a membrane as a separating agent.

There are three main thermal processes: i) multistage flash evaporation (MSF), ii) multiple-effect distillation (MED), and iii) vapour compression (VC). The membrane

processes are reverse osmosis (RO), electro-dialysis (ED), and membrane distillation (MD). MSF and RO are equally important and together these two technologies account for 87% of the worldwide desalination capacity. The membrane processes, particularly RO, will continue to take market share from thermal desalination, with 59% of the total newly built capacity being membrane based [3].

2.1 Thermal Process (Distillation)

Approximately one-half of the worlds' installed desalination capacity uses thermal distillation process to produce fresh water from seawater. Thermal processes are the primary desalination technologies and are used throughout the Middle East, these technologies can produce high purity and low total dissolved solid (TDS) water from seawater and also fuel costs are lower in the region.

- Multi-Stage Flash Distillation (MSF)

MSF is the most commonly employed thermal process for desalination. This process is a most reliable technology with high capacity for the production of desalted water. The schematic diagram of MSF process is shown in Fig. 1.1. MSF contains a number of chambers in series. The feed brine water flows through each chamber with successively lower temperature and pressure, to rapidly vaporize (or “flash”) water from bulk liquid brine. The vapour is then condensed by tubes of the inflowing feed water, thereby recovering energy from the heat of condensation, despite its large energy requirements.

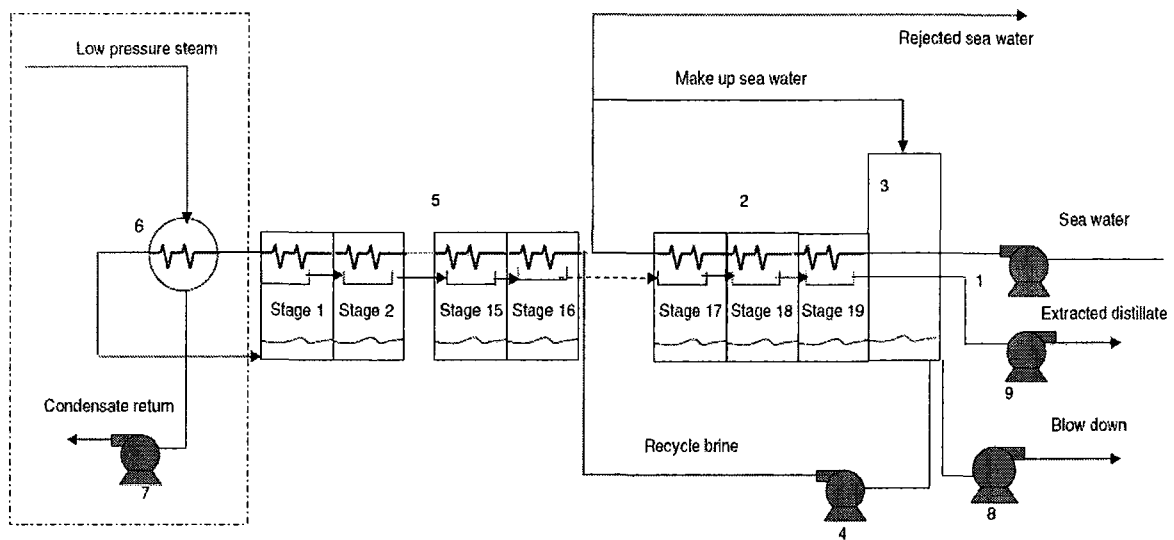


Figure 1.1 Schematic diagram of the MSF desalination plant

(1) Main seawater pump, (2) heat rejection stages (stages 17, 18 and 19), (3) dearator, (4) brine recycle pump, (5) heat recovery stages (stages 1–16), (6) brine heater, (7) condensate pump, (8) blow down pump, (9) distillate pump. [4]

● Multi-Effect Distillation (MED)

Figure 1.2 shows the schematic diagram of MED process. MED is a thin-film evaporation technique, in which the vapour produced by one chamber (or “effect”) subsequently condenses in the next chamber, which has low temperature and pressure, in comparison on the feed side. MED technology is more economical in comparison with MSF as it has lower power consumption.

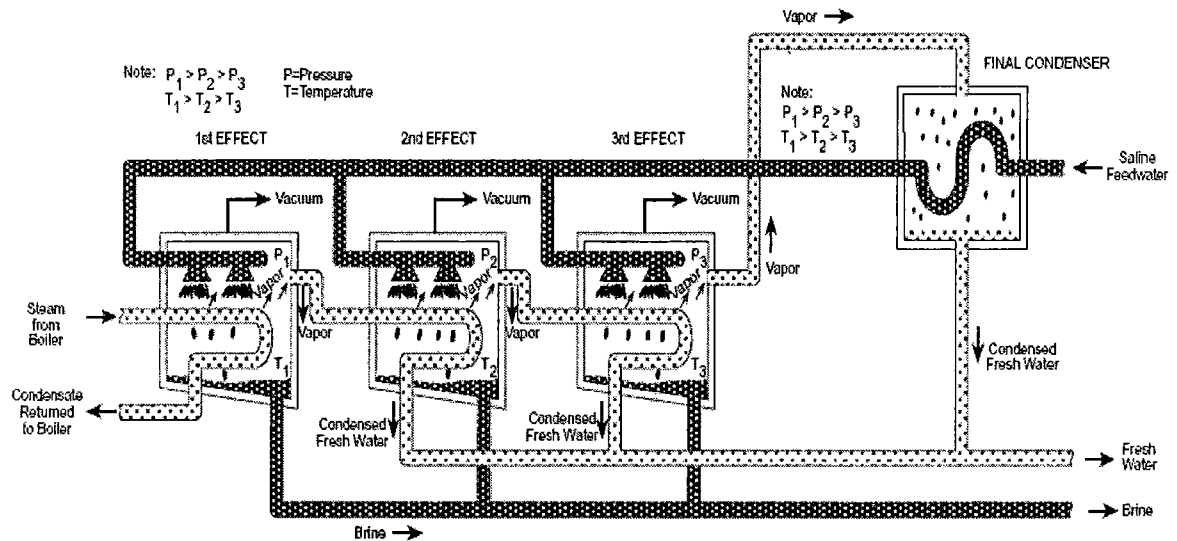


Figure 1.2 Desalination by multiple effect distillation (MED) [5]

- Vapour Compression (VC)

Figure 1.3 shows a schematic diagram of VC. VC is an evaporative process where vapour from the evaporator is mechanically compressed. During the compression the amount of heat released by vapour is reused for the evaporation of feed water. VC is used where cooling water and low-cost steam is not easily available [6].

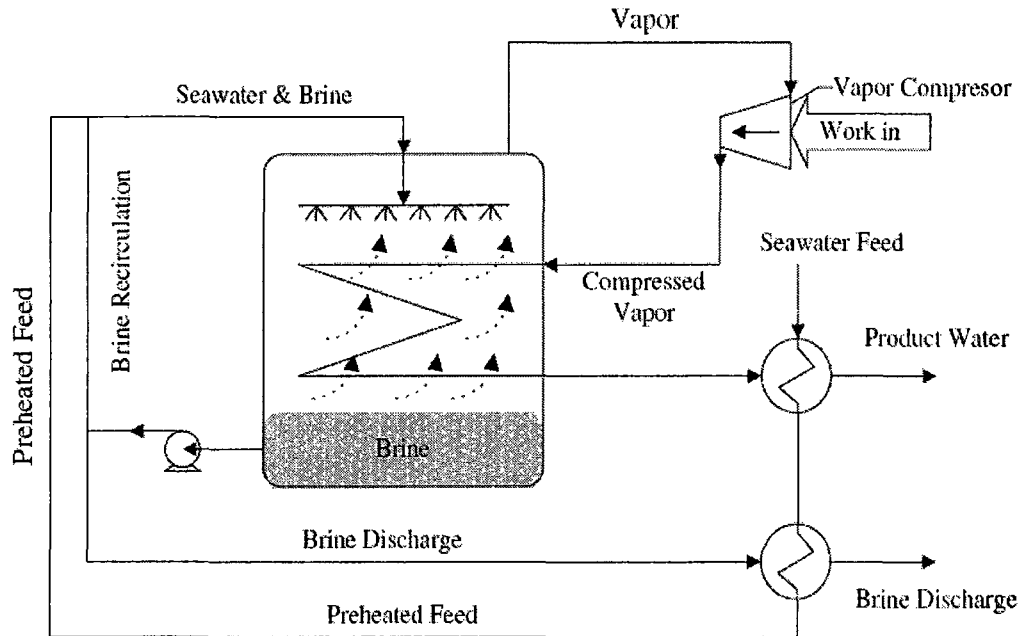


Figure 1.3 Desalination by vapour compression (VC) [7]

Other thermal techniques such as solar distillation and freezing have been developed for desalination, although they have not been commercially successful so far [8].

2.2. Membrane Processes

Membrane desalination process is a new technique in comparison with thermal distillation process, such as MSF, MED and VC. Over the last 50 years, tremendous advancements have been made in the field of membrane technology. In fact, reverse osmosis (RO) represents the fastest growing segment of the desalination market. In 2002, 43.5% of the total desalination plants in use were RO desalination plants [8]. Actually, membrane technology can be used for desalination of both seawater and brackish water. However, it is more commonly used to desalinate brackish water because energy consumption is proportional to the salt content of the desalinating water (feed).

Membrane technology also can remove microorganisms and many organic contaminants from the feed water. Comparing with thermal distillation processes, membrane technology generally has lower capital cost and requires less energy. However, the product water salinity is higher for membrane desalination (<500 ppm TDS) than that produced by thermal technologies (≤ 25 ppm TDS) [3].

Membrane technology operates under either of two driving forces: i) pressure; ii) electrical potential for desalination and water purification. The pressure-driven membrane technologies are commercially available for different desirable applications [7].

- Reverse osmosis (RO)

Figure 1.4 shows a schematic diagram for RO desalination. In RO process, feed water is pumped at a high pressure through permeable membranes. Feed water must be pretreated by removing particles (unwanted, insoluble, colloid and so on) that would be clogged in the system. The quality of the produced water depends on the pressure, the concentration of salts in the feed-water, and the salt permeation constant of the membranes. If the product water quality is not as high as expected, product water quality can be improved by adding a second RO membrane stage, whereby product water from the first RO membrane system will be fed to the second RO membrane stage.

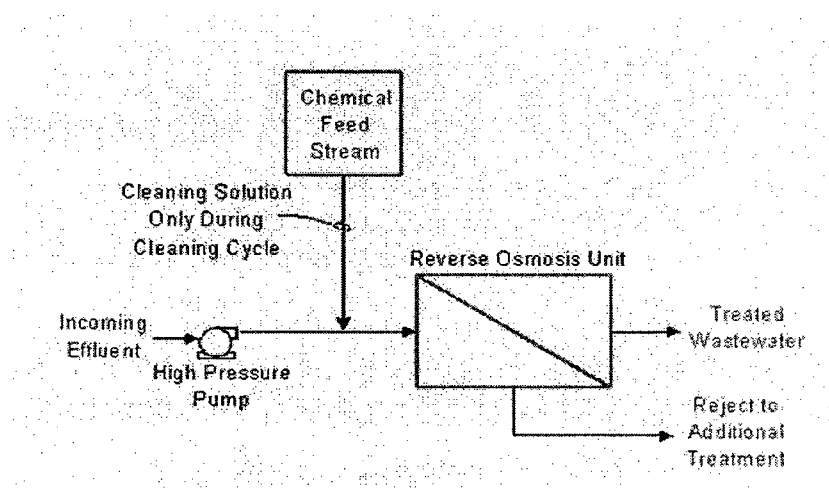


Figure 1.4 Diagram of a reverse osmosis

● Electrodialysis (ED)

ED is another membrane-based process that is important for desalination and operated under a different type of driving force, i.e. electrical potential. Figure 1.5 shows a schematic diagram of ED. In ED applications, hundreds of positively and negatively charged cell pairs are assembled in a stack (charged membrane) to achieve a practical module [7]. The other process called Electrodialysis Reversal (EDR) operates on the same principles as ED, but in it, periodically reverses the polarity of the system to reduce scaling and membrane clogging. Electrodialysis represents approximately 3% of worldwide desalination capacity [8].

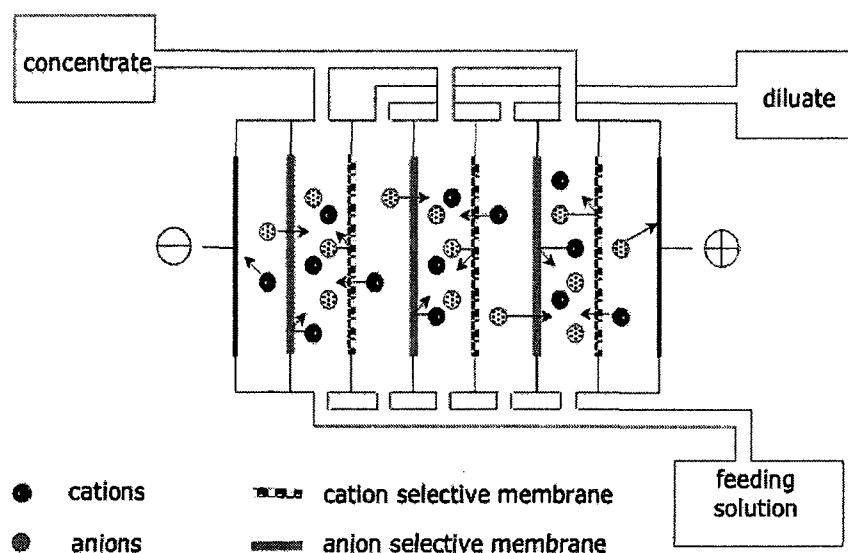


Figure 1.5 Electrodialysis (ED) [9]

Since thermal distillation process consumes more energy, the use of membrane processes for desalination has increased markedly in recent years. Considering the recent improvements in membrane-based desalination, substantial further cost savings could be more difficult to achieve, suggesting the need for a carefully developed research agenda targeted to areas that offer the most promise for cost reduction. As the energy shortage is

becoming more severe, developing low energy cost desalination technology becomes more important. The preferable research topics are as follows [10-17].

- Improving membrane permeability.
- Improving or developing new methods for reducing energy use or recovering energy.
- Improving pretreatment and post-treatment methods to reduce consumption of chemicals.
- Developing less expensive materials to replace current corrosion-resistant alloys used for high pressure piping in seawater reverse osmosis systems.
- Developing new membranes that will enable controlled selective rejection of contaminants.
- Improving methods of integrity verification.
- Developing membranes with more fouling resistant surfaces.

3. MEMBRANE DISTILLATION

Membrane distillation (MD) is a relatively new process that is being investigated worldwide as a low cost, energy saving alternative to conventional separation processes: such as distillation and reverse osmosis (RO). The benefits of MD compared to other more popular separation processes are: (1) 100 % (theoretical) rejection of ions, macromolecules, colloids, cells, and other non-volatiles, (2) lower operating temperatures than conventional distillation, (3) lower operating pressures than conventional pressure-driven membrane separation processes, (4) reduced chemical interaction between membrane and process solutions, (5) less demanding membrane maintenance requirements, and (6) reduced vapour spaces compared to conventional distillation processes. However, MD also has several limitations, which result in a lack of general interest in the process. The primary limit arises from the defining phenomenon itself: the process solution must be aqueous and with limited amount of organic material to prevent wetting of the hydrophobic porous membrane. Therefore, despite MD's performance in

desalination applications, the current outlook for MD in the desalination industry is still gloomy. The greatest leaps in MD technology will come at time as industries are trying to find new less costly and environment friendly processes in comparison with the present processes. Thus, many researchers are devoting their efforts towards determining new applications for MD in the area of food processing, medical, environmental/waste cleanup, in addition to desalination industries. The present effort of this research work will play the biggest role in determining the future of MD [12, 13, 15].

Generally, MD process could use natural energy sources such as wind, solar energy, tide energy, and industrial low quality heat energy (flue gas) as heat source, as MD operating temperature is relatively low. Hence, the potential for desalination by MD process is very high. It could be an alternative process for desalination and water treatment, as well as for medical field, food processing and industrial separation.

Theoretically, the concentration of feed solution has very little effect on the production flux of MD. It also could be used as a crystallizer for heat sensitive crystals [18], nuclear wastewater treatment [16] and for removing toxic compounds from water [19]. The purpose of the present research is to develop a novel PVDF nanofiber membrane for the MD process in both practical and theoretical aspects.

Chapter 2 MEMBRANE DISTILLATION

1. CONCEPT AND MECHANISM OF MEMBRANE DISTILLATION

The concept of membrane distillation (MD) has come from normal distillation process. Both processes (MD and Distillation) are based on vapour-liquid equilibrium. There is phase change in the process. But the operating temperature of membrane distillation is much lower than the boiling point of the solution, which needs to be separated. In Rome on May 5, 1986, IUPAC gave the definition of membrane distillation as follows. The term “membrane distillation” should be applied for membrane operations having the following characteristics: [12]

- The membrane should be *porous*;
- The membrane should not *be wetted* by the process liquids;
- *No* capillary condensation *should* take place inside the pores of the membrane;
- Only *vapour* should be transported through the pores of the porous membrane;
- The membrane must not alter the *vapour-liquid equilibrium* of the different components in the process liquids;
- At least one side of the membrane should be in *direct contact* with the process liquid;
- For each component the driving force of this membrane operation is a *partial pressure gradient* in the vapour phase.

According to the definition, membrane for membrane distillation should be highly porous and highly hydrophobic.

The mechanism of MD is shown on Fig. 2.1. In a MD process, the temperature of feed side must be higher than permeate side, and the volatile components pass through the membrane as vapour and condense on the other side of hydrophobic membrane. Also according to different condensation methods, membrane distillation (MD) is divided to four different types of configurations: i) direct contact membrane distillation (DCMD); ii) air gap membrane distillation (AGMD); iii) sweep gas membrane distillation (SGMD),

and iv) vacuum membrane distillation (VMD).

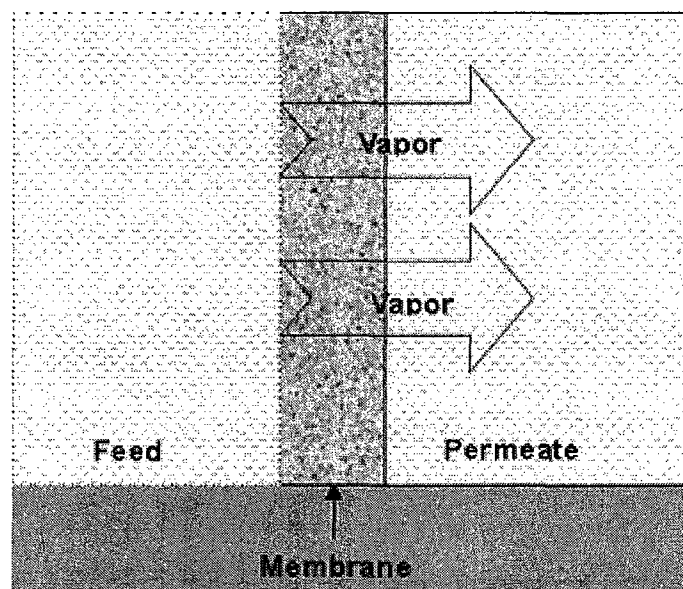


Figure 2.1 Membrane distillation process

2. CONFIGURATIONS OF MEMBRANE DISTILLATION

Four types of membrane distillation configurations are as follows [20]:

- Direct Contact Membrane Distillation (DCMD)

Figure 2.2 shows the mechanism of DCMD. For a DCMD process, one side of the membrane is directly contacted with the feed solution and the other side of the membrane directly contacted with permeate, and also cooling fluid. The temperature of the feed solution is higher than that of the permeate side to create a driving force for vapour transport across the membrane. Because the membrane is the only barrier between both sides (feed side and permeate side), the obtained permeate flux in DCMD is high. Unfortunately, this is also true for energy flow by heat conduction, so that heat loss in DCMD is also very high. That means DCMD may consume a significant amount of energy.

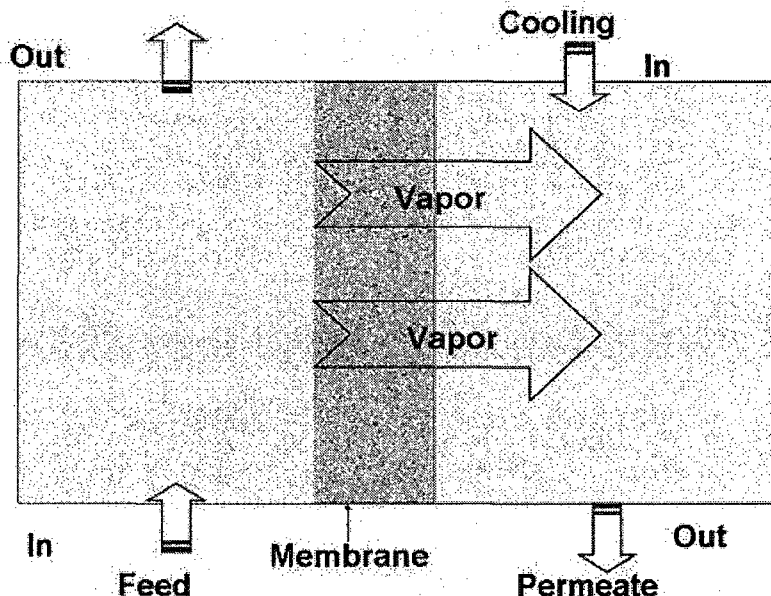


Figure 2.2 Direct contact membrane distillation (DCMD)

- Air Gap Membrane Distillation (AGMD)

Figure 2.3 shows the mechanism of AGMD. In an AGMD process, only the feed solution is directly contacted with a membrane. Permeate is condensed on a cooler surface. There is an air gap situated between the membrane and the cooler surface. Thus, the air gap will reduce energy loss as heat conduction through the membrane. The main drawback of the air gap is that there is an additional resistance to mass transfer. AGMD is suitable for all feed compositions, for which DCMD can be applied. However, it is also suitable for separating other volatile compounds such as alcohol from an aqueous solution [19, 20]. DCMD is not applicable for the latter process, because those substances are likely to wet the membrane at the permeate side as a result of a lower surface tension and/or smaller contact angle with the membrane. In AGMD, the liquid permeate is not in direct contact with membrane surface. Therefore, there is less danger of membrane wetting at the permeate side.

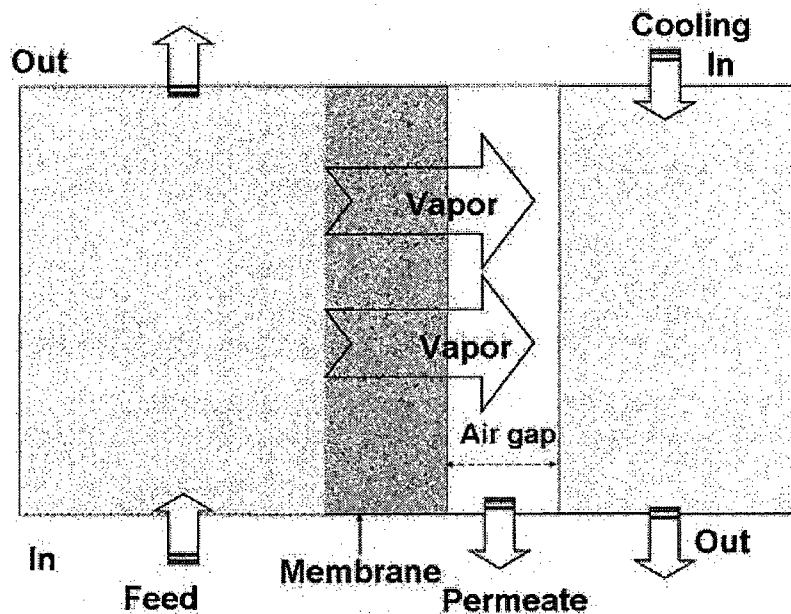


Figure 2.3 Air gap membrane distillation (AGMD)

- Sweep Gas Membrane Distillation (SGMD)

Figure 2.4 shows the mechanism of SGMD, which is also called air stripping membrane distillation. In this process, permeate is removed by a sweeping gas and subsequently externally condensed. Similar to AGMD, it can also be used for removing volatile compounds from water [21]. An advantage of using a sweeping gas is that the resistance to mass transfer of the air gap is substantially reduced. However, the drawback is the dilution of the vapour (permeate) by the sweeping gas, which leads to higher demand on the condenser capacity and higher energy consumption.

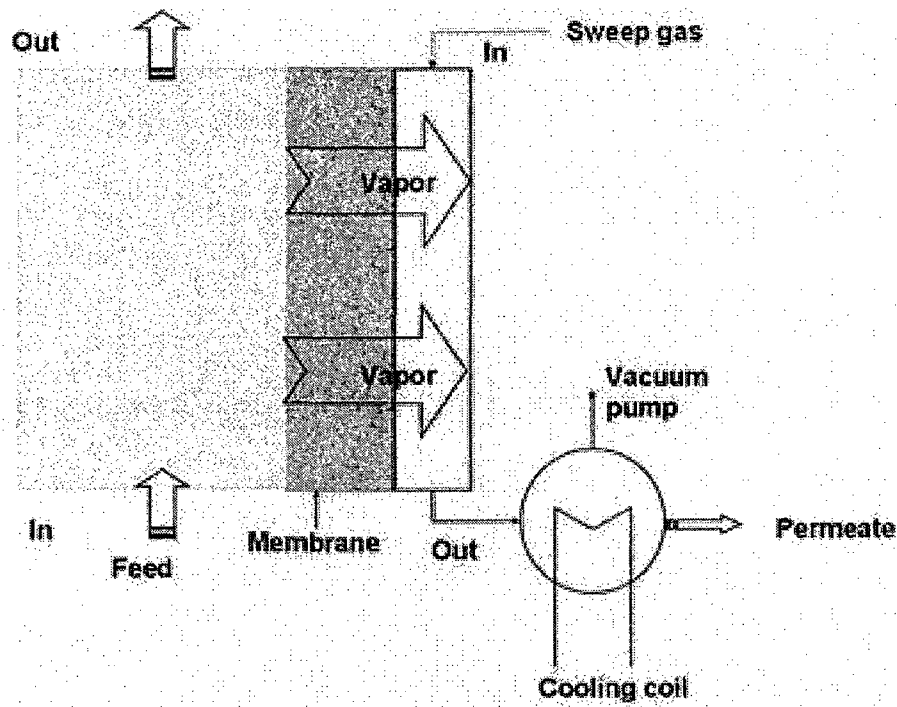


Figure 2.4 Sweep gas membrane distillation (SGMD)

- Vacuum Membrane Distillation (VMD)

Figure 2.5 shows the mechanism of VMD. Instead of using sweeping gas, the vapour can be removed by evacuation and subsequent external condensation. VMD can be used for the separation of various aqueous mixtures with volatile compounds [22-24], and recently it has been proposed as a means for seawater desalination [25].

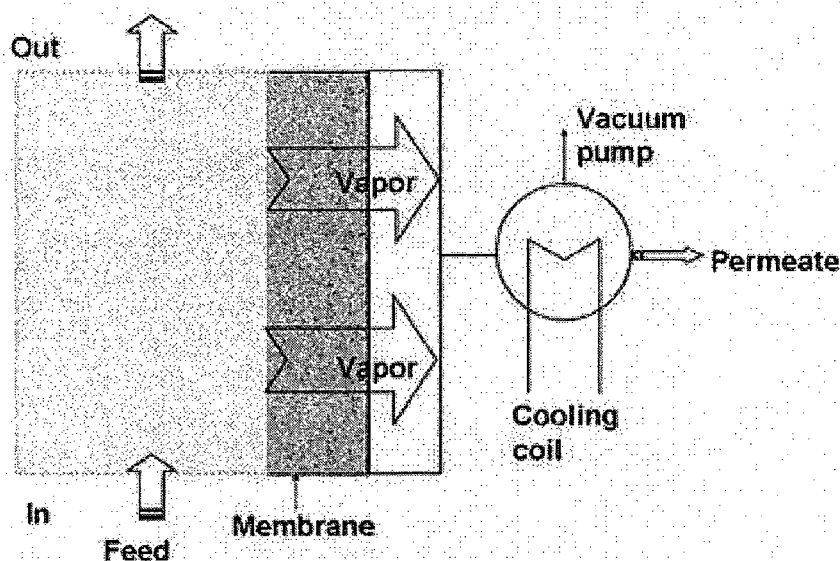


Figure 2.5 Vacuum membrane distillation (VMD)

Generally, membrane distillation is an emerging technology that can be used not only for desalination but also for recycling [25]. Membrane distillation differs from other membrane technologies in that the driving force for desalination is the difference in vapour pressure of water across the membrane, rather than total pressure. The membranes for MD are micro-porous and hydrophobic, which allows diffusion of water vapour, but not liquid water. Concentration polarization does not play a major role in MD, because flux is limited by temperature polarization. An extensive pre-treatment like that for RO is not required [26]. The feed can have a SDI (silt density index) as high as 100, but compounds that make the membranes hydrophilic, such as surfactants and volatiles that are not wanted in the permeate, must be avoided. Elevating feed vapour pressure by heating the feed creates the vapour pressure gradient for MD. However, the feed temperature does not need to reach its boiling point.

The important applications of membrane distillation can be seen in the field of water

purification and in the concentration of product solutions or wastewater treatment [27, 28]. If organic solutes are present in an aqueous solution, the surface tension γ_L will decrease rapidly. If the concentration of organic material does not exceed a certain critical value (so that the liquid on both sides of membrane does not wet the membrane), the membrane distillation process can still be used. On the other hand, if the concentration of the organic material exceeds the critical value, the micro porous membrane will be filled with liquid. In this case, membrane distillation is no longer applicable.

3. SIMILAR PROCESSES FOR MEMBRANE DISTILLATION

There are some other processes, which are similar to MD. To understand the mechanism of those processes will be of great help to develop modeling, by which performance is predicted for membrane distillation process. The following membrane processes have mechanisms similar to MD.

- **Osmotic distillation:**

It is a new membrane technology developed at the end of 80s [29]. High concentration salt solution and separation stream are divided by hydrophobic membrane. With the action of osmotic pressure, water vapour of separation stream will pass through the hydrophobic membrane into salt solution. Then separation stream is concentrated and the salt solution is diluted. In this process, there is no temperature difference. So it can be conducted at room temperature.

- **Membrane absorption:**

In this process, one side of hydrophobic membrane is contacted with an aqueous solution containing a volatile compound; the other side is contact with a different aqueous solution that can absorb the volatile compound. Both sides are at the same temperature and have the same water vapour pressure. The volatile will pass through the hydrophobic membrane and is absorbed on the other side. This phenomenon could be used to remove trace volatile compounds from aqueous solution and for industrial water cleaning [30].

- **Membrane degasser and membrane contactor:**

Normally, oxygen and carbon dioxide are dissolved in water. Corrosion will happen during a long-term transport of such kinds of fluid through pipeline and equipment. By applying vacuum on the other side of a hydrophobic membrane, the dissolved gases will be degassed from water. This degassing process is highly effective, cheap and simple [31]. Membrane contactor is a reverse process of membrane degasser. It is to enhance the dissolved gas in the liquid stream. Artificial lung is a typical example [32].

- **Pervaporation:**

It is not a membrane distillation process. But in many cases, this process is confused with vacuum membrane distillation (VMD). Phase change happens in both processes. Also, vacuum is applied and vapour is condensed. For VMD, the membrane is porous and works as a support to keep the vapour-liquid equilibrium. Separation depends on the vapour pressure difference. For pervaporation, membrane is dense. The permeate dissolves in the membrane and diffuses to the other side of membrane. Separation depends on the property of membrane material and the separation object [33, 34].

4. MEMBRANES FOR MEMBRANE DISTILLATION

The advantages of membrane distillation are that the distillation process takes place at a moderate temperature, a relatively low temperature difference between the two liquids contacting the micro-porous hydrophobic membrane and the process gives relatively high flux. Because entrainment of dissolved particles is avoided, permeate with a high purity is obtained.

However, membrane distillation is only possible if the restrictive condition is fulfilled, that is the pores of the membrane are not filled with liquid. Hence, the wetting power of the liquid with respect to the membrane should be low, and the membrane material should be hydrophobic. In order to fulfill the requirements, hydrophobic materials are required, such as: polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE, Teflon).

5. MEMBRANE PREPARATION FOR MEMBRANE DISTILLATION

There are many methods to make micro-porous membrane, such as: wet phase inversion, stretching, etching, sintering and TIPS (thermally induced phase separation) [35]. Each method has its own advantages. But the most important thing for micro-porous membranes for membrane distillation is that they should have a structure of highly open pores so that vapour can easily transfer through the pores. Membrane also should be highly hydrophobic.

A novel PVDF nanofiber membrane was developed by electrospinning in the present work in Part I. The details of PVDF nanofiber membrane preparation are also described in Part I. The PVDF nanofiber membrane was highly hydrophobic and highly porous. Its pore sizes were in a range appropriate for membrane distillation; i.e. its equilibrium contact angle was over 119° and mean pore sizes were in a range of 1-1.5 μm . Also, it was observed by SEM and AFM that the membrane had more open pores than the membranes fabricated by other methods. In the present research, it is demonstrated that this membrane has a great potential for producing drinking water from seawater.

Attractive characteristics of the electrospun nanofiber membranes were attributable to its i) high porosity, ii) interconnected open pore structure and iii) tailorable membrane thickness.

6. MEMBRANE CHARACTERISTICS

Membranes used in membrane distillation should satisfy the following requirements: i) Membrane should be thin, since the permeate flux is inversely proportional to the membrane thickness. ii) Membrane should not be wetted by the feed solution; i.e. the feed solution should not penetrate into the pores under the experimental conditions.

The phenomenon for membrane wetting can be quantified by the Laplace (Cantor) equation.

$$\Delta P_{entry} = \frac{2\gamma_L}{r_{p,max}} \cos \theta \dots \dots \dots (2-1)$$

Where ΔP_{entry} is the entry pressure difference, γ_L is the surface tension of the solution, θ is the contact angle between the solution and the membrane surface, and $r_{p,max}$ is the largest pore size. In view of Equation (2-1), these non-penetration conditions are: i) membranes should have reasonably small pore sizes (r_p , on the order of micrometer in MD). ii) solution to be treated should have a high surface tension.

As mentioned before, membrane materials suitable for MD, which have been used by many researchers, are polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene (PE) and polypropylene (PP). Those materials are hydrophobic (i.e., they have low surface energies.). The surface energy of these materials is listed in Table 2.1 [36]. PTFE, PVDF are expensive but they have very good chemical resistance and mechanical property. Even though PP and PE are cheaper, they are difficult to be fabricated to nanofibers.

Table 2.1 Surface energy of some materials used in membrane distillation

Membrane material	Surface energy (kJ/m)
PTFE	9.1
PP	30.0
PVDF	30.3
PE	33.2

Table 2.2 shows a number of commercial membranes used for MD research and their properties. In general, the porosity of the membranes used is in a range of 0.06 to 0.85, and the pore sizes are in a range of 0.2 to 2.0 μm . The thickness is in a range of 0.06 to 0.25 mm. However, the thermal conductivities of polymers depend on both temperature and the degree of crystallinity [36, 37]. The reported values of thermal conductivity are in a fairly large range, for example, PP, 0.15-0.20 $\text{Wm}^{-1}\text{K}^{-1}$, PVDF and PTFE, 0.22-0.45

$\text{Wm}^{-1}\text{K}^{-1}$ [36, 38]. As mentioned in Part I, the PVDF nanofiber membrane prepared in this study had porosity of 0.79 ± 4 ; average pore size $1.5 \mu\text{m}$ and thickness 0.15 mm . Since it was formed by random assembly of PVDF nanofibers by electrospinning technology, it had more open pores than membranes fabricated by other methods (The details of PVDF nanofiber membrane preparation and characterization are given in Part I.).

Table 2.2 Membranes used for membrane distillation

Researcher	Membrane material	Porosity	Pore size (μm)	Thickness (mm)	Company
Banat [37]	PVDF	0.75	0.45	0.11	Millipore
Bandini [38]	PP	N/A	0.2	1.5	Akzo
Drioli [39]	Teflon	N/A	N/A	N/A	Gelman
Gujit [40]	PP	0.7	0.1	0.055	Mitsubishi
Hanbury[41]	PTFE	N/A	N/A	N/A	Gortex
Hsu [42]	PTFE	0.85	0.5	0.175	Millipore
Khayet [43]	PTFE	0.80	0.45	0.178	Gelman
Kimura [44]	PTFE	N/A	0.2-3	0.08	Nitto
Lagana [45]	PP	0.7	0.45	0.12	Enka
Lawson [46]	PP	0.85	0.73	0.079	3M
Liu [47]	PTFE	0.85	1.0	0.15	Millipore
Martinez[48]	PVDF	0.75	0.22	N/A	Millipore
Sarti [49]	PTFE	0.6	2.0	0.6	Gelman
Schofield[50]	PVDF	0.75	0.45	0.11	Millipore
Ugrozov[51]	PTFE+PVDF	0.7	0.25	0.12	N/A

7. MEMBRANE PARAMETER, HYDROPHOBICITY AND SELECTIVITY

In MD process, membrane is a physical interface to separate vapour and liquid. MD performance depends on membrane material, pore size, porosity, thickness, thermal conductivity and module configuration. If the operating pressure of MD process is larger than the liquid entry pressure of water (LEP_w) of membrane, the feed solution will pass through the membrane and reduce the rejection [39]. If membrane porosity is high, it means vapour can more easily pass through membrane. The membrane (MD) porosity is directly related to the MD flux [52]. Thickness of the membrane will affect the vapour flux and it also affects the temperature difference between two sides of MD membrane. In other words, the thickness of the membrane is directly related to flux and temperature difference. Thinner membranes will increase the flux; however, thinner membranes will

increase the heat loss in MD process [53]. At the same time, mass and heat transfer are coupled in the membrane distillation process. Compared with other membrane separation processes, MD process is more complex.

Normally, the relationship between membrane distillation flux and membrane morphology can be described as [53]:

$$J \propto \frac{(r^\alpha)\varepsilon}{\tau\delta} \dots\dots\dots(2-2)$$

Where r is membrane average pore size (radius). α is constant of transport, i.e. for Knudsen diffusion: $\alpha = 1$ and for viscous flow: $\alpha = 2$. δ is membrane thickness. τ is membrane tortuosity and ε is porosity. Therefore, membrane distillation flux will increase as the membrane pore size and porosity increase, but will decrease as the thickness and tortuosity of membrane increase. It means geometric parameter of membrane also plays a great role in membrane distillation. Besides, the air in the membrane pores will affect the thermal conductivity of membrane. For a highly porous membrane, more air is in pores (in the membrane), in comparison with less porous membranes. The presence of air in the pores can reduce the heat loss during the membrane distillation process. Therefore, the membrane pore size should be larger but within a certain limit, since feed solution starts to penetrate into the pores when the pore size exceeds the limit. Of course, operating pressure will also affect the liquid (solution) penetration into the membrane pores.

The maximum pore size of membrane and operating pressure of membrane distillation should meet the requirement of Laplace equation:

$$P_{entry} = \frac{2B\gamma_L}{r_{max}} \cos \theta \dots\dots\dots(2-3)$$

Where, P_{entry} is the pressure of liquid entry into the membrane pore, γ_L is the surface tension of the solution, r_{max} is the maximum pore size of membrane, θ is the contact angle between the solution and the membrane surface and B is the geometric parameter of the membrane pore.

It is known that a small amount of surfactant may reduce solution surface tension dramatically. Therefore, it is necessary to remove surfactant in the feed solution.. Organic components also may reduce the surface tension of the feed solution. Franken and coworkers designed a method to measure the limiting concentration of organic components in feed for membrane distillation [12]. If the feed liquid pressure is higher than the liquid entry pressure, liquid will enter membrane pores, a phenomenon called water logging. Once membrane is completely soaked with liquid, membrane is wetted and membrane distillation process will stop. Even if only a fraction of pores are filled with liquid, the performance of membrane will deteriorate. That is the reason why new and better membranes need to be developed for membrane distillation.

Chapter 3 ADVANTAGES AND APPLICATION OF MEMBRANE DISTILLATION

1. ADVANTAGES OF MEMBRANE DISTILLATION

Membrane distillation was first conceived as a process that could operate with a minimum external energy requirement and a minimum expenditure of capital and land for plant [21]. The large vapour space required by a conventional distillation column can be replaced in membrane distillation by a small volume of a micro-porous membrane, which is generally on the order of 100 μm thick. While conventional distillation relies on high vapour velocities to provide intimate vapour-liquid contact, membrane distillation employs a hydrophobic micro-porous membrane to support a vapour-liquid interface. As the result, membrane distillation process and equipment can be much smaller, which translates to a savings in terms of real estate; and the required operating temperatures are much lower, because it is not necessary to heat process liquids above their boiling temperatures. Further, lower process temperatures combined with reduced equipment surface area results in less heat loss to the environment through the equipment surfaces. Feed temperatures in membrane distillation typically are in the range from 60°C to 90°C, although temperatures as low as 30°C had been used. Therefore, low-grade, waste heat and/or alternative energy sources such as solar and geothermal energy can be coupled with membrane distillation systems for a cost efficient, energy efficient liquid separation system. Indeed, membrane distillation systems powered by solar energy have been shown to be cost competitive with reverse osmosis in remote areas [54, 55].

Lower operating temperatures have also made membrane distillation attractive in the food industry where concentrated fruit juices can be prepared with better flavour and color [56] and in the medical field where high temperatures can sterilize biological fluids [57]. As a point of reference, a useful comparison can be drawn between membrane distillation and pressure-driven processes such as RO; nanofiltration (NF); ultrafiltration (UF) and microfiltration (MF), since they share many potential applications. Membrane distillation is a safer, more efficient process than RO for removing ionic components and

non-volatile organic compounds from water. Since membrane distillation is a thermally driven process, operating pressures are generally on the order of zero to a few hundred kPa, relatively low compared to pressure driven processes such as RO. Lower operating pressures translate to lower equipment costs and increased process safety.

Another advantage of membrane distillation systems is its efficiency in terms of solute rejection. Since membrane distillation operates on the principles of vapour-liquid equilibrium, 100% (theoretical) of ions, macromolecules, colloids, cells, and other non-volatile constituents are rejected. However, pressure-driven processes such as RO, NF, UF and MF have not achieved such high levels of rejection, i.e. 100%. Beside these, the desalination process by MD could be very economical.

In RO, NF, UF and MF, the membranes are the part of the process. In MD, the membrane acts only as a physical support for a vapour-liquid interface and does not distinguish between solution components neither on the chemical basis, nor does it act as a sieve. Therefore, membrane distillation membranes can be fabricated from chemically resistant polymers such as polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidenedifluoride (PVDF). Further, membrane fouling is less, because the pores are relatively large compared to the “pores” or diffusion pathways of RO/UF, and are not as easily clogged. Despite all these advantages of membrane distillation, it has received relatively less attention to use it in distillation and desalination industries. The major reason is the lack of suitable membranes for MD. Due to water shortage and energy shortage, MD process will become a more desirable method for desalination in the near future.

2. HISTORY OF MEMBRANE DISTILLATION

The earliest research related with membrane distillation may be that of Kober [58]. He observed that the volume of ammonia sulphate in a sealed cellulose nitrate bag decreased gradually. At the same time, ammonia sulphate crystal appeared outside of the sealed pocket. He noted even at very low temperature, the evaporation rate is high. Then, he

gave two assumptions to this phenomenon: i) the material of sealed bag behave like a gel. Water can diffuse from inside of the sealed bag to outside. This explanation is close to the mechanism of pervaporation. ii) the membrane is porous. Due to surface tension and other factors, only water vapour can pass through. This assumption could not explain the phenomenon of crystal appearing at the outside of the bag. But it is truly the mechanism of membrane distillation. As reverse osmosis, the driving force to utilize membrane distillation is focused on an alternative desalination process to replace the highly energy consuming conventional thermal distillation. Miller applied for a patent in 1964 and the patent was approved in 1968 [59]. The process of Miller is very close to membrane distillation; i.e. feed solution evaporates at a hydrophobic interface. Vapour passes through the hydrophobic interface and condenses. He emphasized that the membrane pore should be small enough to prevent the liquid from going into the membrane pore. He also thought that the operating pressure should be proportional to the concentration of feed solution. This idea may have come from reverse osmosis phenomenon. In 1968, Bodell developed a process, which was very close to sweep gas membrane distillation; i.e. the feed solution is fed to the outer side of hollow fibers and air passes through the inner side of the hollow fibers. The passing gas will carry water vapour, which will be condensed by an outer condenser [60]. Weyl suggested a direct contact membrane distillation process at 1967. In his research, he realized that the temperature difference was the real driving force for membrane distillation and designed a multi-step process to recover the latent heat [61]. A seawater desalination process based on evaporation through membrane was proposed and tested by Findley [62] in the United States and by Van Haute and Henderyckx [63] in Europe in late sixties, but it has not been further developed. This process obtained renewed attention when Gore proposed a spiral-type module using a Gore-Tex membrane in 1982, under the name "Gore-Tex Membrane Distillation" [64]. The Swedish Development Co. also reported test results in 1983 [25]. Enka AG presented a "Trans Membrane Distillation" module using hollow fibers in 1984, at the Europe-Japan Joint Congress on Membranes and Membrane Processes [65]. At the Second World Congress on Desalination and Water Reuse in 1985, several papers were presented [66-69]. This renewed interest is a result of the development of various porous hydrophobic membranes made of polytetrafluoroethylene (PTFE) or

polypropylene.

After the 90s, membrane distillation still focused on the mechanism research, even though the theoretical breakthrough on membrane distillation did not show up. Many researches have been only the further proof of membrane distillation process [70, 71]. But those researches have reflected that membrane distillation has a great potential to meet the requirement of industry and it is slowly but firmly getting into commercialization.

Recently, as the energy price soars up and global warming becomes more serious, more attention is paid to membrane distillation than before. Application field of membrane distillation has been considerably widened. Beside desalination, it was applied for the removal of toxic volatiles from waste water, cyanide waste water concentration, fruit juicy concentration at low temperature, water recycle at air space craft and so on. Table 3.1 shows the summary of membrane distillation researches and applications.

Table 3.1 Summary of membrane distillation researches and applications

Researcher	Year	Application	Type	Status
Weyl	1967	Desalination	DCMD	Patent
Bodell	1968	Desalination	DCMD	Patent
Rodgers	1975	Distillation	DCMD	Patent
Gore	1982	Desalination	DCMD	Commercial
Carlsonn	1983	Desalination	AGMD	Commercial
Gore	1985	Desalination	DCMD	Commercial
Andersson	1985	Food concentration	AGMD	Pilot plant
Kimura	1987	Juice concentration	AGMD	Lab
Drioli	1987	Salt concentration	DCMD	Lab
Lefebvre	1988	Food concentration	OD	Patent
Ford	1988	Desalination	DCMD	Patent
Bandini	1988	Alcohol separation	VMD	Lab
Kubota	1988	Desalination	DCMD	Pilot plant
Sakai	1988	Blood concentration	DCMD	Lab
Franken	1988	Alcohol separation	DCMD	Lab
Schofield	1989	Wastewater	DCMD	Pilot plant
Udriot	1989	Alcohol removal	DCMD	Lab
Gostoli	1989	Alcohol removal	DCMD	Lab

Calibo	1989	Bio separation	DCMD	Lab
Wu	1989	Salt concentration	DCMD	Lab
Semmens	1990	NH ₃ concentration	DCMD	Lab
Ohta	1990	Desalination	DCMD	Pilot plant
Calabro	1990	Waste water	DCMD	Lab
Nakao	1990	Desalination	DCMD	Pilot plant
Loeb	1990	Evaporation	AGMD	Lab
Calabro	1990	Dye concentration	DCMD	Lab
Lefevre	1990	Food concentration	ODMD	Patent
Hogan	1991	Solar desalination	DCMD	Lab
Betts	1991	Volatile removal	DCMD	Lab
Thompson	1991	Juice concentration	OD	Commercial
Bandini	1992	Volatile removal	VMD	Lab
Hogan	1992	Solar desalination	DCMD	Pilot plant
Mulyono	1992	Thermal pump	AGMD	Lab
Tomaszewska	1993	Acid concentration	DCMD	Lab
Sheng	1993	Desalination	DCMD	Pilot plant
Tanigaki	1993	Humidity control	AGMD	Lab
Shen	1993	Cyanide recovery	DCMD	Lab
Depeyre	1993	Alcohol /water	DCMD	Lab
Bryk	1993	Concentration	DCMD	Lab
Saaredra	1993	Volatile removal	VMD	Lab
Dytnersky	1993	Radioactive water	DCMD	Lab
Zolotarev	1994	Metal ion	DCMD	Lab
Rajalo	1994	NH ₃ absorption	DCMD	Lab
Udriot	1994	Azo-component	AGMD	Lab
Qureshi	1994	Alcohol recovery	VMD	Lab
Calabro	1994	Juice concentration	DCMD	Lab
Tomaszewska	1995	Acid concentration	DCMD	Lab
Gostoli	1995	Alcohol removal	DCMD/OD	Lab
Tricoli	1995	NH ₃ absorption	AGMD	Lab
Deblay	1995	Concentration	OD	Patent
Elkina	1995	Azo-component	AGMD	Lab
Chemielewski	1995	Nuclear water	DCMD	Lab
Godino	1996	Desalination	DCMD	Lab
Scarab	1996	Family use	AGMD	Commercial
Massao	1997	LiBr concentration	DCMD	Lab
Chemielewski	1997	Radioactive water	DCMD	Lab
Cabassud	1998	VOC removal	MF+VMD	Pilot plant
Madsen	1998	Air craft	VMD	Lab
Drioli	1998	Juice concentration	OD	Lab
Bandini	1998	VOC removal	VMD	Pilot plant
Mansouri	1999	Oil treatment	DCMD	Lab
Banat	2000	Alcohol/water	AGMD	Lab
Garcia-Payo	2000	Alcohol/water	AGMD	Lab

Gryta	2001	Organic/NaCl	ODMD	Lab
Banat	2002	Desalination	DCMD	Lab
Wirth	2002	Desalination	DCMD	Lab
Brodard	2003	Desalination	ODMD	Lab
Koschikowski	2003	Desalination	DCMD	Lab
Alves	2004	Juice	DCMD	Lab
Ezeji	2004	Fermentation	DCMD	Lab
Alklaib	2005	Desalination	DCMD	Lab
Anheden	2005	Denitrogenation	VMD	Lab
Gujit	2005	Desalination	AGMD	Lab
Mohammadi	2005	Organic solution	VMD	Lab
Alves	2006	Juice	DCMD	Lab
Ding	2006	Ammonia	AGMD	Lab
Drioli	2006	Desalination	AGMD	Lab
Gryta	2006	Water purification	DCMD	Lab
Mariah	2006	Concentrated brines	DCMD	Lab
Arvanitoyannis	2007	Waste water treatment:	DCMD	Lab
Buchaly	2007	Reactive distillation	DCMD	Lab
El-Bourawi	2007	Ammonia	DCMD	Lab

Table 3.1 shows that at the beginning of membrane distillation development, the researches were focused on the desalination market. But most researches were using lab scale equipment. With the progresses of research, application of membrane distillation is expanding. It can be used as: (1) Product concentration while maintaining bacteria free environment, (2) Binary-mixture separation, (3) Volatile component removal at low temperature, (4) Low temperature concentration, (5) Portable fresh water production by desalination, (6) Heavy water separation and recovery at nuclear water plant, (7) Space craft water supply, (8) Electroplating wastewater treatment.

3. RESEARCH OBJECTIVES OF MEMBRANE DISTILLATION

As mentioned earlier, membrane distillation process has many advantages. Based on these advantages some patents have been issued and few commercial systems constructed (Table 3.1). After 50 years of research, however, large scale commercial applications of membrane distillation have not been achieved. Compared with reverse osmosis technology, membrane distillation process can produce higher quality product, but the

membrane distillation are: 1) The membranes that are suitable for the membrane distillation process should have High porosity, High hydrophobicity and Reasonable pore size, but the existing membranes do not satisfy all of those requirements. 2) The mechanism of membrane distillation is still not well-known in sufficient detail. Since membrane distillation couples mass and heat transfer, it is difficult to simulate the process. 3) There are four types of membrane distillation. Each one has its own advantage and disadvantage. A proper design in membrane distillation module is required to reduce the heat loss. 4) The industry is not ready for the change.

The most important thing for membrane distillation is to find a suitable membrane material. As described in Part I, PVDF nanofiber membrane seems to be a reasonable choice for membrane distillation because of its enhanced hydrophobicity and large porosity. Moreover, it is a totally new attempt to use nanofiber membranes for membrane desalination.

In Part II, AGMD process was chosen as a target process for membrane distillation research. Since AGMD is the most complex configuration of MD, AGMD also can produce high quality product and avoid large heat loss. It has most complex heat and mass transfer process among all types of MD processes. Understanding AGMD process will be of great help to understand other MD processes.

In the present research, a novel PVDF nanofiber membrane developed in the laboratory was used in air gap membrane distillation (AGMD) for desalination of saline water and concentration of aqueous ethanol solutions. A modeling of AGMD for desalination was also attempted. Experimental data as well as the theoretical analysis based on the experimental data are presented.

Chapter 4 MECHANISM OF AIR GAP MEMBRANE DISTILLATION (AGMD)

1. THEORETICAL MODELING ANALYSIS OF AGMD FOR ONE VOLATILE COMPONENT (WATER)

The classification of membrane distillation systems is related to the condensation methods adopted. Generally, membrane distillation systems are classified into four different categories: Direct contact membrane distillation (DCMD), Air gap membrane distillation (AGMD), Sweep gas membrane distillation (SGMD) and Vacuum membrane distillation. DCMD and AGMD do not need an external condenser. They are mostly suitable for applications where water is the permeating flux. SGMD and VMD are typically used to remove volatile organics or dissolved gas from an aqueous solution.

1.1. Vapour Liquid Equilibrium of Membrane Distillation

The following analysis is based on only one volatile component. As mentioned earlier, the driving force in membrane distillation is vapour pressure difference across the membrane, which can be imposed by a temperature difference across the membrane, or by a vacuum or a sweep gas on the permeate side of the membrane. To understand the MD process, several assumptions have to be made.

One of the first assumption in membrane distillation is that the kinetic effect is zero or negligible at the vapour/liquid interface. In other words, the vapour and liquid are assumed to be in the equilibrium state corresponding to the temperature at the membrane surface and the pressure within the membrane pores. The following Equation (4-1), named as Kelvin equation, shows the relation between liquid saturated pressures (equilibrium state) with respect to other parameters of the system:

$$P^0 = P_{\infty}^0 \exp\left[\frac{2\gamma_L}{rcRT}\right] \dots\dots\dots (4-1)$$

Where, P^0 is the pure liquid saturation pressure above a convex liquid surface with radius of curvature r , P_∞^0 is the pure liquid saturation pressure above a flat surface, γ_L is the liquid surface tension, C is the liquid molar density, R is the gas constant, and T is temperature.

With the vapour-liquid equilibrium assumption, vapour-liquid equilibrium equations can be applied to determine the partial vapour pressure of each component on each side of the membrane. This gives the boundary conditions for mass transfer within the membrane. For pure liquids the partial vapour pressure is equivalent to the component's saturation pressure P^0 , which also can be determined with the Antoine equation (4-2):

$$P^0 = \exp\left[A - \frac{B}{C + T}\right] \dots \dots \dots (4-2)$$

Where P^0 is in Pa, T is the temperature in K, A , B and C are constants which are reported (water: 23.1964, 3816.44, -46.13; ethanol: 23.4170, 3578.91, -50.50) [72].

It is important to remember that the total pressure, within the membrane may be greater than the saturation pressure due to the partial pressure exerted by dissolved air. As a rule, the total pressures in the membrane are usually equivalent to the static pressure above the liquids in the feed and in permeate holding tanks.

For non-ideal binary mixtures the partial pressures can be determined from:

$$P_i = y_i P = x_i a_i P_i^0 \dots \dots \dots (4-3)$$

Where y_i and x_i are the vapour and liquid mole fractions of i th component respectively,

P is the total pressure, P_i^0 is the saturation pressure of pure i th component, and a_i is the activity coefficient of i th component in the solution. The value of a_i , which is a function of temperature and composition, can either be calculated from one of many available equations or it can be estimated from the available experimental data. The van Laar and NRTL equations have been used successfully in modeling MD of organic-water solutions [73], and Schofield [74-76] used published experimental data to determine the activity of water in NaCl solutions:

$$a_{\text{water}} = 1 - 0.5x_{\text{NaCl}} - 10x_{\text{NaCl}}^2 \dots\dots\dots(4-4)$$

Where, a_{water} is the activity coefficient of water and x_{NaCl} is the mole fraction of sodium chloride (NaCl).

One problem that arises when applying Equations (4-2) and (4-3) is that the complex relationship between P_i and the liquid temperature and composition mandates an iterative solution to the membrane distillation heat and mass transfer equations. However, an approximate solution to the membrane distillation equations may be obtained by employing a couple of simplifying assumptions. First, the Clausius-Clapeyron equation is used to simplify the vapour pressure-temperature relationship:

$$\frac{\Delta P^0}{\Delta T} \approx \frac{dP^0}{dT} = \frac{P^0 \Delta H_v}{RT^2} \dots\dots\dots(4-5)$$

Where, P^0 is the saturation pressure and ΔH_v is the molar latent heat of vaporization [77-78]. The approximation for ideal dilute solutions simplifies the vapour pressure-composition relationship to:

$$P_i = P_i^0 (1 - x) \dots \dots \dots (4 - 6)$$

Where, x is the molar fraction of solute in solution.

When membrane distillation process is applied for desalination, mass transfer is controlled by the following three steps: i).vapour evaporates from liquid, ii) vapour permeates through membrane pore and iii) vapour condenses. At the equilibrium state, the second mass transfer is a dominate step. According to non-equilibrium thermodynamic analysis by Katchalsky [79], membrane distillation flux is:

$$J = \frac{\varepsilon}{\tau} \left[D \nabla c + L \frac{\nabla T}{T} \right] \dots \dots \dots (4 - 7)$$

Where, D is mass diffusion coefficient of water vapour at the average temperature in the air cavity, c is concentration of the volatile component and L is the heat diffusion coefficient. ε is membrane porosity, τ is membrane tortuosity. J is membrane distillation flux, ∇c , is concentration gradient, and ∇T is temperature gradient

On comparing the heat diffusion coefficient with the mass diffusion coefficient D , heat diffusion coefficient, L is too small [80]. Heat diffusion effect could be ignored. The concentration of can be substituted by the vapour pressure, assuming a linear relationship between the vapour pressure and the concentration in the membrane. So, Equation (4-7) can be written to:

$$J = K(P_1 - P_2) \dots \dots \dots (4 - 8)$$

Where, K is related to the mass transfer in the membrane phase and depends on the membrane structure. P_1 and P_2 are water vapour pressure at temperature of feed solution and at temperature of cooling surface, respectively. In a MD process, Knudsen diffusion and molecular diffusion models have been indicated most appropriate [80].

A linear relationship between the water vapour trans-membrane flux and the vapour pressure difference across the membrane is adequately described by Equation (4-8). The mass transfer in membrane distillation also can be described by using temperature difference:

$$J = K \left[\frac{dp}{dT} \right] (T_1 - T_2) \dots \dots \dots (4 - 9)$$

Where, T_1 and T_2 are the temperature of feed solution and the temperature of cooling side, respectively. $\frac{dP}{dT}$ can be calculated from Clausius-Clapeyron equation (Equation (4-5)).

Figure 4.1 illustrates the possible mass transfer resistances in membrane distillation using an electrical analog. Boundary layers next to the membrane can contribute substantially to the overall mass transfer resistance. Indeed molecular diffusion across the boundary layers is often the rate limiting step in membrane distillation mass transfer. Resistance to mass transfer within the membrane results from transfer of momentum to the supported

membrane (viscous or momentum transfer resistance), or from collisions of a diffusing molecule with other molecules (molecular diffusion resistance) or with the membrane itself (Knudsen resistance). The resistances shown in Figure 4.1 are arranged as described by the dusty-gas model (DGM), which is a general model for mass transport in porous media [25, 74, 81-87]. The DGM also includes a pathway for surface diffusion, but this mechanism is considered negligible in membrane distillation modeling. By definition of the membrane distillation phenomenon, molecule-membrane interaction is low and the surface diffusion area in membrane distillation membranes is relatively small (compared to the pore area). The surface diffusion mechanism is included here only as a reminder of its existence, as it may become important with respect to the development of hydrophilic membranes for membrane distillation.

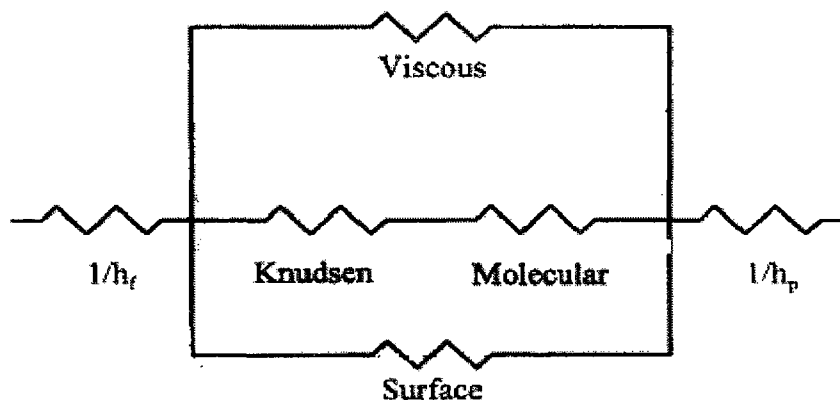


Figure 4.1 Mass transfer resistances inside the membrane and at the boundary layers

A fundamental difference among membrane distillation models found in literatures is the arrangement of the transport resistances in the circuit. In most cases, one or more of the mass transfer resistances may be omitted. For example, in most VMD systems the membrane pores are extremely small compared to the mean free path of the diffusing molecules. Therefore the number of molecule-molecule collisions is negligible compared to the number of molecule-pore wall collisions, and the molecular diffusion resistor may be omitted. Additionally, the vacuum on the permeate side of the membrane prevents the

be omitted.

1.2. Mass Transfer

As motioned before, the AGMD process is the most complex membrane distillation process. Figure 4.2 shows the temperature profile in AGMD.

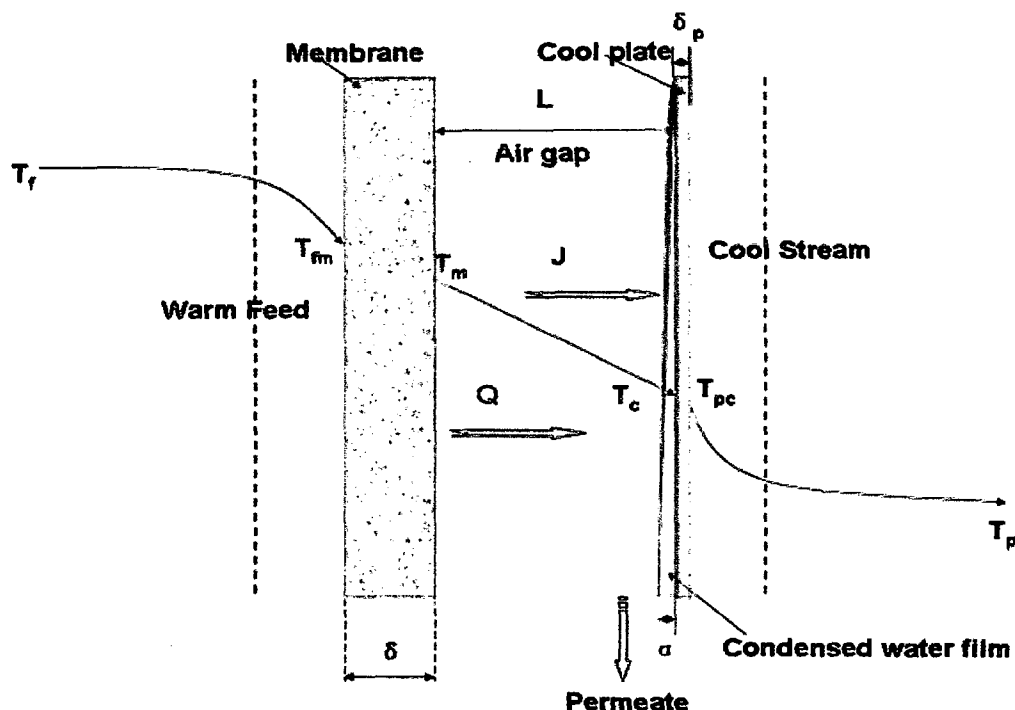


Figure 4.2 Temperature profile of AGMD process

In an AGMD process shown in Fig. 4.2, the vapour from the feed of a higher temperature permeates through the hydrophobic membrane, and the air gap, and then condenses on the cooling surface. Since the characteristic length of the transfer area is typically much bigger than the combined thickness of the membrane, air gap and the cooling plate, the mass transfer in the AGMD process can be reasonably assumed to be one-dimensional.

In addition, the air gap is typically a couple of millimetres so that the air inside is

In addition, the air gap is typically a couple of millimetres so that the air inside is basically stationary. Therefore, a simple mechanistic model of heat and mass transfer for an AGMD process can be established. Let us consider the mass transfer involved in the AGMD process. The vapour, evaporated on the membrane surface, permeates through the porous structure of the membrane via a combined effect of Knudsen diffusion, Poiseuille flow and molecular diffusion. Then the vapour passes through the air gap by molecular diffusion and reach the cooled surface on which the permeate vapour is condensed. However, a thin water film will also form on the cooling surface as shown in Fig. 4.2. The film will also affect the heat transfer. But it is hard to measure the thickness of the water film and it is very thin. In order to simplify the calculation, the effect of condense water film was omitted.

For the vapour permeation through the micro porous membrane, the permeate vapour flux depends on the vapour pressure difference across the membrane and is given by equation (4-8). In equation (4-8), the membrane distillation flux is given as proportional to the vapour pressure difference. In fact, the real driving force of membrane distillation is the temperature difference (equation (4-9)). Considering membrane thickness, the Equation (4-9) can be rewritten as:

$$J = K' \frac{\Delta P}{\delta} = \frac{K'}{\delta} \left(\frac{dP}{dT} \right)_T \Delta T = \frac{K_1}{\delta} \Delta T \dots\dots\dots (4-10)$$

Where, J is the membrane distillation flux, ΔP the cross-membrane vapour pressure difference, and δ is the membrane thickness. K' depends on the domination mode of vapour transfer through the membrane. And also:

$$K_1 = K' \left(\frac{dP}{dT} \right)_T \dots\dots\dots (4-11)$$

One of the mass transfer mechanisms in MD is by diffusive transport of water vapour across the micro porous hydrophobic membrane. The mode of diffusion for water vapour through the stagnant gas phase of the membrane pore can be described either by Knudsen diffusion or molecular diffusion mechanism depending on the pore size characterized by Knudsen number ' K_n ', which is the ratio of mean free path, λ , and pore diameter [88].

$$K_n = \frac{\lambda}{2r} \dots\dots\dots(4-12)$$

Where

$$\lambda = \frac{k_B T}{P \sqrt{2} \pi \sigma^2} \dots\dots\dots(4-13)$$

Where, k_B is the Boltzmann constant, and σ is the collision diameter of the molecule. For saturated water vapour molecule ($\sigma = 2.7 \text{ \AA}$) at 60°C and 20 kPa , the mean free path is $0.7 \text{ }\mu\text{m}$, which is comparable to the typical pore sizes found in membrane distillation membranes. Therefore, the molecule-pore wall to molecule-molecule collision ratio is on the order of unity, and all of the diffusion mechanisms must be considered when modeling membrane distillation process.

● Knudsen diffusion

When the membrane pore size is much smaller than the mean molecular free path ($K_n \geq 10$), the molecules tend to collide more frequently with the pore wall. Under these conditions the mode of water transport is by Knudsen diffusion, which can be represented by Equation (4-14) [84]:

$$J_k = \frac{2r\varepsilon}{\tau\delta} \sqrt{\frac{8M}{\pi RT}} \Delta P \dots\dots(4-14)$$

Where ε is membrane porosity, τ is membrane tortuosity, M is water molar mass, R is gas constant, T is absolute temperature, and P is vapour pressure.

● **Molecular diffusion.**

When air is entrapped within the membrane pores the pressure in the pore becomes nearly equal to atmospheric pressure and K_n becomes lower. When $K_n < 0.01$, the collisions between the gas molecules themselves are more frequent, the mode of diffusion is called molecular diffusion. Water flux across the membrane by this mechanism is represented by Equation (4-15) [89].

$$J_m = \frac{1}{Y_{ln}} \frac{D\varepsilon}{\tau\delta} \frac{M}{RT} \Delta P \dots\dots(4-15)$$

Where $D = 2r$ is membrane pore diameter and ' Y_{ln} ' is logarithmic mean mole fraction of air at the pore inlet and at the pore outlet.

Both equations are useful for predicting the mass transfer through the membrane, each of them having its own limitations. The Knudsen model requires details of membrane pore's geometry (such as pore radius, membrane thickness and tortuosity), whereas molecular diffusion model is not valid at lower partial pressure of the air (as ' Y_{ln} ' tends to zero) [50].

● **Poiseuille flow**

When the pore size is much larger than the mean free path K_n may become < 0.01 . Then,

the Poiseuille flow will become dominant in MD process, which can be represented as equation (4-16) [50]:

$$J_p = \frac{1}{8\mu\delta} \frac{r^2 \varepsilon}{\tau} \frac{M}{RT} \Delta P \dots\dots (4-16)$$

Where, μ is fluid viscosity.

If the membrane pore size is close to mean free path of water vapour molecule, the three type of diffusion will contribute to AGMD process. In most time, electrical analogue is useful to analyse the process. As shown in Fig. 4.3, it is obvious that the total resistance consists of several component resistances. Compared with the similar electrical analogue shown in Fig. 4.1, the boundary layer resistance and the surface contribution is ignored and the air gap resistance is added. The flux through each resistance component is given by J .

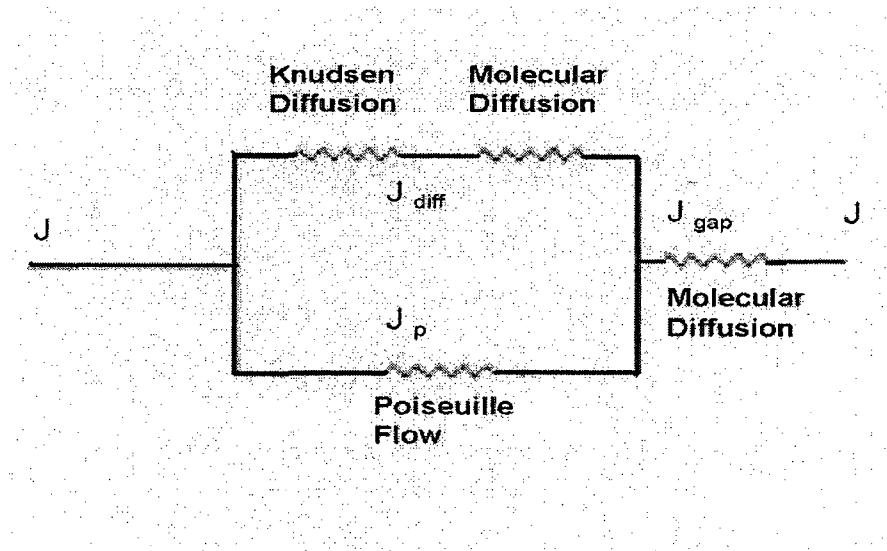


Figure 4.3 Resistance and mass flow mechanism of AGMD process

In Fig. 4.3, the flux of AGMD can be calculated either from the parameters for mass transfer through membrane or for mass transfer through air gap. Since both fluxes are equal to the overall flux J .

$$J = J_{diff} + J_p = J_{gap} \dots\dots(4-17)$$

If three types of flow exist in the AGMD process, according to the analysis of mass transfer through micro porous membrane given above, AGMD flux will be represented by:

$$J = J_{diff} + J_p = \left[\frac{1}{\frac{1}{\frac{2r\varepsilon}{\tau\delta} \sqrt{\frac{8M}{\pi RT}}} + \frac{1}{Y_{ln, air} \frac{D\varepsilon}{\tau\delta} \frac{M}{RT}}} + \frac{1}{8\mu} \frac{r^2\varepsilon}{\tau\delta} \frac{M}{RT} \right] \Delta P \dots\dots(4-18)$$

In equation (4-18) Δp is the vapour pressure difference across the membrane. Usually, Poiseille flow can be ignored in the range of pore sizes involved in MD membranes. Then, Equation (4-18) will become:

$$J = J_{diff} = \left[\frac{1}{\frac{1}{\frac{2r\varepsilon}{\tau\delta} \sqrt{\frac{8M}{\pi RT}}} + \frac{1}{Y_{ln, air} \frac{D\varepsilon}{\tau\delta} \frac{M}{RT}}} \right] \Delta P \dots\dots(4-19)$$

If the vapour pressure difference across the membrane, membrane geometric properties, vapour molecular weight and temperature are known, the AGMD flux can be calculated from Equation (4-19). The equation does not contain any parameters of AGMD module. The only parameter related with operating conditions is temperature and vapour pressure. Except membrane geometric properties, all the data can be obtained from a classic chemistry and physics hand book. Equation (4-19) therefore allows the theoretical estimate of the AGMD process.

For an AGMD process, after water vapour transfers through a membrane, it will diffuse through the air gap and condenses on the surface of cooling plate. The flow mode will follow molecular diffusion. The flux of water molecules through the air gap is J_{gap} . Assuming the flow mode is the same as that of ideal gas, it can be described by the following equation:

$$J = J_{gap} = \frac{D_p}{RTL} \Delta P \dots\dots (4-20)$$

Where, D_p is the diffusion coefficient of water vapour through air gap. Here, Δp is the vapour pressure difference across the air gap.

According to Gates, [90], the diffusion coefficient of water vapour through air, D_p as a function of temperature is:

$$D_p = 21.2 \times 10^{-6} \times [1 + 0.0071 \times (T - 273.15)] \dots\dots (4-21)$$

Where T is absolute temperature.

Combining Equations (4-20) and (4-21), if air gap distance, temperature and vapour pressure are known, the AGMD flux can be calculated at a specific operating condition.

1.3. Heat transfer

As Fig. 4.2 shows, for an AGMD process, heat passes through the boundary layer on the feed side to the surface of the membrane. On the surface, volatile component evaporates and the vapour passes through membrane pore and air gap. At same time, heat will transfer membrane and air gap. Finally, vapour condenses on the surface of the cooling plate. Heat passes through the cooling plate and reaches the cooling stream. The condensed liquid is removed so that the process can be carried on.

In order to simplify the analysis, the following assumptions are made:

- a) Flow rate of cooling stream will not affect the warm feed concentration.
- b) At the membrane surface of the warm feed side and at the surface of the cooling plate, vapour and liquid are at equilibrium state.
- c) Phase change resistance is much smaller than heat resistance.
- d) Effect of concentration polarization is ignored.

A typical AGMD process is exactly following the diagram of Fig. 4.2. For an effective membrane distillation system, where membrane thickness is δ , membrane thermal conductivity is k_m , air gap distance is L , thermal conductivity of air gap is k_l , the thickness of cool plate is δ_p , thermal conductivity of cooling plate is k_2 , hot side convection heat transfer coefficient is h_f and cool stream side convection heat transfer coefficient is h_p , heat transfer of AGMD can be described by the following analysis.

- Hot side boundary layer:

$$Q = h_f (T_f - T_{fm}) \dots \dots \dots (4 - 22)$$

Where, Q is heat flux from the warm feed to the membrane surface. T_f is the temperature of the warm feed solution. T_m is the temperature on the membrane surface.

- Across membrane:

$$Q = N \times \Delta H + \frac{k_m}{\delta} (T_{fm} - T_m) \dots \dots \dots (4 - 23)$$

Where N is evaporated vapour flux, ΔH is latent heat of vaporization. T_{fm} is the temperature on the membrane surface. T_m is the temperature of membrane on other side; k_m is the thermal conductivity of membrane.

- Across air gap :

$$Q = N \times \Delta H + \frac{k_l}{L} (T_m - T_c) \dots \dots \dots (4 - 24)$$

Where N is evaporated vapour flux. ΔH is latent heat of evaporation. T_m is the temperature of membrane on the air gap side. k_l is the thermal conductivity of air gap. T_c is the temperature on the the surface, facing the air gap, of the cooling plate. As mentioned before, heat transfer through condensed water film was ignored.

- Across cooling plate:

$$Q = \frac{k_2}{\delta_p} (T_c - T_{pc}) \dots \dots \dots (4 - 25)$$

Where T_c is the temperature on the surface, facing the air gap, of cooling plate. T_{pc} is the temperature of the surface, facing the cooling stream, of the cooling plate.

- Cooling stream boundary layer:

$$Q = h_p (T_{pc} - T_p) \dots \dots \dots (4 - 26)$$

Where T_{pc} is the temperature at the surface, facing cooling water of the cooling plate, T_p is the bulk temperature of cooling stream.

Assuming evaporated vapour flux, N , is equal to membrane distillation permeate flux J , it can be obtained from mass transfer analysis are from experiment. If the heat transfer coefficients are known, and also the temperature of feed solution and the temperature of the cooling stream are known, combining Equation (4-22) to Equation (4-26), the temperatures at different surfaces of the AGMD process can be obtained. As an AGMD module is chosen, the heat transfer coefficient related to the membrane material and the AGMD configuration can be calculated. The latent heat for water can be found in the literature.

The thermal conductivity of a porous membrane is represented by:

$$k_m = (1 - \varepsilon)k_{material} + \varepsilon k_g \dots\dots\dots (4 - 27)$$

Where, k_m is the thermal conductivity of the porous membrane, $k_{material}$ is the thermal conductivity of polymeric material, and k_g is the thermal conductivity of air. As the membrane thickness is known, the heat transfer coefficient of the porous membrane can be given by:

$$h_m = \frac{k_m}{\delta} \dots\dots\dots (4 - 28)$$

Where h_m is the heat transfer coefficient of the porous membrane, and δ is the thickness of the membrane.

The hot side boundary layer heat transfer coefficient (h_f) and the cold side boundary layer heat transfer coefficient (h_p) are governed by the operating condition. Normally, the boundary layer heat transfer coefficient is analogized with the mass transfer coefficient as Nusselt number:

$$Nu = a Re^b Pr^c \dots\dots\dots(4-29)$$

- Re , Reynolds number $Re = (\rho \cdot v \cdot d_h) / \mu$ (ρ : fluid density, v : fluid velocity, d_h : hydraulic diameter, μ : fluid viscosity)
- Pr , Prandtl number $Pr = (C_p \cdot \mu) / k$ (C_p : specific heat, μ : fluid viscosity, k : thermal conductivity)

For most of the fluid transfer, a , b , and c have the empirical values: i.e. $a = 0.138$ $b = 0.672$. c has two value. For hot fluid, $c = 0.3$. For cool fluid, $c = 0.4$. In AGMD process, the boundary layer heat transfer coefficient can therefore be calculated as [91, 92]:

$$Nu = 0.138 Re^{0.672} Pr^{0.3} \dots\dots\dots(4-30)$$

or

$$Nu = 0.138 Re^{0.672} Pr^{0.4} \dots\dots\dots(4-31)$$

Once the heat transfer coefficients are known, temperatures at the different surfaces of the AGMD process can be obtained. As described before, the temperature difference between two sides of membrane is the driving force for membrane distillation.

1.4. Temperature polarization

In a MD process, normally, a large energy flux increases the temperature difference between the hot water bulk and the evaporating surface and between the evaporating surface and the condensing surface, which leads to a smaller net driving temperature difference between the evaporating and condensing water surfaces. This phenomenon is known as temperature polarization, which reduces the water vapour flux.

Temperature polarization coefficient is generally used to quantify the magnitude of the boundary layer resistances over the total heat transfer resistance. It is defined as:

$$\Theta = \frac{T_{fm} - T_m}{T_f - T_p} \dots\dots\dots(4-32)$$

Θ , often used as indirect index of efficiency for MD process, falls between 0.4 and 0.7 for a satisfying design of the system [21], and approaches unity for mass transfer limited operations.

In DCMD process, evaporation happens at hot side surface of membrane, while condensation conducted at the surface of cooling side. Therefore, the temperature polarization can be described by Equation (4-31). But in AGMD process, the evaporation takes place at the hot side surface of membrane and the condensation takes place at the surface of the cooling plate. The temperature polarization coefficient (Θ') should include membrane and air gap. Then,

$$\Theta' = \frac{T_{fm} - T_c}{T_f - T_p} \dots\dots\dots(4-33)$$

That means the membrane and the stagnant air film of air gap are the main resistances of AGMD process. As shown in Figure 4.2, $T_m \gg T_c$, So, the value of Θ' will larger than the value of Θ .

2. THEORETICAL MODELING ANALYSIS OF AGMD FOR TWO VOLATILE COMPONENTS (ETHANOL / WATER)

If the AGMD process involves two or more volatile components, the theoretical analysis will become more complex. When two components are involved in AGMD process, such as ethanol/water mixtures, the analysis of mass and heat transfer will still follow the similar mechanism as that of a single component. Assuming each volatile component is independent, i.e. the behaviour of evaporation and mass and heat transfer of each volatile component are independent, the calculation follows that of the single volatile component.

2.1. Mass transfer

Since the theoretical analysis of mass transfer for a binary system is too complicated, it is not attempted in this thesis. Rather, the experimental flux data for the components (ethanol and water in this case) will be used in the following heat transfer analysis.

2.2. Heat transfer

All equations from Equation (4-22) to Equation (4-31) that have been derived for the one volatile component system are applicable for the two component system, except;

- a) To evaluate h_f to be used in Equation (4-22), the physicochemical properties of the ethanol/water mixture corresponding to the feed solution mixture should be used, ignoring the concentration polarization.
- b) ΔH in Equations (4-23) and (4-24) should correspond to that of the permeate mixture. It is assumed that the latent heat of evaporation of a binary mixture is the sum of the latent heat of evaporation weighed by the mole fraction of each component.

Then,

$$\Delta H_{mix} = x_w \Delta H_w + x_e \Delta H_e \quad (4-34)$$

Where

$$x_w = \frac{J_{water} / M_{water}}{J_{water} / M_{water} + J_{ethanol} / M_{ethanol}} \quad (4-35)$$

And,

$$x_e = \frac{J_{ethanol} / M_{ethanol}}{J_{water} / M_{water} + J_{ethanol} / M_{ethanol}} \quad (4-36)$$

Therefore

$$(J_{water} + J_{ethanol}) \Delta H_{mix} = J_{water} \Delta H_w + J_{ethanol} \Delta H_e \quad (4-37)$$

ΔH_w , ΔH_e and ΔH_{mix} are the latent heat of evaporation of water, ethanol and water-ethanol mixture, respectively. J_{water} and $J_{ethanol}$ are the flux of water and ethanol, respectively. x_w and x_e are mole fraction of water and ethanol in the permeate, respectively.

2.3. Temperature polarization

Equation (4-33) can be used for the temperature polarization.

Chapter 5 AGMD SYSTEM AND EXPERIMENT

1. AGMD SYSTEM

The schematic representation of the AGMD system used is shown in Fig. 5-1:

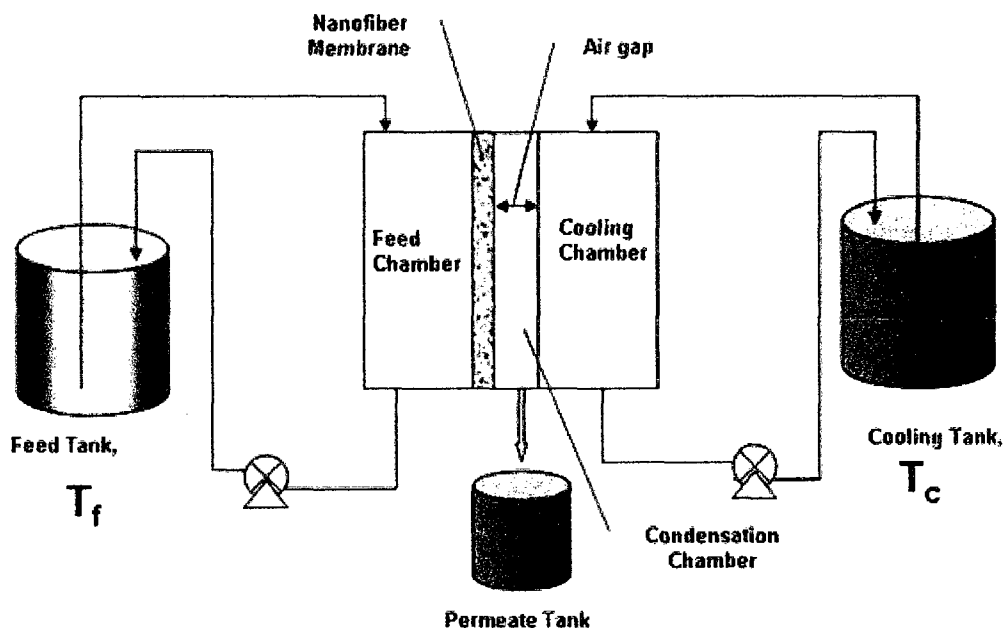


Figure 5.1 Diagram of AGMD system

The feed tank is immersed in a water bath to keep the feed solution temperature constant. The cooling tank is also immersed in a water bath to keep the cooling side temperature constant. The feed solution is recycled by the Masterflex Peristaltic Pump through the feed chamber of the MD cell. The feed pressure is maintained lower than the liquid entry pressure of water (LEP_w), i.e. <5 psig. The air gap of the AGMD module is 2 mm.

Figure 5.2 shows the detailed structure of the AGMD module used in the current study.

Hot feed solution at a set temperature enters into the hot chamber from the centre tube, passes through the separate wall in the middle of chamber, then enters into the tube at the edge of the hot chamber and finally goes back to the feed tank. The cooling fluid at a set temperature is pumped in to the cool chamber and then goes back to the cooling tank. The cooling plate is made of aluminum.

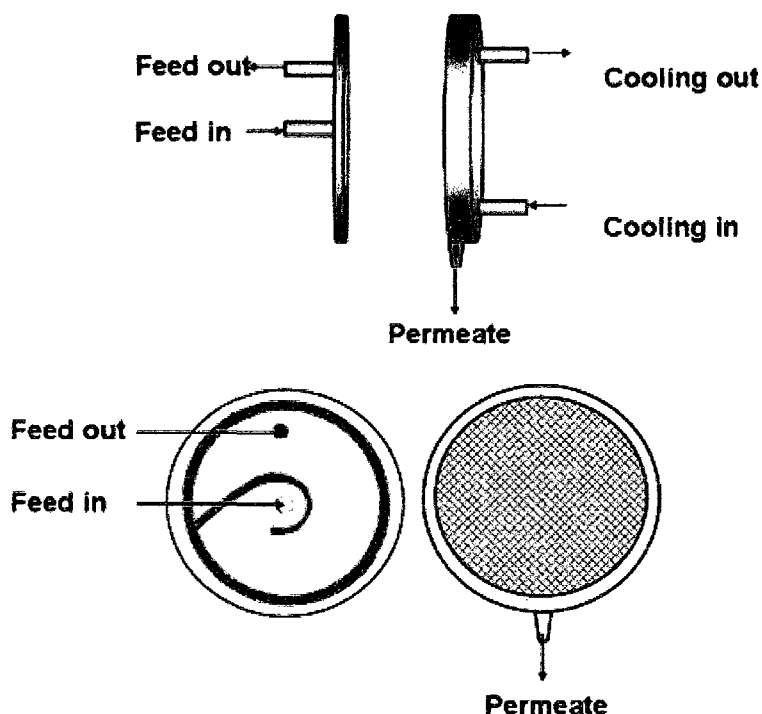


Figure 5.2 Diagram of AGMD module

2. MATERIALS AND METHODS

● PVDF nanofiber membrane

The PVDF nanofiber membrane was made by the electrospinning method. Details of the membrane preparation and characterization are given in Part I. Some important characterization parameters of the PVDF nanofiber membrane are:

- 1) Porosity: $76 \pm 5\%$

- 2) Thickness: 0.15 mm
- 3) LEPw: 17.6 ± 2 psig
- 4) Contact angle: $>120^\circ$
- 5) Average pore size: 1.5 μm

- Feed solutions

Sodium chloride used in the current study was the food grade table salt from Sifto Canada. Ethanol was supplied by Sigma-Aldrich (CR, 99%).

- 1) Sodium chloride solutions of 1, 3, 3.5, 6 and 22 wt% were used for desalination by the AGMD system through PVDF nanofiber membrane.
- 2) Ethanol aqueous solutions of 5 and 10 wt% were used for ethanol concentration by the AGMD system through PVDF nanofiber membrane.
- 3) Cooling fluid was water.

- Operating condition

Feed solution is pumped by Masterflex Peristaltic Pump. The feed solution flow rate is 600 mL/min. Feed pressure is 5 psig. The temperature of feed solution is set at a fixed temperature (35, 43, 51, 60, 65, 71, 80°C). The cooling fluid flow flux is 6000 mL/min. The cooling fluid temperature is set at 20°C .

- Membrane distillation analysis

- a) Desalination: Permeate of AGMD was measured by conductivity meter (OAKTON® CON 11 Conductivity and TDS Meter, USA) to monitor the concentration of NaCl. A series of NaCl solutions with different concentrations (0-15% wt.) were prepared by distilled water.

As shown in Fig. 5.3, the conductivity of NaCl solution has a proportional relationship with its concentration.

In desalination experiments, sodium chloride concentrations (wt %) of the feed and permeate solutions were measured by conductivity meter using a linear calibration curve established between the solution conductivity and the sodium chloride concentration. The salt rejection was calculated by:

$$\text{Rejection} = 1 - \frac{\text{NaCl concentration in Permeate}}{\text{NaCl concentration in Feed}} \times 100\%. \dots (5-1)$$

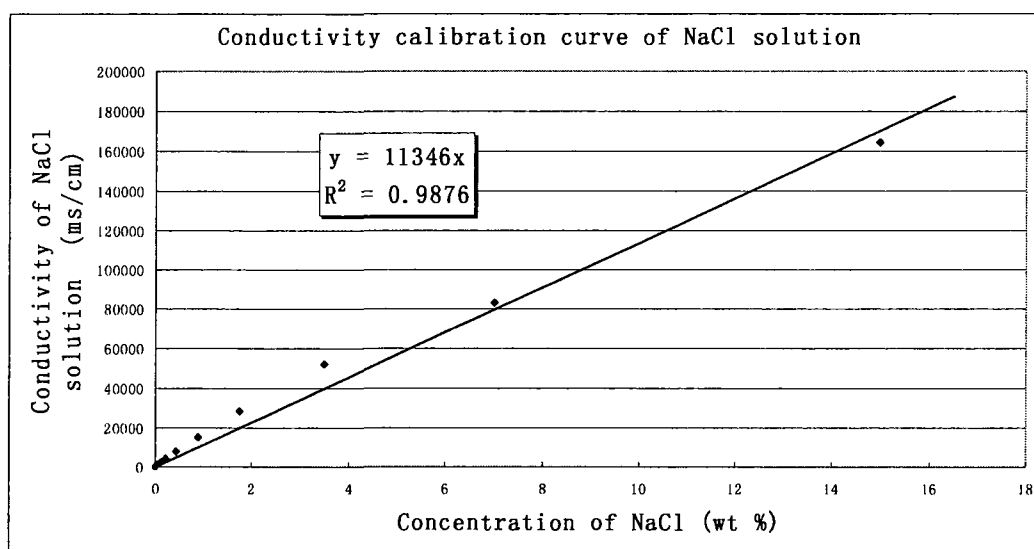


Figure 5.3 Calibration curve of conductivity versus NaCl concentration

- b) For the separation of ethanol/water mixtures the ethanol concentrations (5 and 10 wt %) in the feed and permeate were determined by measuring the weight of the solution (50 mL) by an electronic balance at 25 °C. Then, the solution density was calculated. The ethanol concentration was obtained by using the data from CRC handbook [93] between the ethanol concentration (wt. %) and the density of aqueous ethanol solution shown in Fig. 5.4.

The total permeation rate was obtained by weighing the permeate collected

during a preset permeation period. The permeation flux was obtained by dividing the permeation rate by the effective membrane area (115 cm^2).

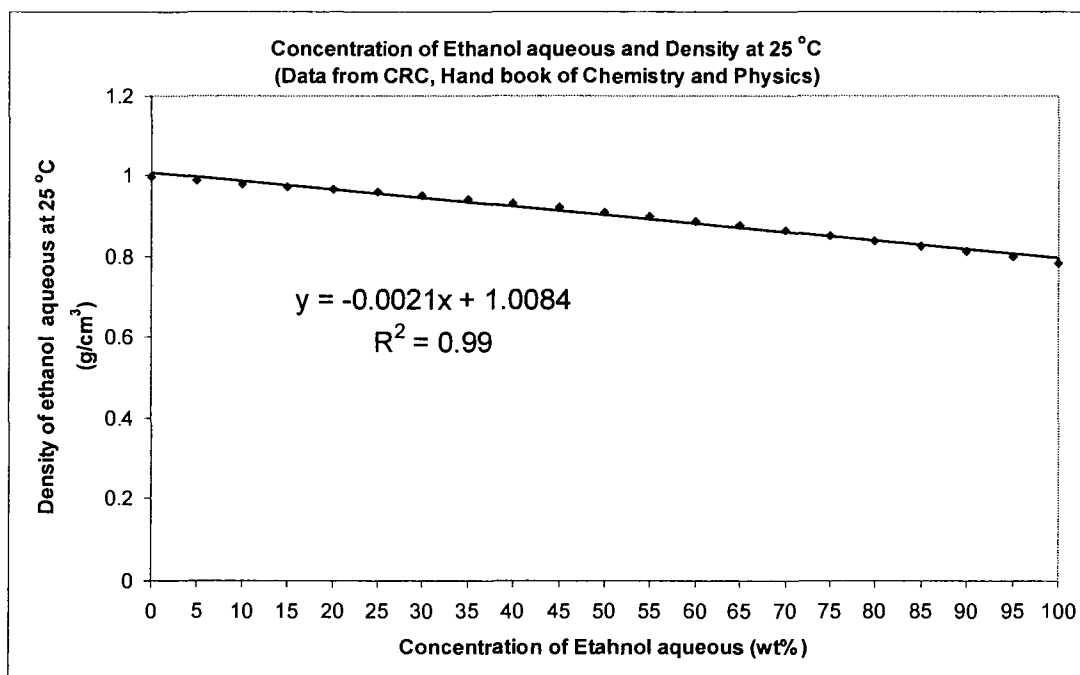


Figure 5.4 Calibration curve of density versus ethanol concentration

Chapter 6 RESULTS AND DISCUSSIONS

1. DESALINATION BY AGMD MEMBRANE DISTILLATION

1.1. Mass Transfer of AGMD

Theoretical analysis of the experimental data was conducted using Equations (4-18) and (4-19). Equation (4-18) allows the theoretical calculation of the flux through the membrane if appropriate membrane characterization parameters such as ε , τ and δ are known. Among those ε and δ are known experimentally and τ is assumed to be equal to unity. Furthermore, $Y_{\text{In, air}}$ is logarithmic mean mole fraction of air at the pore inlet and at the pore outlet and can be obtained by knowing the respective water vapour pressures. As for the pressure difference, Δp , it is unknown since the temperatures on both sides of the membrane, T_{fm} and T_{m} , are unknown but in this analysis T_{f} and T_{p} were used instead, knowing that it is only an approximation.

As expected, the theoretical results shown in Figs. 6.1 (flux versus vapour pressure difference) and 6.2 (flux versus temperature difference) are in a linear and an exponential form respectively and the magnitude of the flux is far greater than the experimental values. Equation (4-20) also allows the flux calculation from the known air gap thickness data. Again, this equation requires the vapour pressures corresponding to T_{m} and T_{c} , but as an assumption those corresponding to T_{f} and T_{p} were used. The results are summarized in Figs. 6.3 and 6.4 as linear and exponential forms. The experimental data obtained for different feed NaCl concentrations are also shown in the figures. This shows that the temperature (or pressure) differences used in the calculation are greater than the real temperature (or pressure) differences.

Comparing Figs. 6.1 and 6.2 with Figs. 6.3 and 6.4, however, it can be said that equation (4-20) resulted in an order of magnitude smaller flux values and they are closer to the experimental ones. These results show that the difference between T_{m} and T_{c} is much closer to T_{f} and T_{p} , which means most of the temperature, and vapour pressure, drop

occurs in the air gap. Temperature drop in the membrane, on the other hand, is very small.

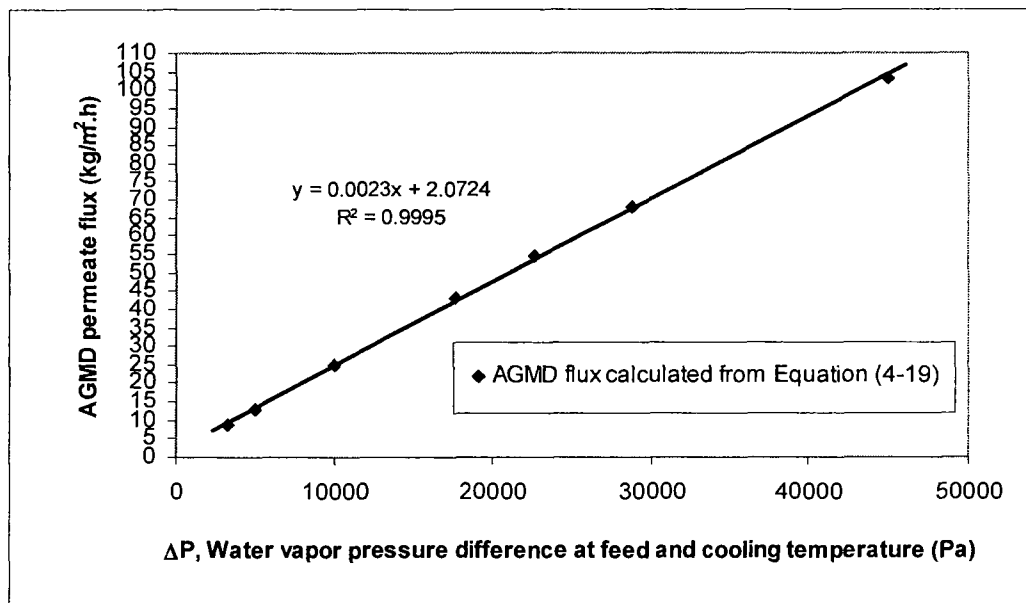


Figure 6.1 AGMD flux versus water vapour pressure difference (Flux calculated from Equation (4-19))

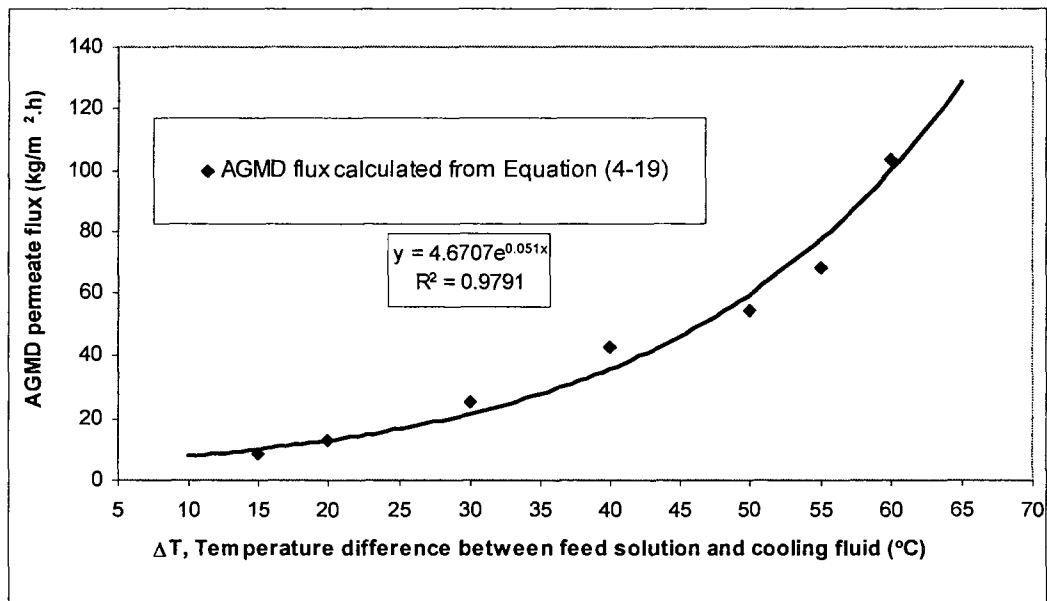


Figure 6.2 AGMD flux versus temperature difference (Flux calculated from Equation (4-19))

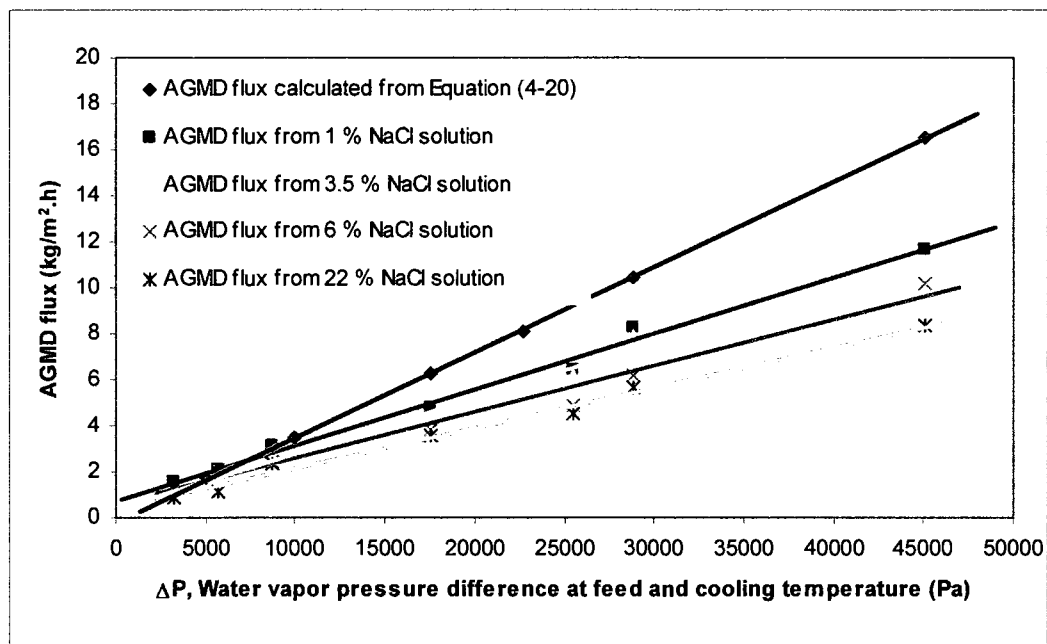


Figure 6.3 AGMD flux versus water vapour pressure difference

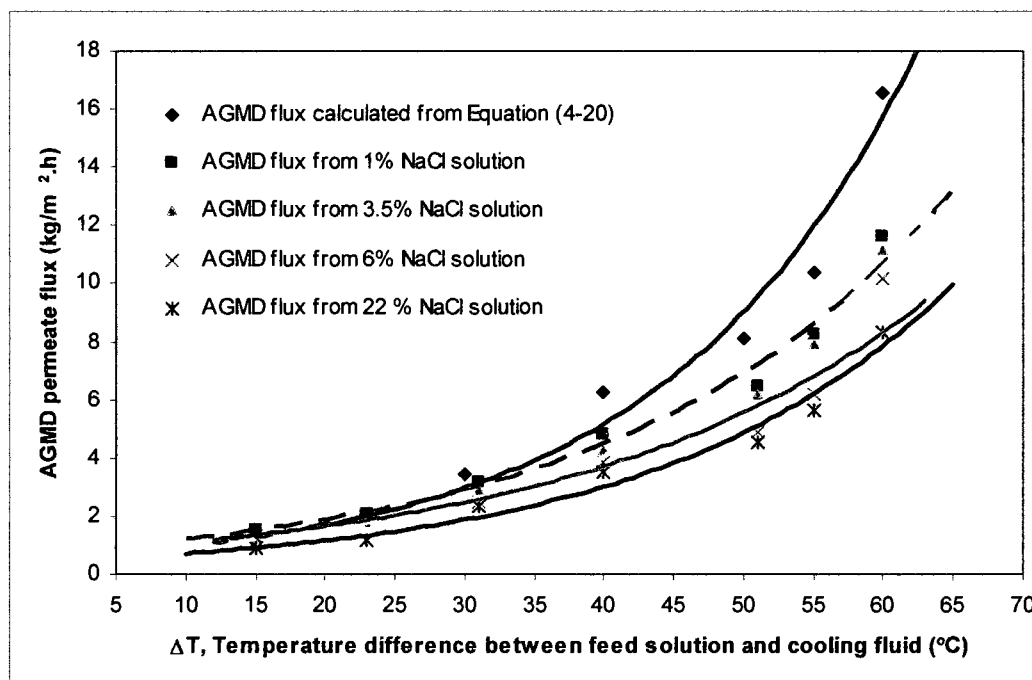


Figure 6.4 AGMD flux versus temperature difference

Fluxes were either calculated from Equation (4-20) or obtained from experiments with 1, 3.5, 6, 22 wt % NaCl solutions.

This conclusion is further confirmed by a more detailed analysis of the heat transport. Based on the results, it also can be found that air gap governs the mass transport of AGMD flux. With air gap increase, the AGMD flux will decrease quickly. Similar results were reported by Kimura et al.[44].

1.2. Heat Transfer of AGMD

1.2.1. Heat transfer coefficient of hot side boundary layer

Temperature at each surface and temperature polarization can be calculated through Equations (4-22)-(4-26). The heat transfer coefficient at each step of the heat transfer is however required for this calculation.

The physico-chemical parameters used to obtain the heat transfer coefficients can be found in the following references. 1) CRC Handbook of Chemistry and Physics [93], 2) Lange's Handbook of Chemistry [94] (for example: THERMAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF NaCl, VISCOSITY MEASUREMENTS OF ALCOHOL-WATER MIXTURES AND THE STRUCTURE OF WATER).

The hot feed solution has a boundary layer, which affects the heat transfer from bulk liquid to membrane surface (as shown in Fig. 4-2). The heat transfer coefficient of the boundary layer can be obtained, similar to the mass transfer coefficient, using the relationship between the dimensionless quantities such as shown by Equations (4-30) and (4-31). It means heat transfer of AGMD is affected not only by the fluid property, but also by the operating conditions.

The AGMD system used in this study is shown in Fig. 5.1. The flow rate of the feed solution required in equations (4-30) and (4-31) was experimentally obtained. The basic physicochemical properties for NaCl solution and ethanol/water mixture were obtained from the literature.

1.2.2. Heat transfer coefficient of sodium chloride solution (h_f)

The feed solution flow rate is 0.0197 m/s, the necessary physicochemical properties such as density, viscosity, thermal conductivity etc. of NaCl solution are found in CRC Handbook. Using these values in Equation (4-30) the heat transfer coefficient, h_f , can be calculated. Table 6.1 summarizes the heat transfer coefficient for NaCl solution, h_f , for different NaCl concentrations and temperatures.

Table 6.1 Heat transfer coefficient (h_f) of NaCl solutions at different temperatures

NaCl solution concentration wt%	Heat transfer coefficient, h_f (W/m ² K)					
	20 °C	30 °C	40 °C	60 °C	80 °C	100 °C
1	189.3	187.8	186.6	184.7	184.2	181.8
3	189.2	187.8	186.7	184.7	183.5	182.1
6	189.0	187.5	186.2	184.4	183.2	182.6
22	175.8	174.0	173.0	171.2	167.0	169.0

1.2.3. Heat transfer coefficient of ethanol aqueous solution (h_f)

Similarly, the heat transfer coefficients for the ethanol/water mixtures can be calculated from Equation (4-31). The results are summarized in Table 6.2.

Table 6.2 Heat transfer coefficient (h_f) of aqueous ethanol solutions

Ethanol concentration wt%	Density kg/m ³	Viscosity N.s/m ²	Thermal conductivity W/m K	Heat transfer coefficient, h_f W/m ² K
1	996.3	0.000105	0.5900	296.1
2	994.5	0.00011	0.5823	294.1
3	992.7	0.000114	0.5747	289.9
4	991	0.000118	0.5673	286.4
5	989.3	0.000123	0.5599	283.3
6	987.8	0.000128	0.5526	280.2
7	986.2	0.000133	0.5454	276.8
8	984.7	0.000139	0.5383	273.5
9	983.3	0.000144	0.5313	270.3
10	981.9	0.00015	0.5244	267.1

1.2.4. Heat transfer coefficient of PVDF nanofiber membrane (h_m)

Thermal conductivity of PVDF polymer is 0.29 W/m K between 323 and 443 K (50 and 170°C) (data from the manufacturer [95]). Thermal conductivities of air are from CRC Handbook of Chemistry and Physics, as shown in Table 6.3.

Table 6.3 Thermal conductivity of air

Name	Thermal conductivity (300 K), W/m K	Thermal conductivity (400 K), W/m K
Air	0.0262	0.0333

Thermal conductivities of water are also from CRC Handbook of Chemistry and Physics [93], as shown in Table 6.4.

Table 6.4 Thermal conductivity of water

Temperature °C	Vapour pressure kPa	Thermal conductivity (W/m K) (Liquid)	Thermal conductivity (W/m K) (Vapour)
0	0.6	0.5610	0.01649
10	1.2	0.5800	0.01721
20	2.3	0.5984	0.01795
30	4.2	0.6154	0.01870
40	7.4	0.6305	0.01948
50	12.3	0.6435	0.02028
60	19.9	0.6543	0.02110
70	31.2	0.6631	0.02196
80	47.4	0.6700	0.02286
90	70.1	0.6791	0.02380
100	101.3	0.6821	0.02479

Both PVDF membrane thickness (0.15 mm) and porosity (0.76 ± 4) were obtained experimentally. Assuming that the PVDF nanofiber membrane pores are filled with air, instead of water vapour, the heat transfer coefficient of PVDF nanofiber membrane was calculated based on Equation (4-27). The results are shown in Table 6.5.

Table 6.5 Heat transfer coefficient (h_m) of PVDF nanofiber membrane

Membrane	h_m	
	Heat transfer coefficient (300 K), W/m ² K	Heat transfer coefficient (400 K), W/m ² K
PVDF	596.7	632.7

1.2.5. Heat transfer coefficient of air at air gap ($h_g = k_1/L$)

The thermal conductivity of the air gap, k_1 , was obtained assuming the air gap was filled with air. This can be justified since the highest average temperature of the air gap is 45°C and the partial vapour pressure of water is 1/10 of atmospheric pressure. Since the thickness of the air gap, L , is 2 mm, the heat transfer coefficient of the air gap, h_g , can also be calculated. The results are shown in Table 6.6.

Table 6.6 Heat transfer coefficient of air gap (h_g)

Air gap	h_g	
	Heat transfer coefficient (300 K), W/m ² K	Heat transfer coefficient (400 K), W/m ² K
Air	8.73	11.1

1.2.6. Heat transfer coefficient of cooling plate ($h_{plate} = k_2/\delta_p$)

The material of cooling plate is aluminum. The thickness is 5 mm. The thermal conductivity of aluminum (237 W/m K) was obtained from CRC Handbook of Chemistry and Physics. The heat transfer coefficient (h_{plate}) is therefore 47400 W/m² K.

1.2.7. Heat transfer coefficient of cooling fluid boundary layer (h_p)

The cooling fluid is water at room temperature (20 °C). The flow rate of cooling water is 0.644 m/s, obtained experimentally. Prandtl number of water was obtained from Perry's Chemical Engineers' Handbook [96], as shown in Table 6.7. The physical properties of water necessary for the calculation of heat transfer coefficients were obtained from CRC Handbook of Chemistry and Physics, as shown in Table 6.8. Similar to the calculation of h_f , the dimensionless correlation (equation (4-31)) was used to calculate the Nusselt number of the fluid, from which the heat transfer coefficient was calculated. The heat transfer coefficient, h_p , of boundary layer of cooling water at 20 °C was calculated to be 2725.2 W/m² K.

Table 6.7 Prandtl number of water

Pressure, bar	Prandtl number		
	300 K	350K	400K
1			
5	5.81	2.32	0.98
10	5.82	2.32	1.34
20	5.82	2.32	1.34

Perry's Chemical Engineers' Handbook (7th Edition) [96]

Table 6.8 Physical properties of water at different temperatures

Temperature °C	Density g/cm	C_p J/g K	Vapour pressure kPa	Viscosity, μ Pa s	Thermal conductivity W/K m
0	0.99984	4.2176	0.6113	1793	0.5610
10	0.99970	4.1921	1.2281	1307	0.5800
20	0.99821	4.1818	2.3388	1002	0.5984
30	0.99565	4.1784	4.2455	979.7	0.6154
40	0.99222	4.1785	7.3814	653.2	0.6305
50	0.98803	4.1806	12.344	547.0	0.6435
60	0.98320	4.1843	19.932	466.5	0.6543
70	0.97778	4.1895	31.176	404.0	0.6631
80	0.97182	4.1963	47.373	354.4	0.6700
90	0.96535	4.2050	70.117	314.5	0.6753
100	0.95840	4.2159	101.325	281.8	0.6791

1.2.8 Latent heat of vaporization for water (ΔH_w)

The latent heat of vaporization for water (ΔH_w) was taken from CRC Handbook of Chemistry and Physics. It is shown in Table 6.9.

Table 6.9 Latent heat of water (ΔH_w)

Temperature °C	Heat of vaporization of water (ΔH_w) J/kg
0	2503
25	2443.9
40	2408.3
60	2360.1
80	2310.3
100	2260.4

The latent heat of ethanol (ΔH_e) at 25 °C was from Lange's Handbook of Chemistry (16th Edition [94]). It is 918.17 J/kg.

Combining Equations (4-22)-(4-26), the temperature of each surface for AGMD can be calculated by:

$$\left\{ \begin{array}{l}
 T_p = T_p \\
 T_f = T_f \\
 N = J \\
 T_c = \left(\frac{h_p}{h_{plate}} + 1 \right) \times T_{pc} - \frac{h_p}{h_{plate}} \times T_p \\
 T_m = \left(\frac{h_p}{h_g} + \frac{h_p}{h_{plate}} + 1 \right) \times T_{pc} - \frac{N \times \Delta H_w}{h_g} - \left(\frac{h_p}{h_g} + \frac{h_p}{h_{plate}} \right) \times T_p \\
 T_{fm} = \left(\frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{plate}} + 1 \right) \times T_{pc} - \left(\frac{1}{h_m} + \frac{1}{h_g} \right) \times N \times \Delta H_w - \left(\frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{plate}} \right) \times T_p \\
 T_{pc} = \frac{1}{\left(\frac{h_p}{h_f} + \frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{plate}} + 1 \right)} \times \left[T_f + \left(\frac{1}{h_m} + \frac{1}{h_g} \right) \times N \times \Delta H_w + \left(\frac{h_p}{h_f} + \frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{plate}} \right) \times T_p \right]
 \end{array} \right.$$

(6-1)

For a given set of experimental T_f and T_p values the vapour flux J was obtained either by calculation (Equations (4-19) and (4-20)) or by experiments. Then, temperatures, T_c , T_m , T_{fm} and T_{pc} were calculated by the above set of equations using the values for the heat transfer coefficient and the latent heat of vaporization.

To simplify the calculation, a single value was used for the heat transfer coefficient at each layer of the heat transfer resistance. As well, latent heat of vaporization at 25°C was used. This approximation is to avoid the complicated iteration process. The used heat transfer coefficient and heat of vaporization values are summarized in Table 6.10.

Table 6.10 Heat transfer coefficient and latent heat of vaporization for water used in calculation

h_f W/m ² K	h_m W/m ² K	h_{g_2} W/m ² K	h_{plate} W/m ² K	h_p W/m ² K	ΔH_w J/kg
189.3	632.7	11.1	47400	2725.1	2443.9

AGMD fluxes calculated from Equations (4-19) and (4-20) are shown in Table 6.11 along with the experimental data. As mentioned earlier, agreement between the values obtained from Equation (4-20) and the experimental values is much better than Equation (4-19).

Table 6.11 Comparison of calculated and experimental AGMD fluxes

Temperature difference ΔT (°C)	Vapour difference ΔP (Pa)	AGMD Flux (kg/m ² .h)					
		Calculated results from Equation (4-19)	Calculated results from Equation (4-20)	Experiment results from NaCl solution			
				1%	3.50%	6%	22%
15	3287.9	8.6	1.10	1.53	1.12	1.33	0.89
20	5042.6	13.0	1.71				
23	5700.6			2.06	1.77	2.05	1.15
30	10005.2	25.1	3.47				
31	8745.7			3.13	2.87	2.47	2.32
40	17593.2	42.8	6.23	4.80	4.27	3.82	3.54
50	22683.2	54.4	8.11				
51	25497.1			6.45	6.19	4.87	4.51
55	28837.2	68.1	10.40	8.23	7.87	6.19	5.63
60	45034.2	103.4	16.53	11.63	11.15	10.17	8.31

Both calculated values, from Equations (4-19) and (4-20), and the experimental flux values were used to solve the set of equations given in (6.1) to obtain the temperatures at different surfaces and the results summarized in Figures 6.5, 6.6 and 6.7 for the feed temperature of 35, 50, and 80°C, respectively.

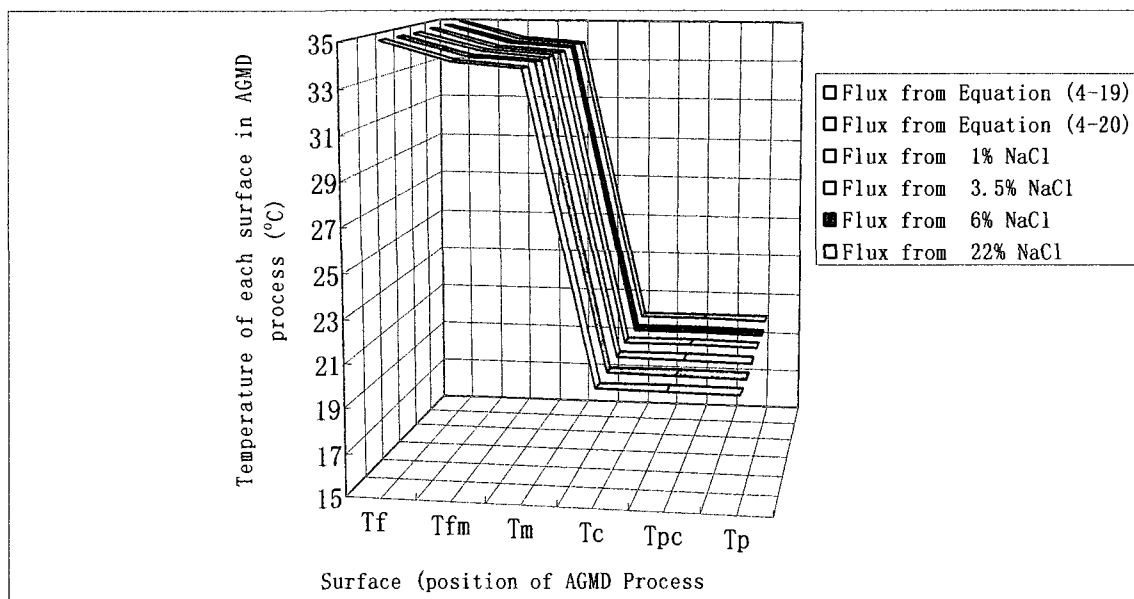


Figure 6.5 Temperature profile of AGMD process
Feed temperature, 35°C; Cooling stream temperature, 20°C.

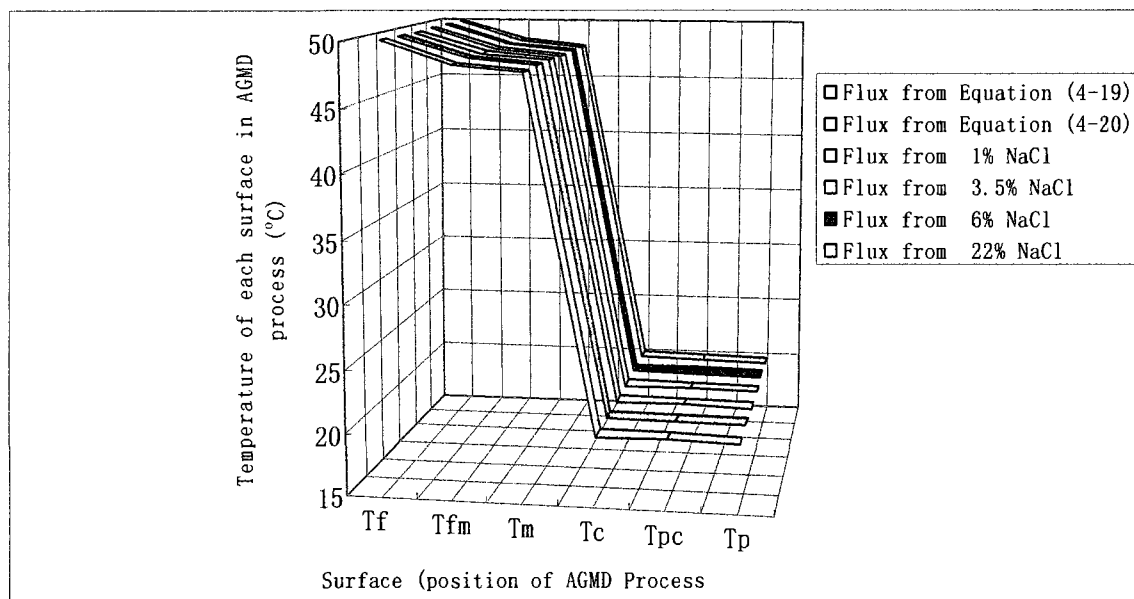


Figure 6.6 Temperature profile of AGMD process
Feed temperature, 50°C; Cooling stream temperature, 20°C.

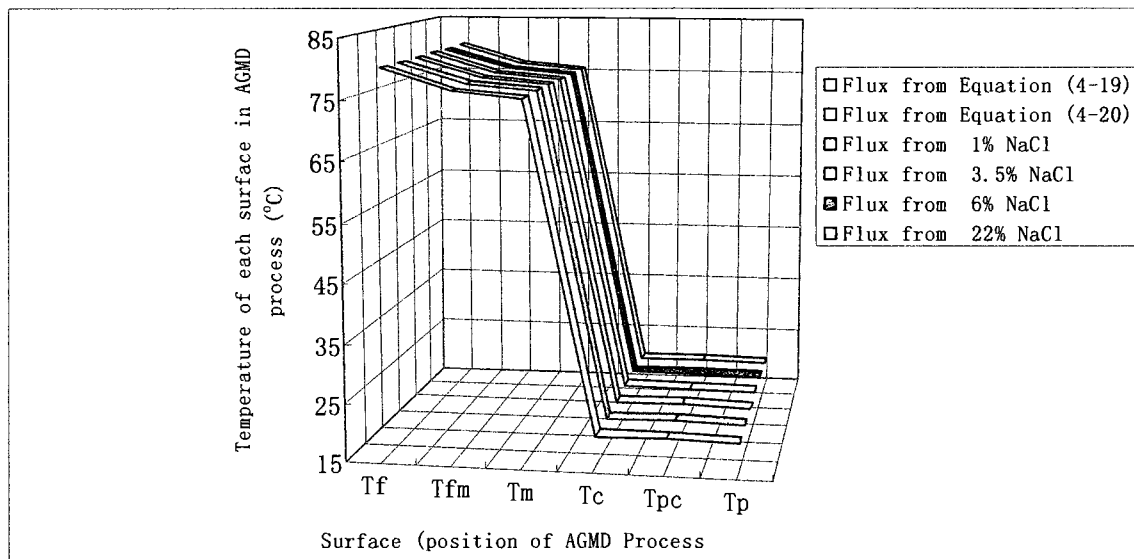


Figure 6.7 Temperature profile of AGMD process

Feed temperature, 80°C; Cooling stream temperature, 20°C.

All the above figures indicate that the major temperature drop occurs from T_m to T_c . This is due to the smallest heat transfer value of air gap, h_g (11.1 W/m² K). There is also a notable temperature drop from T_f to T_{fm} , reflecting the second smallest heat transfer value of boundary layer on the feed solution side, h_f (189.3 W/m² K). The temperature drop from T_{fm} to T_m across the membrane, which is the driving force for the vapour transport, is so small, despite the fact that our current MD system has already achieved fluxes as high as the commercial RO membranes (for example, FILMTEC RO membranes cover a flux performance range from 1 to 14 l/m² h bar) [97]. This heat transfer analysis demonstrates clearly the possibility to achieve a significantly higher vapour flux than the current values, if the AGMD system is properly designed to reduce the air gap resistance.

The temperature polarization coefficients, Θ' , were calculated according to Equation 4-33 and the results shown in Table 6.12. As the table shows the coefficients are above 0.94 in all cases. However, these high values are rather misleading since only a small portion of the temperature drop is utilized as the driving force for the vapour transport through the membrane.

Table 6.12 Temperature polarization coefficients (Θ')

AGMD	Temperature Polarization coefficient (Θ')		
	Feed temperature (35 °C)	Feed temperature (50 °C)	Feed temperature (80 °C)
Flux from Equation (4-19)	0.9397	0.9387	0.9355
Flux from Equation (4-20)	0.9415	0.9413	0.9408
Flux from 1% NaCl	0.9414	0.9414	0.9411
Flux from 3.5% NaCl	0.9415	0.9414	0.9411
Flux from 22% NaCl	0.9415	0.9415	0.9413

2. Salt Rejection of NaCl Solution by AGMD

As Fig. 6.8 shows, the salt rejection by the present AGMD system is over 97%. Theoretically, the salt rejection should reach 100%. But the membrane for membrane distillation in the current research has a pore size distribution, as shown in Part I, and some pores are above the average pore size of 1.5 μm . Therefore the possibility of the NaCl solution leakage through these large pores exists, which lowers the salt rejection below 100%.

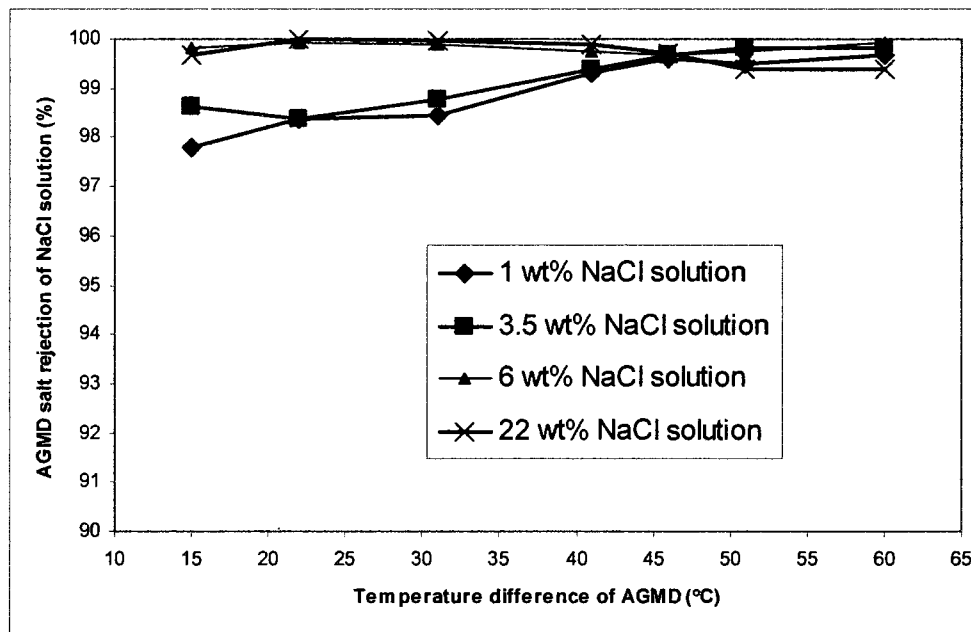


Figure 6.8 Salt rejection of NaCl solution by AGMD

3. Salt Rejection versus Concentration of NaCl Solution in Feed by AGMD

Figure 6.9 shows that NaCl rejection increases as the NaCl concentration in the feed solution increases. This may be due to the increase in viscosity of the sodium chloride solution, which lowers the flow rate of the solution through the large membrane pores.

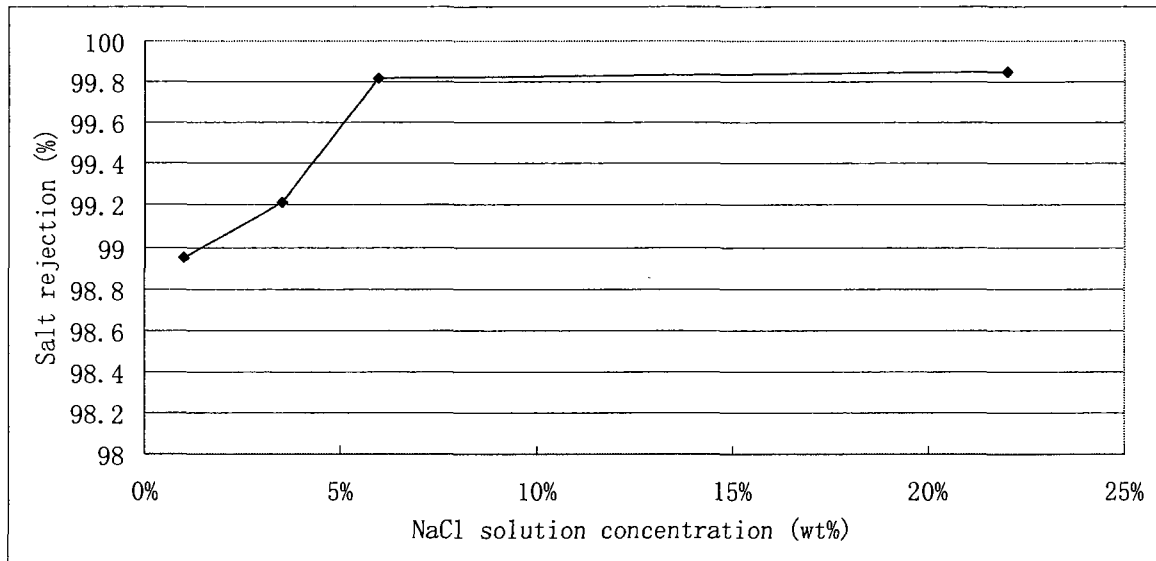


Figure 6.9 Salt rejection versus concentration of NaCl solution
(Temperature difference of AGMD is 60 °C.)

4. Long Term Operation of AGMD

A 25-day separation test has been carried out and the data presented in Fig. 6.10. The figure shows that NaCl rejection does not change considerably during the above operational period. The latest data showed that the membrane was still applicable after the above long term testing. It showed salt rejection of 99.9% for the feed NaCl concentration of 22%.

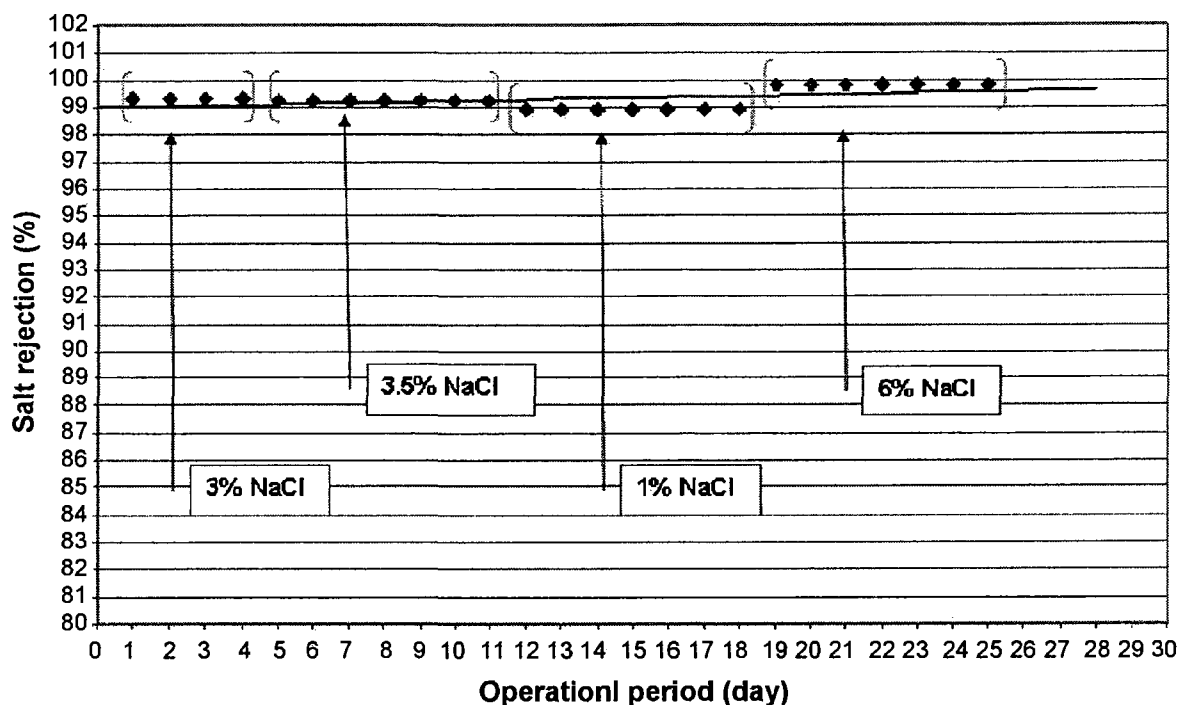


Figure 6.10 Salt rejection versus operational period of AGMD

5. SEPARATION OF ETHANOL/WATER MIXTURES BY AGMD

5.1. Experimental results

AGMD was attempted by the PVDF nanofiber membrane for the alcohol/water mixtures of 5 wt% and 10 wt% ethanol concentration. The mole fractions of ethanol in these mixtures are 0.02 and 0.04, respectively.

The experimental flux data are given in Fig. 6.11. The permeate ethanol concentrations are given in Fig. 6.12. It is clear that ethanol is concentrated in the permeate considerably. As mentioned earlier, the ethanol concentration was determined by measuring the solution density. The linear correlation between the ethanol concentration and density was shown in Fig. 5.4. The data at different temperatures are summarized in Table 6.13.

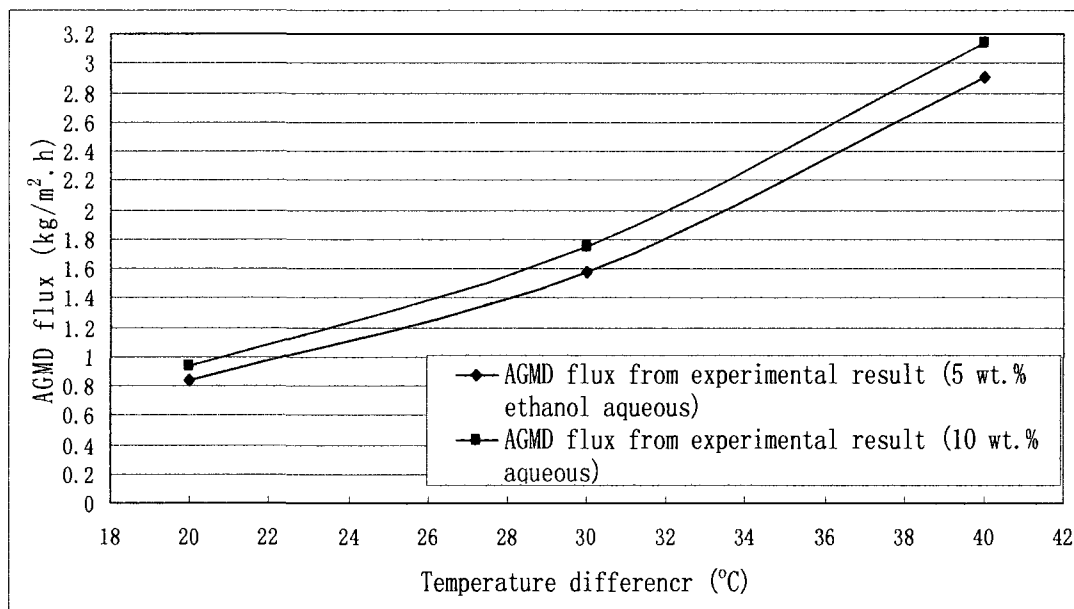


Figure 6.11 AGMD flux for different temperature differences
Feed concentration of aqueous ethanol solutions, 5 wt% and 10 wt%.

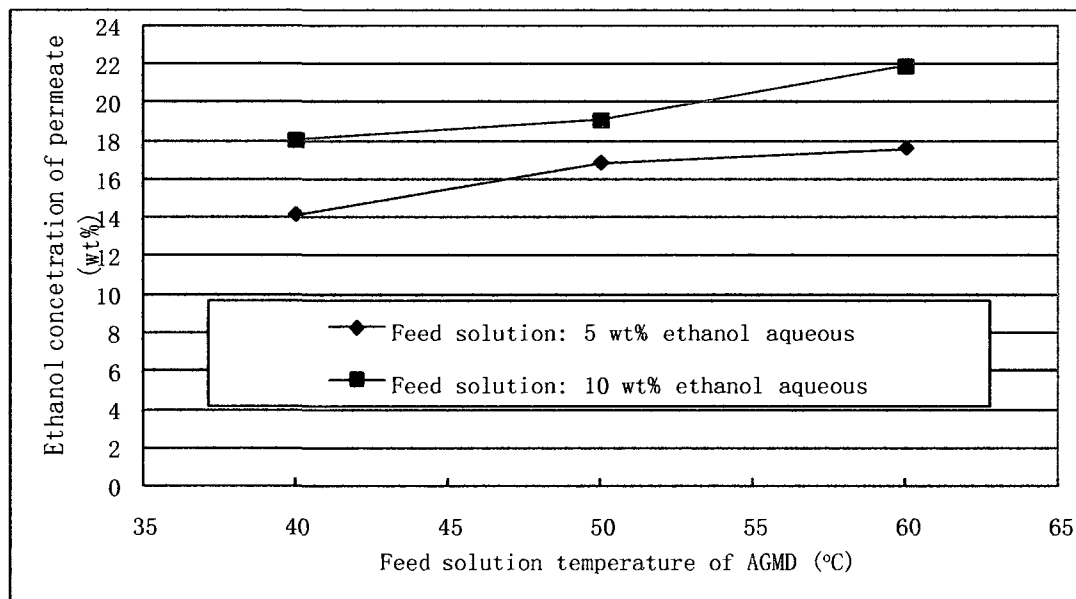


Figure 6.12 Ethanol concentration in the permeate at different temperature differences
Feed concentration of aqueous ethanol solutions, 5 wt% and 10 wt%.

Figure 6.13 is the Vapour Liquid Equilibrium (VLE) chart of ethanol-water binary system from Handbook of Chemical and Environmental Engineering Calculations [98].

From the chart, as the mole fraction of ethanol in water is 0.02 (5 wt%) and 0.04 (10 wt%), in vapour phase the mole fraction of ethanol will be 0.1 and 0.18 respectively. It is 22.1 % and 35.9% in weight percentage from McCabe-Thiele diagram of ethanol water system.

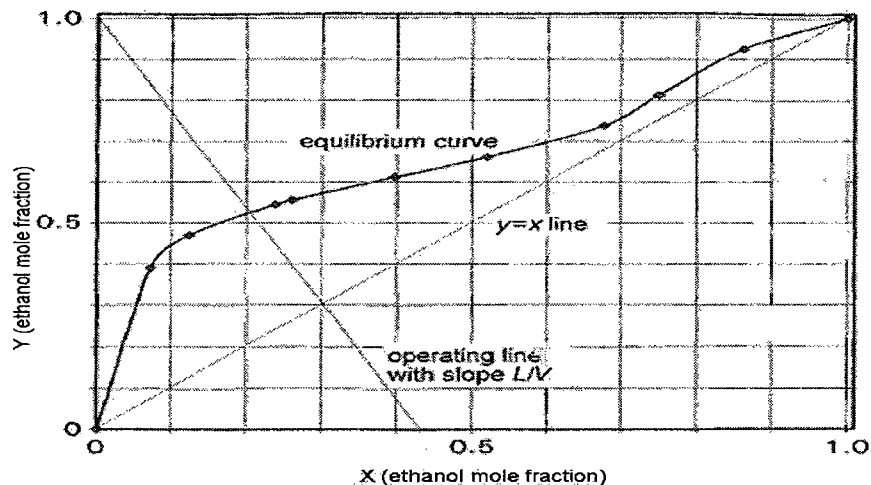


Figure 6.13 McCabe-Thiele diagram (VLE chart) of ethanol-water system [98]

Table 6.13 Density of aqueous ethanol solutions at different temperatures

Ethanol wt%	Density (g/cm ³)				
	10 °C	15 °C	20 °C	25 °C	30 °C
0	0.9997	0.9991	0.9982	0.9971	0.9957
5	0.9910	0.9903	0.9894	0.9881	0.9867
10	0.9839	0.9830	0.9818	0.9804	0.9787
15	0.9780	0.9767	0.9751	0.9733	0.9713
20	0.9725	0.9707	0.9686	0.9664	0.9639
25	0.9666	0.9642	0.9617	0.9589	0.9560
30	0.9597	0.9568	0.9538	0.9506	0.9474
35	0.9516	0.9483	0.9449	0.9414	0.9379
40	0.9424	0.9388	0.9352	0.9315	0.9277
45	0.9322	0.9285	0.9247	0.9208	0.9169
50	0.9216	0.9177	0.9138	0.9098	0.9058
55	0.9105	0.9066	0.9026	0.8985	0.8943
60	0.8992	0.8952	0.8911	0.8870	0.8828
65	0.8877	0.8836	0.8795	0.8752	0.8710
70	0.8760	0.8718	0.8676	0.8634	0.8591
75	0.8641	0.8599	0.8556	0.8513	0.8470
80	0.8519	0.8477	0.8434	0.8391	0.8347
85	0.8395	0.8352	0.8309	0.8266	0.8222
90	0.8265	0.8222	0.8180	0.8136	0.8092
95	0.8128	0.8085	0.8042	0.7999	0.7955
100	0.7978	0.7936	0.7893	0.7850	0.7807

5.2. Heat transfer of AGMD

It is attempted again to obtain temperature profiles in the AGMD system by calculating the temperatures at different surfaces. For this purpose, a set of equations (6-2) were used. The difference between (6-1) and (6-2) is that water flux of (6-1) is replaced by the combined ethanol and water flux in (6-2). As well, latent heat of vaporization of water is replaced by the combined heat of vaporization of ethanol and water in (6-2), assuming that the latent heat of the mixture is the sum of the product of the mole fraction and the latent heat of vaporization of each component. The chosen heat transfer coefficient at each heat barrier is given in Table 6.14 for 20°C. Comparing Tables 6.10 and 6.14, all heat transfer coefficients are equal except for h_f , which is natural because it was assumed that the membrane pores and the air gap are filled with air in both desalination and ethanol/water separation. This is a very crude assumption, which however allows us to go around the tedious iteration procedure and yet provides us with a general picture of the temperature profile in the system. The heating plate is aluminium and cooling media is water in both experiments.

Table 6.14 Heat transfer coefficient and latent heat of vaporization for water and ethanol used in the calculation

h_f of aqueous ethanol soln W/m ² K	h_m W/m ² K	h_g W/m ² K	h_{plate} W/m ² K	h_p W/m ² K	ΔH of water J/kg	ΔH of ethanol J/kg
296.1	632.7	11.1	47400	2725.2	2443.9	918.6

The results of AGMD flux for ethanol/water mixture from experiment are shown in Table 6.15.

Table 6.15 AGMD flux data obtained from AGMD experiments with aqueous ethanol solutions

Feed Temperature (°C)	AGMD Flux (kg/m ² .h)	
	Experiment result from aqueous ethanol solutions	
	5 wt%	10 wt%
40	0.84	0.94
50	1.57	1.75
60	2.90	3.14

$$\left. \begin{aligned}
 T_p &= T_p \\
 T_f &= T_f \\
 N &= J_{\text{water}} + J_{\text{ethanol}} \\
 T_c &= \left(\frac{h_p}{h_{\text{plate}}} + 1 \right) \times T_{\text{pc}} - \frac{h_p}{h_{\text{plate}}} \times T_p \\
 T_m &= \left(\frac{h_p}{h_g} + \frac{h_p}{h_{\text{plate}}} + 1 \right) \times T_{\text{pc}} - \frac{(J_{\text{water}} \times \Delta H_w + J_{\text{ethanol}} \times \Delta H_e)}{h_g} - \left(\frac{h_p}{h_g} + \frac{h_p}{h_{\text{plate}}} \right) \times T_p \\
 T_{\text{fm}} &= \left(\frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{\text{plate}}} + 1 \right) \times T_{\text{pc}} - \left(\frac{1}{h_m} + \frac{1}{h_g} \right) \times (J_{\text{water}} \times \Delta H_w + J_{\text{ethanol}} \times \Delta H_e) - \left(\frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{\text{plate}}} \right) \times T_p \\
 T_{\text{pc}} &= \frac{l}{\left(\frac{h_p}{h_f} + \frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{\text{plate}}} + 1 \right)} \times \left[T_f + \left(\frac{1}{h_m} + \frac{1}{h_g} \right) \times (J_{\text{water}} \times \Delta H_w + J_{\text{ethanol}} \times \Delta H_e) + \left(\frac{h_p}{h_f} + \frac{h_p}{h_m} + \frac{h_p}{h_g} + \frac{h_p}{h_{\text{plate}}} \right) \times T_p \right]
 \end{aligned} \right\}$$

(6-2)

The temperature profiles are given in Figs. 6.14, 6.15 and 6.16. The temperature polarization coefficients, Θ' , are given in Table 6.16. These figures and the table are very similar to Figures 6.5, 6.6 and 6.7 and Table 6.12, which were obtained for desalination. The temperature polarization coefficients are also higher than 0.94.

Table 6.16 Temperature polarization coefficients (Θ')

AGMD	Temperature Polarization coefficient (Θ')		
	Feed temperature (40 °C)	Feed temperature (50 °C)	Feed temperature (60 °C)
Flux from 5 wt% aqueous ethanol solution	0.9439	0.9439	0.9438
Flux from 10 wt% aqueous ethanol solution	0.9439	0.9438	0.9438

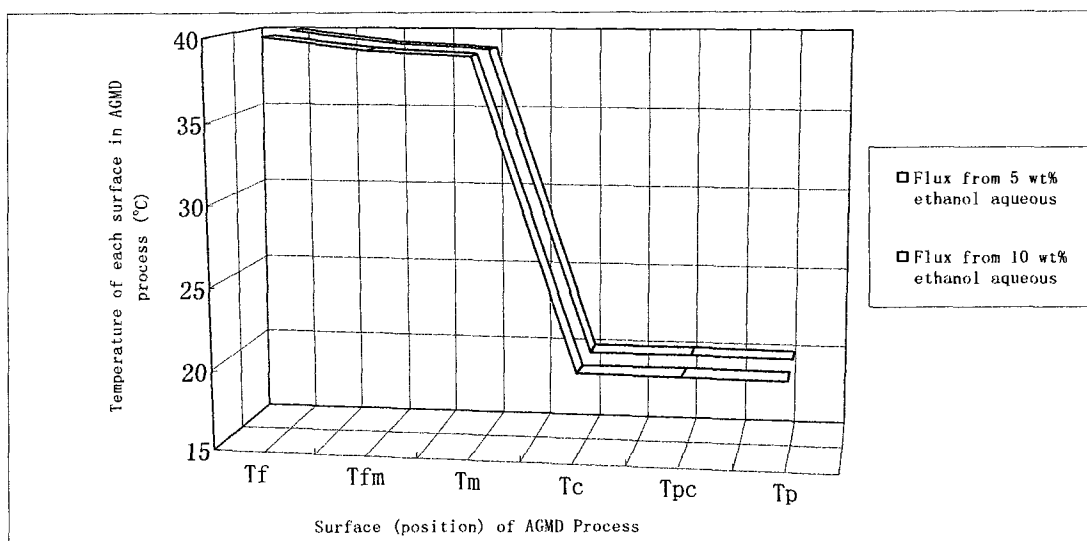


Figure 6.14 Temperature profile of AGMD process with aqueous ethanol solution
Feed temperature, 40°C; Cooling stream temperature, 20°C.

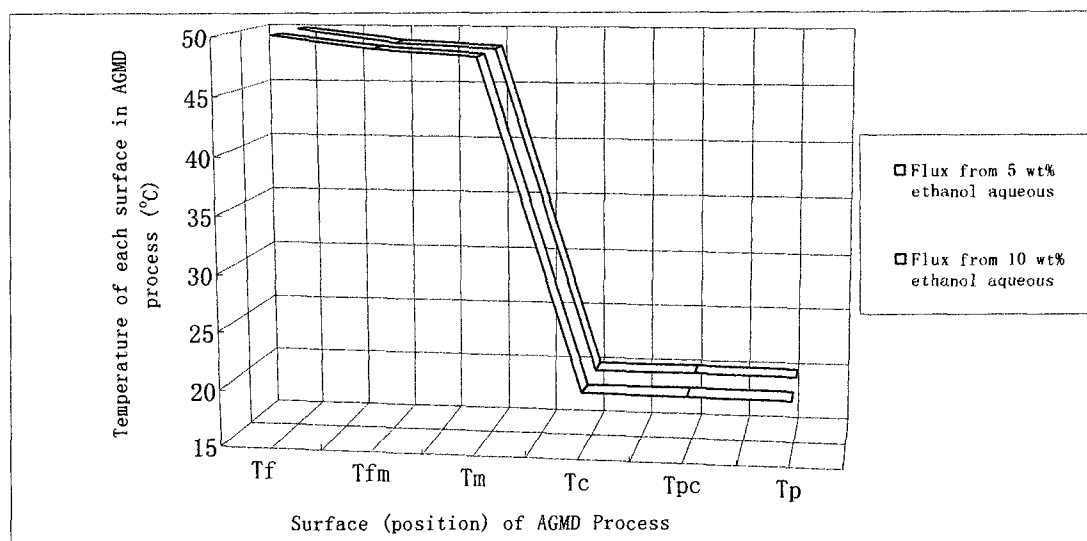


Figure 6.15 Temperature profile of AGMD process with aqueous ethanol solution
Feed temperature, 50°C; Cooling stream temperature, 20°C.

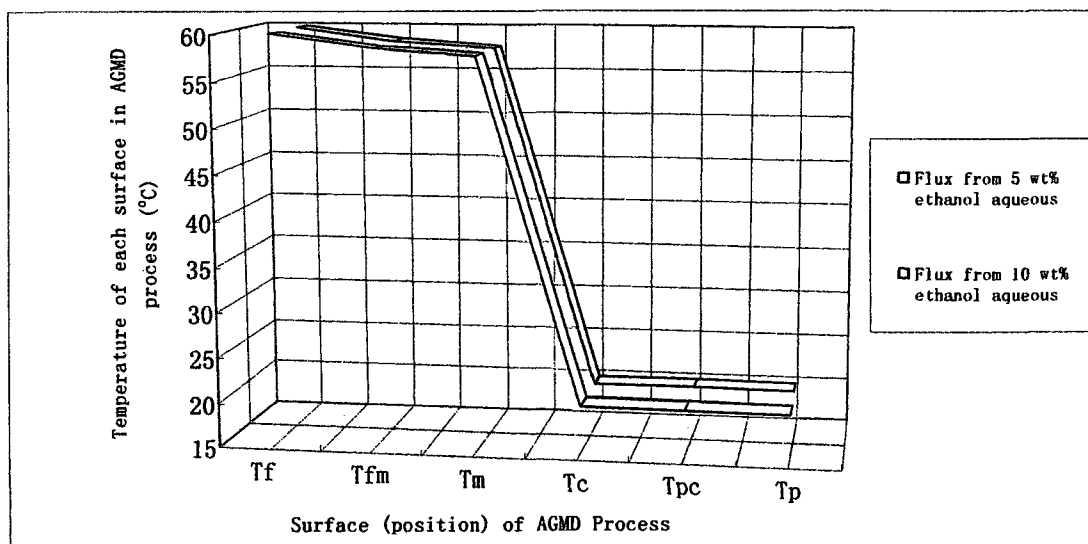


Figure 6.16 Temperature profile of AGMD process with aqueous ethanol solution
Feed temperature, 60°C; Cooling stream temperature, 20°C.

Chapter 7 CONCLUSIONS OF AGMD MEMBRANE DISTILLATION

From the experimental results and the AGMD modeling analysis, the following conclusions can be drawn.

1. Membrane distillation has a great potential as a novel separation process.
2. Membrane distillation can be used as an alternative method for desalination and solution concentration.
3. PVDF nanofiber membrane fabricated by electrospinning can be used for membrane distillation, particularly for AGMD.
4. The AGMD flux can be obtained with sufficiently high accuracy by equation (4-20) that is based on the transport through the air gap.
5. Using 1 wt %, 3.5 wt%, 6 wt% and 22 wt% aqueous NaCl solutions as feed, the highest AGMD flux achieved was $11 \text{ kg/m}^2 \text{ h}$. All the salt rejections were over 98.8 %. The long term running experiment showed that the PVDF nanofiber membrane and the AGMD system were stable for at least 25 days. Thus, AGMD with the newly developed PVDF nanofiber membrane seems to have a potential to compete with commercial micro-filtration membranes.
6. The AGMD system with the newly developed PVDF nanofiber membrane also enabled 5 wt % and 10 wt % aqueous ethanol solutions to be concentrated to 16 wt % and 21 wt %, respectively, when the feed solution temperature was 60°C . The AGMD flux was about $0.84\text{--}3.14 \text{ kg/m}^2\cdot\text{h}$.
7. The temperature polarization coefficient defined by equation (4-33) is above 0.93 for

both single and two volatile components feed solutions. This is because the largest heat resistance occurs at the air gap.

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FUTURE RESEARCH WORKS

1. NANOFIBER MATERIAL RESEARCH

It has been shown in Part I that various nanofibers could be electrospun from different polymers. Thus, the electrospinning technology is a simple, cheap and viable method to fabricate nano-materials. Depending on the polymer, the nano-material has its own specific application. The future research on electrospinning technology can be extended to the following direction:

1) Material Development for Separation Processes

Novel nano-materials can be produced by electrospinning for separation applications other than membrane distillation.

2) Material Development for Bio-engineering

Collagen nanofiber was successfully electrospun. It has a potential to be used for bio-scaffold and drug release control. It may also be used for nerve guiding growth. Possibility of electrospinning nanofibers from other biopolymers such as poly(lactide-co-glycolide) (PLLG), Chitosan and poly(L-lactide) (PLLA) and so on, should also be explored.

3) Development of Inorganic/Organic Blend Nanofibers

It would be interesting to blend TiO_2 , ZnO and other inorganic materials with polymers to electrospin hybrid nano-materials. These composite materials have a great potential in various applications due to considerably increased mechanical strength. For example, electrospinning can spin continuous inorganic or particulate/polymer blend fibers with nanoscaled diameters in the range of 50 to 5000 nm. Also those materials can be as a precursor for making inorganic nanofiber.

4) Development of Carbon Nanofibers

PAN nanofibers have been successfully electrospun. It is known that the diameter of PAN nanofiber can be reduced below 100 nm. PAN nanofibers can serve as a precursor for carbon nanofibers.

2. MEMBRANE DISTILLATION RESEARCH

It has been shown in Part II, PVDF nanofiber membrane was successfully applied for membrane desalination by AGMD. Further research direction of AGMD by nanofiber membranes is as follows:

1) Large scale AGMD Experiment

A pilot plant scale AGMD system needs to enable economic and engineering analysis of AGMD by PVDF nanofiber membranes.

2) Module Design of AGMD

AGMD process performance is affected not only by the membrane, but also by the module configuration and the system design. Optimization is necessary in both aspects to maximize the performance of the AGMD process.

3) Research on Alcohol/Water Mixture and Other Applications

As shown in Part II, AGMD could be used for separation and concentration of alcohol/water mixtures. Because of the complex nature of the binary system, modeling of the heat and mass transfer was not done sufficiently in this thesis. This should be accomplished in the future

4) Other Applications

As mentioned earlier, MD process also can be applied for food industrial, recycling and reuse, heavy water treatment and industrial wastewater treatment. All these possibilities should be explored.

APPENDIX I

Microporous Polypropylene Membrane Development for Desalination by Air Gap Membrane Distillation

1. INTRODUCTION

In membrane distillation process, a microporous hydrophobic membrane is in contact with an aqueous heated solution on one side (feed or retentate). The hydrophobic nature of the membrane prevents a mass transfer in liquid phase and creates a vapour-liquid interface at the pore entrance. Here, volatile compounds evaporate, diffuse and/or convect across the membrane pores, and are condensed and/or removed on the opposite side (permeate or distillate) of the system. The nature of the driving force, in synergy with the hydro-repellent character of the membrane, allows the complete rejection of non-volatile solutes such as macromolecules, colloidal species, ions, etc. Lower temperatures and pressures with respect to those usually used in conventional distillation column are generally sufficient to establish a quite interesting trans-membrane flux, with consequent reduction of energy costs and mechanical requirements of the membrane. Typical feed temperatures vary in the range of 30–80 °C, thus permitting the efficient recycle of low-grade or waste heat streams, as well as the use of alternative energy sources (solar, wind, or geothermal). In addition, the possibility of using plastic equipment also reduces or avoids erosion problems.

In MD, membrane is not involved in the transport phenomena on the basis of its selective properties. Volatile compounds are transferred across the membrane according to vapour-liquid equilibrium principia, whereas the microporous polymeric material acts as physical barrier between two phases and sustains the interfaces where heat and matter are simultaneously exchanged. Since the hydrophobic character of the membrane represents a crucial requirement, membranes have to be made by polymers with a low value of surface energy. Polymers such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) are commonly employed in the preparation of membranes for MD applications. Microporous hydrophobic membranes are manufactured by sintering, stretching, and phase inversion [1-3]: for instance, PP membranes are generally prepared by stretching and thermal phase inversion, PTFE membranes by sintering or stretching, PVDF membranes by phase inversion.

As polypropylene is cheaper and also has very high hydrophobic character. It was chosen as initial polymer for fabricating novel MD membranes in the current research.

Microporous polypropylene membranes have a wide variety of applications as an efficient material for separation. They are used in oxygenators [4], gas separation [5], blood purification [6] and other aspects. So far two methods have been developed for the preparation of microporous membranes. The traditional way is the stretch method [4]. Microvoids will form upon stretching of polymer because of the separation of the lamellae. After heat-setting microporous membranes are obtained [7-12]. This process is simple and easy to perform, but the distribution of membrane pore size is not easy to be controlled. Another method to prepare microporous PP fiber membranes is through the process of thermally induced phase separation (TIPS) [13]. A homogeneous solution is formed at an elevated temperature by dissolving the polymer in a solvent with high-boiling point and low molecular weight. The solution is cooled at a controlled rate or quenched to induce phase separation. After the diluent is removed (typically by solvent extraction) microporous hollow fiber membranes can be obtained [14–17]. However, membranes formed via TIPS are somewhat fragile and a dense skin is easy to form during TIPS process. Therefore, if the porosity is the same, the permeability of the membranes formed via TIPS seems lower than those obtained via the stretch method.

The requirements for the MD membranes are high hydrophobic character and high porosity. The objective of this work is to develop microporous PP membranes with high hydrophobic character and high porosity by the wet phase inversion technique. More specifically, PP is dissolved in a solvent together with a pore former. Xylene or kerosene is chosen as the solvent since it is known that PP can be dissolved in the latter solvents at a high temperature [18]. The PP solution is then cast into a film and the pore former is leached out leaving a micro-porous structure. The porous PP membranes are further characterised and tested for air gap membrane distillation.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

The following materials were used for the experiments.

- Polymer Materials:
 - A: Syndiotactic: Polypropylene (PP), Mw=127K, (Sigma-Aldrich).
 - B: Isotactic: Polypropylene (PP), Mw=250K, (Sigma-Aldrich).
- Pore former (Additive) :
 - PEG (polyethylene glycol) Mw=2,000, (Sigma-Aldrich).
 - PVP (polyvinyl pyrrolidone) Mw=10,000, (Sigma-Aldrich).
 - Dodecylbenzene Sulfonic Acid (DSA), (Sigma-Aldrich).
- Solvent:
 - Xylene (CP, Sigma-Aldrich).
 - Kerosene (CP, Sigma-Aldrich).
- Other chemicals:
 - NaCl (CP, Sigma-Aldrich).

2.2. Membrane preparation

1) Membrane Casting Solution Preparation

The method of membrane preparation is as follows.

7 g of polypropylene was added to 87-93 g of xylene or kerosene in a 250ml glass bottle and the bottle was placed in an oven that was kept at 130 °C. When the polymer was dissolved in the solvent, a clear solution was obtained. While keeping the solution at 130 °C, 3-6 g a pore former (either DSA, or PEG or PVP) was further added to the solution. The solution was stirred at the high temperature to let the pore former and polymer be mixed homogeneously. The compositions of the casting solutions are summarised in Table 1.

Table 1 Composition of membrane casting solution

No.	Solvent	Polymer (PP)	Concentration of Polymer	Concentration of DSA	Concentration of PEG	Concentration of PVP
1	Xylene	Isotactic	7 %	0	0	0
2			7 %	3%	0	0
3			7 %	0	3%	3%
4		Syndiotactic	7 %	0	0	0
5			7 %	3%	0	0
6			7 %	0	3%	3%
7	Kerosene	Isotactic	7 %	0	0	0
8			7 %	3%	0	0
9			7 %	0	3%	3%
10		Syndiotactic	7 %	0	0	0
11			7 %	3%	0	0
12			7 %	0	3%	3%

2) Membrane casting

The polymer solution of high temperature prepared above was poured onto a glass plate which was kept at 90°C. A casting bar designed and fabricated at the Chemical Engineering shop was applied to spread the solution on the glass plate uniformly. After the cast polymer solution film was cooled to the room temperature, it was dried in air for 48 hours. Then, the dry film together with the glass plate was immersed into water where membrane was peeled off from the glass plate spontaneously. The membrane was further washed in warm distilled water (60 °C) to leach out the pore former. The warm water was changed every half hour for two hours. The membrane was air-dried prior to its characterization and AGMD testing.

2.3. Membrane Characterization

- Membrane thickness: Membrane thickness was measured by a micrometer (COMBIMIKE, Mitutoyo MFG. CO., LTD. Japan). Measurement was made for at least five different points of a membrane.
- Contact angle: The equilibrium contact angles were measured both for the dense and the microporous membranes by Goniometer (ST, SCHERR TUMICO, USA). Samples prepared for contact angle measurement were evenly placed on a glass slide and fixed by plastic tape. The sample slide was mounted on the plate holder for contact angle measurement. A water droplet (1 μ L) came from a syringe needle to the top surface of the membrane sample. Then, the equilibrium contact angle was measured.
- Liquid entry pressure of water (LEP_w): LEP_w is the pressure that must be applied to pure water before it penetrates into dried membrane pores. This pressure depends on the pore size and the hydrophobicity of the membrane. LEP_w is also a limited pressure for operation by membrane distillation process.
- Membrane morphology: The membrane morphology was studied by Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM): a) the samples were pasted on a SEM sample holder with a double side carbon adhesive tape. Then, they were put into a sputter-coating chamber to coat with Pt., before being subjected to SEM observation. b) AFM investigation was made by Digital Instrument III, Multi-mode AFM.

2.4. Air Gap Membrane Distillation

In an AGMD process, only the feed solution is directly in contact with a membrane. Permeate is condensed on a cooling surface. There is an air gap situated between the membrane and the surface of the cooling chamber. The system used for AGMD is schematically shown in Figure 1.

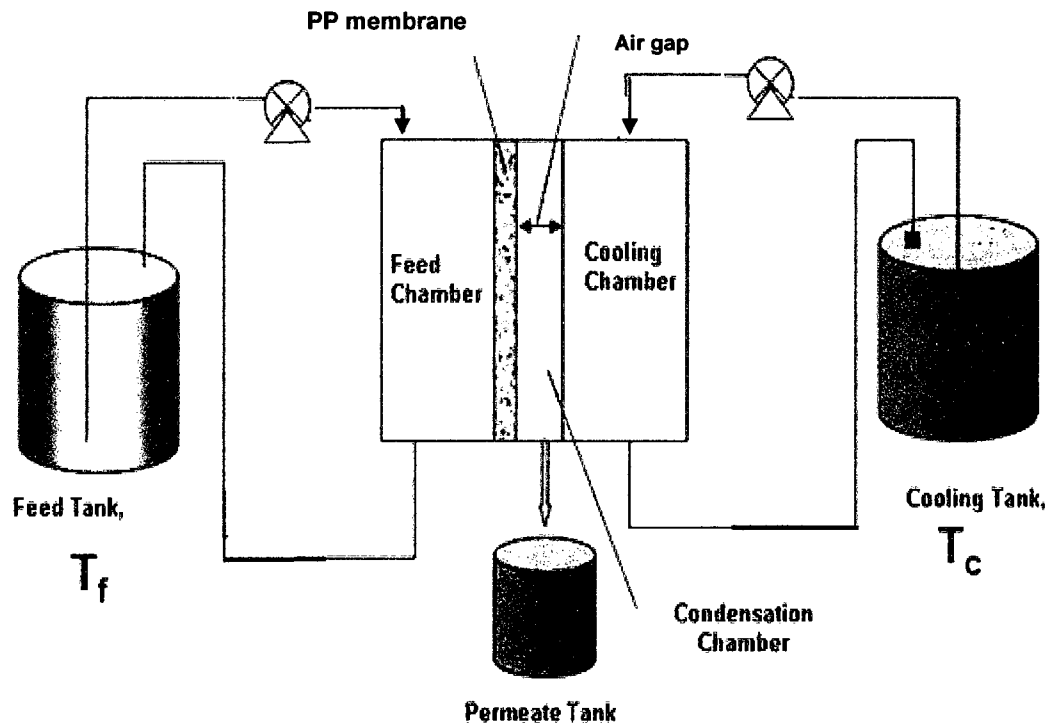


Figure 1 Diagram of AGMD system

The feed which was recycled through the feed line, the cooling water (20 °C) was also recycled. The permeate was collected in a permeate tank. The concentration of permeate was monitored by a conductivity meter (CDM80, Radiometer A/S, Denmark). Based on the NaCl concentration (when the feed is sodium chloride solution) of feed and permeate, the salt rejection is obtained by:

$$\text{Salt rejection} = \left(1 - \frac{\text{concentration in Permeate}}{\text{concentration in Feed}}\right) \times 100\%$$

3. RESULTS AND DISCUSSION

3.1. Membrane Characterization

1) Thickness of membrane

The average thickness of membrane is shown in Table 2, where the membrane number is the same as in Table 2.

Table 2 Thickness of PP membranes

No.	Solvent	Polymer	Thickness of membrane (μm)
1	Xylene	Isotactic	153
2			147
3			138
4		Syndiotactic	116
5			128
6			115
7	Kerosene	Isotactic	137
8			112
9			109
10		Syndiotactic	126
11			118
12			106

From Table 2, the thicknesses of the membranes are in a range of 106-153 μm . No particular trend is observed between the membrane thickness and the membrane composition.

3.1.2. Contact angle of membrane

The equilibrium contact angle of the PP membranes is shown in Table 3.

Table 3 Contact angle of PP membranes

No.	Solvent	Polymer	Contact angle (°)
1	Xylene	Isotactic	110.3±3.3
2			87.6±2.7
3			83.5±1.6.
4		Syndiotactic	106.5±2.5
5			79.4±1.9
6			81.2±2.7
7	Kerosene	Isotactic	106.5±4.3
8			86.3±2.5
9			84.7±3.2
10		Syndiotactic	101.3±2.1
11			83.2±1.3
12			79.6±3.2

Table 3 shows that the contact angles of all the four dense films which were made from the casting solutions without any pore formers are over 100°, regardless of the type of polypropylene and the solvent used. Hence, polypropylene is intrinsically a very hydrophobic polymer. But, the contact angles were considerably reduced when the membranes were made from the casting solutions into which pore formers were added. All of them showed contact angles lower than 90°. The high contact angle of the PP films seems to be due to the dense structure of the film. On the other hand, the lower contact angles of the porous PP membranes are due to the presence of micro-sized pores. It is also possible that the pore formers could not be leached out completely because of their hydrophobic nature, although they are not as hydrophobic as polypropylene

polymer, and the residual pore formers made the membrane surface a little bit more hydrophilic.

3.1.3. Membrane Liquid entry pressure of water (LEPw)

Liquid entry pressure of water (LEPw) is a very important parameter of membranes when they are applied for membrane distillation. The pressure of the feed chamber of the MD setup should not be higher than LEPw, since otherwise the feed liquid will penetrate into the membrane pores and wet the membrane. The method of LEPw measurement can be found in Part I.

The LEPw of PP membranes is shown in Table 4.

Table 4 Liquid entry pressure of water (LEPw) of PP membranes

No.	Solvent	Polymer	LEPw (psig)
1	Xylene	Isotactic	93.3± 3.1
2			39.7±2.3
3			46.3±3.2
4		Syndiotactic	108.2±2.5
5			38.6±5.2
6			42.3±1.6
7	Kerosene	Isotactic	87.3±4.6
8			36.2±1.5
9			47.4±3.6
10		Syndiotactic	96.3±2.8
11			38.6±1.7
12			43.6±3.3

Table 4 shows that, the LEPws of the membranes without pore former (membranes 1, 4, 7 and 10) are higher than 90 psig, except for membrane 7. On the other hand, the porous membranes prepared from the casting solutions with pore formers have significantly lower LEPw values (below 50 psig without exception).

3.1.4. Membrane Structure

a) SEM

Figure 2 shows the SEM images of all the studied PP membranes. Each PP membrane made with a pore former clearly shows a porous structure. The membranes without pore former (membranes 1, 4, 7, 10) have more dense structures. It is interesting to note that no clear porous structures were observed for the latter membranes, even though LEPw data were obtainable. Probably, those membranes also have porous structures, even though they are not detected by SEM. Similar to the TIPS method, for which pores are formed while a semi-crystal polymer solution is cooled by the phase separation, porous structure could also be formed without any pore formers while the solvent is being evaporated.

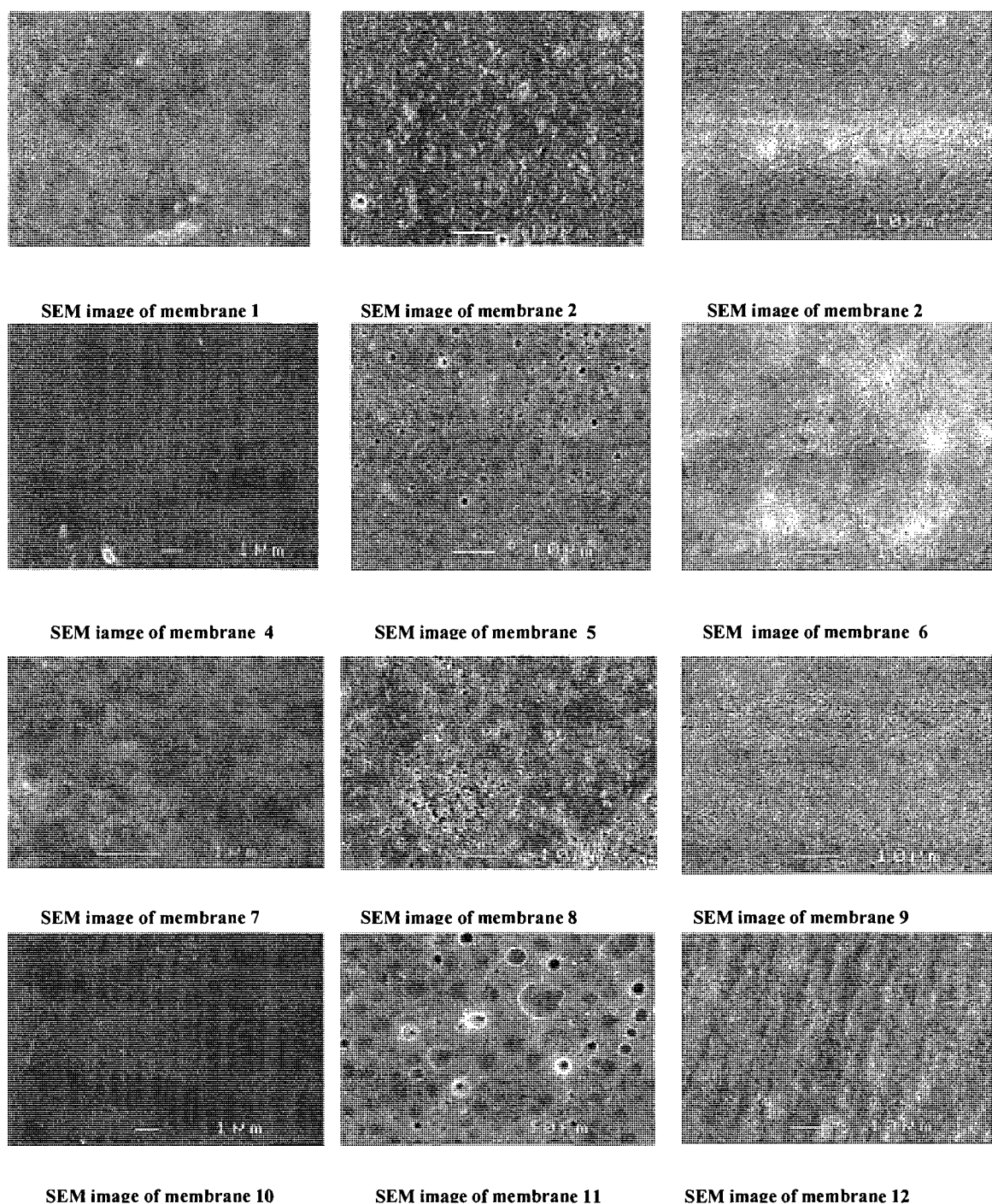


Figure 2 SEM images of PP membranes

b) AFM

Figure 3 shows the AFM images of all the studied membranes. The pore structures of the dense membranes (membranes 1, 4, 7 and 10) are clearly seen. Another interesting

observation is that the macromolecular nodules tend to aggregate when kerosene is used as the solvent, while they tend to remain individual when xylene is used as the solvent.

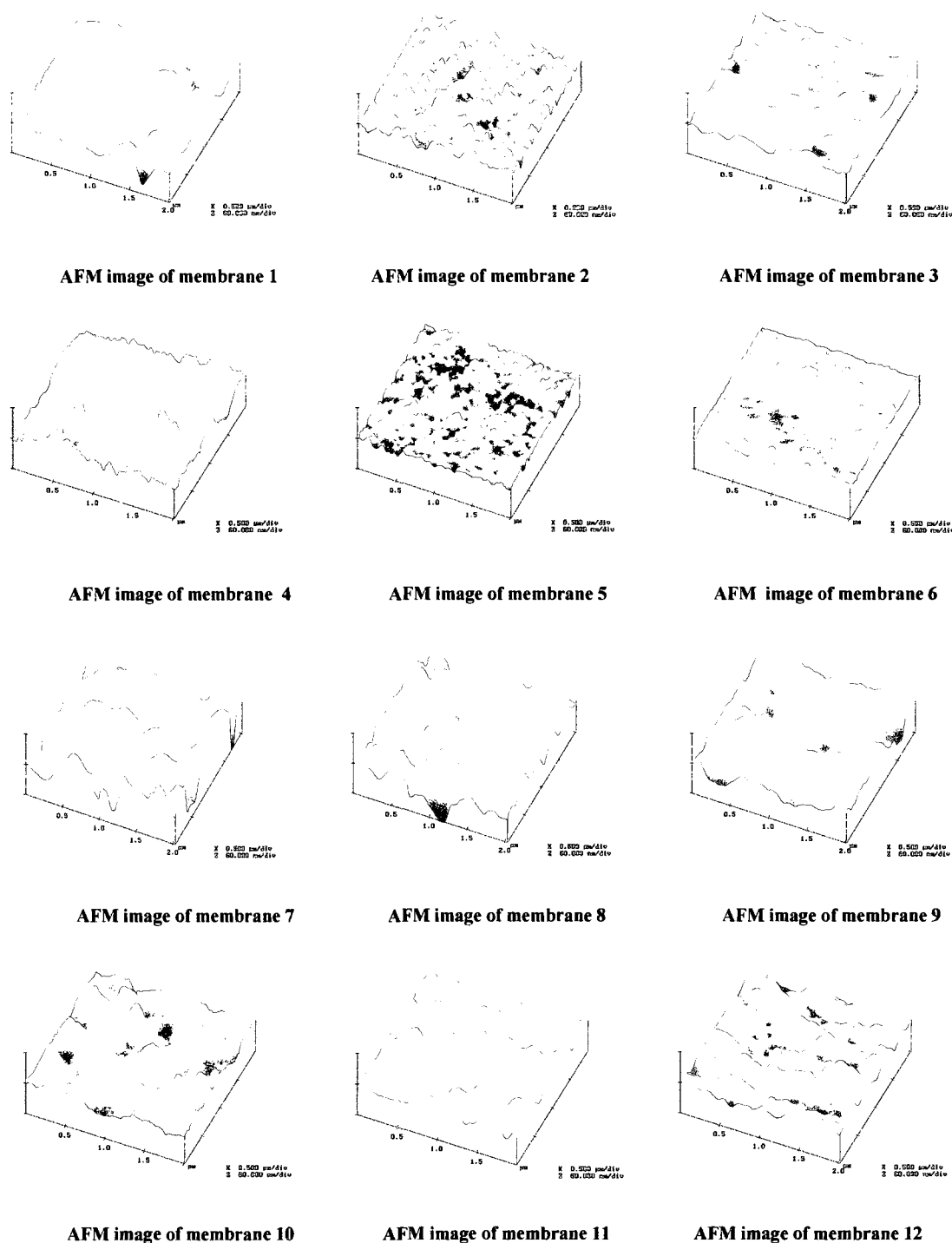


Figure 3 AFM images of PP membrane

3.2. Membrane distillation

The results of AGMD experiments are given in Table 5. Either distilled water or 500ppm NaCl solution was used as feed. Since the LEPw values of all the prepared membranes were higher than 30 psig, the feed pressure was set equal to 30 psig. The temperature of the feed water (solution) was 60 °C and the cooling water was 20 °C.

Table 5 AGMD membrane distillation

No.	Solvent	Polymer	Pure Water (L/m ² .h)	NaCl 500ppm	
				Flux (L/m ² .h)	Rejection %
1	Xylene	Isotactic	0	0	-
2			27.6	18.9	23.6
3			28.3	19.4	37.6
4		Syndiotactic	0	0	-
5			26.5	17.2	33.8
6			30.7	23.2	43.7
7	Kerosene	Isotactic	0	0	-
8			28.4	15.5	39.6
9			31.2	26.4	46.3
10		Syndiotactic	0	0	-
11			36.6	23.2	31.2
12			29.4	21.3	43.1

The membranes prepared without adding pore formers (membrane 1, 4, 7 and 10) did not show any evidence of membrane transport. It provides a strong evidence for the absence of the obvious pores for the vapour transport. However, the membranes prepared with pore formers showed some permeation. When the feed is distilled water, the flux of permeate was higher than 26 kg/m².h. When the feed is the NaCl solution, the permeate flux was significantly lower than distilled water. The highest solute rejection value was

43.6 %. This dictates that some feed NaCl solution leaks through the pores of large sizes in liquid form.

4. CONCLUSIONS

A number of works on fabricating microporous PP membrane for MD and other application [19-22] have been made. This is still another attempt of fabricating PP membranes of high hydrophobicity and high porosity based on the dry-wet phase inversion technique. From the experimental results, the following conclusions have been drawn:

1. Porous polypropylene membranes can be fabricated by the dry-wet phase inversion technique when appropriate solvents, such as xylene and kerosene, and pore formers, such as DSA, PEG and PVP, are used.
2. The membrane pore size is increased by adding a pore former.
3. Solvent has an effect on the membrane structure.
4. The AGMD fluxes of the membranes were 26.5-31.2 L/m² h, when the feed was distilled water, under the AGMD conditions used in this study. When the 500 ppm sodium chloride solution was used as feed, the fluxes were 15.5-26.4 L/m² h. The salt rejections were equal to or below 46.3%, indicating the leak of feed solution through some of the membrane pores.
5. The microporous PP membranes fabricated by the present method are not suitable for membrane distillation. But they may have applications in processes other than membrane distillation.

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APPENDIX II

LIST OF ACRONYMS

AFM	- Atomic Force Microscopy
AGMD	- Air Gap Membrane Distillation
DCMD	- Direct Contact Membrane Distillation
DMAc	- Dimethylacetamide
DMF	- Dimethylformamide
DNA	- Deoxyribonucleic acid
DSC	- Differential Scanning Calorimetry
ED	- Electro Dialysis
EDR	- Electrodialysis Reversal
GIBCO	- Nutrient Mixture (Ham)
GPa	- Gigapascal= 10^6 kPa
HFP	- Hexafluoro-2-propanol
IPA	- Isopropyl alcohol
IUPAC	- International Union of Pure and Applied Chemistry (IUPAC)
KV	- Kilo voltage
LEPw	- Liquid Entry Pressure of Water
MD	- Membrane distillation
MED	- Multiple-effect distillation
MEE	- Multiple effect evaporation
MF	- Microfiltration
MSF	- Multi stage flash

MWCO	- Molecular-weight cut off
Nomex (PA)	- Polyamide (Dupont)
NSF	- National Science Foundation
OD	- Osmotic Distillation
PAN	- Polyacrylonitrile
PC	- Polycarbonate
PE	- polyethylene
PEI	- Polyetherimide
PES	- Polyethersulphone
PLAGA	- poly(lactide-co-glycolide)
PLLG	- poly(lactide-co-glycolide)
PLLA	- Poly(-l-lactides)
PP	- polypropylene
PS	- polysulfone
PTFE	- polytetrafluoroethylene
PVA	- Poly (vinyl alcohol)
PVC	- Poly (vinyl chloride)
PVDF	- polyvinylidenefluoride
PVP	- Poly (vinylpyrrolidone)
RO	- Reverse Osmosis
SDI	- Silt Density Index
SEM	- Scanning electronic microscopy
SGMD	- Sweeping Gas Membrane Distillation

TDS	- Total Dissolved Solid
Tg	- Glass transition temperature
TIPS	- Thermally Induced Phase Separation
Tm	- Melt Temperature
TOC	- Total Organic Carbon
UF	- Ultrafiltration
VC	- Vapour Compression
VMD	- Vacuum Membrane Distillation

NOMENCLATURES

Greek Symbol:

$[\eta]$:	Intrinsic Viscosity (dl/g)
∇c :	Concentration Gradient (mol/l.m)
∇T :	Temperature Gradient (K/m)
α :	Constant of Transport
δ :	Membrane Thickness (m)
δ_p :	Thickness of Cool Plate (m)
ΔH :	Molar Latent Heat of Vapourization (J/kg)
ΔH_e :	Ethanol Latent Heat (J/kg)
ΔH_w :	Water Latent Heat (J/kg)
ΔP :	Across Membrane Vapour Pressure Difference (kPa)
ΔP_{entry} :	Entry Pressure Difference (kPa)
ε :	Porosity
ε_0 :	Vacuum Permittivity
γ_1 :	Fraction
γ_2 :	Fraction
γ_L :	Surface Tension of Solution (N/m)
γ_{LV} :	Interfacial Tension of Liquid/Vapour (N/m)
γ_{SL} :	Interfacial Tension of Solid/Liquid (N/m)
γ_{SV} :	Interfacial Tension of Solid/Vapour (N/m)
η :	Viscosity of Spinning Dope (cP)
η_0 :	Viscosity of Solvent (cP)
λ :	Molecule free path (m)
μ :	Fluid Viscosity (cP)
μ :	Fluid Viscosity (cP)
μ_p :	Mean Pore Diameter (m)
μ_s :	Mean Particle Size (m)

θ :	Contact Angle
θ :	Temperature polarization coefficient
θ' :	Temperature Polarization Coefficient
θ_1 :	Contact Angle for Component 1
θ_2 :	Contact Angle for Component 2
θ_e :	Effective Contact Angle
ρ :	Fluid Density (g/l)
ρ_m :	Density of Membrane (g/l)
ρ_{pol} :	Density of Polymer Material (g/l)
σ :	Surface Tension of Spraying Liquid (N/m)
σ_g :	Geometric Standard Deviation
σ_p :	Mean Diameter of Particle (m)
σ_s :	Mean Pore Diameter of Membrane (m)
τ :	Membrane Tortuosity

English symbol:

A:	Constant
A_0 :	Intercept
A_1 :	Slope
a_i :	Activity coefficient
a_{water} :	Activity coefficient of water
B:	Empirical coefficient
B:	Constant
C:	Constant
C:	Liquid molar density
c:	Polymer concentration (g/l)
C_f :	Polystyrene latex suspension concentration in feed (g/l)
C_p :	Polystyrene latex suspension concentration in permeate (g/l)
C_p :	Specific heat capacity (J/kg.K)

d :	Droplet diameter (m)
D :	Empirical coefficient
D :	Mass diffusion coefficient
d :	Membrane pore diameter (m)
d_p :	Pore size (m)
d_s :	Particle diameter (m)
E :	Strength of electrical potential (V/m)
f :	Solute rejection
h_g	Heat transfer coefficient of air gap (W/m ² .K)
h_f :	Hot side convection heat transfer coefficient (W/m ² .K)
h_m	Heat transfer coefficient of PVDF nanofiber membrane (W/m ² .K)
h_p :	Cool stream side convection heat transfer coefficient (W/m ² .K)
J :	Flux (kg/m ² .h)
k :	Huggins--Martin constant
k :	Heat conductivity (W/m.K)
k_l :	Heat conductivity of air gap (W/m.K)
$k_{l,e}$:	Membrane heat conductivity of ethanol (W/m.K)
$k_{l,w}$:	Membrane heat conductivity of water (W/m.K)
k_2 :	Thermal conductivity of cooling plate (W/m.K)
k_B :	Boltzman constant
k_g :	Thermal conductivity of air (W/m.K)
k_m	Membrane heat conductivity (W/m.K)
$k_{material}$:	Heat conductivity of polymeric material (W/m.K)
K_n :	Knudsen number
L :	Heat diffusion coefficient
L :	Air gap distance (m)
M :	Water molar mass
N :	Evaporated vapour flux
N_e :	Evaporated ethanol vapours flux
N_w :	Evaporated water vapour flux

P^0 :	Liquid saturation pressure above a convex (kPa)
P_{entry} :	Entry vapours pressure (kPa)
P_{liq} :	Vapour partial pressure at liquid surface (kPa)
Pr :	Prandtl number
P_{vop} :	Vapour partial pressure close to the condensate surface (kPa)
Q :	Charge of the particle
Q :	Heat transfer from warm feed to membrane surface
R :	Gas constant
Re :	Reynolds number
$r_{p, \text{max}}$:	Largest pore size (m)
r_p :	Membrane average pore size (m)
T :	Temperature (K)
T_1 :	Temperature of feed solution (K)
T_2 :	Temperature of cooling side (K)
T_c :	Temperature on the the surface, facing the air gap (K)
T_f :	Temperature of warm feed solution (K)
T_{fm} :	Temperature on the membrane surface (K)
T_g :	Glass transition temperature (K)
T_m :	Melt point temperature (K)
T_m :	Temperature on the membrane surface (K)
T_m :	Temperature of membrane (K)
T_p :	Temperature of the surface, facing cooling stream, of the cooling plate (K)
T_p :	Bulk temperature of cooling stream (K)
T_{pc} :	Temperature at the surface, facing cooling water, of the cooling plate (K)
v :	Fluid velocity (m^3/s)
V_T :	Total or bulk volume of material (m^3)
V_v :	Volume of void-space (m^3)
X_{NaCl} :	Mole fraction of sodium chloride
Y_{ln} :	Mole fraction of air at the pore inlet and at the pore outlet.