# CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE (PVDF) HOLLOW FIBER MEMBRANE ON DIFFERENT LITHIUM CHLORIDE (LiCl) LOADING FOR CARBON DIOXIDE ($CO_2$) REMOVAL

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**NOR ATIKAH BINTI MOHD**

Thesis submitted in partial fulfilment of the requirements
For the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering**
**UNIVERSITI MALAYSIA PAHANG**

JUNE 2015

# SUPERVISOR'S DECLARATION

I hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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| Signature | : |
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| Position | : Lecturer |
| Date | : JUNE 2015 |

# STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : NOR ATIKAH BINTI MOHD
ID Number : KC11016
Date : JUNE 2015

# DEDICATION

Special Dedication of This Grateful Feeling to My…

Beloved family,
That always loves me,
My friends, my fellow colleague,
Supportive Supervisor
Dr. Rosmawati binti Naim,
and all friends.

For all your care, support and believed in me.

# ACKNOWLEDGEMENT

Bismillahirrahmanirrahim, Allhamdulillah, my source of strength, protection, guidance, and blesses were obtained from Allah and I would be able to face all the impediments and the hardships of completing this research.

Firstly, I am grateful to who have supported me to make this work a success. I would like to take this great opportunity to express deep gratitude to my research supervisor, Dr. Rosmawati bt Naim, for her guidance and valuable advices to complete this research.

I would also like to thank University Malaysia Pahang (UMP) for providing good facilities in the campus and FKKSA laboratory for providing excellent lab facilities to carry out this research.

Last but not least, I am full of praise and thanks to my beloved family, friends and colleagues for their help, support and understanding during completion of this research.

# ABSTRACT

In this study, hollow fiber membranes (PVDF – LiCl) were studied as one of the efficient alternatives for carbon dioxide removal. The membranes were prepared via phase inversion method by using the wet spinning process. An aqueous dimethylacetamide (DMAc) solution was used as a solvent. The experimental was conducted to investigate the effect of different lithium chloride (LiCl) concentration on the membrane properties and membrane structure. The prepared fibers were characterized in term of gas permeation, critical water entry pressure (CEPw), water contact angle and morphology analysis. Results of gas permeation test showed that with increasing of LiCl concentration, the pore size of membrane became smaller and increased in the effective surface porosity. The cross-section, inner surface and outer surface of membranes were examined via scanning electron microscopy (SEM). It gave a result that by addition of LiCl, membrane structure change from finger-like to sponge-like layer, which resulted in a high wetting pressure and $N_2$ permeation rates. Membrane with 5% LiCl gave higher hydrophobicity than plain PVDF and 3% LiCl membrane. It was suggested that higher hydrophobicity of PVDF membrane may be an effective way for long-term operating performance of $CO_2$ removal. Therefore, these results concluded that small pore size, high surface porosity and high wetting resistance are the important factors in producing an efficient membrane for $CO_2$ removal.

# ABSTRAK

Dalam kajian ini, membran gentian geronggang (PVDF - LiCl) telah dikaji sebagai salah satu alternatif berkesan untuk penyerapan karbon dioksida. Membran disediakan melalui kaedah fasa penyongsangan dengan menggunakan proses berputar pelarut. Larutan dimethylacetamida (DMAc) telah digunakan sebagai pelarut. Eksperimen ini dijalankan untuk mengkaji kesan kepekatan litium klorida (LiCl) yang berbeza terhadap sifat membran dan struktur membran. Gentian yang tersedia telah dicirikan dari segi penyerapan gas, tekanan kemasukan air kritikal (CEPw), sudut sentuhan air dan analisis morfologi. Keputusan ujian penyerapan gas menunjukkan bahawa dengan peningkatan kepekatan LiCl, saiz liang membran menjadi lebih kecil dan peningkatan keliangan permukaan berkesan. Keratan rentas, permukaan dalaman dan permukaan luar membran telah diperiksa melalui mikroskop imbasan elektron (SEM). Ia menunjukkan keputusan apabila ada penambahan LiCl, struktur membran berubah daripada seperti bentuk jejari kepada seperti bentuk lapisan span, yang mengakibatkan tekanan kebasahan dan kadar penyerapan $N_2$ menjadi tinggi. Membran dengan 5% LiCl memberi *hydrophobicity* yang lebih tinggi daripada PVDF biasa dan membran 3% LiCl. Ia telah dicadangkan bahawa membran PVDF yang mempunyai *hydrophobicity* tinggi boleh menjadi cara yang berkesan untuk prestasi operasi jangka panjang bagi penyingkiran $CO_2$. Oleh itu, kesimpulannya bahawa saiz liang kecil, keliangan permukaan yang tinggi dan rintangan kebasahan tinggi adalah faktor penting dalam menghasilkan membran berkesan untuk penyingkiran $CO_2$.

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## LIST OF SYMBOLS

| | |
|---|---|
| cm | centi meter |
| $K_o$ | slope |
| nm | nano meter |
| ppm | part per million |
| $P_o$ | intercept |
| µm | micro meter |
| $^oC$ | degrees Celcius |

## LIST OF ABBREVIATIONS

| | |
|---|---|
| CEPw | Critical water entry pressure |
| $CO_2$ | Carbon dioxide |
| EPA | Environmental protection agency |
| NMP | N-methylpyrrolidone |
| PE | Polyethylene |
| PES | Polyethersulfone |
| PP | Polypropylene |
| PS | Polysulfone |
| PTFE | Polytetrafluoroethylene |
| PVDF | Polyvinylidene fluoride |
| LiCl | Lithium cloride |
| $N_2$ | Nitrogen gas |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background Study

Carbon dioxide ($CO_2$) is one of the most important greenhouse gases that result from human activities such as industrial and domestic usage. Carbon dioxide ($CO_2$) emissions have a negative impact on global warming. Therefore, it is very important to remove carbon dioxide ($CO_2$) from the flue gas stream and the local industry as an effort to deal with issues of climate change in the future (Mansourizadeh and Ismail, 2011). In addition, human concerns regarding the level of carbon dioxide ($CO_2$) emissions to the atmosphere will affect the economy and demand for gas purification equipment will increase in the future (Rahbari Sisakht et al, 2012).

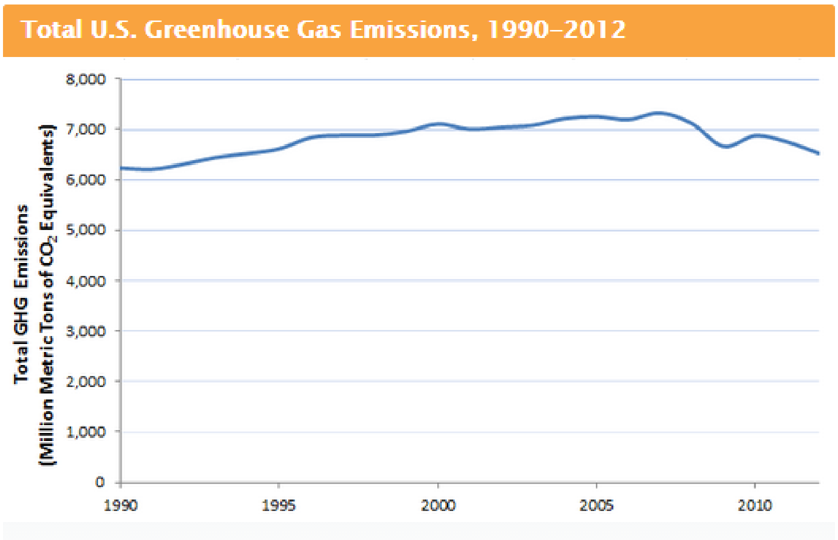

**Figure 0-1**: Emission estimates from the Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2012

Based on Figure 1-1, line graph showed the total United State (U.S.) greenhouse gas emissions for 1990 to 2012. The total greenhouse gas emissions steadily increased from just over 6,000 million metric tons of carbon dioxide equivalents in 1990 to over 7,000 million around 2000. Between 2007 and 2009, the greenhouse gas emissions decline to about 6,600 million metric tons of carbon dioxide equivalents, followed by a slight rebound in 2010 and 2011 to around 6,800 million metric tons and a slight decline in 2012 to around 6,500 million metric tons. Hence, it can be summarized that carbon dioxide ($CO_2$) emissions in the United States increased by about 5% between 1990 and 2012.

Releasing of carbon dioxide to atmosphere can bring harm to the environment because the acid contents in carbon dioxide ($CO_2$) gas are hazardous. According to United State Environment Protection Agency (EPA), in 2012, greenhouse gas emissions totalled 6,526 million metric tons of carbon dioxide ($CO_2$). This problem caused temperature of the planet increase (global warming). Currently, the amount of carbon dioxide in the atmosphere is increasing at the rate of about one part per million per year (ppm). If this continues, some meteorologists expect that the temperature of the earth will increase by about 2.5 degrees celsius and it could be to cause glaciers to melt, which would cause coastal flooding. The changing climate impacts society and ecosystems, such as climate change can increase or decrease rainfall, influence agricultural growth, affect human health, cause changes to forests, animal habitats and other ecosystems.

Therefore, it is important to lower the negative impact of environment. Priority should be given to the technologies with enhanced carbon dioxide ($CO_2$) removal efficiency that can minimize the impacts. Membrane technology is one of the promising alternatives for carbon dioxide ($CO_2$) removal due to its favourable mass transfer performance (Mansourizadeh and Ismail, 2011).

Numerous studies have been conducted for $CO_2$ removal by using the hollow fiber membrane, e.g. Nishikawa et al. (1995), Klaassen and Jansen (2001), Chen and Li (2005), Rongwong et al. (2009), Mansourizadeh et al. (2010), Khaisri et al. (2011), Mansourizadeh, A. (2012), Naim et al. (2013), and Rezaaei et al. (2015). For carbon dioxide ($CO_2$) absorption study, some of the microporous hydrophobic membrane was used, which are polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). Although the physical and chemical properties of membranes is well understood, the improvement of the membrane structure must be always explored by the researchers to get the most effective membrane structure for efficient $CO_2$ removal. In this study, polyvinylidene fluoride (PVDF) was used because it is hydrophobic polymers dissolved in the some solvent, which can be used in phase-inversion process for the preparation of asymmetric membranes. This membrane showed in easy controlled membrane structure and morphology (Rezaei et al, 2014).

In recent years, several methods have been carry out for capturing of carbon dioxide ($CO_2$), such as chemical and physical absorption, solid adsorption, cryogenic distillation, and membrane separation (Naim and Ismail, 2013). Microporous hollow fiber membrane contactor system for carbon dioxide ($CO_2$) absorption is has attracted researchers' attention to apply this in carbon dioxide ($CO_2$) absorption because gas and liquid can contact on the gas-liquid interface at the mouth of each membrane pore (Naim et al., 2013). Mansourizadeh, (2012) studied that the membrane was the most important element of the membrane contactor. Effective membrane required high hydrophobicity, high surface porosity, low mass transfer resistance and excellent resistance to get a better result performance.

Li and Chen (2005) reported that Qi and Cussler were the first to establish the idea of the hollow-fiber contactor using a microporous polypropylene (PP) hollow fiber membrane for absorption of carbon dioxide ($CO_2$) and aqueous sodium hydroxide solution was used as an absorbent.

In this study, a microporous PVDF membrane is one of the promising candidates for use in membrane contactors due to relatively high hydrophobicity, high chemical resistance and reasonable material cost (Rajabzadeh et al, 2009). PVDF is the only hydrophobic polymer that can be dissolved in common solvents to prepare asymmetric membranes via phase-inversion process (Mansourizadeh and Pouranfard, 2014). LiCl was used as an additive in PVDF/ Dimethylacetamide (DMAc) solution systems for the evolution of high performance hollow fiber membranes. The influence of LiCl concentration on the final membrane structure and the resulting of gas permeation, critical water entry pressure (CEPw), and water contact angle were analyzed (Yeow et al, 2005). This work therefore aims to determine the most efficient characteristics of hollow fiber membrane to reduce the carbon dioxide by using absorption method.

## 1.2 Problem statement

One of the main challenges of membrane gas absorption technology is the pore wetting that occurs during the research. This problem can reduce the mass transfer coefficient of the membrane module. The main cause of pore wetting is capillary condensation (Naim et al., 2013). According to Dindore et al. (2004), they reported that this problem depends on a number of membrane properties such as pore size, hydrophobicity, surface roughness and chemical resistance to solvents, on the surface tension of solvent and operating conditions of absorption process. Therefore, it is possible to lower the wet ability of membranes by reducing the membrane pore size and increasing the surface of membrane (Rongwong et al., 2009).

## 1.3 Objectives

The following are the objectives of this research:

1) To prepare the PVDF hollow fiber membrane via phase inversion process.
2) To study the effect of lithium chloride (LiCl) loading on the membrane properties and membrane structure.

## 1.4 Scope of this research

The following are the scope of this research:-

1) The polyvinylidene fluoride (PVDF) polymer dope making by using lithium chloride (LiCl) as an additive and spinning process for obtaining hollow fiber membrane.

2) Characterization of PVDF hollow fiber membrane in term of gas permeation, critical water entry pressure (pr), water contact angle and morphology analysis by using scanning electron microscopy (SEM).

## 1.5 Organisation of the thesis

*Chapter 1* Present the research background of $CO_2$ removal by membrane gas absorption process, determine the motivation, problem statement, objectivities, scope f the research and structure of this thesis.

*Chapter 2* Present the overview of the research. A general definition and type of membrane module were defined. A description of hollow fiber membrane, lithium cloride as an additives and as well as behaviour of membranes that can also be described with additional dimensionless numbers. This chapter also provides a brief review on previous research done on hollow fiber membrane and a method to prepared hollow fiber membranes..

*Chapter 3* gives a description of the methodology of this research work including the chemicals and equipment's used. The methods of membranes fabrication and characterization also was described in details, and observe the changes of membrane surface morphologies by scanning electron microscopy (SEM) in this chapter.

*Chapter 4* Investigate the effects of different concentration of lithium chloride (LiCl) on membrane fiber characteristics and morphology.

*Chapter 5* Presents about the final conclusion and summarise of this study.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Overview

This chapter will point out about the definition and the basic concept of membrane technology, membrane structure that have been used nowadays, membrane module in gas removal industry and also characteristic of membranes involve in this research.

## 2.2 Introduction to membrane

### 2.2.1 Membrane definition

Membrane can defined in various terms of definition, basically as thin layer of semi-permeable barrier, which separate two phases and restrict transport of various chemical when a driving force is applied across the membrane (Baker, 2004), and also can described as a selective barrier between two phases, the term ‘selective’ being inherent to a membrane or a membrane process (Mulder, 1996). Membrane can be thick or thin, its structure can be homogenous or heterogeneous, solid or liquid, symmetric or asymmetric and transport can be active or passive, which passive transport can be cause by a pressure, concentration or a temperature difference (Mulder, 1996). This membrane process are increasingly used nowadays for environmental application such removal of carbon dioxide ($CO_2$).

### 2.2.2 Carbon dioxide ($CO_2$) removal

Carbon dioxide ($CO_2$) is one of the acid gases which have to be removed from natural gas, to prevent the corrosion problem and the global warming problems. The removal of the carbon dioxide ($CO_2$) is important as carbon dioxide ($CO_2$) can cause corrosion as well as greenhouse effect with approximately 55% of the global warming. Therefore, the removal of the carbon dioxide ($CO_2$) from the natural gas must be done before further bad impacts to environment and health. In industrial gas processing, there is an increasing interest in gas absorption processes for the selective removal of acid gases from the raw gas streams. The processes of removing carbon dioxide ($CO_2$) can be done by using membrane separation, chemical absorption, physical absorption, cryogenic methods, and biological fixation and by gas permeation (Mansourizadeh and Ismail, 2011b).

Absorption process can offer a very high selectivity and a high driving force for transport even at very low concentration in the reaction (Klaassen et al, 2008). Besides that, another advantages of absorption process over conventional contacting devices are have high surface area per unit contactor volume, independent control of gas and liquid flow rates without any flooding, loading, weeping, foaming or entrainment problems, small size, modular, and easy to scale up or down (Gabelman and Hwang, 1999).

Since 1980, much research has been completed to remove carbon dioxide ($CO_2$) from flue gas using gas-liquid membrane contactor system. For this purpose, researchers have considered a number of factors such as membrane materials, absorption solution, and membrane module to improve the performance of the removal of carbon dioxide ($CO_2$) (Rahbari Sisakht et al., 2012).

### 2.2.3 Advantages and disadvantages of membrane

Membranes process has numerous numbers of advantage and disadvantage compared to other conversional methods.

The advantages of membrane include:

- Membranes can be produced with extremely high selectivity for the components to be separated/remove. In general, the values of this selectivity are much higher than typical values for relative volatility for distillation operations.
- Because of the fact that a very large number of polymers and inorganic media can be used as membranes, there can be a great deal of control over separation/removal selectivity.
- Membrane processes are able to recover minor but valuable components from a main stream without substantial energy costs.
- Membrane processes are potentially better for the environment since the membrane approach require the use of relatively simple and non-harmful materials.

The disadvantages of membrane include:

- Membrane modules often cannot operate at much above room temperature. This is again related to the fact that most membranes are polymer-based, and that a large fraction of these polymers do not maintain their physical integrity at much above 100 $^{o}$C. This temperature limitation means that membrane processes in a number of cases cannot be made compatible with chemical processes conditions very easily.
- Membrane processes can be saddled with major problems of fouling of the membranes while processing some type of feed streams. This fouling, especially if it is difficult to remove, can greatly restrict the permeation rate through the membranes and make them essentially unsuitable for such applications.

## 2.3 Membrane structure

The proper choice of membrane should be determined by their specific application. There are two type of membrane structure that commonly used which is asymmetric and isotropic membrane (nonporous and microporous). The different between these two structures are the physical and chemical properties (Nunes and Peinemann, 2006).

### 2.3.1 Symmetric and Asymmetric membranes

#### 2.3.1.1 Symmetric membrane

Symmetrical membranes are the properties of the membrane do not change throughout the cross-section of the membrane. Typical thickness of symmetric membranes ranges roughly from 10-200 µm. The resistance to mass transfer is determined by the total membranes thickness. A decrease of membrane thickness results in an increased permeation rate.

#### 2.3.1.2 Asymmetric membrane

Asymmetric or as known as anisotropic are non-uniform over the membrane cross section and they consist of a number of layers each with different structure permeability and chemical composition. The asymmetric consists of a very dense top layer with thickness about 0.1 to 0.5 µm supported by a porous sublayer about 50-150 µm. The asymmetric membranes combine high permeant flow, provided by a very thin selective top layer and reasonable stability (Mulder, 1996). Because the nature of this membrane itself have a thin top layer that acts as a selective barrier film, and a porous sublayer that offer good mechanical strange makes this membrane have been widely used for gas and liquid separation process.

### 2.3.2 Isotropic membrane

Isotropic membranes have a uniform composition structure all through, and they can be porous or dense. The resistance to mass transfer in these membranes are determined by the total membrane thickness. A decrease in membrane thickness brings about an increased permeation rate. Isotropic membrane divided by nonporous and microporous membrane.

#### 2.3.2.1 Nonporous membrane

These types of membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. Dense membranes have the weakness of low flux unless they can be made extremely thin. Therefore, dense membrane properties are joined into the top "skin" layers of asymmetric membranes. The transmembrane of dense nonporous isotropic membrane fluxes through this membrane relatively make it too low for practical separation process and rarely used in membrane separation process. On the other hand, this nonporous isotropic membrane is commonly used in laboratory work to characterize the membrane properties. Most gas separation, pervaporation, and reverse osmosis processes use dense membrane to perform the separation (Baker, 2004).

#### 2.3.2.2 Microporous membrane

This isotropic microporous membrane almost behave like fibre filter and separate by sieving mechanism that determined by the pore diameter and particle size. The pores in the membrane may vary between 1nm- 20 micron (Baker, 2004). By comparing with the isotropic nonporous membrane, the isotropic microporous membranes have higher fluxes and more widely used as microfiltration membrane. The microporous membrane acts as a fixed interface between the gas and the liquid phase without dispersing one phase into another that offers a flexible modular and energy efficient device (Mansourizadeh and Ismail, 2009). Besides, it is also used as inert spacers in a battery and fuel cell applications and as the rate controlling element in controlled drug delivery device (Hazah, 2012).

The simplest form of microporous membrane is a polymer film with cylindrical pores or capillaries. However, more commonly microporous membranes have a more open and random structure, with interconnected pores. They are very similar in structure and function to conventional filters. However, in contrast with conventional filters, these pores are extremely small, on the order of 0.01 to 10 micrometer in diameter (Baker, 2004).

#### 2.3.2.3 Electrical Charged membrane

These types of membranes are also referred to as ion-exchange membranes. They can be dense or microporous, with the pore walls carrying fixed positively or negatively charged ions. A membrane fixed with positively-charged ions is called an anion-exchange membrane because it binds anions (negativeely charged ions) in the surrounding fluid. The reverse is true for a cation-exchange membrane.

Separation is accomplished mostly by exclusion of ions of the same charge as the fixed ions on the membrane structure, and is influenced by the charge and concentration of ions in the solution. This type of membranes is utilized for processing electrolyte solutions as a part of electro dialysis (Baker, 2004).

### 2.3.3 Liquid membrane

Liquid membranes have turn out to be progressively increased in the context of facilitated transport, which uses "carriers" to specifically transport components, for example, metal ions at a generally high rate over the membrane interface.

Generally, development of a thin fluid film is not an issue. Difficulty is encountered, however, in keeping up and controlling this film and its properties during a mass separation process. Reinforcement is important to avoid break-up of the film. Liquid membranes are utilized on a pilot-plant scale for selective removal of heavy-metal ions and organic solvents from industrial waste streams. They have also been utilized for the separation of oxygen and nitrogen.

## 2.4 Membrane module

A membrane module is a pack of the membrane area into the least volume, to lower the capital and operating cost with providing acceptable flow hydrodynamics in the vessel. The effectiveness of the membrane separation process usually depends on the module configuration because the active separation membrane area can affect the membrane module configuration. There are four type of membrane which is tubular, spiral wound, plate and frame and hollow fibres.

### 2.4.1 Tubular membrane module

The tubular module are now generally restricted to ultra-filtration, which is has advantage of resistance to membrane fouling outweighs the high cost. These modules enclose as many as 5 to 7 smaller tubes, each 0.5 to 1.0 cm in diameter (Hazah, 2012). The membrane is often on the inside of a tube and the feed solution is pumped through the tube and permeate is removed from each tube from each tube and sent to permeate collection header.

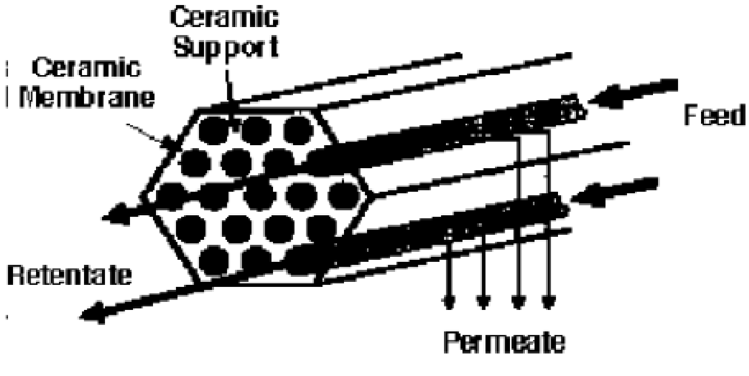

**Figure 2-1**: A schematic drawing of a tubular membrane module (Hazah, 2012).

### 2.4.2 Hollow fibe membrane module

The hollow fiber module also has been widely used for desalination that usually consists of bundle of hollow fibers in a pressure vessel. The system of hollow fiber module will pressurised from the shell side, and the filtrate passes along the fiber wall and exits through the open fiber ends. Bore-side of hollow fiber modules can also be used where the feed is circulated through the fiber (Mansourizadeh and Ismail, 2010a). The most advantages of hollow fiber modules are the ability to pack a very large membrane to single module.

Li and Chen (2005) reported that Qi and Cussler were the first to establish the idea of the hollow-fiber contactor using a microporous polypropylene (PP) hollow fiber membrane for absorption of carbon dioxide ($CO_2$) and aqueous sodium hydroxide (NaOH) solution was used as an absorbent. The fibers used in the contactor are generally not selective. Membranes with a higher selectivity have lower permeability and produce a smaller flux. Thus, the advantage of using non-selective membrane is potentially to get a higher flux.

For carbon dioxide ($CO_2$) absorption study, some of the microporous hydrophobic membrane was used, which are polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). In this study, polyvinylidene fluoride (PVDF) is used because it is hydrophobic polymers dissolved in the same solvent, which can be used in phase-inversion process for the preparation of asymmetric membranes. Microporous PVDF membranes are also used in membrane contactors due to high hydrophobicity, high chemical resistance and reasonable cost of materials.

On the other hand, polyvinylidene fluoride (PVDF), another hydrophobic polymer, has good chemical and thermal resistance, and in contrast with aforementioned polymeric materials are soluble in common organic solvents. Hence it can easily be converted to asymmetric membranes via phase inversion method, resulting in easy controlled membrane structure and morphology (Rezaei et al, 2014).

**Figure 2-2**: A parallel flow hollow fiber module (Gabelman and Hwang, 1999)

### 2.4.3 Plate and frame membrane module

Plat and frame membrane module were one of the earliest type of membrane modules and were widely used in separation process. But, because of their relatively high cost they have replace in most application by spiral wound modules and also hollow fiber modules. Nowadays, the plate frame module used only in electrodialysis and pervaporation system in a limited number of reverse osmosis and ultrafiltration applications with highly fouling condition (Hazah, 2012).

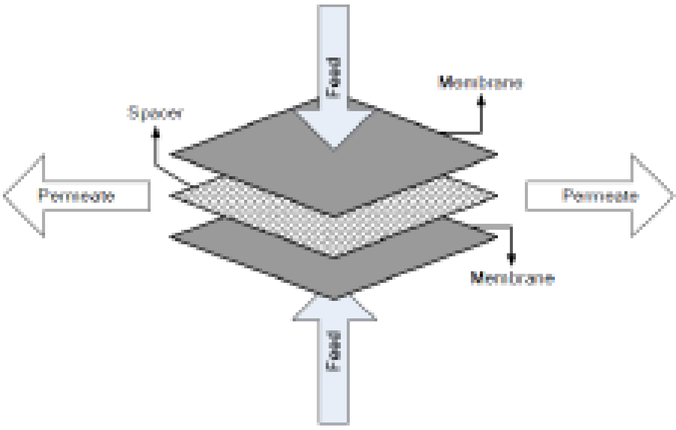

**Figure 2-3**: A schematic drawing of a plate and frame membrane module (Mulder, 1996)

### 2.4.4 Spiral wound membrane module

The spiral wound module very popular in industry for nanofiltration or reverse osmosis membrane. This module has a flat sheet membrane wrapped around a perforated permeate collection tube. The feed flows on one side of the membrane and permeate is collected on the other side of the membrane meanwhile spirals in towards the centre collection tube. The low price and very compact design of spiral wound module was originally made exclusively for water desalination caught the attention to other industry (Klaassen, 2005). But nowadays after redesign have made, this module can be used for a variety of industrial application such as in the dairy industry, the pulp and paper industry and other else.

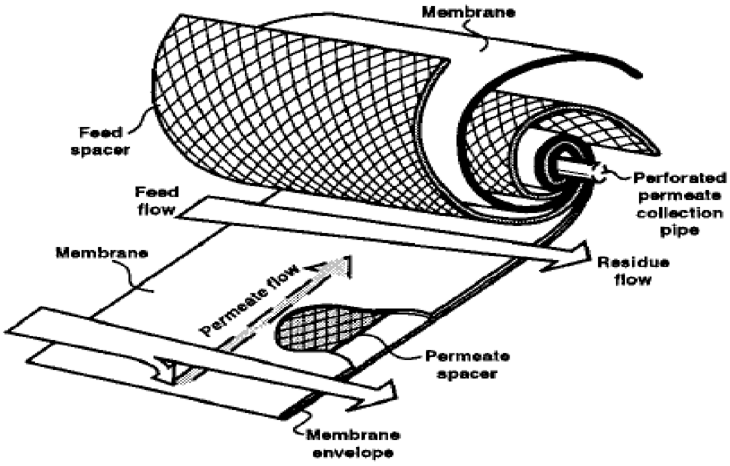

**Figure 2-**4: A schematic drawing of a spiral wound membrane module (Mulder, 1996)

The choice of the most suitable membrane module type for a particular membrane separation must balance a number of factors. The comparison and principal module design parameters that enter into the decision are summarized in Table 2-1.

**Table 2-1**: Comparisons of parameters for membrane module design (Baker, 2004)

| Parameter | Hollow fine fiber | Capillary fibers | Spiral-wound | Plate-and-frame | Tubular |
|---|---|---|---|---|---|
| Manufacturing cost (US$/m$^2$) | 5-20 | 1050 | 5-100 | 50-200 | 50-200 |
| Concentration polarization fouling control | Moderate | Good | Moderate | Good | Very Good |
| Permeate-side pressure drop | High | Moderate | Moderate | Low | Low |
| Suitability for high-pressure operation | Yes | No | Yes | Yes | Marginal |
| Limited to specific types of membrane materials | Yes | Yes | No | No | No |

Based on factors summarize above, that presented that cost is difficult to quantify because the actual price of the same module design varies widely on the application. Generally, high-pressure modules are more expensive than low-pressure or vacuum modules. Concentration polarization control is a particularly important issue in liquid separations such as reverse osmosis and ultrafiltration. Another factor is the ease with which various membrane materials can be fabricated into a particular module design. Almost all membranes can be formed into plate-and-frame, spiral-wound and tubular modules. Hollow fiber and capillary fiber modules also a choice for membrane application. Finally, the suitability of the module design for high-pressure operation and the relative magnitude of pressure drops on the feed and permeate sides of the membrane can also be important factors.

## 2.5 Polymer membrane

### 2.5.1 Polyvinylidene fluoride (PVDF)

Vinylidene fluoride ($CH_2$=$CH_2$) is polymerized promptly by free-radical initiators to form a high molecular weight, partially crystalline polymer (Ramakrishna et al, 2011). PVDF has melting point range of 155-192oC. It can be autoclaved and its resistance to common solvents is great (Kroschwitz, 1990). It also has excellent mechanical properties and resistance to severe environmental stresses. The membrane is usually hydrophobic. They are famous for microfilteration and ultrafiltration processes. They have better resistance to chlorine over the polysulfone family (Mulder, 1996). PVDF have strong chemical resistance against corrosive chemicals including acids, bases, oxidants and halogens, makes it an excellent polymeric membrane material and popular among various research groups (Lovinger, 1982).

### 2.5.2 Polypropylene (PP)

Polypropylene ($(-CH_2\text{-}CH(CH_3)-)_n$ can be processed by injection molding, melt-extrusion, thermal inversion and blow molding. It is widely used in the form of hollow fibers. The versatility of this product, coupled with its low cost and inertness to water and microorganisms encourages its usage as membranes. They have been employes as stretched membrane and sintered polymer membrane type (Ramakrishna et al, 2011).

### 2.5.3 Polytetrafluroethylene (PTFE)

The monomer of PTFE is a colourless, tasteless, odourless, non-toxic gas. The polymerization is highly exothermic. PTFE has excellent heat resistance and wide working range of temperatures (-100$^o$C to 260$^o$C). Their property makes it an ideal candidate as a membrane materials but it is available only as microfiltration membranes.

PTFE is extremely hydrophobic. They are microporous, with a pore size of 0.1-5 µm (Ramakrishna et al, 2011).

### 2.5.4 Polycarbonate (PC)

Polycarbonate possesses high impact strength, creep resistance and thermal stability. They are applied for filtration of suspensions and biological solutions. They have microporous structure with 0.02 to 20 µm pore diameter. A few other membrane materials which are employed for manufacturing microfiltration and ultrafiltration membranes industrially are Polyvinyl Alcohol (PVA), Polyvnyl Chloride (PVC), Polyacrylonitrile (PAN) (Mulder, 1996).

## 2.6 Membrane Applications

### 2.6.1 Water treatment

Several studied have been done on the use of membrane contactors in wastewater treatment. For example, Johnson et al (1997), investigated for bubble free aeration in wastewater treatment that offers several advantages including absence of foaming and higher aeration rates , Semmens et al (1990), used to test a microporous polypropylene membrane contactor operated in dead end mode that used to trap flocculent solids that resulting a gas permeable coating allowed the fibers to run for over 300 h with no decrease in oxygen transfer efficiency, and Pankhania et al (1994), demonstrated the removal of toluene from air and subsequent biological destruction using a microporous polypropylene hollow fiber module.

In addition, several troublesome pollutants from extraction method have been investigated extensively, such as pollutants that include phenol, toluene, 2-chlorophenol, benzene, chloroform, trichloroethylene, carbon tetrachloride, nitrobenzene, tetrachloromethane and acrylonitrile, with hexane, isopropyl acetate, kerosene, silicone oil and sunflower oil as extraction solvents (Gabelman and Hwang, 1999). Table 2-2 described the pros and cons of using membrane techniques in wastewater and process water treatment.

**Table 2-2**: pros and cons of using membrane techniques in wastewater and process water treatment

| Advantages | Disadvantages |
|---|---|
| • material reliability | • high purchase price of the membranes |
| • less chemicals required | • residue (very concentrated filtrate) has to be collected or further treated |
| • relatively simple follow-up, once the installation is correctly set | - |
| • efficient use of energy | - |
| • no change in state of aggregation necessary | - |

### 2.6.2 Gas absorption and stripping

The processes of removing carbon dioxide ($CO_2$) can be done by using membrane separation, chemical absorption, physical absorption, cryogenic methods, and biological fixation and by gas permeation (Mansourizadeh and Ismail, 2011b). In industrial gas processing, there is an increasing interest in gas absorption and stripping processes for the selective removal of acid gases from the raw gas streams. Absorption process can offer a very high selectivity and a high driving force for transport even at very low concentration in the reaction (Klaassen et al, 2008). Besides that, another advantages of absorption process over conventional contacting devices are have high surface area per unit contactor volume, independent control of gas and liquid flow rates without any flooding, loading, weeping, foaming or entrainment problems, small size, modular, and easy to scale up or down (Gabelman and Hwang, 1999).

Since 1980, much research has been completed to remove carbon dioxide ($CO_2$) from flue gas using gas-liquid membrane contactor system. Example of researcher completed their research are Karoor and Sirkar, (1993) that studied the absorption of pure $CO_2$, pure $SO_2$, $CO_2$ from $CO_2/N_2$ mixtures, and $SO_2$ from $SO_2$/air mixtures into water and Qi and Cussler, (1985) also reported on absorption of $CO_2$ into aqueous sodium hydroxide using hydrophobic hollow fibers. For this purpose, researchers have considered a number of factors such as membrane materials, absorption solution, and membrane module to improve the performance of the removal of carbon dioxide ($CO_2$) (Rahbari-Sisakht et al, 2012).

### 2.6.3 Biomedical application

The prepared hollow fibers are being applied in various processes such as gas separation, ultrafiltration, reverse osmosis, dialysis, etc. Membrane technology is of major importance in medical applications, in particular in a number of life saving treatment methods. Membranes are used in drug delivery, artificial organs, tissue regeneration, diagnostic devices, as coatings for medical devices, bio-separations and others (Chwojnowski et al, 2009). In addition, Amor et al, (2011) tested the suitability of different hollow-fiber membranes for improved xenon dissolution in blood.

## 2.7 Phase inversion technique

The phase inversion method is the most versatile membrane preparation process. This method also can be described as a demixing process whereby the initially homogeneous polymer solution is transformed in a controlled manner from a liquid state (polymer solution) to a solid state. Mulder (1996) has further discovered that the description of the phase inversion process in “Basic Principles of Membrane Technology”. The basic concept of most phase inversion processes is a ternary system consisting of polymer, solvent and non-solvent. In general, the preparation involves several steps: (1) choice of correct polymer; (2) choice of proper solvent/non-solvent; (3) choice of correct additives; (4) spinning the dope solution; (5) choice of the coagulant bath and its operating condition; (6) eventual post-treatment of the membrane. There are several ways of phase inversion transformation can be accomplished which are immersion precipitation, thermally induced phase separation (TIPS), Evaporation-induced phase separation and vapor-induced phase separation.

### 2.7.1 Immersion precipitation

Phase separation is a widely used method for making microporous polymer membrane. Commonly, most of the membranes used in microfiltration, ultrafiltration and as support material for composite membrane are prepared by immersion precipitation (Wang et al, 2006). The basic process for immersion precipitation can be carried out with three component; polymer, solvent and non-solvent. Polymer and solvent are used to prepare spinning solution and non-solvent is used as coagulation bath. In the process, a viscous spinning solution can be first spin on a suitable condition, and then the polymer solution is immersed in a non-solvent coagulation bath (typically water). The demixing and precipitation occurs due to the exchange between solvent (polymer solution) and the non-solvent (coagulation bath). Depending on the rate of polymer precipitation, there are two types of membrane can be obtained; symmetric and asymmetric membrane.

### 2.7.2 Thermally induced phase separation (TIPS)

One of the most significant developments in preparation of membrane is the inversion of the thermal process. In this technique, a polymer (typically a polyolefin or a polyfluorocarbon) is dissolved (in the case of highly crystalline polymer above its melting point) and by cooling demixing will take place. TIPS are been used to form microporous polymeric membrane of controlled pore characteristics from a variety of crystalline and thermoplastic polymers, including polyolefins, condensation and oxidation polymers, copolymers and blends (Witek-Krowiak et al, 2012). In addition, this method is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying. Commercially available TIPS polypropylene membranes have proved useful in cross-flow and are being investigated for possible use in membrane distillation.

### 2.7.3 Evaporation-induced phase separation

This is the one of eldest techniques for preparing membranes and was widely studied (Witek-Krowiak at al, 2012). A polymer is dissolved in volatile solvent and a less volatile non-solvent. By evaporation, the polymer solution shift to the demixing region and finally phase separation occurs resulting in a porous membrane (microfltarion/ultrafiltration). This technique is also known as a solution casting method.

### 2.7.4 Vapor-induced phase separation

This method was developed in the beginning of the 20th century. Here the non-solvent is introduced via the vapour phase (Strathmann et al, 1975). A polymer solution is spin as a hollow and exposed in an atmosphere with water vapour. The water (non-solvent) diffuses into this hollow and absorption of non-solvent causes demixing/precipitation. Porosity and pore size can be varied by the choice of solvent and polymer concentration in the solution. The type of polymer used and techniques of membrane fabrication was summarizing in Table 2-3.

**Table 2-3:** Summary of commonly used polymers and fabrication techniques for membrane preparation.

| Polymers used for membrane fabrication | Fabrication techniques | Average pore size of the membrane |
|---|---|---|
| Cellulose acetate/triacetate | Phase inversion | 3–5 Å |
| Aromatic polyamide | Solution casting | - |
| Polypiperzine | | -- |
| Polybenziimidazoline | | - |
| Polyamides | Interfacial polymerization | 0.001–0.01 μm |
| Polysulfones | Layer-by-layer deposition | - |
| Polyols | Phase inversion | - |
| Polyacrylonitrile (PAN) | Phase inversion | 0.001 – 0.1 μm |
| Polyethersulfone (PES) | Solution wet-spinning | - |
| Polysulfone (PS) | | - |
| Polyethersulfone (PES) | | - |
| Polyvinylidene fluoride (PVDF) | | - |
| Polyvinylidene fluoride (PVDF) | Phase inversion | 0.1–10 μm |
| Polytetrafluorethylene (PTFE) | Stretching | - |
| Polypropylene (PP) | Track-etching | - |
| Polyethylene (PE) | | - |
| Polyethersulfone (PES) | | - |
| Polyetheretherketone (PEEK) | | - |
| Polytetrafluorethylene (PTFE) | Phase inversion | 0.1–1 μm |
| Polyvinylidenefluoride (PVDF) | Stretching<br>Electrospinning | - |

However, among these techniques, immersion precipitation and thermally induced phase separation are the most commonly used method in the fabrication of polymeric membranes with various morphologies. Table 2-4 described the immersion precipitation method for membrane formation.

**Table 2-4:** Main polymers used in membrane formation via immersion precipitation

| Polymer | Advantages | Disadvantages |
|---|---|---|
| Cyanoacrylate (CA) | • Hydrophilicity<br>• Flexibility in fabrication<br>• Low cost | • Low thermal resistance (b30 °C)<br>• Low chemical resistance<br>• pH range (2–8)<br>• Poor resistance to chlorine |
| Polysulfone (PS) and Polyethersulfone (PES) | • High thermal resistance (up to 75 °C)<br>• Wide pH tolerances (1–13)<br>• Good chlorine resistance<br>• Flexibility in membrane fabrication (wide range of pore size)<br>• High mechanical characteristics | • Low operating pressure limits<br>• Hydrophobicity |
| Polyvinylidene fluoride **(**PVDF) | • High mechanical strength and chemical resistance<br>• High thermal stability (up to 75 °C) | • Hydrophobicity |
| Polyamide (PA) | • Wide pH tolerance<br>• High thermal stability<br>• High mechanical properties | • Poor chlorine resistance |

## 2.8 Chapter Summary

In this chapter, membranes have been introduced. The characteristics and types of membranes also have been elaborated. This chapter have continued with literature review of carbon dioxide ($CO_2$) removal, which focuses on the membrane technology that available to capture carbon dioxide ($CO_2$). The method used in preparation of hollow fiber membrane also be determined, and the type of technique and general applications of membrane were discussed.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Overview

In this study, hydrophobic porous polyvinylidene fluoride (PVDF) hollow fiber membranes are prepared by wet spinning process. Microporous PVDF membranes are also used due to high hydrophobicity, high chemical resistance and reasonable cost of materials. In order to prepare hollow fiber membranes with low mass transfer resistance, Dimethylacetamide (DMAc) aqueous solution was used as solvent and lithium chloride (LiCl) as an additive.

To study the LiCl loading on PVDF hollow fiber membrane for carbon dioxide ($CO_2$) removal, this study started with the preparation of sample solution to created hollow fiber membrane via phase inversion method. Figure 3.1 shows the general overall process of the experiment.

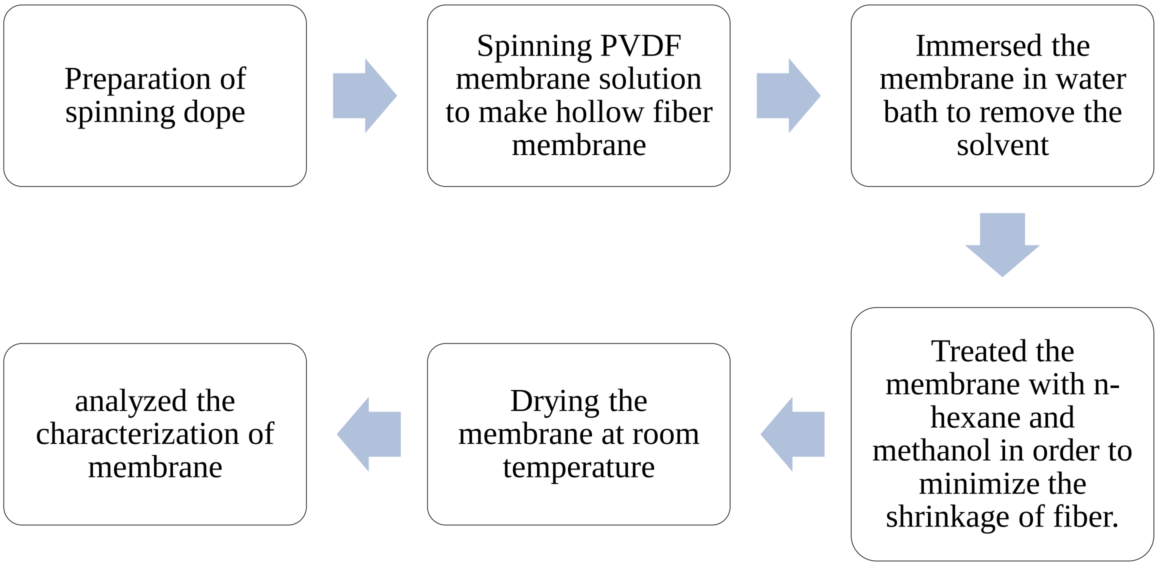

**Figure 3-1:** The summary of fabrication process of PVDF hollow fiber membrane

## 3.2 Chemicals

PVDF polymer pellets, Dimethylacetamide (DMAC) (>99.5%) as the solvent were supplied by MERCK. LiCl was used as the additive. Aqueous Dimethylacetamide (DMAc) solution was used as the bore fluid and tap water as coagulation bath in the spinning process. Methanol (99.9%) and n-hexane (99%) was used as post-treatment for the prepared membranes. LiCl, methanol and n-hexane obtained from Faculty of Chemical Engineering and Natural Resources Lab, University of Malaysia Pahang.

## 3.3 Fabrication of PVDF hollow fiber membrane

The PVDF polymer pellets were dried at 60°C in a vacuum oven for 24 h to remove moisture content. The PVDF polymer pellets were weighed and mixed with Dimethylacetamide (DMAc) solvent. The spinning dopes were prepared at 60 °C using stirring until the solution became homogeneous. The homogeneous polymer solution was kept for 24 h at room temperature before spinning. After spinning, the hollow fibers prepared were immersed in the water bath for 3 days to remove the DMAc solvents and the additives. Then, in order to minimize the possibility of shrinkage fibers, membranes were treated in methanol and n-hexane before dying at room temperature (Yeow et al, 2005). The solutions compositions are given in 3-1.

**Table 3-1:** Spinning dope composition

| Spinning dope | D1 | D2 | D3 |
|---|---|---|---|
| PVDF (wt.%) | 17 | 17 | 17 |
| LiCl (wt.%) | 0 | 3 | 5 |
| DMAc (wt.%) | 83 | 83 | 83 |

**Table 3-2**: Spinning conditions of PVDF hollow fiber membranes**.**

| | |
|---|---|
| Dope extrusion rate (ml/min) | 4.50 |
| Dope extrusion rate (ml/min) | 4.0 |
| External coagulant | Tap water |
| Air gap distance (cm) | 0.5 |
| Spinneret o.d./i.d. (mm) | 0.5/0.5 |
| Coagulation temperature (°C) | 25 |

## 3.4 Characterization of membranes

Porous surface modified PVDF hollow fiber membranes with different amounts of LiCl as an additive were fabricated via the dry-wet spinning process. The fabricated membranes were characterized in term of gas permeation, critical water entry pressure (CEPw) and water contact angle (Rahbari-Sisakh et al, 2013).

### 3.4.1 Critical water entry pressure (CEPw)

Critical water entry pressure (CEPw) test was conducted to evaluate wetting resistance of the prepared membranes. To measure CEPw, a hollow fiber was glued with epoxy resin at one end and the other end was potted to stainless steel membrane module. The distilled water was fed into the lumen side of the hollow fiber membranes. The nitrogen pressure was supplied and slowly increased at state interval. At each pressure interval, the membrane module was kept at the constant pressure for five min to check if any water droplet appeared on the outer surface of the fiber. CEPw was considered as the pressure for the first water droplet on the outer surface of the hollow fiber.

### 3.4.2 Water contact angle measurement

The contact angle measurement is a technique to evaluate the membrane surface hydrophobicity/hydrophilicity by using goniometer with water as the liquids. As for contact angle measurement, samples of the hollow fibers were dried in a vacuum oven at $60^{o}$C for 12 hours. A droplet of water was placed on the surface of hollow fiber and the contact angle was measured. The contact angle was measured between water droplets and outer surface of the hollow fibers. The contact angle values of each sample were measured at 10 various position of the sample and then averaged (Mansourizadeh et al, 2010).

### 3.4.3 Gas permeation test

Gas permeation tests were done to measure the mean pore size and the effective surface porosity. Two hollow fibers were glued with epoxy resin at one end and the other end was potted to stainless steel tubing with a length of 10 cm (Rahbari et al, 2012). For a significant porous membrane, the total gas permeation rate through the membrane can be considered as the combination of Poiseuille flow and Knudsen flow (Mansourizadeh et al, 2010). Equation 1 was used to calculate the gas permeance:

$$J_A = \frac{2r_p\varepsilon}{3RTL_p}\left(\frac{8RT}{\pi M}\right)^{0.5} + \frac{r_p^2\varepsilon}{8\mu RTL_p}\bar{P} \quad \text{or} \quad J_A = K_0 + P_0\bar{P} \qquad (1)$$

where $J_A$ is the gas permeance (mol/m$^2$ s Pa); $r_p$ and $L_p$ are pore radius and effective pore length, respectively (m); $\varepsilon$ is surface porosity; $R$ is gas constant 8.314 (J/mol K); $\mu$ is gas viscosity (kg/m s); $M$ is gas molecular weight; $T$ is gas temperature (K); and $\bar{P}$ is mean pressure (Pa).

By plotting $J_A$ with mean pressures according to Eq. (1), mean pore size and effective surface porosity over pore length, $\varepsilon/L_p$, can be calculated from the intercept ($K_0$) and slope ($P_0$) as following:

$$r_p = 5.333\left(\frac{P_o}{K_o}\right)\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \qquad (2)$$

$$\frac{\varepsilon}{L_p} = \frac{8\mu RTP_o}{r_p^2} \qquad (3)$$

In the gas permeation method, pure $N_2$ was used as the test gas. The test apparatus used was based on the volume displacement method. The test module containing two hollow fibers with the length of about 10 cm was used to determine the gas permeability. The pressure was increased at 50 kPa intervals up to 300 kPa. The $N_2$ permeation rate was measured at 25 °C in the lumen side using soap-bubble flow meter. The gas permeability was then calculated according to outer diameter of the hollow fiber.

### 3.4.4 Scanning Electron Microscopy (SEM)

Hollow fiber membranes were fractured in liquid nitrogen to have a clean brittle fracture, and then sputter-coated with platinum (Pt). The SEM micrographs of the cross-section, inner and outer surfaces of the fabricated hollow fibers were taken by SEM at different magnifications.

## 3.5 Chapter Summary

In this chapter, the chemicals used in this study have been listed. The origin and preparation of samples also have been summarized. Besides that, the preparation method and characterization of membrane have been stated. Phase inversion method was elaborated in this chapter, which have been used in this study to prepare the spinning dope of hollow fiber membranes.

# CHAPTER 4

# RESULT AND DISCUSSION

## 4.1 Overview

This paper presents a study of the characterization and structure of the membrane and based on different additives loading in membrane solution. The result was obtained from several researchers to indicate as reference for the current experimental of membrane for carbon dioxide removal. The result was discussed based on the characterization of membrane and its structure.

## 4.2 Material selection

### 4.2.1 Polyvinylfluoride (PVDF)

PVDF has been chosen as the focus of this review as it is the most popular polymer that used for $CO_2$ removal. PVDF plays an important role in various industries, such as pulp and paper, nuclear-waste processing and chemical processing. These roles proved that PVDF have remarkable chemical and physical properties. Besides that, high hydrophobicity, high chemical resistance and reasonable material cost are the other most important criteria for selecting polymeric material for gas (Rajabzadeh et al, 2009). Other factors affecting the selection of polymer may include that PVDF are only hydrophobic polymer that can be dissolved in common solvents to prepare asymmetric membranes via phase-inversion process (Mansourizadeh and Pouranfard, 2014), and it's also typical polymers used for low pressure membranes. Microporous PVDF membranes show good gas absorption performance as well as good stability compared to others (Khaisri et al, 2011).

### 4.2.2 Lithium Cloride (LiCl)

Lithium chloride (LiCl) has been used as pore forming agent to prepare porous PVDF membranes for different applications. The presence of LiCl in polymer solution will cause the phase inversion process and structure of membrane change. With the high concentration of LiCl in the PVDF polymer solution, the microvoid formation was suppressed and it enhanced permeate flux at low concentration (Mansourizadeh and Ismail, 2010). LiCl was choosen due to the resulting in great performance of PVDF hollow fiber membrane.

### 4.2.3 Dimethylacetamide (DMAc)

The solution of membrane was prepared by adding PVDF in Dimethylacetamide (DMAc). For water soluble solvents used, the most common solvent is DMAc. It is base and strong polar high boiling point solvents for PVDF. It is less volatile solvent used in the spinning dope that can affect the solvent evaporation. Therefore, the use of DMAc solvent becomes a most efficient tool to prepare desired membranes. In fact, the high absorption performance such as permeability of $CO_2$ can be enhanced by using DMAc.

## 4.3 Morphological of hollow fiber membrane

The effect of LiCl loadings on the structure of the PVDF membranes was examined through Spectroscopy Electron Microscopy (SEM). It was found that the morphology of prepared hollow fibers is strongly dependent on the percentage of additive used in the spinning dopes (Mansourizaded and Ismail, 2010). The morphology was presented based on outer surface, inner surface and cross-sectional images as shown Figure 4-1.

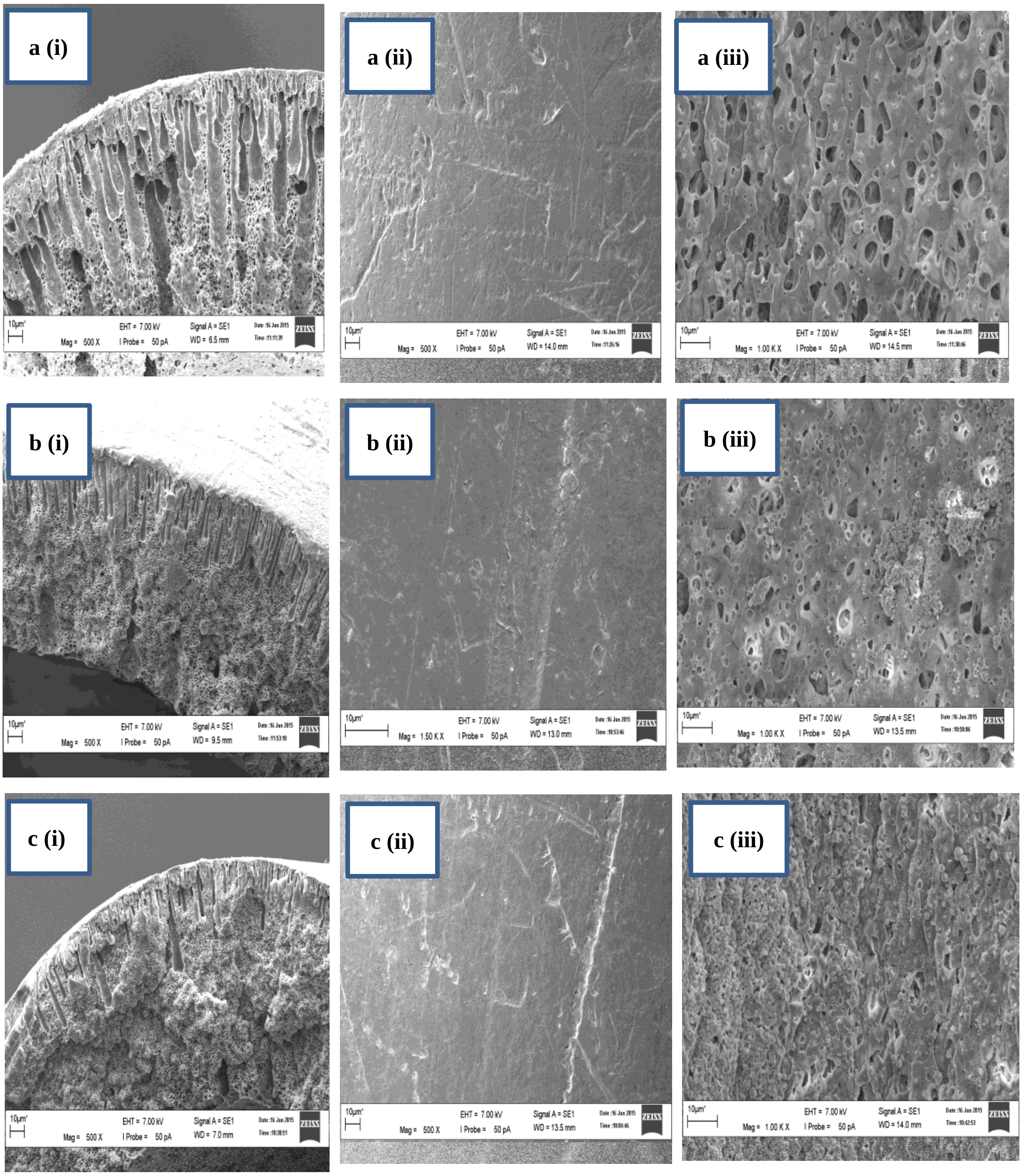

**Figure 4-1**: SEM micrographs of PVDF–LiCl membranes, (a) Plain PVDF, (b) PVDF–3% LiCl, and (c) PVDF–5% LiCl; (i) cross-section, (ii) outer surface and (iii) inner surface

As presented in the cross-sectional images above, the membrane structure consisted of two different layer which are finger-like layer that stretched from the outer to the inner membrane layer and sponge-like layer, irrespective of the LiCl loadings.

According to the Fig 5 a (i), plain PVDF membrane resulted in membranes with almost large finger-like layer and a thin sponge-like layer. The finger-likes enlarged close to the inner surface. This structure can be related to low viscosity of the dope solution and fast phase inversion rate between the coagulant medium and solvent which resulted in large finger like shapes and thin sponge-like layer (Naim et al, 2012). It seems that this structure was not favorable for increasing gas permeability. In addition, by increment to 3 wt. % lithium chloride (LiCl) in the spinning dope, the finger-like size was reduced, which provided an almost balance finger-like/sponge-like structure. This performance associated with the increasing on pores number in hollow fiber membrane. Effective surface porosity pointed the high value at this point that means the small pore size appeared to partially block water to penetrate through the pores and wet the membrane. On the other hand, addition of 5 wt.% LiCl in the spinning dope provided a large sponge-like structure with very small finger-likes. This membrane has small mean pore size and higher effective surface porosity. This structure expected to provide higher permeability gas removal application. Generally, for cross-section morphology, the membrane structure changed from finger-like to sponge-like by increasing the amount of LiCl in the spinning dopes.

## 4.4 Characterization of hollow fiber membrane

Different lithium chloride (LiCl) concentrations were considered in the spinning dopes in order to prepare the asymmetric membranes with high permeability (low mass transfer resistance) and hydrophobicity (high wetting resistance). The hollow fiber membranes were characterized in terms of gas permeability, critical water entry pressure and overall porosity. The results are given in Table 4-1.

**Table 4-1:** Characterization of the PVDF hollow fiber membranes

| Membrane | $N_2$ permeance ($1x10^{-6}$ $mol/m^2.s.Pa$) | Mean pore size (nm) | Effective surface porosity, ($10^3$ $m^{-1}$) | CEPw ($10^5$ Pa) | Contact angle (Θ) |
|---|---|---|---|---|---|
| PVDF | 0.91 | 3.56 | 49.73 | 3.00 | 40.58 |
| PVDF/3% LiCl | 3.91 | 0.42 | 2206.50 | 4.00 | 55.70 |
| PVDF/5% LiCl | 4.13 | 0.36 | 2721.55 | 7.50 | 57.28 |

Critical water entry pressure ($CEP_w$) test was conducted to examine wetting resistance of the prepared membranes. Therefore, using hydrophobic membranes with a high wetting resistance are desired for long-term gas absorption applications. From Table 4-1, the $CEP_w$ of the membranes increased by increasing LiCl concentration in the spinning dopes, which can be associated to the membranes structure. Pore size, surface hydrophobicity and pressure difference are the key parameters for membrane wetting according to Laplace–Young equation (Rajabzadeh et al, 2009). In plain PVDF membrane, pressure supplied was the lowest because the greater pores size allows water to penetrate easily through the pores and wet the membrane at a low pressure of 300 kPa. The wetting pressure was increased respectively as the increasing of concentration of LiCl. This was supported by smaller mean pore radius (0.42 and 0.36 nm) of the membranes. Wetting pressure is inversely proportional to membrane pore size according to Laplace-Young equation (Naim et al, 2012). Therefore, the addition of LiCl resulted in smaller mean pore sizes which can reduce the possibility of the membrane wetting.

In addition, measured contact angle of 57.28° was the highest among three samples. With the increment of LiCl concentration from 3wt% to 5wt%, it was confirmed that membranes have high hydrophobicity. Therefore, by using hydrophobic membranes with a high wetting resistance are desired for long-term gas absorption applications. These data proved that the addition of concentration LiCl in polymer dope was resulting membrane mean pore size decreased as the CEPw increased. However, it should be noted that mean pore sizes obtained using the gas permeation method only show the trend of the pore size change. The actual size of the pores could not be determined accurately using this method (Yeow et al, 2005).

From the calculation and data obtained in the gas permeation test, $N_2$ permeance as a function of mean pressure was plotted in Figure. 4-2.

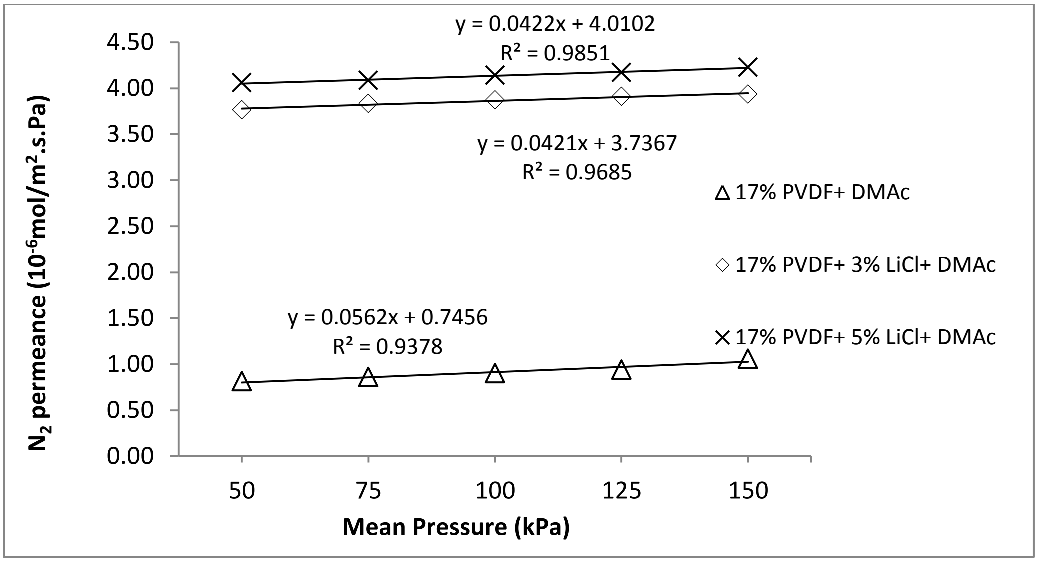

**Figure 4-2:** Measured $N_2$ permeance of the PVDF hollow fiber membranes

Figure 4-2 shows $N_2$ permeance of the membranes as a function of mean pressure. The solid lines indicate the best linear fit to the data. Based on Eq. (1) given, the values of $P_0$ and $K_0$ can be obtained from intercept and slope of the lines in Figure 4-1 respectively. That value can then be used to calculate the mean pore size and the effective surface porosity using Eqs (2) and (3). The results are given in Table 4-1. From Figure 4-1 , the slope of $N_2$ permeance line for the plain PVDF membranes is lower than the prepared membranes by using LiCl in the spinning dopes. On the other hand, the slope of lines for the prepared membranes using 3wt. % and 5 wt. % LiCl is significantly high. It seems that the Knudsen flow governs the $N_2$ permeation through the membranes, which can confirm existence of small pore sizes. Moreover, addition of LiCl in the spinning dopes significantly increased the intercept of the lines, which indicates higher permeability of the membranes. As it can be seen, $N_2$ permeances calculated for all the membranes show an increase with the increase in mean pressure.

# CHAPTER 5

# CONCLUSION

## 5.1 Conclusion

This research is focusing on the characterization of PVDF hollow fiber membrane when manipulating the concentration of LiCl additives. In order to improve the membrane structure for carbon dioxide ($CO_2$) absorption, porous hydrophobic PVDF hollow fiber membranes were prepared via a simple wet phase-inversion process. LiCl was introduced into the spinning dope as phase-inversion promoter and DMAc solution was used as the solvent. The effect of LiCl concentration on the membrane characteristics was investigated. Effect of those parameters was evaluated based on gas permeation, contact angle and critical water entry pressure (CEPw). Results of gas permeation test indicated that an increase of the additive concentration in the spinning dope resulting the increased in $N_2$ permeation rate. From the study, among the different concentration of LiCl additives studied, 5% of LiCl provided the good result characteristics of membrane that efficiently enhanced $CO_2$ absorption. Therefore, it can be concluded that high wetting resistance are the important factors for membrane contactor applications which can be achieved by improving the membrane structure. Besides that, produced membrane can be applied in diverse application such as removal of $CO_2$ from flue gas, volatile organic compounds (VOCs) from wastewater, water purification and membrane distillation in separation industry. High liquid entry pressures of membrane absorption is ideal for long term operation and are suitable for gas-gas and gas-liquid system.

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## 5.2 Recommendation and future work

Membrane science and the use of hollow fiber as membrane materials are the rising technology used for a wide range of industrial applications, especially if incorporated in carbon dioxide removal. The use of new membrane materials is still unexplored option in this new technological area. Much research work continues to be done to provide improvements in the separator systems. Therefore, it becomes even more important to found new and more effective processes for the formation of hollow fiber from both new and existing polymer. Also, as mixtures of different polymers are being used in making hollow fiber membrane, the possibility and understanding in which various processing conditions that affected the final properties of membrane are required. Continuing, additional approaches need to be found to controlling the separation performance of hollow fiber membrane, such as pore size. Understanding of ways to achieve such a most minimum size of pore for avoiding the wetting membrane occurred.

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# APPENDICES

## A1:Raw data of contact angle measurement

**Table A1-1**: Data of 10 reading of contact angle measurement

| Sample | PVDF | PVDF + 3% LiCl | PVDF + 5% LiCl |
|---|---|---|---|
| **1** | 41.59 | 55.46 | 53.13 |
| **2** | 36.46 | 65.94 | 59.32 |
| **3** | 32.42 | 56.43 | 63.12 |
| **4** | 34.62 | 48.45 | 54.95 |
| **5** | 40.51 | 59.85 | 57.33 |
| **6** | 45.67 | 64.73 | 54.3 |
| **7** | 50.76 | 52.55 | 54.82 |
| **8** | 39.77 | 46.9 | 57.44 |
| **9** | 43.46 | 51.95 | 58.23 |
| **10** | 40.57 | 54.74 | 60.14 |
| **Average** | **40.58** | **55.7** | **57.28** |

## A2:Analysed data for gas permeation

**Table A2-1**: Gas permeation data for membrane 17%PVDF + DMAc

| Pressure (bar) | Mean P (Pa) | Mean P (kPa) | V (m3/s) | n (mol/s) | JA ($10^{-6}$ mol/m2.s.Pa) | Slope | Intercept | Pore radius (nm) | Effective surface porosity |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 25000 | 25 | 3.4189E-07 | 1.3982E-05 | 1.07 | 1.79214 x!0$^{-12}$ | 7.1586 x $10^{-7}$ | 3.36457 | 49733.6386 |
| 0.75 | 37500 | 37.5 | 4.4473E-07 | 1.81875E-05 | 0.93 | | | | |
| 1 | 50000 | 50 | 0.00000052 | 2.12659E-05 | 0.81 | | | | |
| 1.25 | 62500 | 62.5 | 6.6435E-07 | 2.71693E-05 | 0.83 | | | | |
| 1.5 | 75000 | 75 | 8.2285E-07 | 3.3651E-05 | 0.86 | | | | |
| 1.75 | 87500 | 87.5 | 9.8005E-07 | 4.00801E-05 | 0.88 | | | | |
| 2 | 100000 | 100 | 0.00000115 | 4.70303E-05 | 0.90 | | | | |
| 2.25 | 112500 | 112.5 | 1.2403E-06 | 5.07226E-05 | 0.86 | | | | |
| 2.5 | 125000 | 125 | 0.0000015 | 6.13439E-05 | 0.94 | | | | |
| 2.75 | 137500 | 137.5 | 1.5985E-06 | 6.53731E-05 | 0.91 | | | | |
| 3 | 150000 | 150 | 2.0208E-06 | 8.26405E-05 | 1.06 | | | | |

**Table A2-2**: Gas permeation data for membrane: 17%PVDF + DMAc + 3% LiCl

| Pressure (bar) | Mean P (Pa) | Mean P (kPa) | V (m3/s) | n (mol/s) | JA ($10^{-6}$ mol/m2.s.Pa) | Slope | Intercept | Pore radius (nm) | Effective surface porosity |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 25000 | 25 | 1.2506E-06 | 5.11462E-05 | 4.28 | 1.11446 x $10^{-12}$ | $3.7601 \times 10^{-06}$ | 0.422012167 | 2206504.529 |
| 0.75 | 37500 | 37.5 | 1.7164E-06 | 7.01933E-05 | 3.92 | | | | |
| 1 | 50000 | 50 | 0.0000022 | 8.9971E-05 | 3.76 | | | | |
| 1.25 | 62500 | 62.5 | 2.8402E-06 | 0.000116151 | 3.89 | | | | |
| 1.5 | 75000 | 75 | 0.00000336 | 0.00013741 | 3.83 | | | | |
| 1.75 | 87500 | 87.5 | 3.9182E-06 | 0.000160239 | 3.83 | | | | |
| 2 | 100000 | 100 | 4.5235E-06 | 0.000184993 | 3.87 | | | | |
| 2.25 | 112500 | 112.5 | 5.2217E-06 | 0.000213545 | 3.97 | | | | |
| 2.5 | 125000 | 125 | 5.7148E-06 | 0.000233714 | 3.91 | | | | |
| 2.75 | 137500 | 137.5 | 6.1703E-06 | 0.000252339 | 3.84 | | | | |
| 3 | 150000 | 150 | 0.0000069 | 0.000282182 | 3.94 | | | | |

**Table A2-3:** Gas permeation data for membrane 17%PVDF + DMAc + 5% LiCl

| Pressure (bar) | Mean P (Pa) | Mean P (kPa) | V (m3/s) | n (mol/s) | JA ($10^{-6}$ mol/m2.s.Pa) | Slope | Intercept | Pore radius (nm) | Effective surface porosity |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 | 25000 | 25 | 1.2856E-06 | 5.25748E-05 | 4.26 | $1.02189 \times 10^{-12}$ | $3.9988 \times 10^{-06}$ | 0.363863646 | 2721553.768 |
| 0.75 | 37500 | 37.5 | 1.9268E-06 | 7.87967E-05 | 4.25 | | | | |
| 1 | 50000 | 50 | 2.4526E-06 | 0.0001003 | 4.06 | | | | |
| 1.25 | 62500 | 62.5 | 3.0893E-06 | 0.000126338 | 4.09 | | | | |
| 1.5 | 75000 | 75 | 0.0000037 | 0.000151315 | 4.08 | | | | |
| 1.75 | 87500 | 87.5 | 4.2395E-06 | 0.000173377 | 4.01 | | | | |
| 2 | 100000 | 100 | 0.000005 | 0.00020448 | 4.14 | | | | |
| 2.25 | 112500 | 112.5 | 5.5417E-06 | 0.000226631 | 4.08 | | | | |
| 2.5 | 125000 | 125 | 0.0000063 | 0.000257644 | 4.17 | | | | |
| 2.75 | 137500 | 137.5 | 6.7166E-06 | 0.000274682 | 4.04 | | | | |
| 3 | 150000 | 150 | 7.6599E-06 | 0.000313257 | 4.23 | | | | |