EFFECT OF ADDITIVE ON ASYMMETRIC POLYVINYLIDENE FLUORIDE MEMBRANE FOR CO_2/N_2 SEPARATION

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A thesis submitted in fulfilment

of the requirements for the award of the degree of

Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

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I declare that this thesis entitled “Effect of Additive on Asymmetric Flat Sheet Membrane for CO_2/N_2 Separation” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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For those who love chemistry and engineering

ACKNOWLEDGEMENT

First and foremost, the acknowledgement was for my supervisor, Dr Sunarti Binti Abdul Rahman. Due to her patience, guidance, ideas and also critics have made this research possible. I also want to express my thank Mr Masri for his cooperation and guidance during the experiment runs in the laboratory and also for the helps in searching for related information for this experiment.

I also would like to thank my fellow friends and family for their moral support and advice since I began learning to read until this report was finished. Without their support and contribution, I will not be able to acquire this opportunity to place myself in the place I stand nowadays. A special appreciation also deserve by the laboratory staff, and other staff in the Faculty of Chemical and Natural Resources Engineering for their contribution that ease up my business in various areas especially when in the process of completing this research. Without your help, this research cannot be done without thousand of difficulties.

I would like also thanks all the researcher I have cited, without the information from their previous research, this research cannot be made possible. Last but not least, I would like to congratulate myself for the completion of this thesis. Writing is always an obstacle and my weakness in whatever things I do. By completing this thesis shows that with effort, I also can write.

ABSTRACT

The developments of the membrane process for gas separation now get attention especially for commercial industry. The aim of this study is to determine the effect of concentration of additive in Polyvinylidene Fluoride (PVDF) dope solution and to study the performance and characteristic properties of fabrication of membrane for CO_2/N_2 gas separation. In this research the N-methyl-2-pyrrolidinone (NPM) is used as solvent and Lithium Nitrate ($LiNO_3$) is used as addictive. The ratio of PVDF/NMP/H_2O is 15 wt% PVDF/82 wt% NMP/3 wt% H_2O for dope solution. The different quantities of additive with different concentration are added to dope solution (0.2wt%, 1.8%wt and 5wt %). For the physical and chemical characterization membrane, the Scanning Electron Microscopy (SEM) and Fourier Transform Radiation (FTIR) will be used. These researches have to calculate the gas permeability and the selectivity after single gas permeation test with different pressure. The PVDF membrane with good condition in term of selectivity, chemical stability, and thermal stability for CO_2/N_2 was developed. Refer to SEM analysis, the reducing of clear image for finger-like pores and sponge-like structure as 0.2wt% $LiNO_3$ > 1.8wt% $LiNO_3$ > 5wt% $LiNO_{3.}$ As the percentage of additive increase, the image of pores and structure will be less clearly. Compare to morphology image without additive, 15wt% PVDF membrane pore and structure is quite larger and longer. The additional of additive resulting the pore and structure become smaller. Membrane with additive of 5wt% $LiNO_3$ into the dope solution could form the membrane stronger strain strength than the PVDF commercial membrane. For FTIR analysis, membranes without additive have the functional group of alkenes, alkyl halide and aromatic group. Membranes with additive have the functional group of alkenes, alkyl halide, aromatic, amine and nitro group. Gas permeation analysis, 0.2wt% $LiNO_3$ produces a high performance for gas separation. It has a higher permeability and selectivity result. The relation of gas permeation test and SEM morphology test is the larger pore on cross section membrane will be cause the good permeability on CO_2/N_2 pure gas. Permeability of membrane with additive is give a high performance compared with membrane which does not have additive.

Keywords: Polyvinylidene Fluoride, Lithium Nitrate, Additive, Membrane, Gas Separation

ABSTRAK

Perkembangan proses membran untuk pemisahan gas kini mendapat perhatian terutama bagi industri komersial. Tujuan kajian ini adalah untuk menentukan kesan kepekatan tambahan Fluorida Polyvinylidene (PVDF) dalam larutan dope dan untuk mengkaji prestasi dan sifat-sifat fabrikasi membran untuk CO_2/N_2 pemisahan gas. Dalam kajian ini N-metil-2-pyrrolidinone (NPM) digunakan sebagai pelarut dan Nitrat Litium ($LiNO_3$) sebagai tambahan. Nisbah PVDF/NMP/H_2O adalah 15% berat PVDF/82% berat NMP/ 3% berat H_2O untuk larutan dope. Kuantiti and kepekatan yang berbeza aditif ditambah kepada larutan dope (0.2wt%, 1.8wt% dan 5wt%). Untuk pencirian membran fizikal dan kimia, Mikroskopi Elektron Imbasan (SEM) dan Fourier Transform Sinaran (FTIR) akan digunakan. Membran dengan keadaan baik PVDF dalam jangka selektiviti, kestabilan kimia, dan kestabilan haba untuk CO_2/N_2 telah dibangunkan. SEM analisis, mengurangkan imej yang jelas seperti liang jari dan span struktur sebagai 0.2wt%$LiNO_3$> 1.8wt%$LiNO_3$> 5wt%$LiNO_3$. Semakin peratusan tambahan menaik, imej liang dan struktur akan menjadi kurang jelas. Bandingkan imej morfologi tanpa aditif, 15wt% PVDF liang membran dan struktur adalah agak besar dan panjang. Tambahan aditif yang mengakibatkan liang dan struktur menjadi lebih kecil. Membrane dengan tambahan (5wt% $LiNO_3$) ke dalam penyelesaian dadah boleh membentuk tekanan membran kekuatan lebih kuat daripada membran PVDF komersial. FTIR analisis, membran tanpa bahan tambah mempunyai kumpulan berfungsi alkena, alkil halida dan aromatik. Membran dengan tambahan mempunyai kumpulan berfungsi alkena, alkil halida, aromatik, Amine dan nitro. Analisis Gas penyerapan, 0.2wt% $LiNO_3$ menghasilkan prestasi tinggi untuk pemisahan gas. Ia mempunyai kebolehtelapan yang lebih tinggi dan hasil selektiviti. Hubungan ujian penyerapan gas dan SEM ujian morfologi adalah liang yang lebih besar di atas membran keratan rentas akan menyebabkan kebolehtelapan yang baik pada CO_2/N_2 gas tulen. Kebolehtelapan membran dengan tambahan adalah memberi prestasi yang tinggi berbanding dengan membran yang tidak mempunyai tambahan.

Kata Kunci: Fluorida Polyvinylidene, Nitrat Litium, Additive, Membrane, Pemisahan Gas

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LIST OF ABBREVIATION

PVDF	-	Polyvinylidene Flouride
NMP	-	N-methyl-2-pyrrolidinone
$LiNO_3$	-	Lithium Nitrate
H_2O	-	Water
CO_2	-	Carbon Dioxide
N_2	-	Nitrogen
SEM	-	Scanning Electron Microscopy
FTIR	-	Fourier Transform Radiation
IUPAC	-	International Union of Pure and Applied Chemistry
^oC	-	Degree Celsius
P	-	Permeability
D	-	Diffusion
P_i	-	Permeability for Gas Component
Q	-	Gas Flowrate
A	-	Area
ΔP	-	Pressure in System
P_j	-	Permeability of Another Gas Component
α	-	Selectivity

CSDS - Chemical Safety Data Sheet

IR - Infrared

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CHAPTER I

INTRODUCTION

This chapter will give the ideas about the significant of the research formulation. This first chapter will cover up the subtopic of background of study or information, problem statement, research objectives, research questions, scope of proposed research, expected outcomes and significance of the proposed research.

1.1 Background of Study

The topic of this research is to study the effect of hydrophobicity of PVDF membrane on CO_2/N_2 separation. The development of separation of gas mixtures using membrane process has exhibited a remarkable progress during the last two decades. The reason why there are strong interest toward the synthesis of gas separation membrane are the materials provided is better selectivity, chemical stability and thermal stability than those that already exist. In addition, nonpolymeric and inorganic membrane has attraction in recent years in studies aimed at upgrading the performance materials for gas separation.

PVDF is short term for polyvinylidene fluoride, which are a pure thermoplastic fluoropolymer and a highly non-reactive. PVDF is generally used in applications requiring the highest purity, strength, and resistance to solvents, acids, bases and heat and low smoke generation during a fire event. Furthermore, PVDF is an especially for plastic material in the highest purity, strength, and resistance to solvents, acids, bases and heat and low smoke generation during a fire event. The properties of PVDF are explained in context of chemical properties, physical properties and structure of PVDF. The IUPAC name of polyvinylidene fluoride is poly-1, 1-difluoroethene. The melting point of PVDF is around 177 °C. The density of it is 1.78. PVDF is typically 50–60% crystalline and has a glass transition temperature (Tg) of about -35 °C. The appearance of PVDF is basically in whitish or translucent solid. The mechanical properties of polyvinylidene fluoride is oriented to molecular chains and poled under tension. Furthermore, the thermal conductivity of PVDF is 1.39 Btu/hr-.ft-deg F. The important properties of PVDF is water absorption (230 deg C, 10 Kg) is < 0.04 gm/10 min.

Based to the topic, study the effect of hydrophobicity of PVDF membrane on CO_2/N_2 separation, there has explanation about hydrophobicity aspect. The hydrophobicity is the physical property of a molecule that will repelled from a mass of water. Hydrophobic molecules prefer to be non-polar molecule and also non-polar solvents. The molecule tends to bonding with itself because they are unable to form hydrogen bond. It will cause the hydrophobic interaction which in itself is misleadingly named as the energetic force comes from the hydrophilic molecules. The two immiscible phase (hydrophilic vs. hydrophobic) will change, so their corresponding interfacial area will be minimal. This can call phenomenon of phase separation.

The PVDF membrane is more get attention as membrane material because it has more outstanding properties such as thermal stability, high mechanical strength; chemical resistance and high hydrophobicity compare other polymeric materials. PVDF membrane also applied in ultrafiltration and microfiltration for general separation purpose and now currently explored as potential candidates in the application of membrane contractor and membrane distillation. In addition, PVDF particularly microporous membranes can use to exhibit high efficiency for particle removal. PVDF also can be used for western blots for immobilization of proteins because of its non-specific affinity for amino acids.

1.2 Problem Statement

The global climate change is a big concern especially in concept of the CO_2 emission from the combustion of fossil fuels in power plants. The CO_2 capture technique is used in order to overcome the global climate problem. The PVDF as hydrophobic polymers is suggested to be contactors for CO_2 capture. This membrane has a high degree of hydrophobicity and strong chemical resistance. Furthermore, the PVDF is a polymer which gains more attention to industry as a potential membrane material recently. Basically, the PVDF have characteristic as a high hydrophobic nature and excellent chemical resistance. The fabrication of PVDF membrane is the way to develop a better and good kind of polymeric membrane in order for gas separation industry. The development of PVDF membrane would be improve the performance of the existing membrane in term of chemical, physical and other characteristics. Moreover, the addictive were selected specifically to study the effect addictive on the membrane performance. The characteristic of hydrophobicity of PVDF was study by adding the additive in the polymer. The roles of different additives vary in different polymer/solvent/non-solvent systems.

1.3 Research Objectives

1. To develop PVDF membrane with lithium nitrate as additive.
2. To study performance of fabrication of membrane for CO_2/N_2 separation process.
3. To characterise the physical and chemical properties of the PVDF membrane.

1.4 Scope of Research

1. Study the effect of additives $LiNO_3$ with different concentration on the fabrication of PVDF.
2. Study the performance of PVDF membrane using single gas permeation test using different pressure (0.5 bar, 1.0 bar, 1.5 bar)
3. Characterize the membrane using SEM and FTIR.

1.5 Rationale and Significant

The fabrication of PVDF membrane is important for development of membrane for gas separation process. The fabrication of PVDF membrane with better condition of characteristic is needed in the industrial sector to reduce the overall cost operation cost. The economic country will be increase in order increases the development of production of good quality of membrane. The addition of $LiNO_3$ as additive into the dope solution could be form the PVDF membrane good performance in term of strain strength than the PVDF commercial membrane nowadays.

CHAPTER II

LITERATURE REVIEW

2.1 Concept of Membrane

2.1.1 History of Membrane

According to Gwen V. (2001), the history of existence membrane begins when the early 1930’s-40’s, Danielli and davson studied triglyceride lipid bilayers over a water surface. They found the triglyceride lipid bilayers arranged themselves with the polar heads facing outward. Figure 2.1 show the Danielli and Davson model. The model of membrane show the triglyceride lipid bilayers arranged themselves.

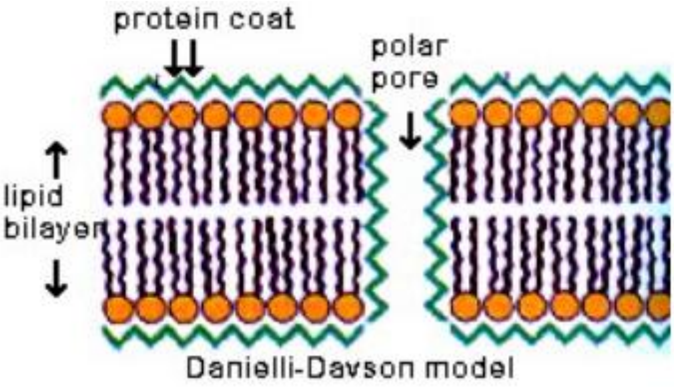


Figure 2.1: Danielli and Davson model structure of membrane (Gwen V., 2001)

Furthermore, in the 1950's, Robertons take a note when he done a research on the structure of membranes seen in electron micrographs. There are no spaces for pores in the electron micrographs. He make hypothesis that the there are rail rock track appearance from the binding of osmium tetroxide to proteins and polar group of lipids. Figure 2.2 show the Robertson model. His model explains the membrane general structure of membrane with no space for pore in membrane but only like rail rock track appeared.

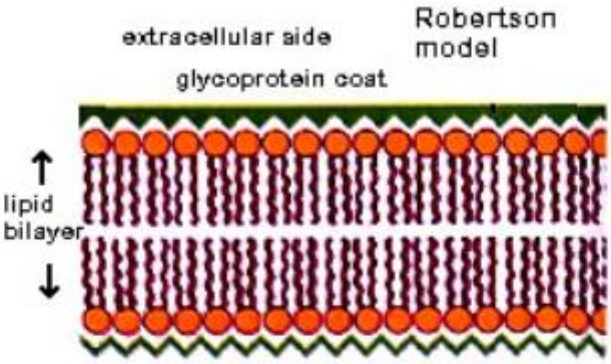


Figure 2.2: Robertson model structure of membrane (Gwen V., 2001)

Therefore, in 1966, Lenard and Singer done a experiment and there are over 30% of membrane proteins were twisted into an alpha helix. This observation show there is many spherical proteins. Singer then studied the phospholipids bilayers and found that they can from a flattened surface on water without any requirement for protein coat. Later than that, Singer found that inside of membrane has a proteins molecule.

2.1.2 Definition of Membrane

The membrane can be defined as a barrier which separates two phases and confine the transport of various chemicals in a selective manner. A membrane can be classified as homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge or be neutral or bipolar (G. Srikanth). The membrane is functional to protect the surface. Therefore, it’s also functioning as covering separating two regions. It will be connecting the structures or organs of an animal or a plant. According to Lukas (2010), membrane can be defined as phospholipids bilayer mixed with membrane proteins. The lipid is not continuous but it contains non-lipid molecular in particular proteins.

Moreover, according to Marcel (2003), definition of membrane is a selective barrier between two phases and term of selective being inherent to a membrane or a membrane process. Refer to term of selective, it specific to macroscopic definition.

2.1.3 Function of Membrane

According to Regina (2012), membrane will be functioning to protect the integrity of the cell by allowing certain substances into the cell, while keeping other substances out. It also will be act as a base of attachment for the cytoskeleton in some organisms and the cell wall in the others. Therefore, the cell of membrane serves to help support the cell and help maintain its shape. According to Gwen V. (2001), membrane is vital because it can separate the cell from the outside of cell. Then, the reason why membrane separate compartment inside the cell is membrane wants to protect important process which happens inside the cell membrane.

In addition, the function of cell membrane is serving as mechanisms for cell-cell communication. Then, cell membrane will be act as a boundary between cytoplasm of the cell and outer surrounding. It is very selective permeable and controls the exchanger of substance into and out of cell membrane. According to Wil N.K. et. al. (2002), the membrane is usually impermeable for most ions and solutes and can be controlling the composition of the cytoplasm. Then the cytoplasm membrane has crucial function in maintain the internal condition for energy transduction and metabolism. In addition, membrane can be control and manage the flow of information between other molecules and also received the signal from other molecule (Bernard S. B., 1996). Membrane also involve in process of release and capture of energy. The example of process involves in capture and release energy are oxidation phosphorylation and photosynthesis.

2.1.4 General Structured of Membrane

The membrane is a known as the flexible containers. Inside the membrane, there are many structured with different functioned. For the future understanding for the structure of membrane, figure 2.3 shows the overall structure in a membrane. According to Stephen (2005), membrane is can be see within cells (the plasma membrane surrounding cells) which consist of phospholipids (other lipids and membrane proteins) arrayed by lipid bilayer or hydrophobic exclusion into two-dimension fluids. Then, phospholipids are amphipathic molecules which have both a hydrophobic and hydrophilic end. Another important structure in membrane is lipid bilayer. Lipid bilayer can exist as bilayer in aqueous solution.

According to Suzanne (2004), the fluid mosaic describes the lipid membrane. The chains are aligned parallel to each other. The non-polar ends of the chains contact each other in middle of the bilayer make it a barrier impermeable to most aqueous soluble molecules but small or non-polar agents to pass. Furthermore, in biological theory, membranes have a major component which is lipids, proteins and sugars (Bernard S. B., 1996). Figure 2.4 will be show the cell membrane structure consist of lipids, proteins and sugars. The membrane structure consists of two-layered of lipids and there are a proteins molecule embedded in lipids gaps. The structure in membrane is highly fluid, so, the proteins molecule an move freely in the plane of the membrane. Moreover, the sugars molecule attaches to lipids and proteins molecule because there are have covalent bond between them.

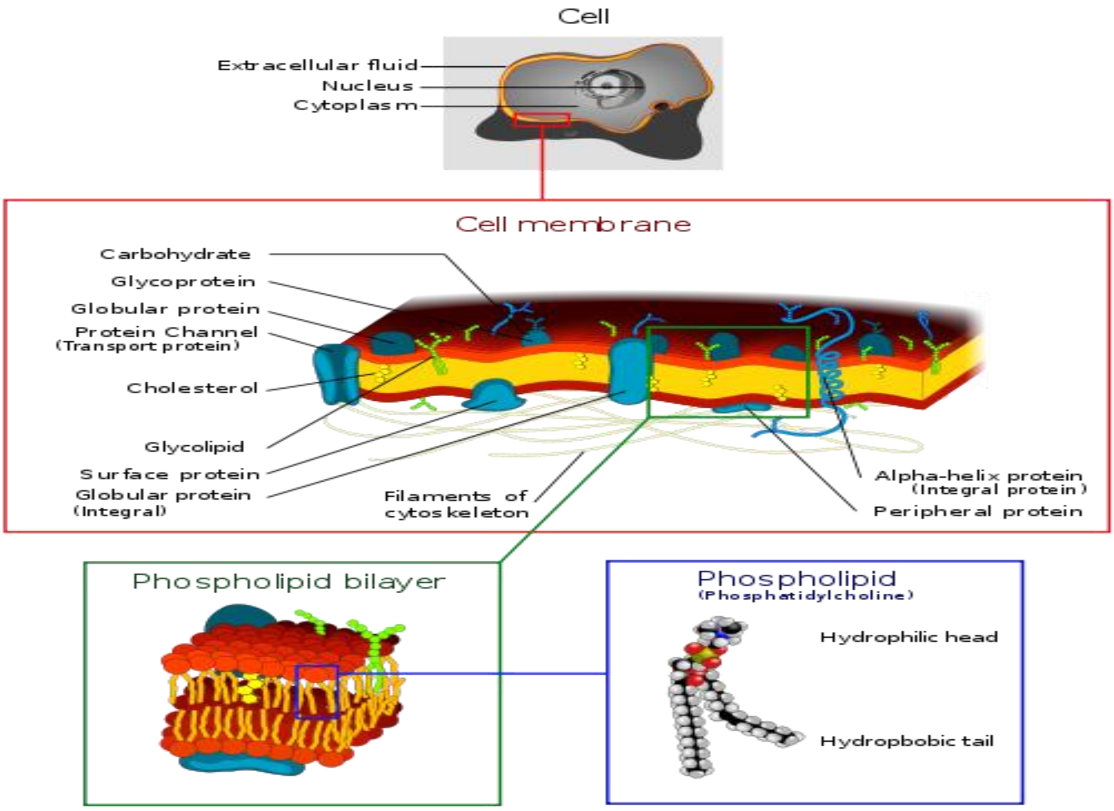


Figure 2.3: **The overall structure in a membrane.**

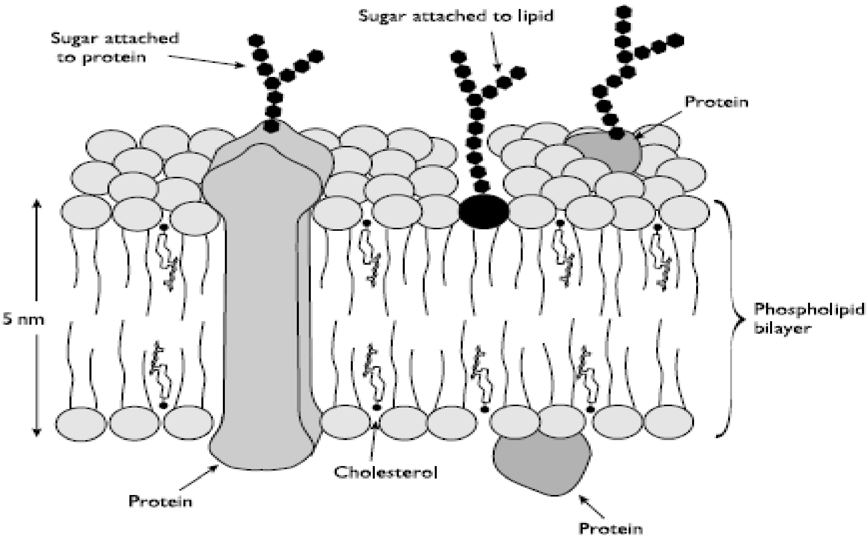


Figure 2.4: **The biological structure of membrane consists of lipids, proteins and sugars (Bernard S.B., 1996)**

2.1.5 Membrane Structures

According to Keith and Hughes (199), the function of the membrane will depend on its structure as this essentially determines the mechanism of separation and its application. There are two kind of structure are generally found in the membrane which are symmetric membrane, asymmetric membrane and composite membrane.

2.1.5.1 Symmetric and Asymmetric Membranes

The definition of symmetric membrane is the membrane which has the same or constant diameter of pores throughout the cross section of the membrane. The symmetric membrane usually used in filtration but also in other separation such as per-traction, liquid membranes and utilize. Example of materials for fabrication of symmetric membrane are ceramic, metals, carbon and polymers.

The definition of asymmetric membrane is the membrane which has the different size of the pore size at the surface compare with the pore at the bottom side. Generally, asymmetric membranes are used in reverse osmosis (RO), gas permeation (GP) and pervaporation (PV).

According to Seeram R., Zuwei M., and Takeshi M. (2011), the thickness of symmetric membranes can be assume in range of 10-200µm. The resistance to mass transfer can be determined from the total membrane thickness. Therefore, a decrease in membrane thickness will be affected the increasing of permeation rate. In addition, asymmetric membranes (aniosotropic) have a different chemical and physical structured related to its thickness. The asymmetric usually is a 'thin' skin on a surface membrane with small pore size and its thickness is around 0.1-0.5 µm. It's have a dense layer which can be supported by a porous structure with larger pore size and a thickness can be assume around 50-150 µm. According to Klein (1991), asymmetric generally known as superior membrane compare to symmetric membrane because there are flux determining top layer is very thin. Thus, refer to this unique ultra structure, the rejection only happens at the surface and retained particles do not enter the body of the membrane. The resistance to mass transfer is determined largely by the thin top layer. The support layer does not add any significant hydraulic resistance to the flow of solvent through the membrane.

2.1.6 Module of Membrane

According to Heirner et, al. (2006), the main criteria for design module membrane are high membrane packing density, reliability, ease of membrane or module replacement, control of concentration polarization and low cost. The membrane normally produced in three different configurations such as flat sheet, hollow fibers or capillaries and tubes. According to Singer et, al (1972), the cell membrane functions as a semi-permeable barrier, allowing a very few molecules across it while fencing the majority of organically produced chemicals inside the cell.

2.1.6.1 The Plate and Frame Membrane Module

This kind of membrane module is used on an industrial in many scope of membrane separation process including to ultrafiltration, reverse osmosis and gas separation. This plate and frame membrane modules is the membrane which can easily be exchanged. So, it makes this membrane module suitable for batch-type operations and multi-purpose applications using different membranes for different separation tasks. The membranes, porous membrane support plates, and spacers forming the feed flow channel are clamped together and stacked between two endplates and placed in a housing. Figure 2.5 shown the schematic drawing illustrating the concept of a plate-and-frame membrane module.

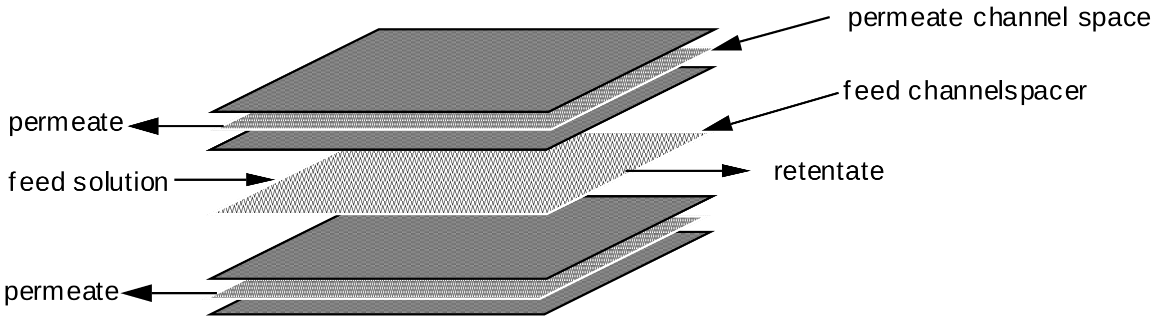


Figure 2.5: Schematic drawing illustrating the concept of a plate-and-frame membrane module (Singer et, al, 1972)

Moreover, the plate and frame module also have another variation which is the spiral wound module. This kind of module is basically used for reverse osmosis, ultrafiltration and gas separation. Small spiral wound units consist of just one envelope which limits the total membrane area that can be installed in one unit to about 1 to 2 m^2. The limitation of the surface area which installed in a module containing one single envelope is because of the pressure drop encountered by the permeate moving down the permeate channel to the central collection tube. Figure 2.6 shown the schematic drawing of a spiral-wound membrane module.

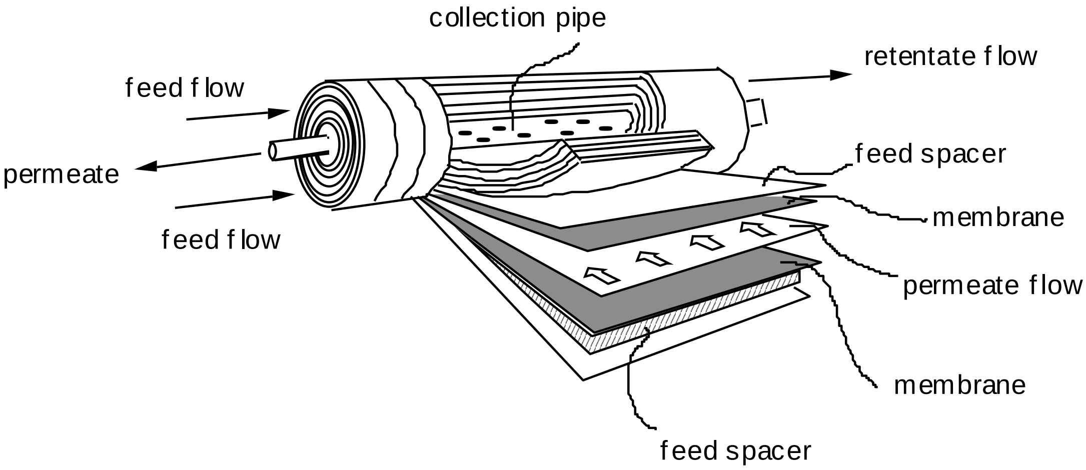


Figure 2.6: Schematic drawing of a spiral-wound membrane module (Singer et. al. 1972)

2.1.6.2 The Tubular Membrane Module

The tubular membrane module is consists of membrane tube placed into porous stainless steel of fiber glass reinforced plastics pipes. The main advantage of the tubular module is that concentration polarization effects and membrane fouling can be easily controlled, and plugging of the membrane module is avoided even with feed solutions that have very high concentration of solid matter and thus high viscosity. The disadvantage of the tubular module design is the low surface area, that can be installed in a given unit volume, and the very high costs. Therefore, tubular membrane modules are generally only applied in applications where feed solutions with high solid content, and high viscosity have to be treated and other module concepts fail due to membrane fouling and module plugging. Figure 2.7 shown the schematic drawing for the tubular membrane module.

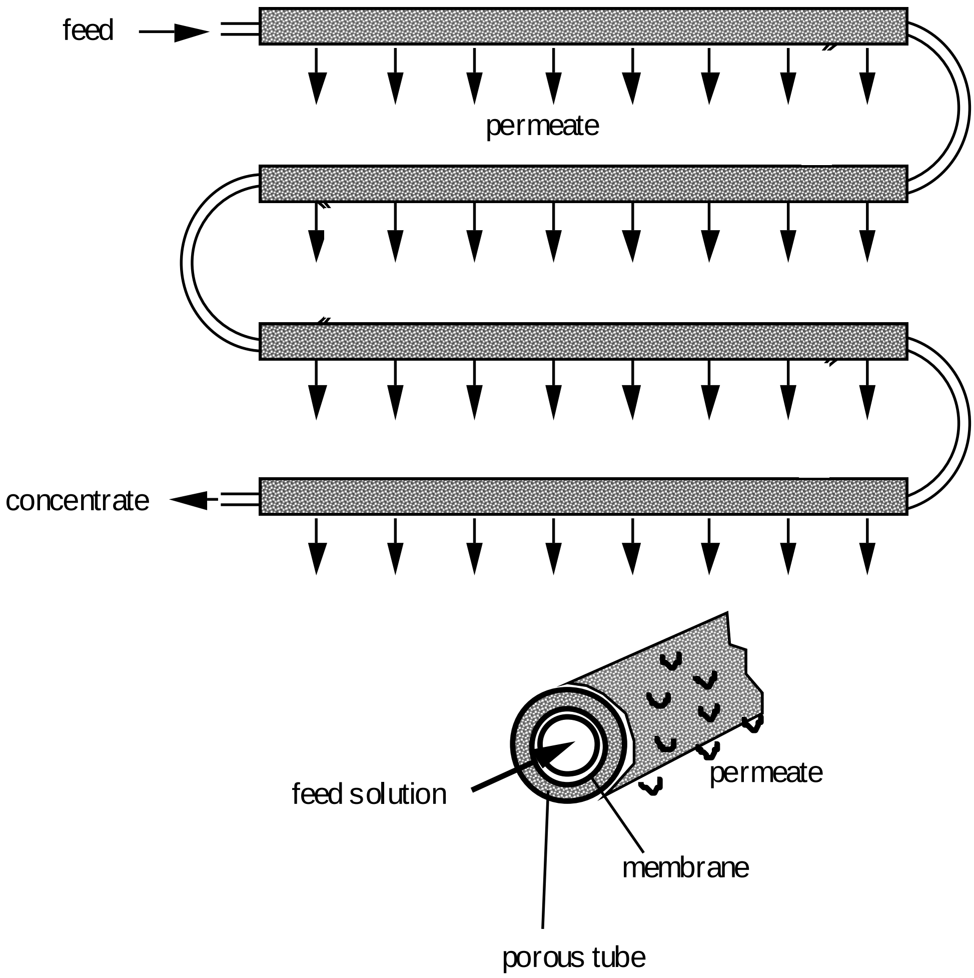


Figure 2.7: Schematic drawing illustrating the tubular membrane module (Singer et, al, 1972)

2.1.6.3 The Hollow Fiber Membrane Module

Another type of module membrane is the hollow fiber module. This module has the highest packing density of all module types available on the market today. Its production is very cost effective and hollow fiber membrane modules can be operated at pressures in excess of 100 bars. The main disadvantage of the hollow fiber membrane module is the difficult control of concentration polarization and membrane fouling. Therefore, an extensive pretreatment is required when hollow fiber membranes are used for the treatment of liquid mixtures. The main application of the hollow fiber module is today in reverse osmosis desalination of sea water and in gas separation. Figure 2.8 shown the schematic drawing illustrating the construction of a hollow fiber module.

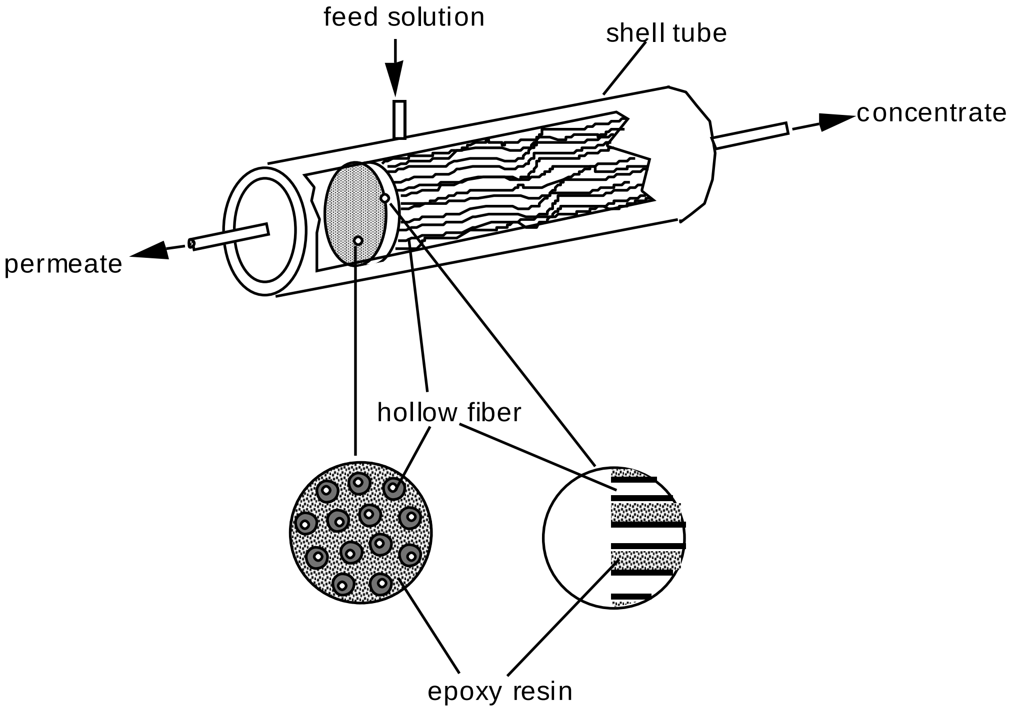


Figure 2.8: Schematic drawing illustrating the construction of a hollow fiber module (Singer et, al, 1972)

2.1.7 The Process Involve Membrane

According to Lenntech (2011), the membrane separation process is based on the presence of semi permeable membranes. The principle used is the membrane acts as a very specific filter that will allow water flow throungh but at same time it catches suspended solids and other substances. According to Ahsan (2006), the main types of membrane process are ultrafiltration, microfiltration and reverse osmosis. Furthermore, referring to Marcel M.,(2003), types of membrane process are microfiltration, ultrafiltration, reverse osmosis, nanofiltration, pressure retarded osmosis and piezodialysis.

2.1.7.1 Ultrafiltration

According to Ahsan (2006), ultrafiltration (UF) is the process of separating extremely small particles and dissolved molecules from fluids. The primary basis for separation is molecular size, although in all filtration applications, the permeability of a filter medium can be affected by the chemical, molecular or electrostatic properties of the sample. Ultra filtration can only separate molecules which differ by at least an order of magnitude in size. Molecules of similar size cannot be separated by ultra filtration. Ultrafiltration is typically used to separate proteins from buffer components for buffer exchange, desalting, or concentration. UF is more efficient because it can simultaneously concentrate and desalt solutes. It does not require a phase change, which often denatures labile species, and UF can be performed either at room temperature or in a cold room. Table 2.1 show the summary of ultrafiltration (Marcel M., 2003).

Table 2.1: The summary of ultrafiltration (Marcel M., 2003)

Membranes:	Asymmetric Porous
Thickness:	150µm (or monolithic for some ceramics)
Pore size:	1-100 nm
Driving force:	Pressure (< 10 bar)
Separation principle:	Sieving mechanism
Membrane materials	Polymer (e.g polysulfone, polycrylonitrile) Ceramic (e.g zirconium oxide, aluminium oxide)
Main applications:	-dairy (milk, whey, cheese making) -food(potato starch and proteins) -metallurgy (oil-water emulsions, electro paint recovery) -pharmaceutical (enzymes, antibiotics, pyrogens) Automotive (electron paint) -water treatment

2.1.7.2 Microfiltration

According to Ahsan (2006), micro filtration (MF) is the process of removing particles or biological entities in the 0.025 µm to 10.0µm range from fluids by passage through a microporous medium such as a membrane filter. Membrane filters can be used for final filtration or pre-filtration, whereas a depth filter is generally used in clarifying applications where quantitative retention is not required or as a pre-filter to prolong the life of a downstream membrane. Microfiltration can also be used in sample preparation to remove intact cells and some cell debris from the lysate.

Table 2.2: The summary of microfiltration (Marcel M., 2003)

Membranes:	Symmetric Porous
Thickness:	10-150µm
Pore size:	0.05-10µm
Driving force:	Pressure (< 2 bar)
Separation principle:	Sieving mechanism
Membrane materials	Polymeric, ceramic
Main applications:	-analytical applications -sterilization (food and pharmaceuticals) -ultrapure water (semiconductors)

2.1.7.3 Reverse Osmosis

According to Ahsan (2006), reverse osmosis (RO) separates salts and small molecules from low molecular weight solutes (typically less than 100 daltons) at relatively high pressures. RO membranes are normally rated by their retention of sodium chloride while ultrafiltration membranes are characterized according to the molecular weight of retained solutes. Reverse osmosis systems are primarily used to purify tap water to purities that exceed distilled water quality.

Table 2.3: The summary of reverse osmosis (Marcel M., 2003)

Membranes:	Asymmetric or composite
Thickness:	Sublayer = 150μm, toplayer = 1μm
Pore size:	< 2nm
Driving force:	Pressure: brackish water 15-25 bar Seawater 40-80 bar
Separation principle:	Solution-diffusion
Membrane materials	Cellulose triacetate, aromatic polyamide, polyamide and poly(ether urea) (interfacial polymerization)
Main applications:	-desalination of brackish and seawater -production of ultrapure water (electronic industry) -concentration of milk (dairy industry)

2.1.8 Membrane Transport Mechanism

The membrane transport is a mechanism to regulate the passage of solute to enter the biological membrane namely lipid bilayers. The structure of membrane itself will help to control the transportation processes. According to Singer et, al, (1972), figure 2.9 show the model of common molecule in membrane such as phospholipid, polar (hydrophilic) and two non-polar (hydrophobic).

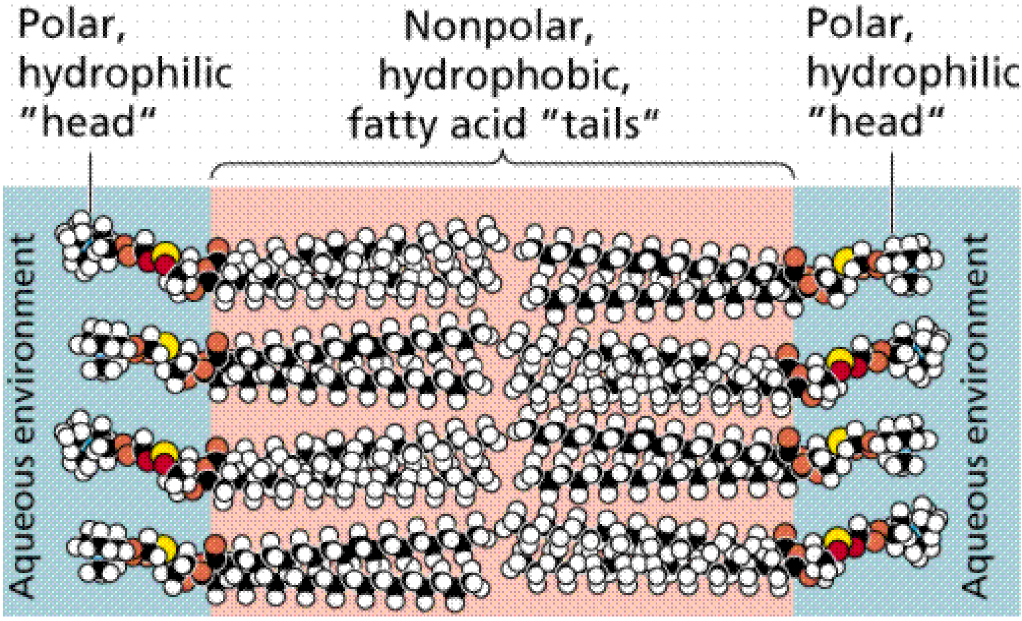


Figure 2.9: The model of common molecule in membrane such as phospholipid, polar (hydrophilic) and two nonpolar (hydrophobic) (Singer et, al, 1972)

2.1.8.1 Active Transport Mechanism

The transport mechanisms have to categories. The categories of transport mechanism are passive transport mechanism and active transport mechanism. According to Bergmann (2001), the active transport mechanism is the movement of a molecule across a membrane or another barrier that is driven by energy other than stored in the concentration gradient or the electrochemical gradient of the transported molecule. This type of transport requires usually the expenditure of ATP and the help of specific transport proteins. The example of process which used the theory of active transport mechanisms are Active transport via protein pumps and Bulk flow mechanism (Endocytosis and Exocytosis).

Active transport via protein or the Na^+ K^+ pump present in the cell membranes of all animal cells and is the most abundant and important of all membrane pumps. The Na^+ K^+ pump is a complex pump, simultaneously pumping three sodium ions out of the cell and two potassium ions into the cell for each molecule of ATP split. This means that, apart from moving ions around, it also generates a potential difference across the cell membrane. According to Kjell (2012), the membrane transport mechanism for the Na^+ K^+ pump is showed in figure 2.10.

Endocytosis is the transport of materials into a cell. Materials are enclosed by a fold of the cell membrane, which then pinches shut to form a closed vesicle. Strictly speaking the material has not yet crossed the membrane, so it is usually digested and the small product molecules are absorbed. When the materials and the vesicles are small (such as a protein molecule) the process is known as pinocytosis (cell drinking), and if the materials are large (such as a white blood cell ingesting a bacterial cell) the process is known as phagocytosis (cell eating). Figure 2.11 is shown the membrane transport mechanism of Endocytosis process.

Exocytosis is the transport of materials out of a cell. It is the exact reverse of endocytosis. Materials to be exported must first be enclosed in a membrane vesicle, usually from the RER and Golgi body. Hormones and digestive enzymes are secreted by Exocytosis from the secretory cells of the intestine and endocrine glands. Figure 2.12 is shown the membrane transport mechanism of Exocytosis process.

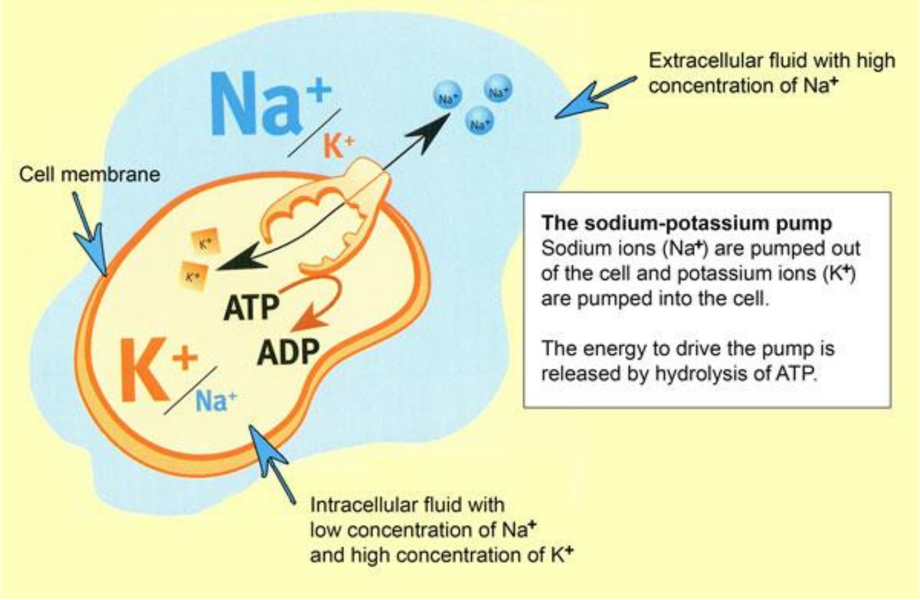


Figure 2.10: The membrane transport mechanism for the Na^+ K^+ pump (Kjell, 2012)

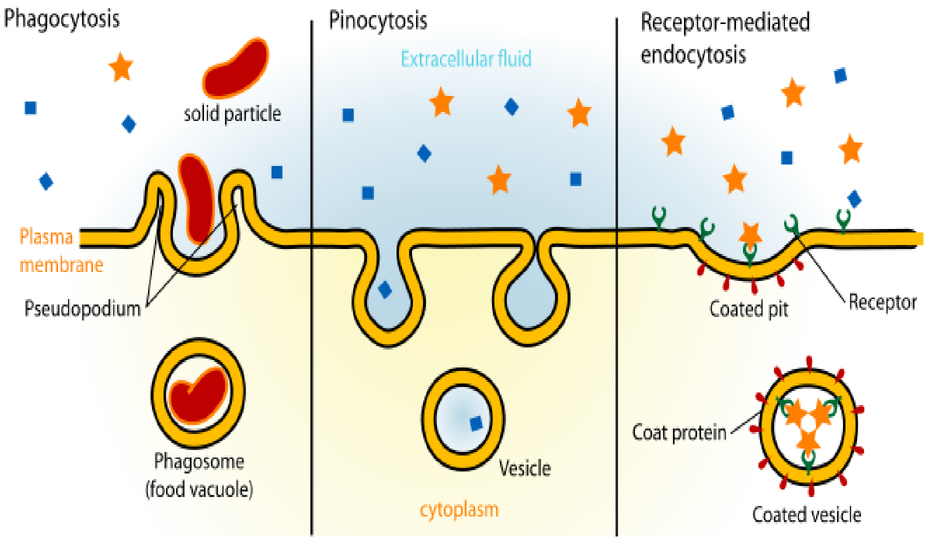


Figure 2.11: The membrane transport mechanism of Endocytosis process (Kjell, 2012)

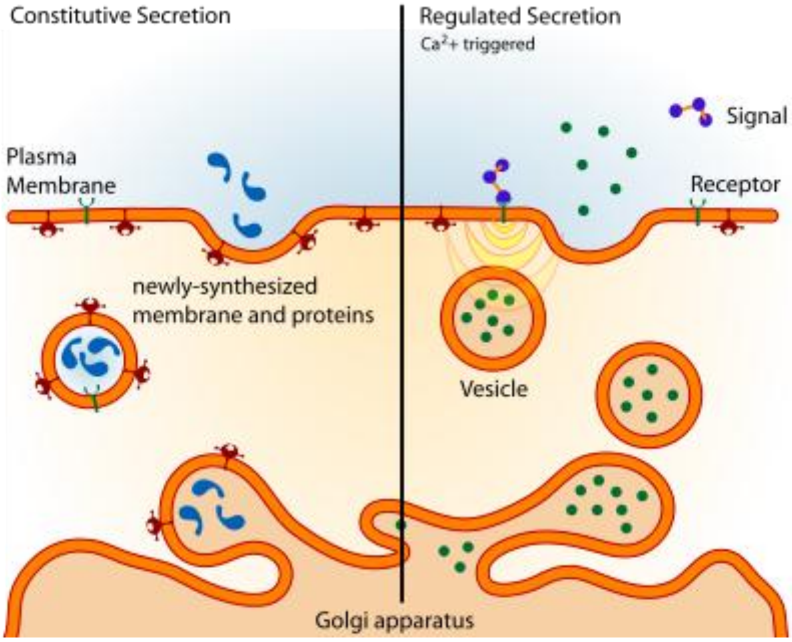


Figure 2.12: The membrane transport mechanism of Exocytosis process (Kjell, 2012)

2.1.8.2 Passive Transport Mechanism

According to Kjell (2012), passive transport is the transport of substances across a membrane by a trans-membrane protein molecule. The transport proteins tend to be specific for one molecule (a bit like enzymes), so substances can only cross a membrane if it contains the appropriate protein. This is movement across the membrane without any energy input. The common passive transport systems are diffusion, facilitated diffusion and osmosis.

Diffusion refers to the process by which molecules intermingle as a result of their kinetic energy of random motion. Consider two containers of gas A and B separated by a partition. The molecules of both gases are in constant motion and make numerous collisions with the partition. If the partition is removed as in the lower illustration, the gases will mix because of the random velocities of their molecules. In time a uniform mixture of A and B molecules will be produced in the container.

Facilitated diffusion is the movement of specific molecules down a concentration gradient and passing through the membrane via a specific carrier protein. Thus, rather like enzymes, each carrier has its own shape and only allows one molecule (or one group of closely related molecules) to pass through. It is passive and requires no energy from the cell.

Osmosis is a special example of diffusion. It is the diffusion of water through a partially permeable membrane from a more dilute solution to a more concentrated solution (down the water potential gradient). An isotonic solution has the same concentration as a cell, so no visible changes occur (this is called dynamic equilibrium). A hypotonic solution is less concentrated than the cell, so in this case the cell swells and bursts (or in the case of a plant cell, the cell walls prevent bursting, so there is an increase in turgor pressure). A hypertonic solution is more concentrated than the cell, so the cells shrivels up (in plants this also happens and the cell membrane pulls away from the cell wall, this is called plasmolysis).

2.1.9 Membrane used for Gas Separation

According to Keith and Hudges (1996), the main properties of membrane to be made it effective for gas separation membrane are chemical resistance, mechanical stability, thermal stability, high permeability, high selectivity and stable operation.

2.1.10 Industrial Application of Gas Separation Membrane

According to Freemantl (2005), gas separation membrane currently used in industry for hydrogen separation such as hydrogen/nitrogen separation in ammonia plants and hydrogen/hydrocarbon separation in petrochemical application. Gas separation membrane also used for separation of nitrogen from air and $CO_{2.}$ In addition, gas separation membrane also used for organic vapor removal from air or nitrogen streams and for water removal from natural gas. Mostly membrane material for gas separation is polymer.

Currently, the gas separation membranes are most widely used on industry for hydrogen separation like hydrogen/nitrogen separation in ammonia plants and hydrogen/hydrocarbon separation in petrochemical application. Membrane also used to remove the CO_2 and water from natural gas, aroma recovery in perfume industry/ fragrance and flavor separation in food industry

2.2 Concept of Gas Separation

2.2.1 Definition of Gas Separation

Gas separation can be defined as the process of separating various hydrocarbon components in natural gas to be used at its fullest value. Membrane can be defined as a barrier between two fluids, which allows selective transfer of some species through a driving force. In separation of gases, membranes are often polymeric and the driving force is the partial pressure of species. The gas molecules dissolve in the membrane at high-pressure side, diffuse through it and release at low-pressure side. Depending on the type of gas molecules and the structure of the membrane, some molecules pass the membrane faster than others and hence, separation occurs.

2.2.2 Material Requirement of Membrane for Gas Separation

Generally, the membrane application on the gas separation offer many benefit such as simple flow schemes, low energy consumption, reliable continuous operation and competitive capital cost. Therefore, the physical properties of membrane its self make membrane is good choice to be used in gas separation process. According to Chien et, al (2005), the most important physical constants for gas separation are permeability and selectivity. Polymers with both high permeability and selectivity are desirable. Higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units. Higher selectivity results in a higher purity gas product. Another important factor is to make a highly permeable and selective membrane with good mechanical and thermal stability.

2.2.3 Technique for Gas Separation

Gas separation membrane usually works according to the principle of selective permeation through a membrane surface. The basic method or techniques used to separate gases are by sorbents/ solvent, membrane and cryogenic distillation. In addition, another technique also applied in the gas separation such as crystallization, paper-chromatography, thin-layer chromatography and open column chromatography.

2.2.3.1 Separation with Sorbent/ Solvents

Amine scrubbing technology was established over 60 years ago in the oil and chemical industries, for removal of hydrogen sulphide and CO2 from gas streams Commercially, it is the most well established of the techniques available for CO2 capture although practical experience is mainly in gas streams which are chemically reducing, the opposite of the oxidizing environment of a flue gas stream. Solid adsorbents, such as zeolites and activated carbon, can be used to separate CO2 from gas mixtures. In pressure swing adsorption (PSA), the gas mixture flows through a packed bed of adsorbent at elevated pressure until the concentration of the desired gas approaches equilibrium. The bed is regenerated by reducing the pressure.

2.2.3.2 Separation with Membrane

Gas separation membranes allow one component in a gas stream to pass through faster than the others. There are many different types of gas separation membrane, including porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. Membranes cannot usually achieve high degrees of separation, so multiple stages and/or recycle of one of the streams is necessary. This leads to increased complexity, energy consumption and costs. Several membranes with different characteristics may be required to separate high-purity CO2. Solvent assisted membranes are being developed to combine the best features of membranes and solvent scrubbing. Much development is required before membranes could be used on a large scale for capture in power stations.

2.2.3.3 Separation by Cryogenic Distillation

CO_2 can be separated from other gases by cooling and condensation. Cryogenic separation is widely used commercially for streams that already have high CO2 concentrations (typically >90%) but it is not used for more dilute CO2 streams. Cryogenic separation has the advantage that it enables direct production of liquid CO2, which is needed for certain transport options, such as transport by ship.

Cryogenics would normally only be applied to high concentration, high pressure gases, such as in pre-combustion capture processes or oxygen fired combustion. A major disadvantage of cryogenic separation of CO2 is the amount of energy required to provide the refrigeration necessary for the process, particularly for dilute gas streams. Another disadvantage is that some components, such as water, have to be removed before the gas stream is cooled, to avoid blockages.

2.2.4 Process/ Mechanism in Separation Gas of N_2 and CO_2

According to Lee et, al. (2003), hydrogen is separated from a hydrogen/nitrogen/carbon dioxide mixture by an electrochemical separation method. By applying a direct current to a proton-conducting membrane, hydrogen can be electrochemically dissociated on the platinum catalyst of the anode, transported across the hydrated cation exchange membrane, and then recovered on the catalytic cathode. The separation of pure hydrogen from a hydrogen/nitrogen/carbon dioxide mixture by a low-temperature electrochemical separation system is investigated. The apparatus for separating hydrogen is similar to that used in a PEMFC for producing an electrical current. Therefore, the electrochemical parameters, i.e., activation loss, ohmic loss, and mass transport loss, are generally in accordance with those of a PEMFC. When the gas mixture is supplied to the anode side of an electrochemical cell using a proton exchange membrane and direct current is passed through it, hydrogen is ionized on the platinum catalyst sites in the porous, gas-diffusion electrode and the resulting H+ protons are selectively transported through the membrane to the cathode where hydrogen gas is evolved. Pure hydrogen gas can be separated without pressurization and the separation rate can be easily controlled by the applied current.

2.2.5 Membrane Gas Separation Market

According to LePree et, al. (2012), membrane technology has been available since the mid 1980s, but has become more prevalent in gas processing operations as new developments have helped it filter into more applications. New materials allow the membrane modules to operate at more extreme parameters, such as higher temperatures and pressures, and there have been modifications to the chemistry of making the membrane polymer. Therefore, it will be able to withstand increasingly harsh conditions. Limited budgets and the need for high performing operations are causing chemical processors and petroleum and gas refiners to seek out find the budget of processes. When it comes to gas processing operations, such as carbon-dioxide removal, hydrogen purification and air separation, membrane technologies will be compare with favorably to other available systems and will continue to do so for years to come as research and development work is currently underway for future applications.

According to Foo (2011), as were noted by the US National Research Council, the technological frontiers of the membrane technology should be concerned more in the developing of new membrane materials and the identification of new ways of using perm selective membranes. New membrane materials to be used is still a big option in the research of this brand new technology, as most of the researchers are always intend to get a better improvement for this separation process. membrane-based hybrid system serve as a good example, as it is a combination of conventional unit operations and membrane separation processes, which often results in separation processes that offer significant advantages over the exclusive use of either component process. Such advantages may include more complete separation, reduced energy requirement, lower capital cost, and lower production cost.

2.3 Concept of Polyvinylidene Fluoride (PVDF) Membrane

Generally, the PVDF is short form of Polyvinylidene Fluoride. According to Francis et, al (1964), PVDF is a new member in the family of fluorine containing polymers. PVDF contains carbon, hydrogen and fluorine. Moreover, PVDF is one of the higher fluorine containing polymer.

2.3.1 Properties of PVDF

PVDF is produced by the polymerization of vinylidene difluoride. The IUPAC name of PVDF is poly-1,1-difluoroethene. The molecular formula for PVDF is $–(C_2H_2F_2)n-$. Table 2.1 is showing the mechanical and physical properties of PVDF.

Furthermore, the others properties of PVDF are Low density in comparison to other fluoro plastics, Absorbs practically no water, Good dimensional stability, High chemical resistance, good hydrolytic stability, weather resistant, radiation resistant and physiologically safe.

Table 2.4: The mechanical and physical properties of PVDF

Property	**Units**	**Value**
Melting	C	174
Glass transition	C	~ -30
Density	g/cm^3	1.8
Heat capacity	Joule/(gK)	1.9
Tensile strength	Psi	78000
Serving temperature long term	C	140
Dielectric constant (60 Hz)	-	9
Dielectric strength	KV/mm	160
Volume resistivity	Ohm/cm	1×10^{14}
Refraction index		1.42

2.3.2 PVDF Membrane Material

PVDF membrane is basically are microporous membrane. It can be prepared in order to exhibit high efficiency for particle removal. There are two type of PVDF membrane such as hydrophobic PVDF membranes and hydrophilic PVDF membranes with specific pore size around 0.2 or 0.4 µm. In the pierce PVDF membrane, there are proprietary alterations. So, it will make PVDF membrane more resistant to discoloration which often with other commercially available PVDF membrane filters (Yu, 2010). According to Membrane Solution, PVDF filter media is a microporous membrane and can be provided to exhibit high efficiency for cleaning particle. PVDF membrane has a low critical surface energy and conventional. PVDF membrane also are hydrophobic and microporous. This membrane is not wet with aqueous fluids. It consists of reinforced-type PVDF membrane. Therefore, it can be ensure wet air and other gas pass through smoothly even in condition of differential pressure is very low.

2.3.3 Surface Modification of PVDF Membrane

There are many researches done in order to increase the ability of PVDF membrane in term of their properties. According to Nripen et, al (2005), the surface modification of microporous PVDF membrane is done be process of atom transfer polymerization (ATRP). This research is indicate that t by changing polymerization time, it is possible to tune the ion-exchange capacity and the average pore size in rational ways. Furthermore, the surface modification of PVDF porous membranes via poly (DOPA) coating and heparin immobilization is done (Zhu et, al (2008). Result from this research is t the hydrophilicity of PVDF membranes was significantly improved by the incorporation of poly (DOPA) and heparin. The effects of poly (DOPA) and heparin on membrane surface morphologies were also investigated by scanning electron microscopy (SEM).

2.3.4 Crystalline Properties of PVDF

According to Zhenya et, al. (2009), the properties of polyvinylidene fluoride (PVDF) is a semi-crystalline polymer containing an amorphous phase and also a crystalline phase. The crystalline phase gives thermal stability and flexibility of amorphous. PVDF membrane is stable when it is attacked by the corrosive organic compound and chemical such as alkaline, acids, fungal and algae. Furthermore, PVDF membranes also have high flexibility and hard to cracking. According to Liu et, al. (2011), PVDF is a semi-crystalline polymer that usually contains 59.4 wt% fluorine and 3 wt% hydrogen. The commercial PVDF is generally produced by polymerisation in emulsion or suspension using free radical initiators, forming a repeating unit of $–CH_2–CF_2–$. The spatial arrangement of the CH_2 and CF_2 groups along the polymer chains can contribute to the unique properties of PVDF generated from its crystalline structure. Polymer crystalline and the resultant membrane morphology are among important factors in determining the mechanical strength properties, as well as the impact resistance of the membranes.

2.3.5 Thermal Stability of PVDF

According to Liu et, al. (2011), fluoropolymers are thermally more stable than hydrocarbon polymers. The high electro negativity of fluorine atoms on the chain and the high bond dissociation energy of the C–F bond provide the high stability of the fluoropolymers. Although generally stable and inert, PVDF has been observed to experience degradation during high temperature operations. Madorsky and co-workers were first to extensively study the thermal degradation of PVDF at moderate and high temperatures in vacuum. Nguyen provided a systematic review on the thermal stabilities of PVDF based on the available literatures that reported about their investigations on the degradation processes conducted at early stages. General agreement was made based on the literatures concerning the mechanism of the PVDF polymer degradation process. PVDF is thermally degraded primarily by the evolution of HF (dehydro fluorination) and followed by the formation of double bonds.

2.3.6 Membrane Patent of PVDF

According to Xioa et, al. (2009), as a semi-crystalline polymer, poly (vinylidene fluoride) (PVDF) is fit for membrane material due to its excellent chemical resistance, physical and thermal stability, high strength and flexibility. However, the hydrophobicity of PVDF remains a problem and limits its application, thus, hydrophilic modification of PVDF membranes is one of the hotspots in membrane science.

According Ren (2009), PVDF membranes are focused on flat sheet configuration and relatively less research on the fabrication of PVDF asymmetric hollow fiber membranes has been carried out. In those studies, the influences of various dope concentration, additives, spinning conditions, coagulations. On the membrane morphology and membrane performance were investigated, aiming at identifying optimal polymer dope formations and spinning conditions. However, the effect of dope theology in the spinning process on the performance and morphology of PVDF hollow fiber membranes has not received much attention though this factor has been studied detailed for other membrane materials.

2.3.7 Performance of PVDF Membrane

According to Cui et, al. (2009), many studies have attempted to improve the performance of PVDF membranes using various techniques, including physical blending, chemical grafting, and surface modifications. The blending of polymers has the advantage of easy preparation using the thermally induced phase separation. The addition of organic hydrophilic materials can improve some properties of membranes, but reduces membrane strength. Recent studies of PVDF-blending modifications have focused on blending the polymer with inorganic materials. Several papers have been reported that, in the process of membrane preparation via non-solvent induced phase separation (NIPS) method a unique polymer/inorganic particle membrane material can be developed to change the membrane porous structure and enhance the hydrophobic properties of membranes by the addition of an inorganic particle to a polymer. Inorganic materials that can be blended with PVDF include silica zirconium dioxide (ZrO_2), aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2). The PVDF blend membrane morphology and elasticity are both significantly affected by the mass of inorganic materials added.

According to Yan et, al. (2005), to improve the performance of PVDF membranes uses various techniques, including physical blending, chemical grafting, and surface modifications. The blending of polymers has the advantage of easy preparation using phase inversion. The addition of hydrophilic materials to the dope solution increases the water permeability of a membrane with similar pore size and pore distribution, due to an increase in pore density as well as in the hydrophilicity of the membrane surface and inside the pores. Polymethyl methacrylate (PMMA) is an organic material that is commonly blended with PVDF. The addition of hydrophilic PMMA not only improves the membrane pore size distribution and pore structure, but also enhances its permeation performance without a loss of retention. Additional organic materials that can improve PVDF membrane properties include polymethy acrylate (PMA).

2.3.8 Application of PVDF Membrane

Because of the polyvinylidene fluoride (PVDF) membranes are have the chemical flexibility and stability; PVDF can be used as the topcoat of architectural membrane structures, tent fabrics, and roof materials. Continues modification of PVDF membrane with super hydrophobic property will make it as the coating layer surface (Zhenya Gu, 2009). In addition, PVDF membrane also has application in Chemical Process Industry. Hydrophobic PVDF membranes have high binding affinity for nucleic acid and proteins. It can be used for application such as Western, Southern, Northern and dot blots (Yu, 2010). PVDF membranes are having ability to apply in off shore oil industry (multilayer structures for oil and gas, high purity fluid transportation, plumbing and lithium batteries.

According to Herlace (2000), the two main application of PVDF are N-Termina; Sequencing and Immuno blotting, both of which benefit from the qualities of PVDF. Furthermore, Bio-Rad offers to grades for PVDF, Immun-Blot PVDF for western bloting and Sequi-Blot PVDF for protein sequencing.

2.4 Concept of Hydrophobicity

2.4.1 Definition of Hydrophobicity

Hydrophobicity is one of property of membrane which will influence the separation process. Generally, hydrophobicity or hydrophobic is call “water fearing” when the property of it is do not dissolve easily in water context and are usually non-polar. According to Kuo et, al. (2008), the porous membrane has the property of hydrophobic which can prevent the aqueous solution penetration into the membrane pores. Therefore, the larger pores of the membrane and higher hydrophobicity with high permeate flux under a high rejection will be expected. Hydrophobic material is function to prevent the processed liquids from wicking and wetting into the membrane pores and forming direct bridges between the two streams of water (Dumee et, at., 2011).

2.4.2 Process Involve in Hydrophobicity

Hydrophobic is described as the segregation and having repulsion between water and non-polar substances. It observed to be having tendency of non-polar substances to aggregate in aqueous solution and not include in water molecule. According to Temell (2011), hydrophilic properties give effect to the monomers used during polymerization provide accommodation processes involving non- aqueous solvent. So, it is important to know the changes made during the polymerization reaction towards the formation of relatively hydrophobic polyamide membranes. The hydrophobicity of a surface membrane can be improve by apply the chemical modification which will lower the surface energy or by the introduction of proper surface roughness (Kuo, 2008). Furthermore, the techniques to fabricate the hydrophobic porous membrane are stretching; non-solvent induced phase separation (NIPS) and also thermally induced phase separation (TIPS).

2.4.3 Hydrophobicity of PVDF Membrane

The membrane of PVDF is highly hydrophobic. According to Herculer (2000), the hydrophobicity of PVDF membrane makes it an ideal support for binding proteins in electro phoretic and dot application. The hydrophobicity of the PVDF membrane makes it impossible to wet the membrane with aqueous solutions. Methanol or an alternative organic solvent is required to pre-wet the membrane prior to equilibration in transfer buffer. The membrane prevents the penetration of the aqueous solution into its dry pores by its hydrophobic nature until the liquid entry of the water is exceeded.

According to Yan (2005), the hydrophilicity of the membrane and its porous structure play important roles in membrane-separation processes. A suitable porous membrane must have high permeability, good hydrophilicity, and excellent chemical resistance to the feed streams. In order to obtain high permeability, membranes should have high surface porosity and good pore structure. An asymmetric membrane is ideal for this purpose. Polyvinylidene fluoride (PVDF) is one material that can form such asymmetric membranes. This polymer is thermally stable and resistant to corrosion by most chemicals and organic compounds. PVDF-based membranes show outstanding anti-oxidation activities, strong thermal and hydrolytic stabilities, and good mechanical and film-forming properties. PVDF membranes can thus be used in many ultrafiltration processes through various modifications.

2.5 Concept of Flue Gas

2.5.1 Definition of Flue Gas

Flue gas is the gas exiting to the atmosphere via a flue, which is a pipe or channel for conveying exhaust gases from a fireplace, oven, furnace, boiler or steam generator. Quite often, the flue gas refers to the combustion exhaust gas produced at power plants. Its composition depends on what is being burned, but it will usually consist of mostly nitrogen (typically more than two-thirds) derived from the combustion air, carbon dioxide (CO_2), and water vapor as well as excess oxygen (also derived from the combustion air).

2.5.2 Properties Condition of Flue Gas

According to Herzog (1999), the major component of flue gas is nitrogen, which enters originally with the air feed. If there were no nitrogen, CO2 capture from flue gas would greatly simplify. This is the thinking behind the oxygen approach, where instead of air, the power plant is fed oxygen produced by an air separation plant. However, combustion with oxygen yields temperatures too large for today's materials, so some flue gas must be recycled to moderate the temperature. Applying this process is easier for steam turbine plants than gas turbine plants. In the former, relatively straightforward boiler modifications are required.

2.5.3 Relation of Flue Gas and Gas Separation Process of CO_2/N_2

Ambient air contains about 79 volume percent gaseous nitrogen (N_2), which is essentially non-combustible, the largest part of the flue gas from most fossil-fuel combustion is un combusted nitrogen. The next largest part of the flue gas is carbon dioxide (CO_2), which can be as much as 10−25 volume percent or more of the flue gas. This is closely followed in volume by water vapor (H_2O) created by the combustion of the hydrogen in the fuel with atmospheric oxygen. Much of the 'smoke' seen pouring from flue gas stacks is this water vapor forming a cloud as it contacts cool air.

2.5.4 The Effect of Gas Separation CO_2/N_2

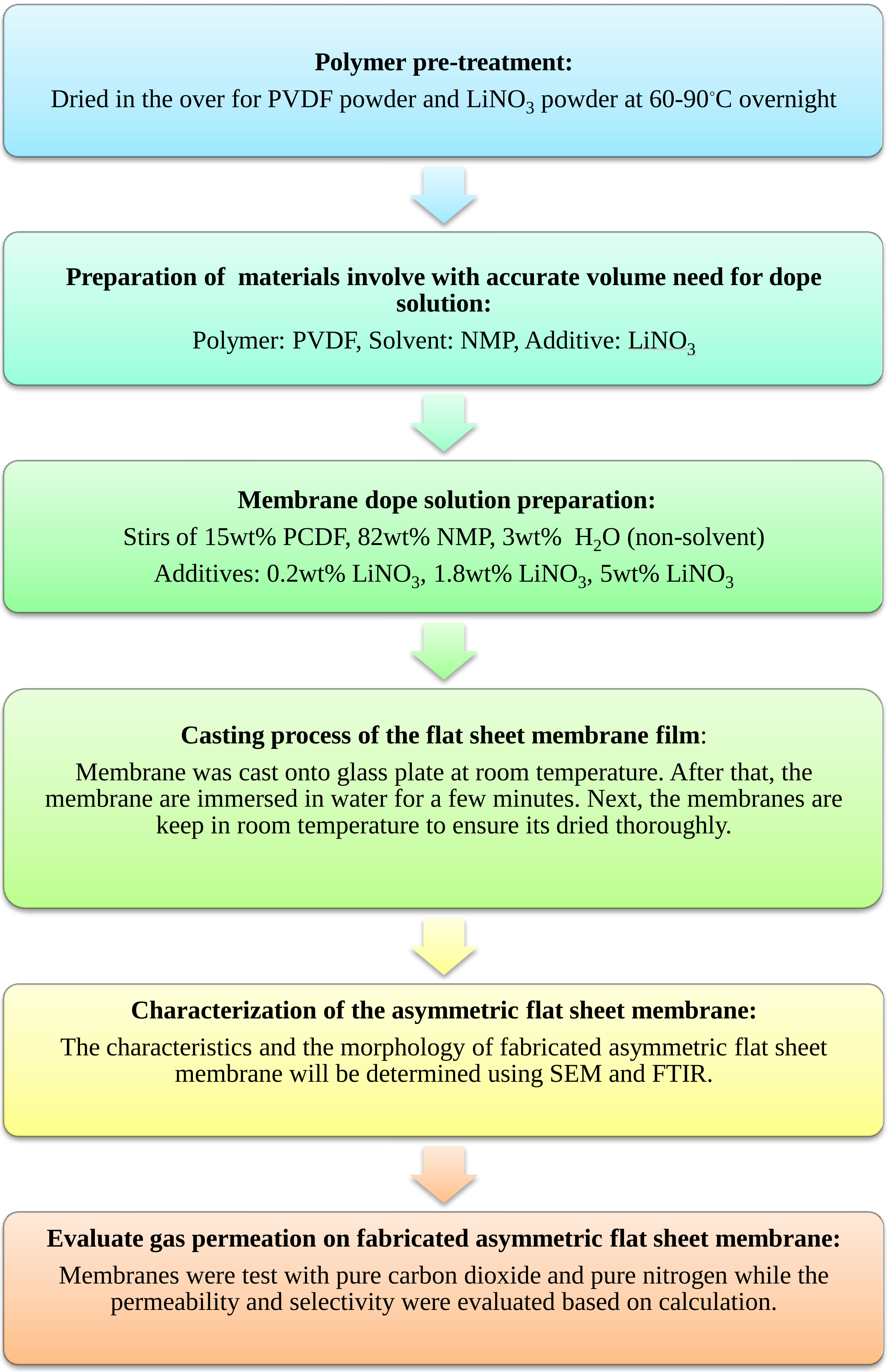
The emissions from this power plant in New Mexico contained excessive amounts of sulfur dioxide before flue-gas desulfurization was installed. According to Bae (2009), greenhouse gas concentrations in the atmosphere are a strong motivation to reduce CO2 emissions from industrial processes. Burning of fossil fuel to generate electricity is a major source of CO2 in the atmosphere, but the capture and sequestration of CO2 from flue gas emissions of power plants is a daunting challenge. Flue gases consist of nitrogen (typically more than two-thirds), CO2, water vapor, oxygen, and minor components such as carbon monoxide, nitrogen oxides, and sulfur oxides. Several technologies have been considered for CO2 separation from nitrogen-rich streams, including absorption, membranes, and adsorption separations.

CHAPTER III

METHODOLOGY

3.1 Chapter Overview

This chapter will discuss about the materials used to fabricate the asymmetric flat sheet membrane. Besides that, in this chapter will be cover the experimental methods together with the experimental procedure to prepare PVDF membrane and to test the new fabrication membrane. The main procedures are preparation of material involves, PVDF dope solution preparation, casting process of the dope solution to form an asymmetric flat sheet membrane film, post treatment for test defect and membrane characteristic test. There are three tests which used to study the characteristic of new membrane and will be discuss later. The overview of methodology approached through this study as figure 3.1.



Polymer pre-treatment:

Dried in the over for PVDF powder and $LiNO_3$ powder at 60-90°C overnight

Preparation of materials involve with accurate volume need for dope solution:

Polymer: PVDF, Solvent: NMP, Additive: $LiNO_3$

Membrane dope solution preparation:

Stirs of 15wt% PCDF, 82wt% NMP, 3wt% H_2O (non-solvent)

Additives: 0.2wt% $LiNO_3$, 1.8wt% $LiNO_3$, 5wt% $LiNO_3$

Casting process of the flat sheet membrane film:

Membrane was cast onto glass plate at room temperature. After that, the membrane are immersed in water for a few minutes. Next, the membranes are keep in room temperature to ensure its dried thoroughly.

Characterization of the asymmetric flat sheet membrane:

The characteristics and the morphology of fabricated asymmetric flat sheet membrane will be determined using SEM and FTIR.

Evaluate gas permeation on fabricated asymmetric flat sheet membrane:

Membranes were test with pure carbon dioxide and pure nitrogen while the permeability and selectivity were evaluated based on calculation.

Figure 3.1: Research design flowchart

3.2 Materials Selection

The selection of suitable polymer, solvent and additive is an important in order to make sure all objectives can be achieved. Therefore, this sub-chapter will be discuss about the selection of the materials used and any benefit will be get while using that materials in this research.

3.2.1 Polymer selection

3.2.1.1 Polyvinylidene fluoride (PVDF)

The polymer used in this study was PVDF purchased from Sigma Aldrich (M) Sdn Bhd. PVDF that we used is without any modification. The name of polymer that we select to be used in this study is Polyvinylidene fluoride (PVDF). PVDF is a fluoropolymers family. PVDF is a homopolymer of Vinylidene fluoride (CF_2 = CH_2). Moreover, the functional groups of PVDF polymer are alkenes group (C-H) and alkyl halides group (C-F). Compared to other fluoropolymers, PVDF polymer is an easier melt process because it has low melting point of around $177^{o}C$. Figure 3.2 show the structure of PVDF polymer. Table 3.1 shows the properties of PVDF polymer.

The featured of PVDF polymer are excellent mechanical strength, excellent abrasion resistance, excellent aging resistance, resistance to UV and nuclear radiation, good permeation resistance and smooth, anti-fouling surfaces. Then, the applications of PVDF polymer are fluid handling, fire-safe componentry, chemical process/storage and semiconductor equipment.

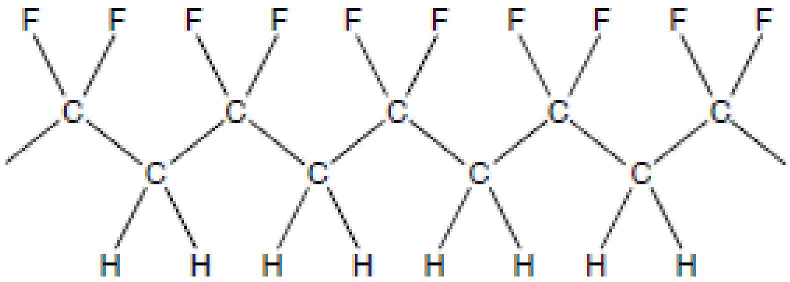


Figure 3.2: Poly (vinylidene fluoride) structure (Kurt A.W., 2006)

Table 3.1: The Properties of PVDF polymer

Physical Properties	**Descriptions**
Density	1.78 g/cc
Water Absorption	0.03 %
Moisture Absorption at Equilibrium	0.015%
Melt Flow	1.1 g/10 min
Mechanical Properties	**Descriptions**
Tensile Strength, Yield	50 MPa
Elongation at Yield	7%
Tensile Modulus	1.7 GPA
Electrical Properties	**Descriptions**
Electrical Resistivity	2e+014 ohm-cm
Surface Resistance	Min 1e+015 ohm

Dielectric Constant	7.7
Dielectric Strength	21 kV/mm
Dissipation Factor	0.231
Comparative Tracking Index	600 V
Thermal Properties	**Descriptions**
Melting Point	168 ^{o}C
Maximum Service Temperature, Air	135 ^{o}C
Glass Temperature	-40 ^{o}C
Flammability	V-0
Oxygen Index	43%

3.2.2 Solvent selection

3.2.2.1 N-methyl-2-pyrrolidone (NMP)

NMP is chosen as solvent in fabrication of flat sheet membrane. Anhydrous N-methyl-pyrrolidene (NMP) supplied from Sigma Aldrich (M) Sdn Bhd was used as the solvent without any further purification. NMP is a good solvent with broad of solubility for resins and high thermal stability and high chemical. NMP is completely soluble with water at any temperature and also soluble with organic solvents. Moreover, NMP is generally colorless to slightly yellow liquid, with a faint amine odor. NMP is contains 5-member-ring compound containing nitrogen. Figure 3.2 show the structure of NMP solvent. Table 3.3 shows the properties of NMP solvent.

The characteristics of NMP are it has a flash point compared to similar solvents, thermally and chemically stable and not corrosive, mixes with water in all proportions, the boiling point is high, handling is easy and the freezing point is low and it is highly polar and miscible with most organic solvents (alcohol, ethers, ketones, aromatic hydrocarbons, chlorinated hydrocarbons, etc). Inorganic and organic substances are highly soluble in it.

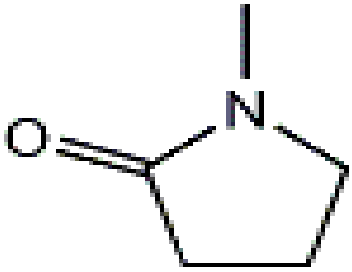


Figure 3.3: The structure of NMP solvent

Table 3.2: The properties of NMP solvent

Physical Properties	**Descriptions**
Form	Liquid
Colour	Colourless
Odour	Amine-like
Melting Point	-24^{O}C
Boiling Point	202 ^{O}C
Flash Point	86 ^{O}C
Ignition Temperature	270 ^{O}C
Danger of Explosion	Product does not present an explosion hazard
Explosion Limits (Lower)	1.3 Vol%

Explosion Limits (Upper)	9.5 Vol%
Vapour Pressure	At 20 ^{O}C: 0.38 hPa
Density	At 20 ^{O}C: 1.03 g/cm^3
Viscosity Dynamic	At 25 ^{O}C: 1.65 mPas
Solubility in/miscibility with water	Fully miscible

3.2.3 Non-solvent and Coagulation medium

3.2.3.1 Water

For this study, water is chosen and will be used in dope solution for fabrication of flat sheet membrane and also used as coagulation medium. Water can be acts as a dissolving agent or that is capable of dissolving another substance. The chemical formula of water is H_2O (H-OH). The water molecule is contains one oxygen and two hydrogen atoms which connected by covalent bonds. Water can be in solid state (ice), gases state (water vapor or steam) and liquid crystal state near hydrophilic surfaces. Water is can be transparent in the visible of electromagnetic spectrum. Furthermore, water is a good polar solvent and usually refers to the universal solvent. Table 3.3 show the properties of water

Table 3.3: The properties of water

Physical Properties	Descriptions
Molar Mass	18.015288 g/mol
Appearance	White solid or almost colorless, transparent
Density	1000 kg/m^3, liquid 917 kg/m^3, solid
Melting Point	0 ^oC
Boiling Point	100 ^oC
Viscosity	at 20 ^oC

3.3 Gas for permeation test

For gas permeation test in this research, pure gas which used is carbon dioxide and nitrogen. After doing the fabrication of flat sheet membrane, CO_2/N_2 gas separation test will be done. Table 3.4 will be showing the properties of penetrants.

Table 3.4: The properties of penetrants

	Carbon Dioxide	**Nitrogen**
Molecular Formula	CO_2	N_2
Molar Mass	44.01 g/mol	16.043 g/mol
Kinetic Diameter		
Viscosity		
Appearance/ Odor	Colorless /.Odorless gas	Colorless gas, liquid or solid
Melting Point	-78^OC	-210 ^OC
Boiling Point	-57 ^OC	-195.79 ^OC

3.4 Additive

3.4.1 Lithium Nitrate

LiCl is purchase from Sigma Aldrich (M) Sdn Bhd was an additive. LiCl is chosen as non-solvent additive in order used to study the effect of additive elements in PVDF dope solution. Next, lithium nitrate is an inorganic compound with the formula $LiNO_3$. The uses of $LiNO_3$ are corrosion inhibitor, mold releasing agent, chemical reagent, pharmaceutical catalyst, concrete admixture, glass and ceramic additive. $LiNO_3$ is made by reacting lithium carbonate with nitric acid. The functional group for lithium nitrate is nitro group (N = O) and alkyl halide group (C-Li). Figure 3.4 show the structure of lithium nitrate. Table 3.5 shows the properties of lithium nitrate.

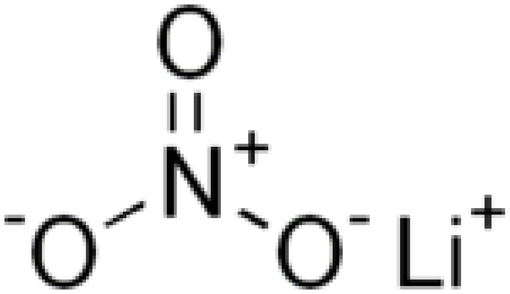


Figure 3.4: The structure of lithium nitrate

3.5: The properties of lithium nitrate

Physical Properties	Descriptions
Molecular Formula	$LiNO_3$
Molar Mass	68.946 g/mol
Appearance	White to light yellow solid
Density	2.38 g/cm^3
Melting Point	2.55^{o}C
Boiling Point	873 ^{o}C

3.5 Dope Solution Preparation

To do the dope solution for asymmetric flat sheet membrane, the main materials must to prepare first which are polymers, solvent, additive and non-solvent. First, the polymer and additive must be dried in a vacuum to eliminate any moisture content during storage of chemical. The condition of vacuum is at 80-90^{o}C for at least 24 hours (overnight). In airtight glass bottle, a specified quantity of polymer was taken and then a known quantity of the solvent was added gradually. Then, water as non-solvent also added in the solution. The polymer used in this study is PVDF and the solvent used in this study is NMP. The ratio concentration of reagents is PVDF/NMP/H_2O (15wt%/ 82wt %/ 3wt %). The different quantities of additives which are $LiNO_3$ were added to the solution. The quantities of additives are 0.2 wt%, 1.8 wt% and 5 wt%. The solution was kept agitated for several hours for complete dissolution. Calculated quantities of additives were subsequently added and kept for deairation. To dissolution of PVDF/NMP with $LiNO_3$, the solution was stirred continuously at temperature around 60^{o}C for 4 hours. The mechanical stirred used was set at 200-350 rpm. The stirring process is done to make sure that the polymer, solvent, non-solvent and additive can mix well in order to form homogeneous solution. The 1000ml beaker as replacement of round bottom solution vessel was used to prepare the solution. Moreover, the thermometer is used to measure the temperature during stirring process. The processing temperature should be controlled by the heater so that the temperature does not exceed the boiling point of the solvent. In this study, the dope solution was prepared within a range of temperature between 60^{o}C to 80^{o}C. The homogeneous polymer solution was kept stagnant to remove bubbles. The gas bubble formed from the mixing process is removed by placing the Scott bottle contained dope solution into the ultrasonic water bath for 5 to 6 hours respectively. The dope solution is now ready to go through membrane casting process. The same steps are repeated to prepare the dope solution by using different percentage of additive. Figure 3.5 show the apparatus setup for dope solution preparation. The overall process of the dope solution preparation method will show as figure 3.6.

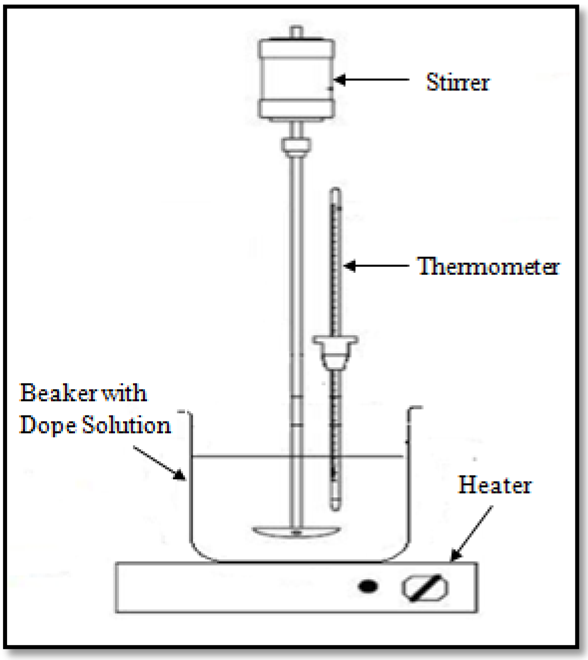


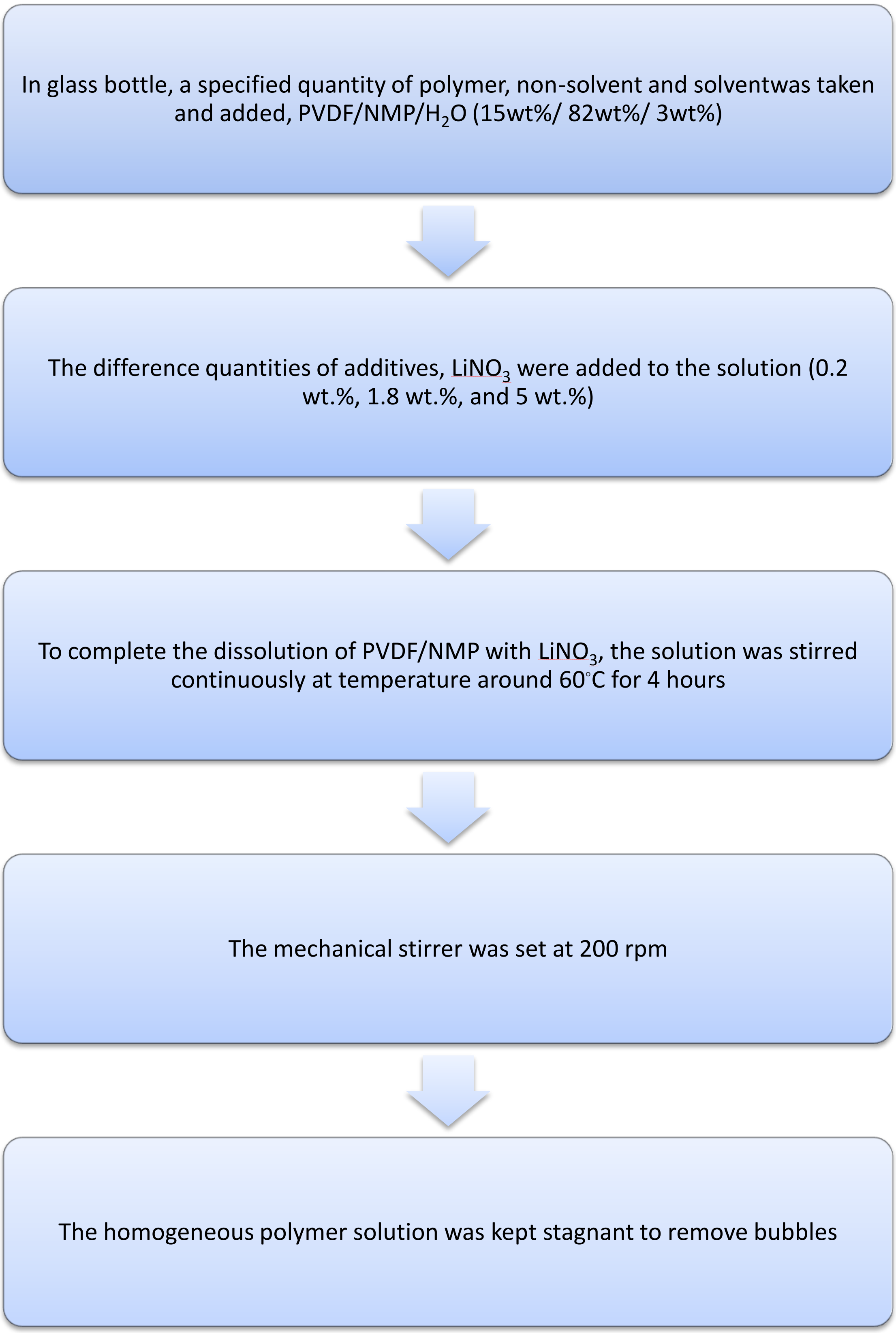
Figure 3.5: The apparatus setup for dope solution preparation (Cheer, 2002)

Figure 3.5 show the apparatus set up for dope solution preparation. The dope solution preparation is done in a fume hood chamber because to avoid from the dope solution contaminate with other substance/chemical during the experiment was carried out. Besides, fume hood is used to prevent from the exposure to hazardous vapors form during stirring process.

3.6 Casting Process of the Dope Solution

The polymer solution was cast on a glass plate with the thickness of 300 μm by a Gardner knife. The thickness of the membranes was control by varying the thickness of adhesive tapes at the sides of the glass plate. The glass plate was kept in an environment of controlled temperature and humidity during membrane casting. PVDF membranes were prepared according to dry/ wet phase separation process.

The casting process is done at room temperature (30^{o}C). A small amount of dope solution was poured onto a glass plate with casting rod gap setting of 0.4 μm. To remove the membrane film from the glass plate, the cast membrane was immersed into water to initiate delamination and slightly peel the membrane film from the glass plate. No deliberate solvent evaporation period as allowed. After that the membrane is transferred and immersed into the coagulation medium which is water. Then, the membranes were peeled off and further dried in the air for 1-2 days. The overall casting process will be show in figure 3.7.



In glass bottle, a specified quantity of polymer, non-solvent and solventwas taken and added, PVDF/NMP/H_2O (15wt%/ 82wt%/ 3wt%)

The difference quantities of additives, $LiNO_3$ were added to the solution (0.2 wt.%, 1.8 wt.%, and 5 wt.%)

To complete the dissolution of PVDF/NMP with $LiNO_3$, the solution was stirred continuously at temperature around 60°C for 4 hours

The mechanical stirrer was set at 200 rpm

The homogeneous polymer solution was kept stagnant to remove bubbles

Figure 3.6: The dope solution preparation method

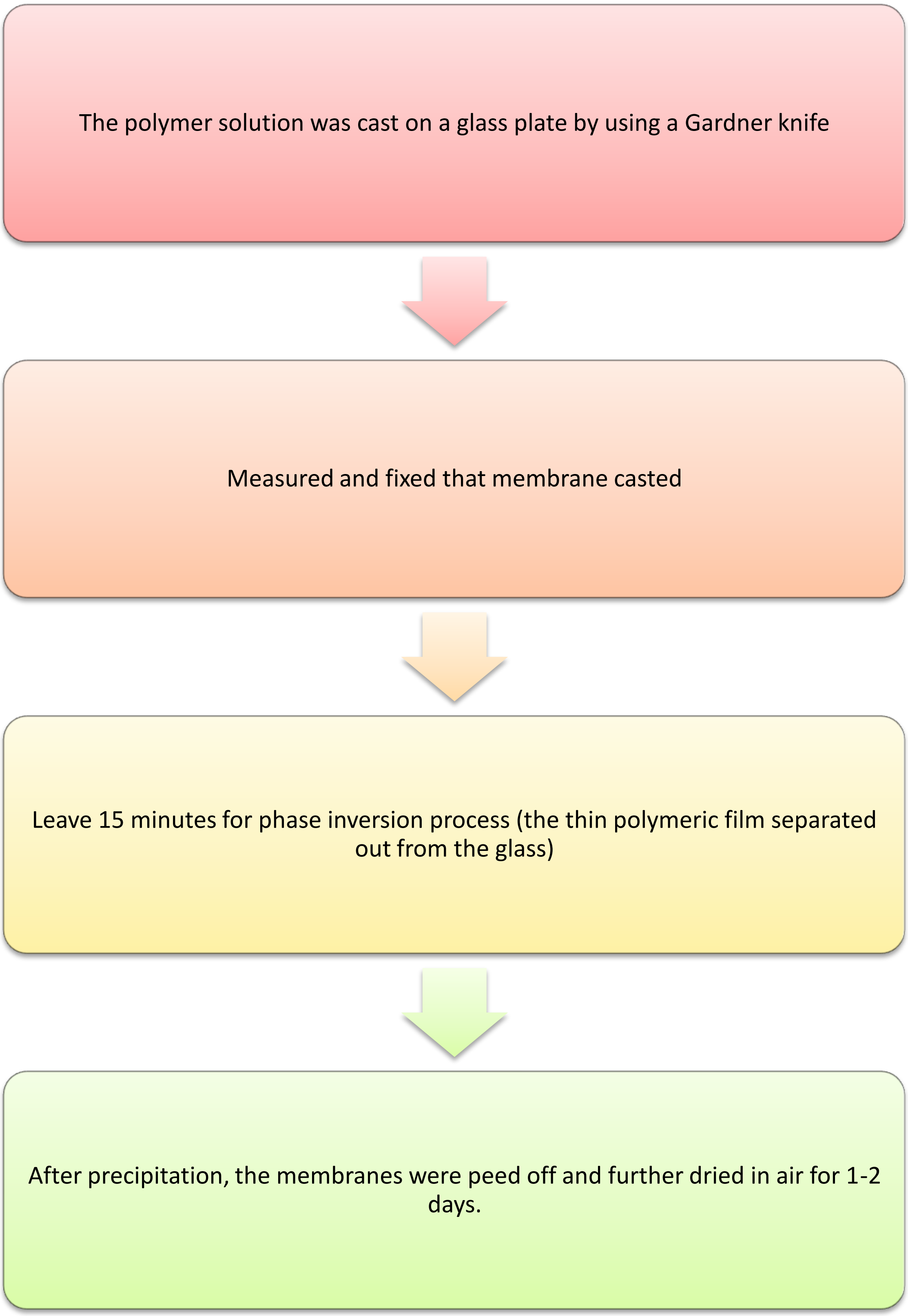


Figure 3.7: **Casting Process of the polymer solution**

3.7 Membrane Characterization

The prepared membrane is characterized using two methods which are by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Radiation (FTIR). There are several parameters that will be evaluated from this study which were: morphological studies and effect of concentration of polymer.

3.7.1 Scanning Electron Microscopy (SEM)

The Scanning electron microscopy is a scientific instrument that uses a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield topography, morphology, composition and crystallographic information. Electron Microscopes (EMs) function exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition. The steps of working scanning electron microscopy are:

i. A stream of electrons is formed (by the Electron Source) and accelerated toward the specimen using a positive electrical potential.
ii. This stream is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam.
iii. This beam is focused onto the sample using a magnetic lens.
iv. Interactions occur inside the irradiated sample, affecting the electron beam.

The SEM was used to produce image of high resolution which is means that closely spaced features examined at high magnification. The SEM developed by Professor Dr. Charles Oatlev in the 1950s. Hictachi High-Technologies is form in 2001. The current model of Hitachi High-Technologies product are S-3700N, an analytical style SEM ideal for studying large, heavy and tall samples, S-3400N, a user-friendly, more compact model that utilizes new technology in electron optics and SU1510, a compact, high performance SEM that can handle large samples and provides high-resolution imaging. The example images of instruments SEM were shown in figure 3.8 and 3.9.

Figure 3.8: Image of instrument SEM

Figure 3.9: Image of instrument SEM

3.7.2 Fourier Transforms Infrared Radiation (FTIR)

FTIR is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular finger prints of the sample. Like a finger print no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FTIR is a qualitative analysis that detects the chemical bonds, molecular structure and functional groups in the sample by producing an infrared absorption spectrum. The images of instrument FTIR are show in figure 3.10 and 3.11.

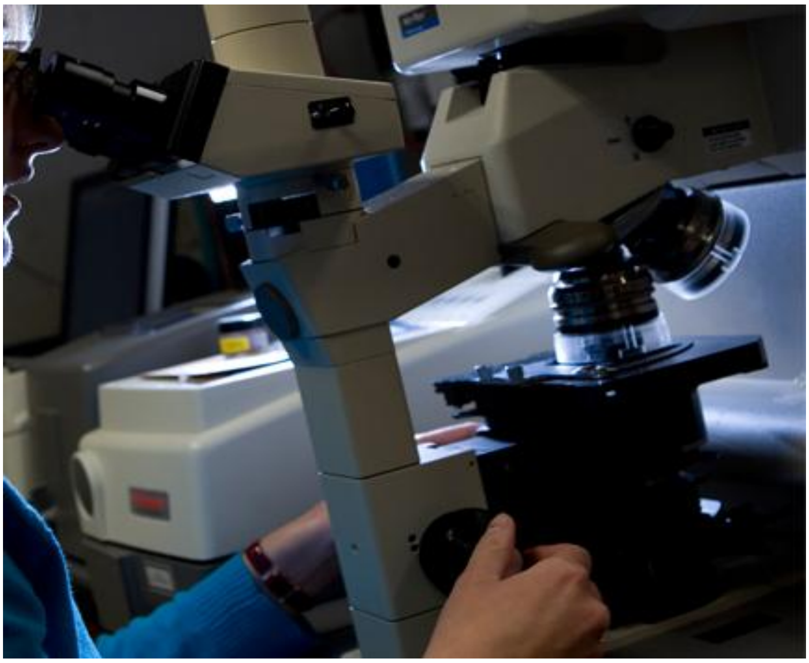


Figure 3.10: Image of instrument FTIR

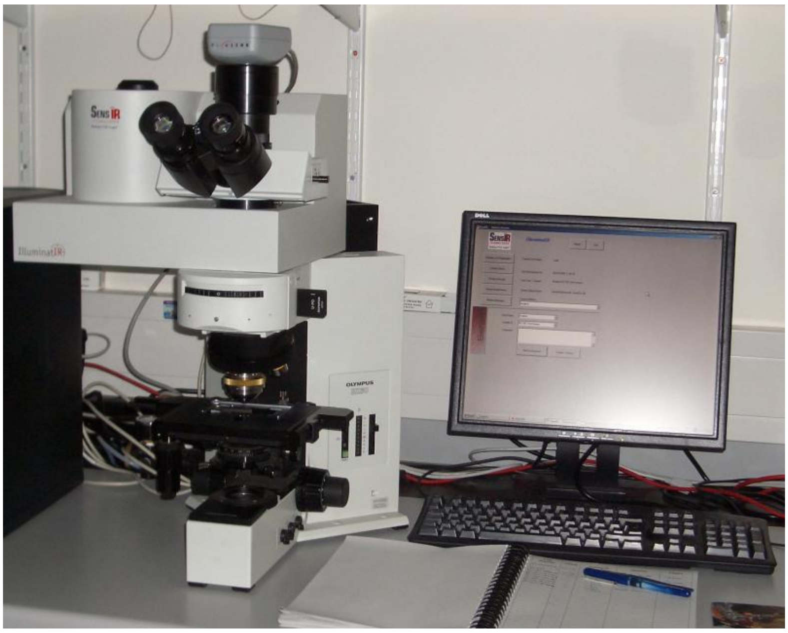


Figure 3.11: Image instrument of FTIR

3.8 Membrane Gas Permeation Test

The asymmetric flat sheet membrane is test with pure gas permeation test. The pure gases used for this test are carbon dioxide and nitrogen. Gas permeation test is done to study the separation gas ability of a fabrication membrane. Firstly, the membrane will be cut into a small circle with diameter 48cm. The size of circle membrane must to suite with the permeate core in order to avoid any leakage of pure gas. Then, the circle membrane will be pleated and folded around the permeate core. The separation of pure gas across fabricated membrane will be tested at pressure 0.5 bar, 1.0 bar and 1.5 bar. When the permeability unit already setup, the pure gas will be turn on and flowing through the membrane fitted in it. The volume different of the soap water by each membrane and the time of the first bubble formed was taken. Figure 3.12 shows the gas permeation test apparatus and Figure 3.13 shows the cross-sectional view of assembled permeation cell and gas flow direction.

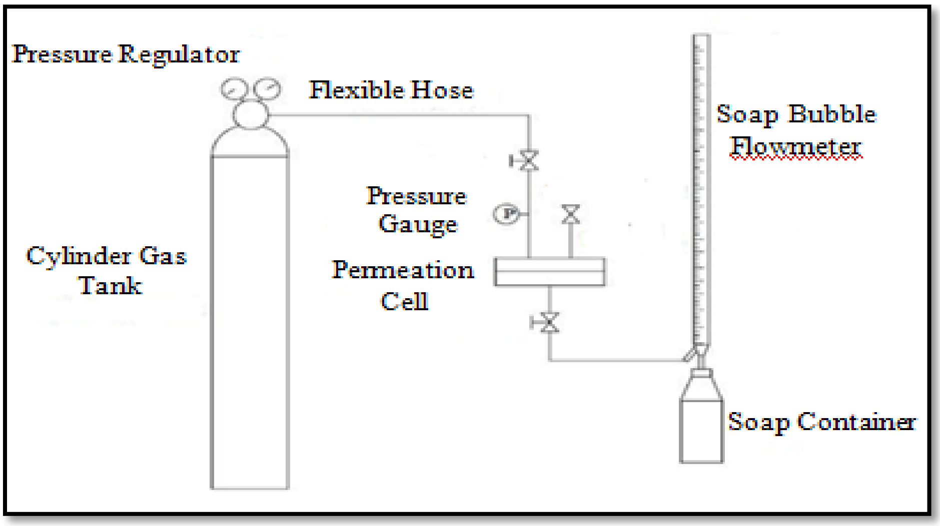


Figure 3.12: The gas permeation test apparatus (Cheer, 2002)

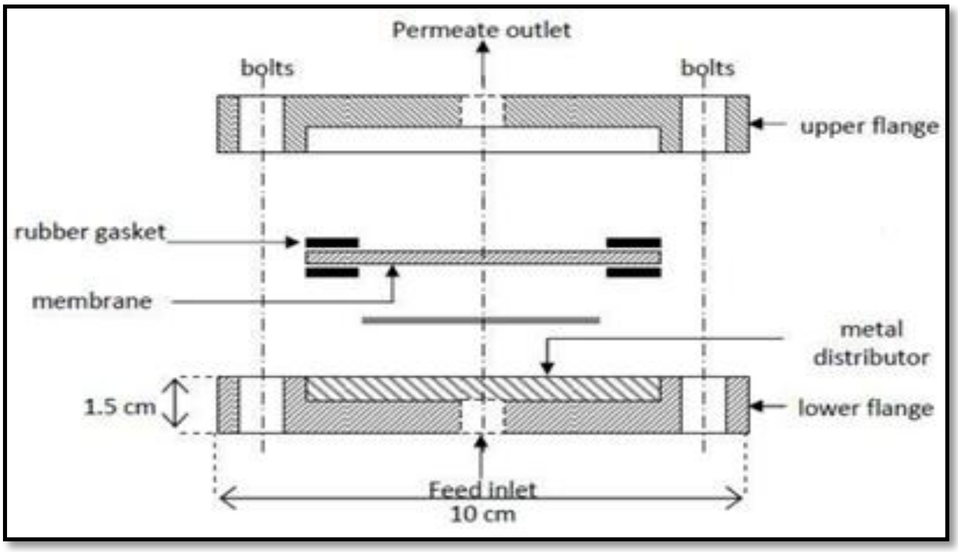


Figure 3.13: The cross-sectional view of assembled permeation cell and gas flow direction (Cheer, 2002)

The permeability is defined as the transport flux of material through the membrane per unit driving force per unit membrane thickness. Its value must be experimentally determined. In general, permeability of a polymer for a gas mixture increases with decreasing size and increasing solubility (or condensability) of the gas.

The membrane selectivity is used to compare the separating capacity of a membrane for 2 (or more) species. The membrane selectivity, a (also known as the perm-selectivity) for one component (A) over another component (B) is given by the ratio of their permeability. Selectivity obtained from ratio of pure gas permeability's is called the ideal membrane selectivity or the ideal perm-selectivity. This is an intrinsic property of the membrane material.

The gas permeability (P) was calculated using this equation:

$$p = \frac{VI}{At\,\Delta p} \text{ [cm}^3 \text{ (STP) cm/(cm}^3 \text{ s cm Hg)]} \qquad (3.1)$$

The permeance (P/I) for membrane was calculated using this equation:

$$\frac{P}{I} = \frac{V}{At\Delta p} \text{ [(cm}^3 \text{ (STP)/(cm}^2 \text{ s Hg]}$$

I = the thickness of the membrane (cm)

A = the effectiveness membrane area in cm^3

V = the volume (cm^3) displaced in time t(s)

Δp = the Transmembrane pressure (cm Hg)

Selectivity, $\alpha = P_i / P_j$ (3.2)

Where: P_i = Permeability of CO_2 gas component

P_j = Permeability of N_2 gas component

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Effect of the additives on the membrane morphology

The SEM photographs of cross section of 15wt% PVDF fabrication membrane, 0.2wt% $LiNO_3$ membrane, 1.8wt% $LiNO_3$ membrane and 5wt% $LiNO_3$ membrane specimens are taken under identical magnification. Figure 4.1, 4.2 and 4.3 shows the morphology of the flat sheet asymmetric membrane containing $LiNO_3$ as the additive with different percentage and the morphology of the flat sheet asymmetric made from the dope containing without additive is presented in figure 4.4. The comparisons of cross section image for with additive and without additive, SEM image clearly show the asymmetric nature of these membranes. Referring to discussion on 4.2, 0.2wt% $LiNO_3$ was produce high performance of fabricated asymmetric flat sheet membrane. From this result we can assume that 0.2wt% $LiNO_3$ membrane have a big pore size compare others membrane which can allow the gases to permeate easily through the membrane.

The typical morphology of 0.2wt% $LiNO_3$ membrane is show in figure 4.1(a) and 1(b). Figure 4.1(a) can be observed that the cross section of membrane have a thicker substrate with a finger-like macrovoid structure. In other figure (figure 4.1(b)), the cross section of membrane have finger-like structure and sponge-like structure. Then, for figure 4.2(a) and 4.2(b) are shows that the morphology cross section image of 1.8wt% $LiNO_3$ membrane sample. The SEM photograph of figure 4.2(a) is having finger-like pores. Figure 4.2(b) is showing the cross section of membrane have a less sponge-like structure. Furthermore, the morphology pictures for 5wt% $LiNO_3$ will be seemed in figure 4.3(a) and 4.3(b). For image of figure 4.3(a) and (b) showing a symmetric flat sheet membrane have a finger-like structure but have less sponge-like structure. Therefore, from observation of three different percentage of additive, we can conclude that the increasing percentage of molecular weight $LiNO_3$ will be result the low appearance of finger-like pores and sponge-like structure. But the presence of additive can be altered the inner side and outer side to finger-like structure compare with morphology without additive (Panu S. et. al. (2010). Further discussion for morphology of without additive will be discussed referring to figure 4.4(a) and 4.4(b).

As shown in figure 4.4(a) and (b), there are microscopic observations for SEM analysis of cross section 15% PVDF membrane sample with absence of $LiNO_3$ additive. The morphology images for cross section membrane sample figure 4.4(a) are having larger and longer macrovoids finger-like pores and thicker skin with relatively dense structure. For figure 4.4(b) show the morphology image of membrane is finger-like pores with sponge-like structure. But the membrane is having a thick skin of outer side.

All observations were believed to be associated with the change of the kinetic and thermodynamic properties of the system before and after $LiNO_3$ addition (Li D. et. al., (2004). Lithium nitrate is made by reaction of lithium hydroxide with nitric acid. $LiNO_3$ addition increases the dope's thermodynamic instability in the reaction of water, which makes a rapid phase demixing and resulted in reaction macrovoid formation (Lei S. et.al., 2008).

Furthermore, $LiNO_3$ have strong interactions with the polymer and solvent which was supported by the significant increase in viscosity of $LiNO_3$ added to dope solutions compare without present of additive. The good interactions among the components in a dope solution tend to delay the dope precipitation (the kinetic effect) and partially offset the thermodynamic impact of $LiNO_3$ addition (Atchariyawut s. et. al., 2006). Resulting, the increase of percentage of additives will cause the size of finger-like pores and sponge-like structures were reduced. Moreover, when compare morphology of flat sheet membrane of with additive and without additive, the size of pore of with additive is quite small. Therefore, the additional of additive of 5wt% $LiNO_3$ into the dope solution could form the membrane stronger strain strength than the PVDF commercial membrane.

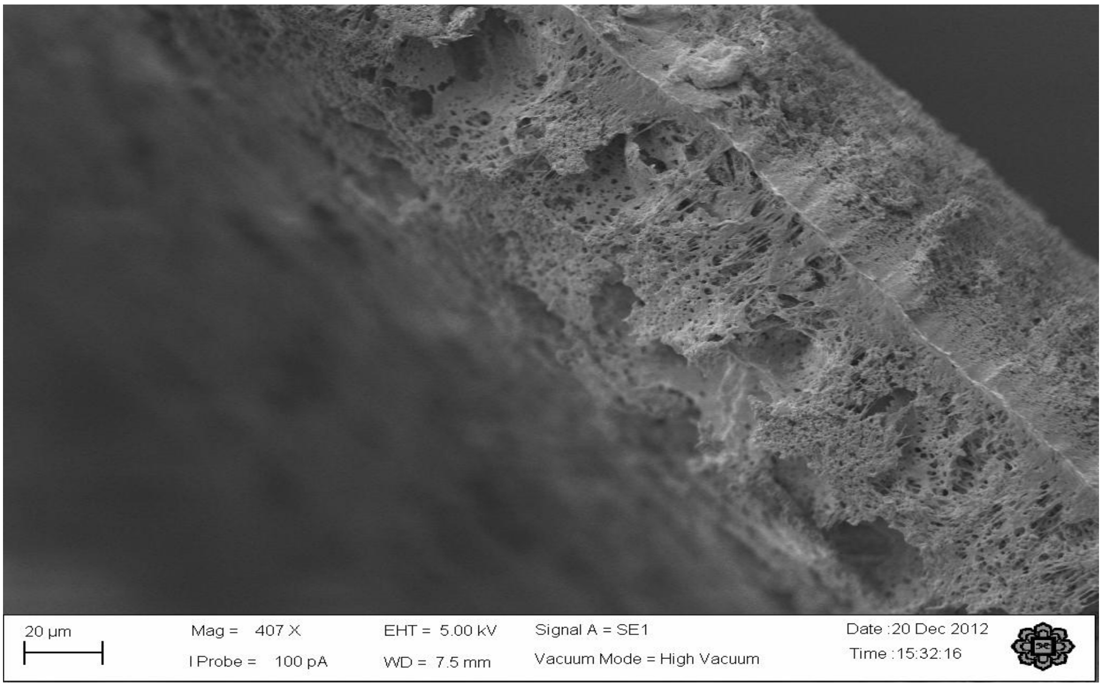


Figure 4.1(a): **Morphology cross section image of 0.2wt% $LiNO_3$ membrane sample**

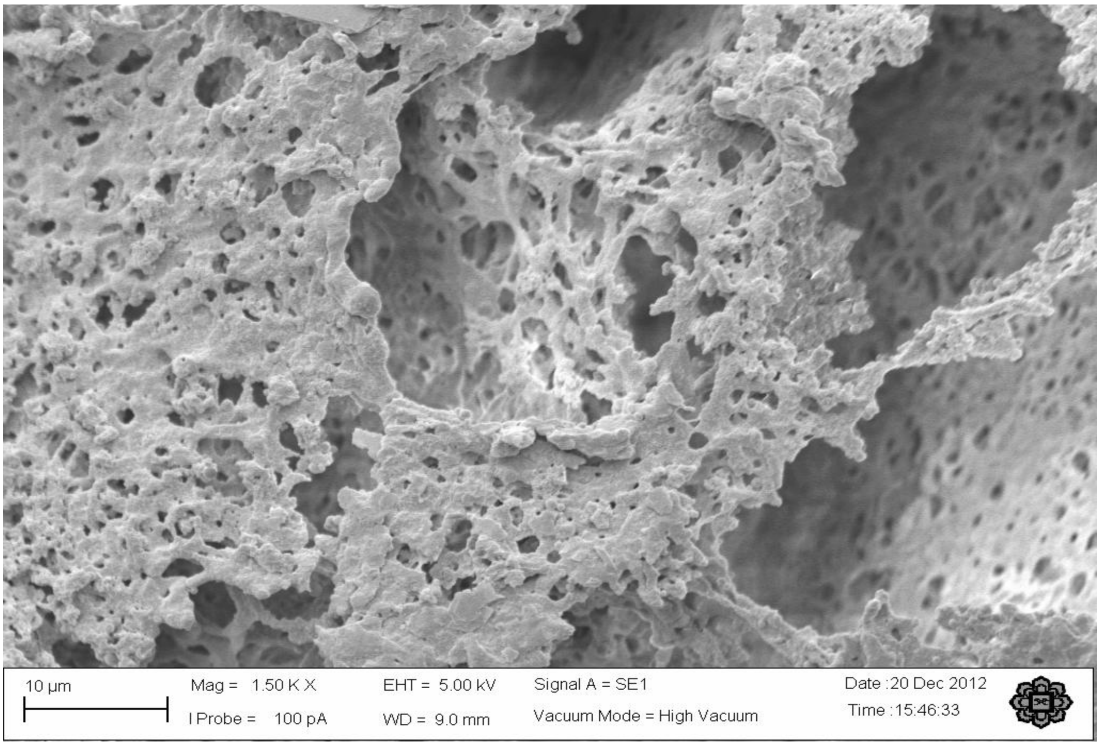


Figure 4.1(b): **Morphology cross section image of 0.2wt% $LiNO_3$ membrane sample**

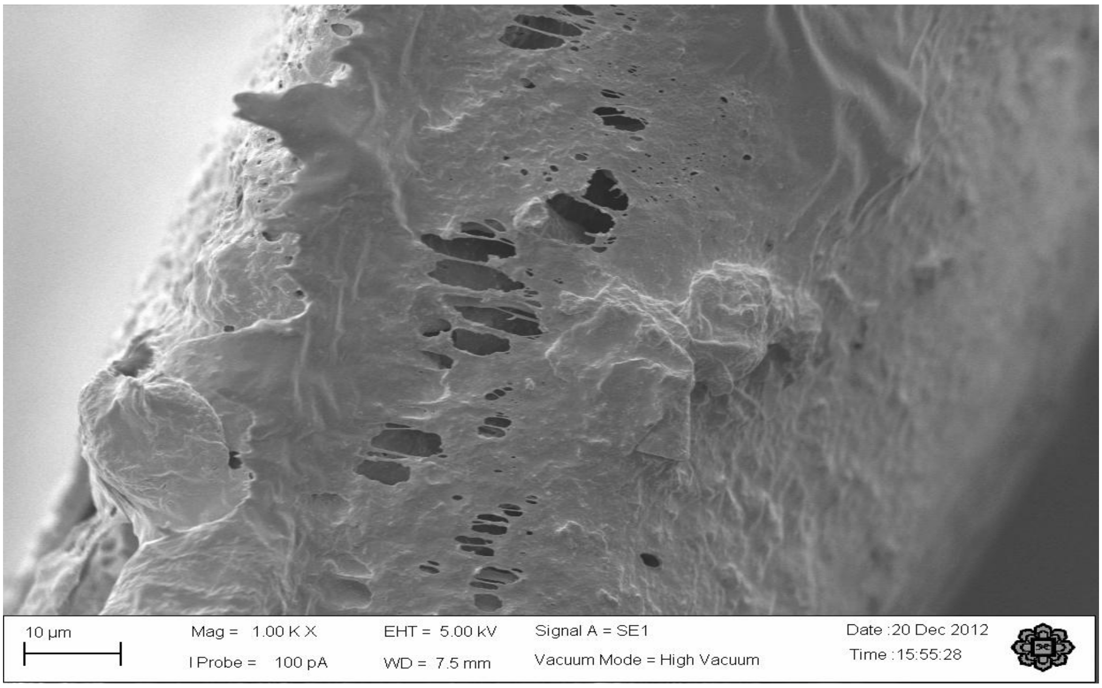


Figure 4.2(a): **Morphology cross section image of 1.8wt% LiNO$_3$ membrane sample**

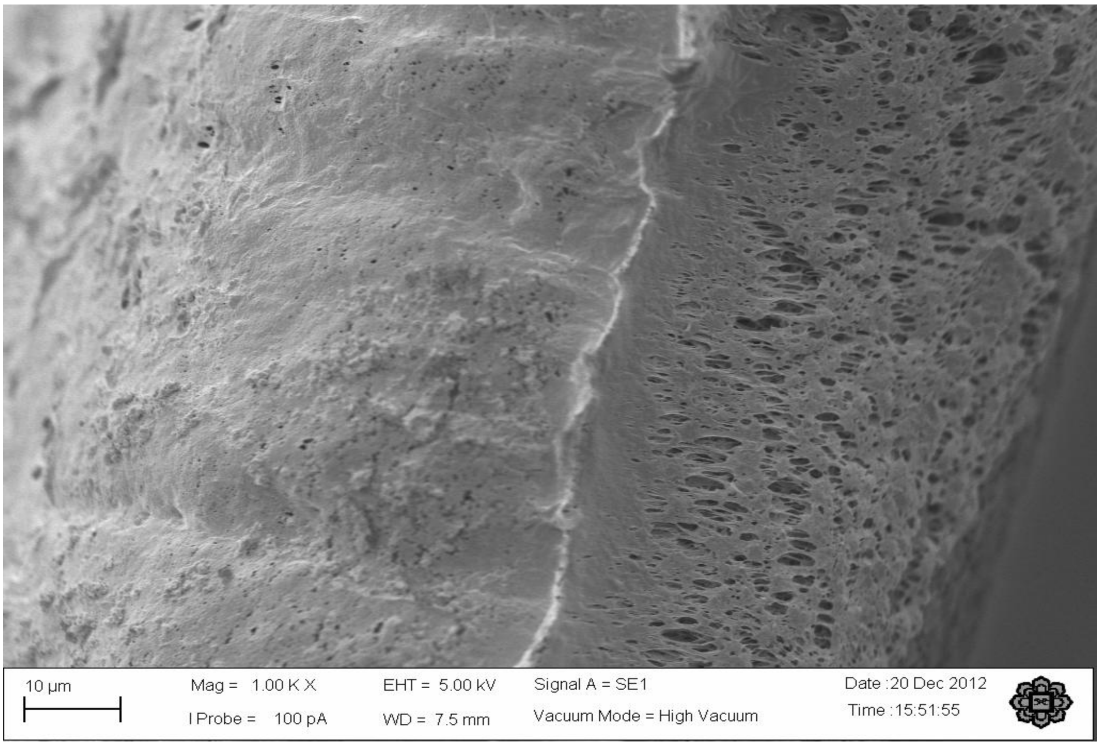


Figure 4.2(b): **Morphology cross section image of 1.8wt% LiNO$_3$ membrane sample**

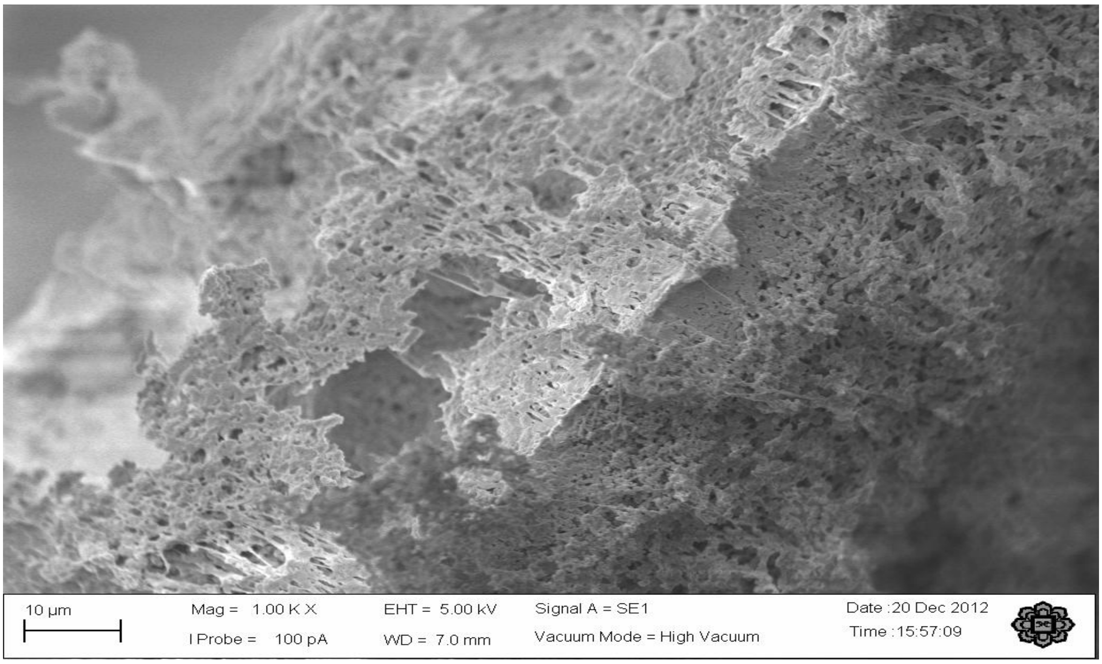


Figure 4.3(a): **Morphology cross section image of 5wt% $LiNO_3$ membrane sample**

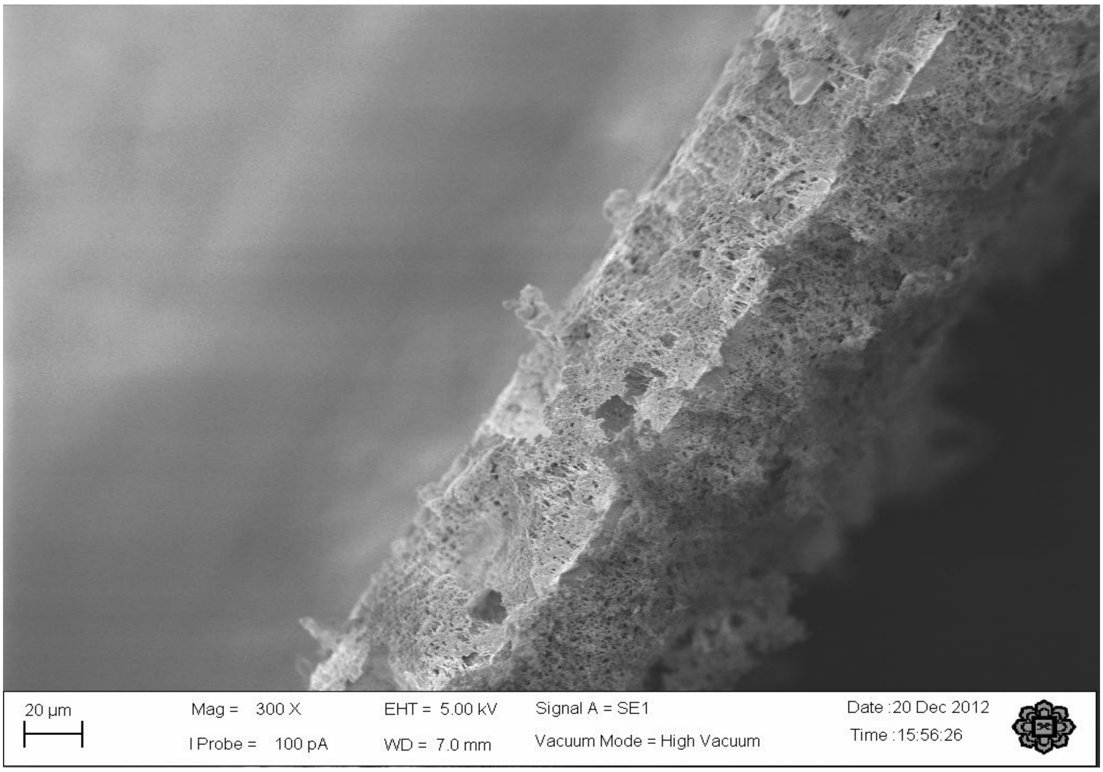


Figure 4.3(b): **Morphology cross section image of 5wt% $LiNO_3$ membrane sample**

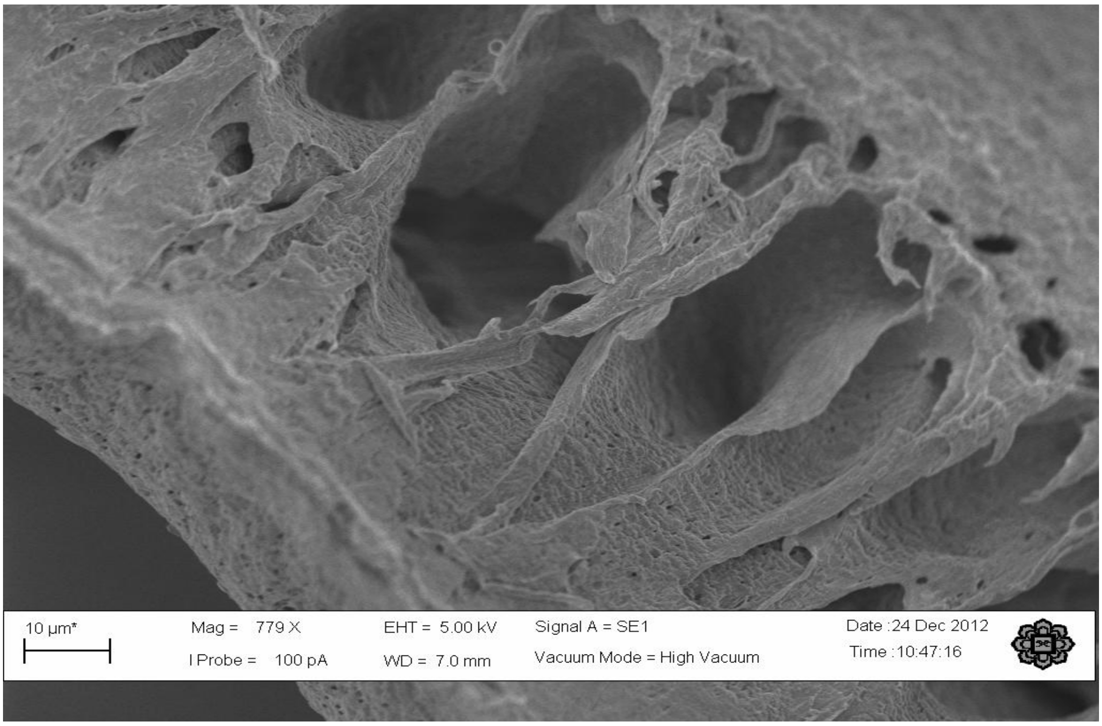


Figure 4.4(a): **Morphology cross section image of 15% PVDF membrane**

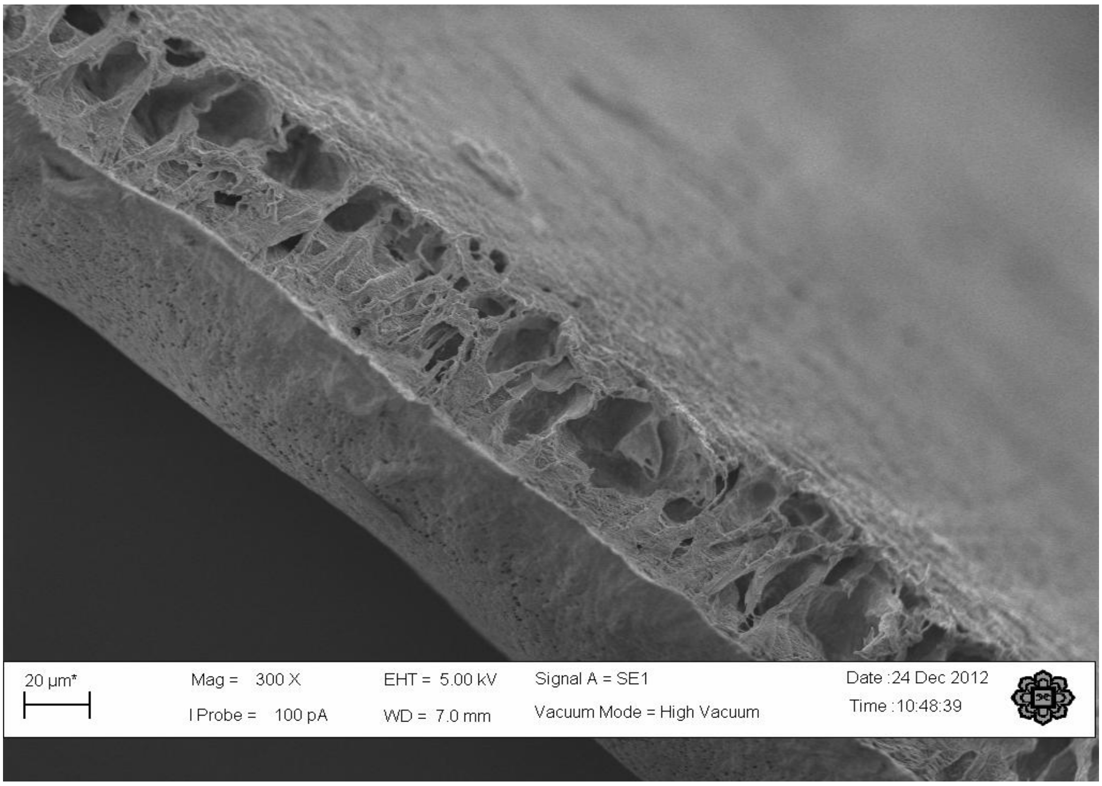


Figure 4.4(b): **Morphology cross section image of 15% PVDF membrane**

4.2 Effect of the Additive on the FTIR Analysis of membrane

FTIR (Fourier transform infrared spectroscopy) is a technique which is used to gain information about the sample. From FTIR we will be identify the unknown materials in fabricated membrane, determine the quality of consistency of the membrane sample and determine the amount of components in a mixture. Therefore, the information about the chemical bonding or molecular structure of materials will be gain after doing FTIR test. Generally, the bonds and group of bonds will be vibrating at characteristic frequencies. The membrane sample is exposed to infrared rays absorbs infrared energy in FTIR machine. This process is at specific frequencies which refer are characteristic to that molecule in the membrane sample. One part of membrane sample will be subjected to a modulated infrared (IR) beam. Next, the membrane's reflectance and transmittance of the infrared rays at different frequencies is translated into an infrared absorption plot. The plot will be consist of reverse peak, absorbance, and wavelength of membrane sample. Figure 4.4 show the FTIR absorbance peak for PVDF/NMP/H_2O membrane sample, Figure 4.5 show the FTIR absorbance peak for 0.2wt% $LiNO_3$ additive in PVDF/NMP/$LiNO_3$ membrane sample, Figure 4.6 show the FTIR absorbance peak for 1.8wt% $LiNO_3$ additive in PVDF/NMP/H_2O membrane sample and Figure 4.7 show the FTIR absorbance peak for 5wt% $LiNO_3$ additive in PVDF/NMP/H_2O membrane sample.

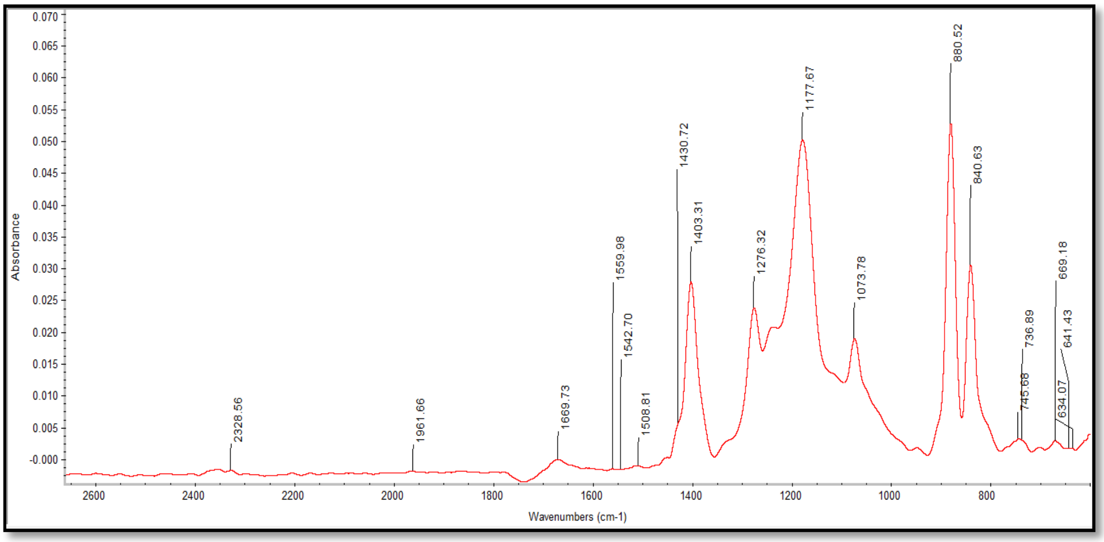


Figure 4.4: FTIR Absorbance Peak for 0.2wt% $LiNO_3$ Additive

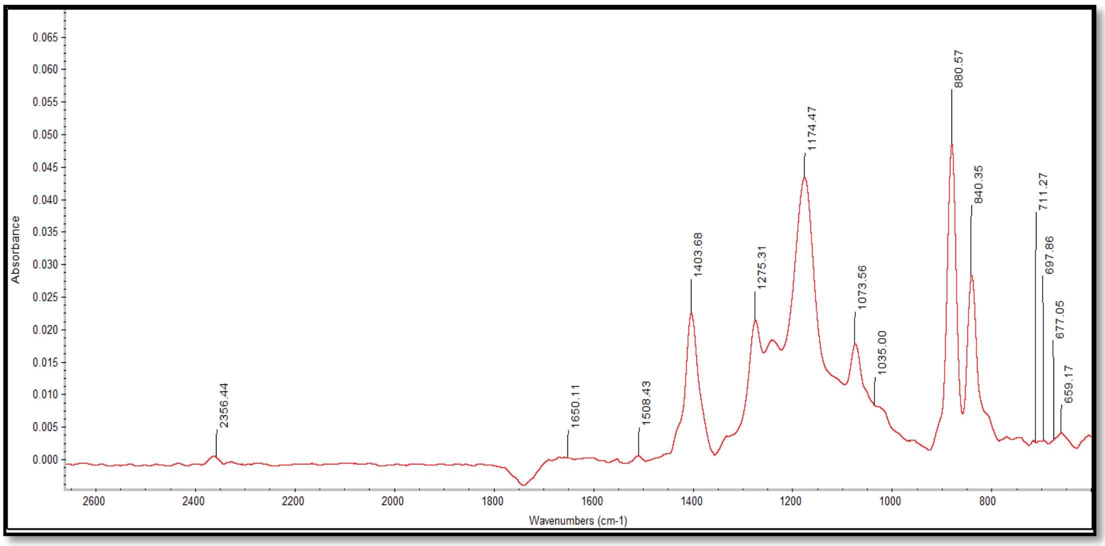


Figure 4.5: FTIR Absorbance Peak for 1.8wt% $LiNO_3$ Additive

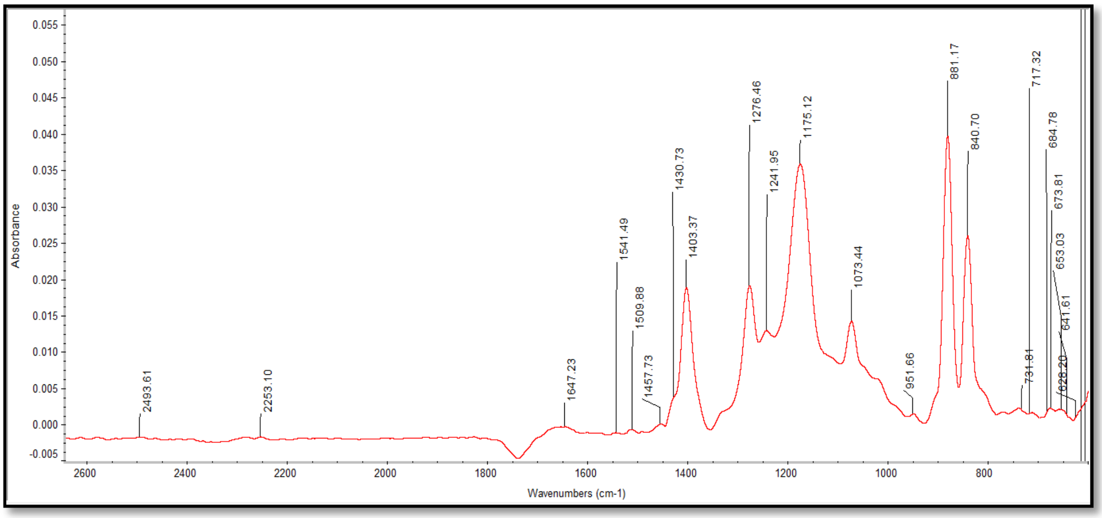


Figure 4.6: FTIR Absorbance Peak for 5wt% $LiNO_3$ Additive

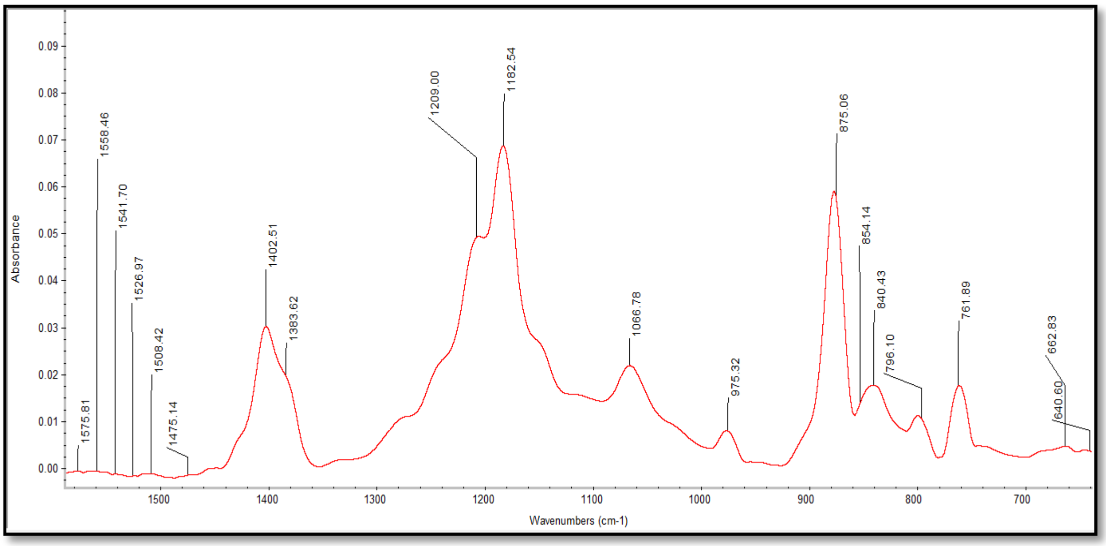


Figure 4.7: FTIR Absorbance Peak for 15wt% PVDF Polymer

Figure 4.4, 4.5 and 4.6 show the comparison of FTIR analysis for fabrication of asymmetric flat sheet membrane that produced using different percentage of additive. Function of FTIR test is to determine functional group of materials in membrane sample. The spectrum reveals the occurrence of interaction between the characteristic of PVDF as polymer, NMP as solvent, H_2O as non-solvent and $LiNO_2$

as non-solvent additive. In FTIR test, the frequency shifts involving characteristics group and absorption intensity changes will be happen when there have interaction between all materials in membrane sample.

Refer to figure 4.4 for 0.2wt% $LiNO_3$, the characteristic IR absorption bands for PVDF polymer at 875.06cm^{-1} which corresponding to the –CH_2- bond in the alkenes functional group. In PVDF polymer also have -CF_2- bond in alkyl halide functional group at 1182.54cm^{-1}. Moreover, the characteristic IR absorption bands for NMP as solvent is correspond at 1403.68cm^{-1} which show the C=C bond in the aromatic functional group. NMP solvent also have amine functional group with C-N bond at 1209.00cm^{-1}. Special case for this research is having fabrication of membrane with adding of additive. In this membrane sample have additive materials when 1402.51cm^{-1} and 1508.42cm^{-1} wavenumbers is refer to N=O bond in nitro functional group.

Furthermore, figure 4.5 show the 1.8wt% $LiNO_3$ of membrane sample. In this sample have the characteristic IR absorption bands for PVDF as polymer is at 880.52cm^{-1} refer to the –CH_2- bond in the alkenes functional. PVDF polymers also have alkyl halide functional group (-CF_2- bond) at 1403.31cm^{-1}. NMP as solvent have aromatic functional group at 1430.72cm^{-1} in C=C bond. In NMP solvent also have amine functional group in C-N bond at 1177.67cm^{-1}. The appearance of additive $LiNO_3$ in this membrane sample is prove at 1508.81cm^{-1} which for nitro functional group in N=O bond.

In addition, figure 4.6 show the 5wt% $LiNO_3$ of membrane sample. This sample have polymer, solvent, non-solvent and additive. PVDF as polymer is show in FTIR wavenumbers when at 881.17cm^{-1} which corresponds to alkenes functional group in $–CH_2$- bond. In PVDF also have alkyl halides functional group which at 115.12cm^{-1} for $–CF_2$- bond. Next, the present of NMP as solvent is prove that at 1403.37cm^{-1} correspond to aromatic functional group in C=O bond. The amine functional group also have in NMP solvent when at FTIR result shows 1276.48cm^{-1} in C-N bond. The appearance of $LiNO_3$ additive is prove when at 1457.73cm^{-1} and 1509.88cm^{-1} of nitro functional group in N=O bond.

Figure 4.7 show the FTIR analysis for fabrication of asymmetric flat sheet membrane that produced using 15wt% PVDF polymer without additive element. The spectrum reveals the occurrence of interaction between the characteristic of PVDF as polymer, NMP as solvent, and H2O as non-solvent. The characteristic IR absorption band for PVDF polymer is show at 838.65cm^{-1} wavenumbers which corresponding to the $–CH_2$- bond in the alkenes functional. For alkyl halides functional group in PVDF polymer is show at 1068.21cm^{-1} in $–CF_2$- bond. The presence of NMP solvent is show at.1403.71cm^{-1} which correspond to aromatic functional group for C=C bond.

Therefore, from doing FTIR analysis we can say that there are proving for the presence of PVDF as polymer, NMP as solvent, H_2O as non-solvent and $LiNO_3$ as additive in our fabrication asymmetric flat sheet membrane sample. Table 1 show the summary result for FTIR analysis for all membrane samples.

4.3 Effect of performance of PVDF membrane and with different percentage of additive on CO_2/N_2 permeation gas test

In order to evaluate the result from permeation test, we have to calculate average of time taken, volumetric flowrate, gas permeability value and gas selectivity value. All of calculation can be done by using equation 3.1 in chapter 3.

4.3.1 Effect of pressure on CO_2 permeation for 15wt% PVDF membrane

The performance of PVDF membrane on CO_2/N_2 gas separation will be evaluated with and without additive. The kind of additive used for this research is lithium nitrate ($LiNO_3$). Furthermore, different percentage of additive is used in order to study the effect of additive on performance of PVDF membrane. According to Lei et. al. (2008), the presence of additive on PVDF membrane fabrication dope solution will improved the permeation and selectivity test. Therefore, this research will discuss the effect of only PVDF membrane on permeation gas test and the effect when PVDF membrane have a different percentage of lithium nitrate as additive on permeation gas test.

Table 4.1 show the result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test of 15% w/v PVDF membrane sample and figure 4.5 is represent the result in table 4.1, the result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test for 15% w/v PVDF membrane sample

Table 4.1 and figure 4.8 show the result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test of 15% w/v PVDF membrane sample. To calculate the permeability and selectivity value for gas permeation test, we have to know the value of area of flat sheet PVDF membrane, time taken for the soap water move, selected pressure of pure gas used and volume different of the soap water by each membrane. By referring to table 4.1 and figure 4.8, it shows that as pressure for 15% w/v PVDF membrane sample increase, time taken for soap water move will be decrease. Its mean, the gas separation for CO_2 gas on 15% w/v PVDF membrane will be faster when used higher value of pressure. In other way, volumetric flowrate will be affected by average time taken. When average time taken of soap water move is slow/decrease, the volumetric flowrate value will be increase. The value of volumetric flowrate is inverse proportional to average time taken.

Table 4.1: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test of 15% w/v PVDF membrane sample

Remarks: Volume: 20mL (20 cm3), Time (sec)		
% w/v PVDF membrane sample	pressure (cmHg)	Average Time Taken (sec)
15	37.50	6.48
	75.01	2.95
	112.51	2.01
% w/v PVDF membrane sample	pressure (cmHg)	Volumetric Flowrate, Q(cm3/sec)
15	37.50	3.09
	75.01	6.78
	112.51	9.43

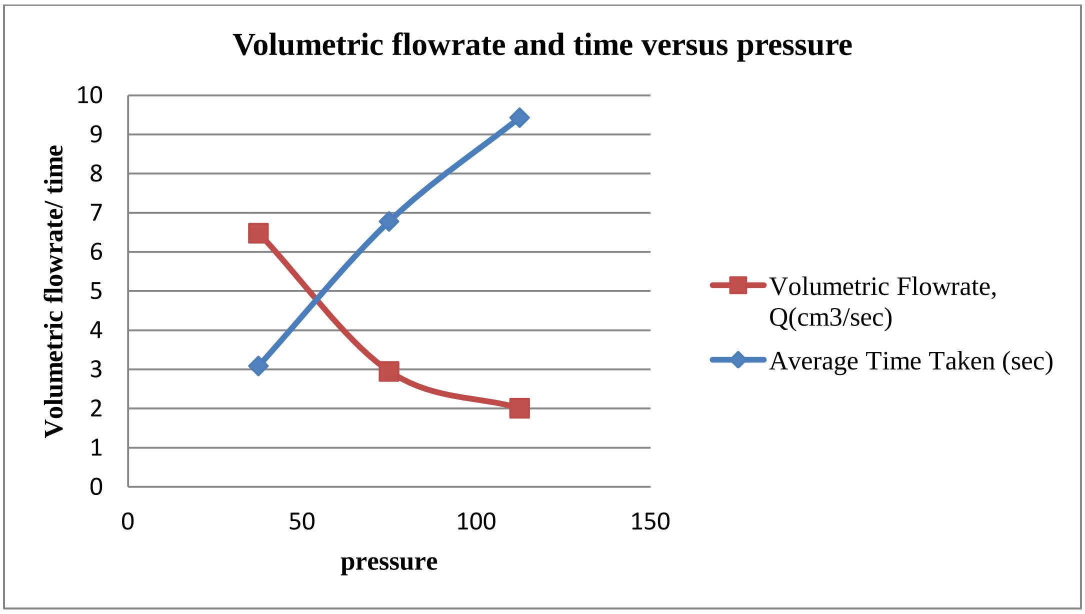


Figure 4.8: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test for 15% w/v PVDF membrane sample

4.3.2 Effect of pressure on N_2 permeation for 15wt% PVDF membrane

In addition, table 4.2 and figure 4.9 shows the result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for N_2 permeation test of 15% w/v PVDF membrane sample. For table 4.2 and figure 4.9, there are some differences with previous table and figure. Gas permeation test for N_2 gas is opposite to gas permeation test for CO_2. When pressure used is increase, the average time taken for soap water move will be decrease. Its mean that, the flow of N_2 gas separation is much slower compare to the flow of CO_2 gas separation. Apart from that, the result of volumetric flowrate will be affected by average time taken. Average times taken for N_2 is slower/decrease, the volumetric flowrate value will be increase. The value of volumetric flowrate is inverse proportional to average time taken. The kinetic diameter of CO_2 gas is small compare of N_2 gas. So, it effects the gas separation through membrane. gas permeation of CO_2 much faster than $N_{2.}$

Table 4.2: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for N_2 permeation test of 15% w/v PVDF membrane sample

Remarks: Volume: 20mL (20cm3), Time (sec)		
% w/v PVDF membrane sample	pressure (cmHg)	Average Time Taken (sec)
15	37.50	6.90
	75.01	3.60
	112.51	2.92
% w/v PVDF membrane sample	pressure (cmHg)	Volumetric Flowrate, Q(cm3/sec)
15	37.50	2.90
	75.01	5.56
	112.51	6.84

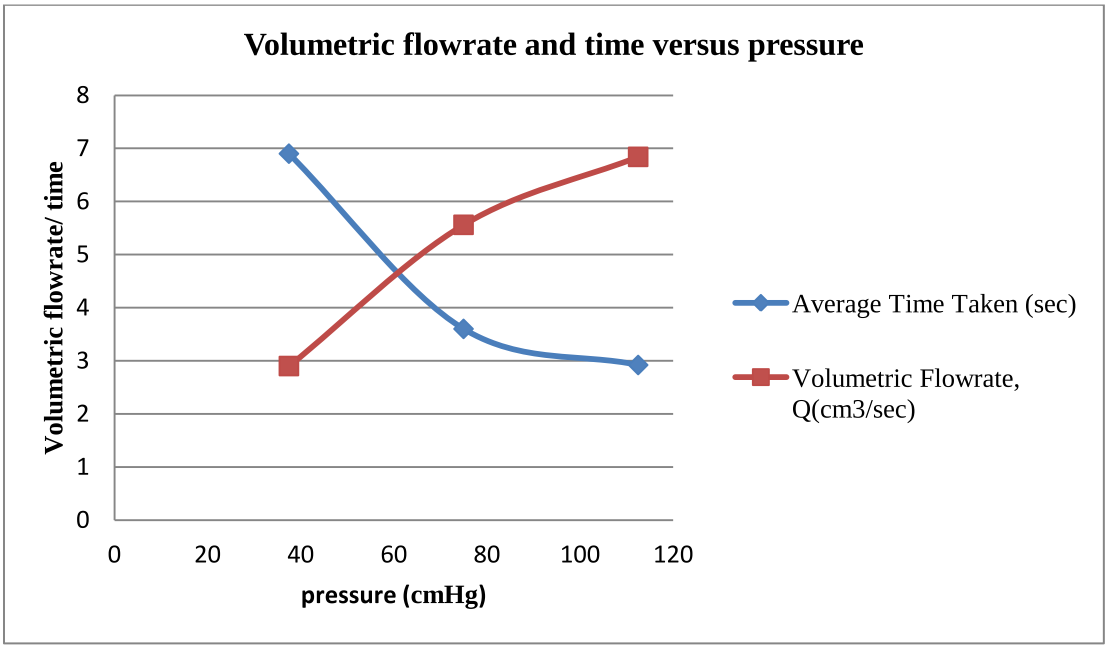


Figure 4.9: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for N_2 permeation test of 15% w/v PVDF membrane sample

4.3.3 Effect of pressure on permeability of CO_2/N_2 separation for 15% w/v PVDF membrane

Table 4.3 and figure 4.10 showing the results of permeability (p/l) for CO_2 and N_2 for 15% w/v PVDF membrane sample. Whereas, figure 4.4 showing the results of CO_2/N_2 selectivity (α) for 15% w/v PVDF membrane sample. The gas separation characteristic and performance can be determine by evaluate Figure 4.10 (plotting graph for permeability of CO_2 and N_2 pure gas) and figure 4.11 (plotting graph for CO_2/N_2 selectivity of each membrane produced against different the feed pressure.

According to figure 4.10, the permeability test is only doing on one type of membrane which is 15% w/v PVDF membrane. The manipulated variable is different value of feed pressure used. For CO_2 gas, the permeability result is increase from pressure 37.5031 cm Hg to 75.0062 cm Hg. Then, the permeability result is decrease from pressure 75.0062 cm Hg to pressure 112.5092. Furthermore, for N_2 gas, the permeability result is decrease as pressure rate increase from 37.5031 > 75.0062 > 112.5092. The significant differences of gas permeance among membrane prepared from three different pressure rates could be explained by referring to their morphologies as discuss on SEM test. Because of this dope solution 15% w/v PVDF membrane is solutions only have PVDF polymer, NMP solvent and H_2O non-soluble element and also do not have any dip coating chemical or additive chemical mix with them, so there is no increasing effective layer thickness. According to Ahmad A. L.

et. al. (2009), through the dip coating process, the effective layer thickness will be increase. An increase in effective layer thickness will be attributed to the increase in skin layer thickness, rather than originated from pore penetration.

Table 4.3: Results of permeation test for CO_2 and N_2 for 15% w/v PVDF membrane sample

% w/v PVDF membrane sample	pressure (cm Hg)	permeability		Selectivity (α) (CO2/N2)
		p/l (CO2)	p/l (N2)	
15	37.50	4553	4273	1.01
	75.01	4995	4096	1.22
	112.51	4632	3360	1.38

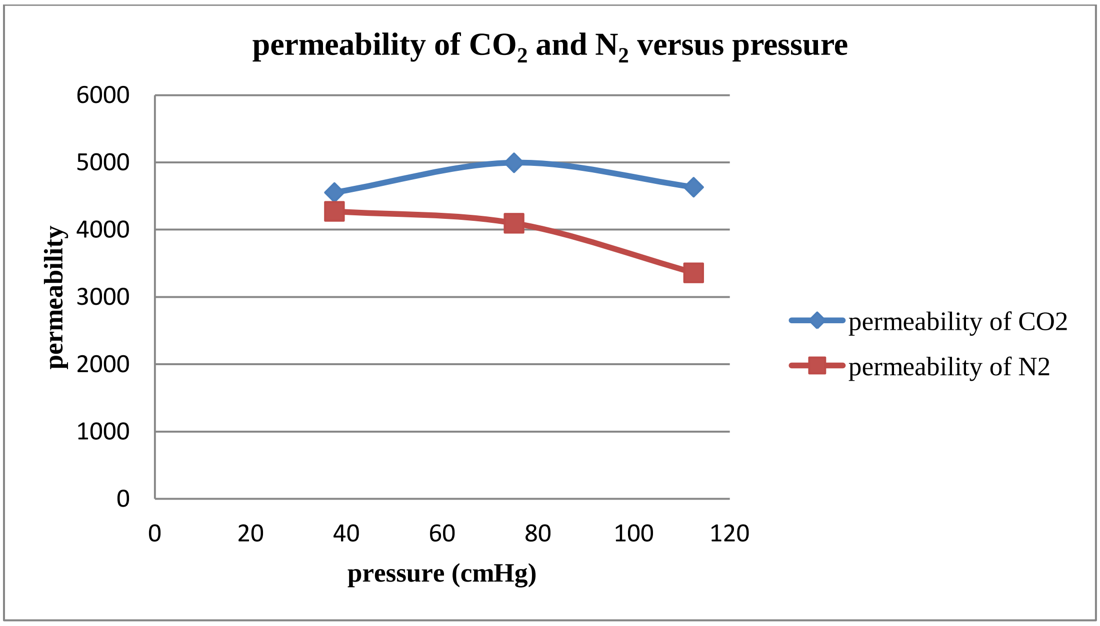


Figure 4.10: Results of permeability (p/l) for CO_2 and N_2 for 15% w/v PVDF membrane sample

4.3.4 Effect of pressure on selectivity of CO_2/N_2 separation for 15% w/v PVDF membrane

Besides that, figure 4.11 showing the results of CO_2/N_2 selectivity (α) for 15% w/v PVDF membrane sample. The selectivity value is getting from dividing two permeability of pure gas. Referring to figure 4.11, the selectivity of CO_2/N_2 gas is increasing with increase of feed pressure. According to Morreale B.D. et. al. (2009), the permeability values is dependence on differences in the partial pressure driving force exponent, n. From this paper, in order to determine value of selectivity, they used Arrhenius equation. The selectivity value is directly proportional to pressure with constant value of thickness of flat sheet PVDF membrane. The selectivity value for three different pressures is increasing as 1.0655 < 1.2194 < 1.3787. The value of permeability and selectivity is in term of GPU (Gas Permeation Units).

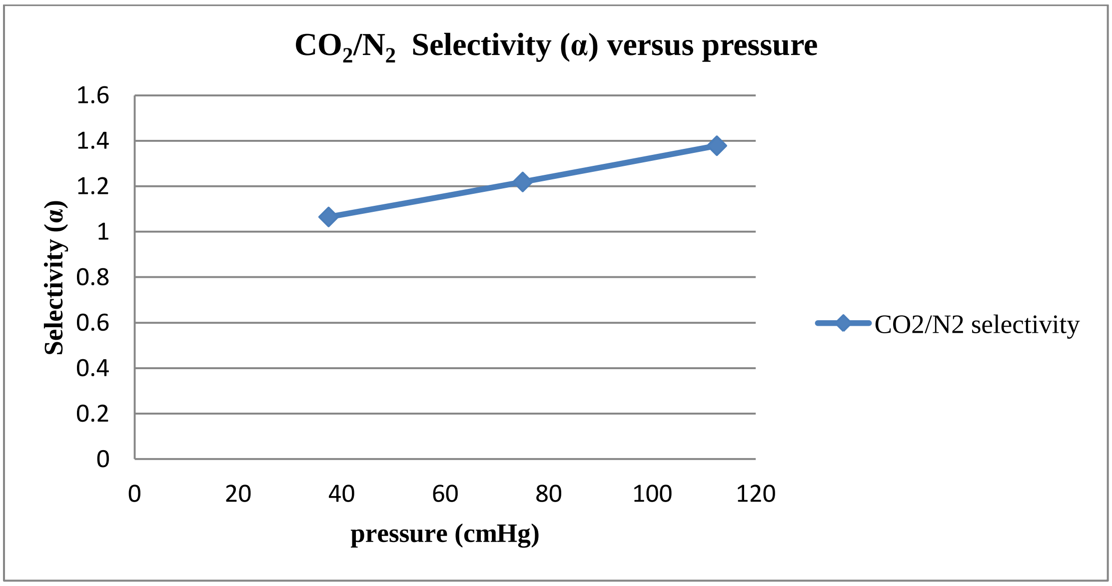


Figure 4.11: Results of CO_2/N_2 selectivity (α) for 15%w/v PVDF membrane sample

4.3.5 Effect of pressure on CO_2 permeation for 0.2%, 1.8% and 5% of $LiNO_3$ membrane

Table 4.4 and figure 4.12 are showing the result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test of 0.2%, 1.8% and 5% of $LiNO_3$ membrane sample. Different with table and figure before because this time dope solution have some percentage of additive. Additive used to study performance of PVDF membrane is lithium nitrate and we also study effect when used various percentages of additive. Referring to figure 4.12, as feed pressure increase, the average time taken will be decreases. Moreover, percentage of $LiNO_3$ additive used increase from o.2% w/v, 1.8% w/v and 5% w/v, the average time take is increase. Example, for 0.2% w/v $LiNO_3$, the average time taken is 3.2825>1.5675>1.4225. For 1.8% w/v $LiNO_3$, the average time taken is 5.115>1.6625>1.265. For 5% w/v $LiNO_3$, the average time taken is 5.935>2.9875>1.99425. From this result its show that, when used high percentage of additive, the time taken for soap water reach $20cm^3$ of burette is much slower. Soap water of 0.2% w/v $LiNO_3$ is move faster as increase pressure used compare with 5% w/v $LiNO_3$. In addition, the volumetric flowrate is inversely proportional to average time taken. For average time taken, 0.2% w/v $LiNO_3$ is fastest compare others membrane. For volumetric flowrate, 5% w/v $LiNO_3$ is fastest compare others membrane.

Table 4.4: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test of 0.2%, 1.8% and 5% of $LiNO_3$ membrane sample

Remarks: Volume: 20mL (20 cm3), Time (sec)		
% LiNO3 additive	pressure (cmHg)	Average Time Taken (sec)
0.2	37.50	3.28
	75.01	1.57
	112.51	1.42
1.8	37.50	5.12
	75.01	1.66
	112.51	1.27
5	37.50	5.94
	75.01	2.99
	112.51	1.94
% LiNO3 additive	pressure (cmHg)	Volumetric Flowrate, Q(cm3/sec)
0.2	37.50	6.09
	75.01	12.76
	112.51	14.06
1.8	37.50	3.91
	75.01	12.03
	112.51	15.81
5	37.50	3.37
	75.01	6.69
	112.51	10.30

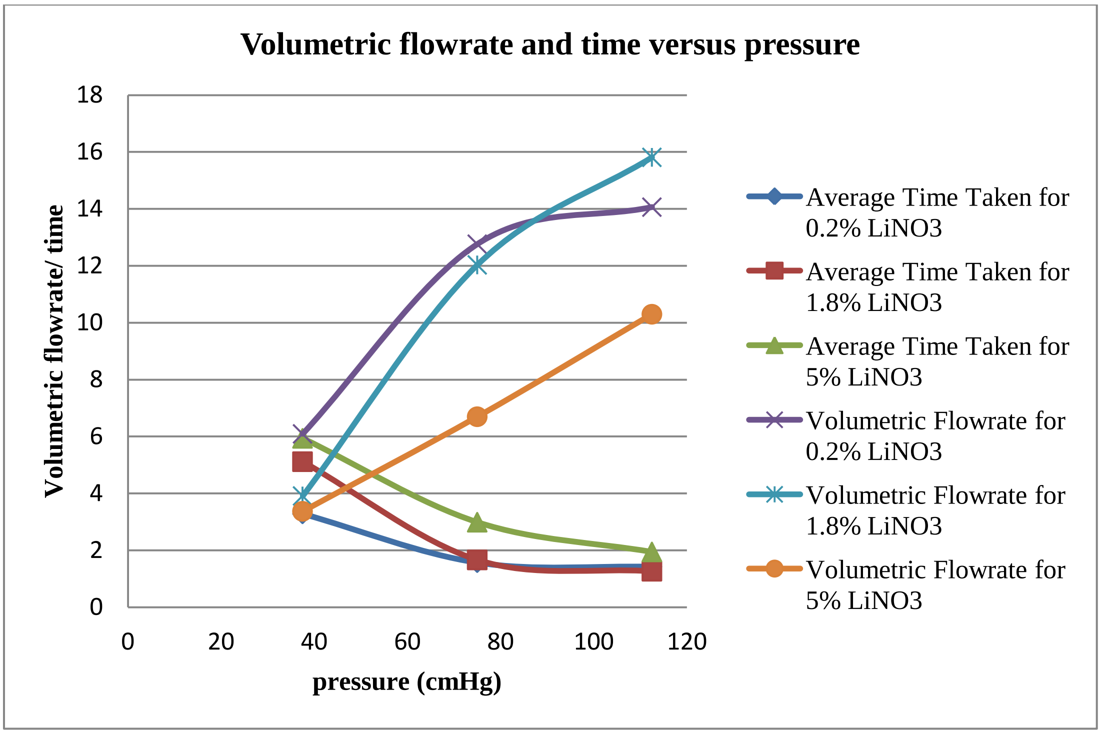


Figure 4.12: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for CO_2 permeation test of 0.2%, 1.8% and 5% of $LiNO_3$ membrane sample

4.3.6 Effect of pressure on N_2 permeation for 0.2%, 1.8% and 5% of $LiNO_3$ membrane

Table 4.5 and figure 4.13 are showing the result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for N_2 permeation test of 0.2%, 1.8% and 5% of $LiNO_3$ membrane sample. For figure 4.5 we can see that the average time taken of N_2 gas is much slower than CO_2. Gases for permeability can be classified into two groups which are fast gas penetrants (CO_2) and slow gas penetrants (N_2). But it stills same with CO_2 which is as increasing of percentage of additive, the soap water move faster. And as high feed pressure used, the average time taken for soap water move is also faster. Furthermore, the volumetric flowrate for N_2 also still same as CO_2.

Volumetric flowrate is inversely proportional to average time taken. As increasing of percentage $LiNO_3$ additive, the volumetric flowrate is increase.

Table 4.5: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for N_2 permeation test of 15% PVDF membrane sample

Remarks: Volume: 20mL (20 cm3), Time (sec)		
% LiNO3 additive	pressure (cm Hg)	Average Time taken (sec)
0.2	37.50	15.01
	75.01	7.83
	112.51	4.17
1.8	37.50	12.21
	75.01	7.69
	112.51	4.41
5	37.50	12.38
	75.01	3.22
	112.51	2.36
% LiNO3 additive	pressue (cmHg)	Volumetric Flowrate, Q(cm3/sec)
0.2	37.50	1.33
	75.01	2.56
	112.51	4.79
1.8	37.50	1.64
	75.01	2.60
	112.51	4.53
5	37.50	1.62
	75.01	6.21
	112.51	8.48

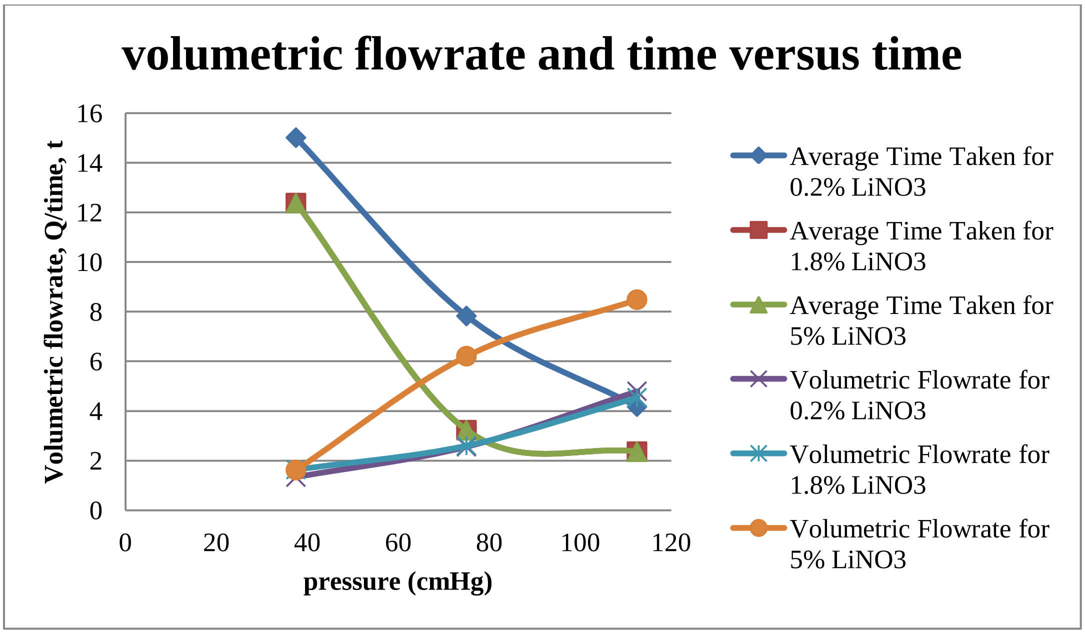


Figure 4.13: Result of average time taken (sec) and volumetric flowrate, Q (cm^3/sec) for N_2 permeation test of 0.2%, 1.8% and 5% of $LiNO_3$ membrane sample

4.3.7 Effect of pressure on permeability of CO_2/N_2 separation for 0.2%, 1.8% and 5% of $LiNO_3$ membrane

According to figure 4.14, 4.15 and 4.16, CO_2 and N_2 permearance values increase in the order of 5% w/v $LiNO_3$ < 1.8% w/v $LiNO_3$ < 0.2% w/v $LiNO_3$ of additive in the dope solution. The significant differences of the gas permeance among three membrane contain different percentage additive prepared could be explained by referring to their morphologies as discuss in sub- chapter 4.1 (effect of the additives on the membrane morphology). The permeance of 0.2% w/v LiNO3 additives is much higher for both the gases compare to others membrane with different percentage of additives. The increasing of permeance rate of the 0.2% w/v LiNO3 additives will be indicates the possibilities of membrane pore have a big pore size compare to others membrane. In addition, a big pore size will be allows the gases to permeate easily through the membrane. Therefore, if membrane will be consequently have lower selectivity. 5% w/v $LiNO_3$ membrane has a small pore size gives a lower permeance rate of both of the gases (CO_2 and N_3). This is because; the gases hardly slip through the small pore size membrane which give the membrane high selectivity value. So, from the research, it shows that best additive percentage to produce high performance of PVDF asymmetric flat sheet membrane is 0.2% w/v $LiNO_3$.

Moreover, we have compare selectivity result for asymmetric flat sheet membrane with and without additive to chosen whether with additive or without additive produce high performance. For sample without additive the selectivity result is 1.065529346, 1.219425742 and 1.378654388 refer to 37.5031cm Hg, 75.0062cm Hg and 112.5092cm Hg respectively. In other hand, for sample with additive chosen 0.2wt% $LiNO_3$, the selectivity result is 4.573080198, 4.988113121 and 2.933216203 refer to 37.5031cm Hg, 75.0062cm Hg and 112.5092cm Hg respectively. Hence, the result of selectivity for separation of pure gas CO_2/N_2 is with presence of 0.2wt% $LiNO_2$ additive give a good performance for separation pure gas compare without additive. The selectivity rate for membrane without additive is lower than membrane with present of additive. From this result we can say that, when doing fabrication of membrane with adding $LiNO_3$ additive, the performance of membrane its self is getting increase. Referring to pervious research Lei S. et. al. (2008), larger and longer macrovoids with finger-like pores can be observed in sample fabricated asymmetric flat sheet with $LiCl_2$ additive. The larger and longer will allow the permeation of pure gas through asymmetric flat sheet membrane.

Table 4.6: Results of permeation test for CO_2 and N_2 for 0.2%, 1.8% and 5% of LiNO3 membrane sample

% LiNO3 additive	pressure (cm Hg)	permeability		selectivity (α) (CO2/N2)
		(p/l) CO2	(p/l) N2	
0.20%	37.50	8977.35	1963.09	4.57
	75.01	9393.16	1883.11	4.99
	112.51	6905.84	2354.36	2.93
1.80%	37.50	5761.61	2414.14	2.39
	75.01	8863.36	1916.79	4.62
	112.51	6905.84	2226.30	3.10
5%	37.50	4965.57	2381.47	2.09
	75.01	4932.33	4572.64	1.08
	112.51	5057.17	4166.94	1.21

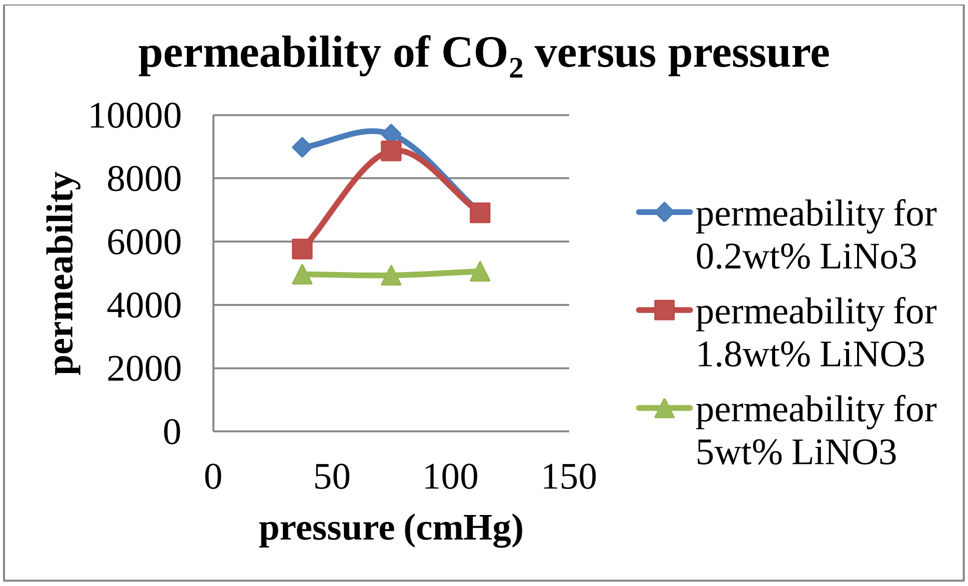


Figure 4.14: Results of permeation test for CO_2 for 0.2%, 1.8% and 5% of LiNO3 membrane sample

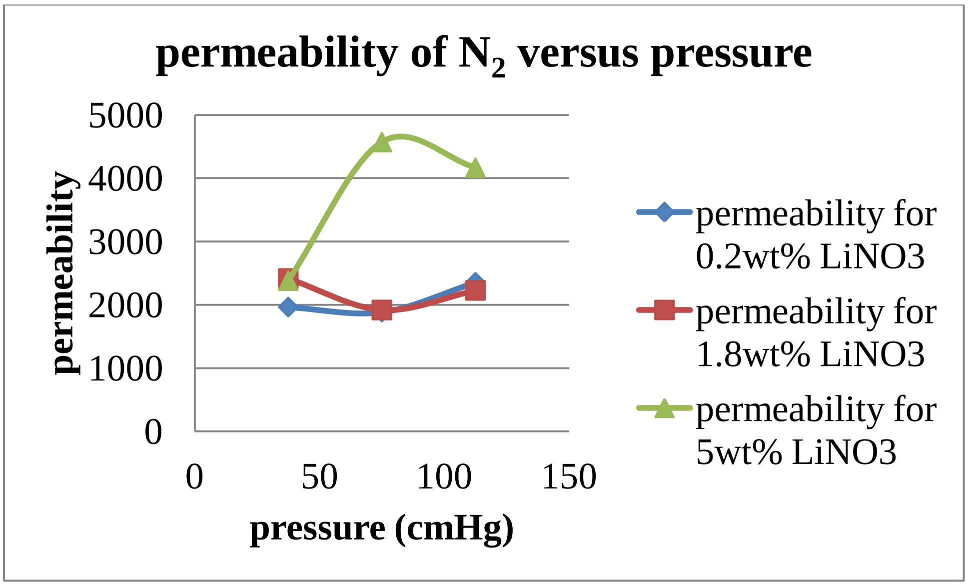


Figure 4.15: **Results of permeation test for N_2 for 0.2%, 1.8% and 5% of LiNO3 membrane sample**

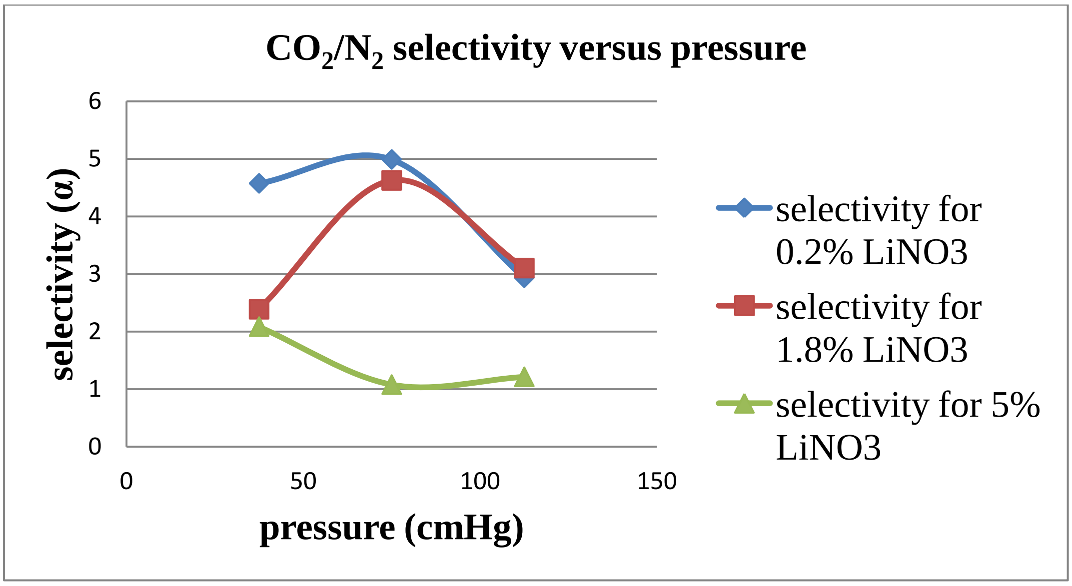


Figure 4.16: **Results of CO_2/N_2 selectivity (α) for N_2 for 0.2%, 1.8% and 5% of LiNO3 membrane sample**

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In the present research, the effect of typical additive, $LiNO_3$ on the fabrication of PVDF/NMP flat sheet asymmetric membrane were studies and compared with the fabrication of membrane without additive. Based on the analyses for PVDF/NMP which without/with an additive, the way an additive affected membrane preparation was investigated in terms of membrane morphology, structure, FTIR analysis and gas permeation test.

Refer to analysis of SEM test; it was found that the addition of $LiNO_3$ reduced the thermodynamic stability of the dope solution. The reducing of clear image for finger-like pores and sponge-like structure as 0.2wt% $LiNO_3$ > 1.8wt% $LiNO_3$ > 5wt% $LiNO_3$. As the percentage of additive increase, the image of pores and structure will be less clearly. Compare to morphology image without additive, 15wt% PVDF membrane pore and structure is quite larger and longer. The additional of additive resulting the pore and structure become smaller. Therefore, the additional of additive of 5wt% $LiNO_3$ into the dope solution could form the membrane stronger strain strength than the PVDF commercial membrane. Membrane with additive will be keeping the similar rigidity.

Based on analysis of gas permeation test, the size of pore will be effect the continuous movement of pure gas through the flat sheet membrane. Based on the result, among three different additive used. 0.2wt% $LiNO_3$ produces a high performance for gas separation. It have a higher permeability and selectivity result. Therefore, the relation of gas permeation test and SEM morphology test is the larger pore on cross section membrane will be cause the good permeability on CO_2/N_2 pure gas. Moreover, we have compare with permeability result of membrane have additive and without additive. Permeability of membrane on gas separation with additive is give a high performance compared with membrane which does not have additive. It refers result of permeability and selectivity.

In addition, after doing analysis of FTIR we can know the molecular structure and functional group which have on membrane sample. This research, we have two type of sample which are membrane sample without additive (PVDF/NMP/H_2O) and membrane sample with additive (PVDF/NMP/$LiNO_3$). In membrane sample have additive, it have the functional group of alkenes, alkyl halide, aromatic, amine and nitro group. Then, for membrane sample which without additive, it have the functional group of alkenes, alkyl halide and aromatic group.

Research of using additive in order to fabricate and improve the performance of membrane is very encourage which will be benefit to industry and economic of country. All of objective can be achieved by doing three analysis test on membrane. The fabrication of PVDF membrane will be improving the performance of that membrane in order to satisfy the industrial market needed. The effect of additives on the fabrication is the main objective in this research by referring to structure of morphology image, the performance in gas permeation test and knowing characteristic of membrane on FTIR test.

5.2 Recommendation

Based on the study conducted, some recommendations are given for future work.

1) Asymmetric membrane should be prepared with a variety of additive in order to study the effect of additive on membrane fabrication and performance such as Lithium chloride.
2) Different percentage of additive should be used to know the effect of concentration of additive on formation of membrane such as in range of 10wt% - 0.1%.

3) Wet casting and dry casting should be used to see which casting method is suitable for casting dope solution with and without additive.
4) Comprehensive studies on other fabrication parameters of asymmetric membrane such as evaporation temperature, coagulation temperature and drying method must be carried out to further optimize membrane formation process.
5) Many analysis should be carry out to study the performance of fabrication of asymmetric membrane such as dynamic contact angle, mechanical property test, measurements of pore size and pore flux distribution, measurements of pure water flux and MWCO.

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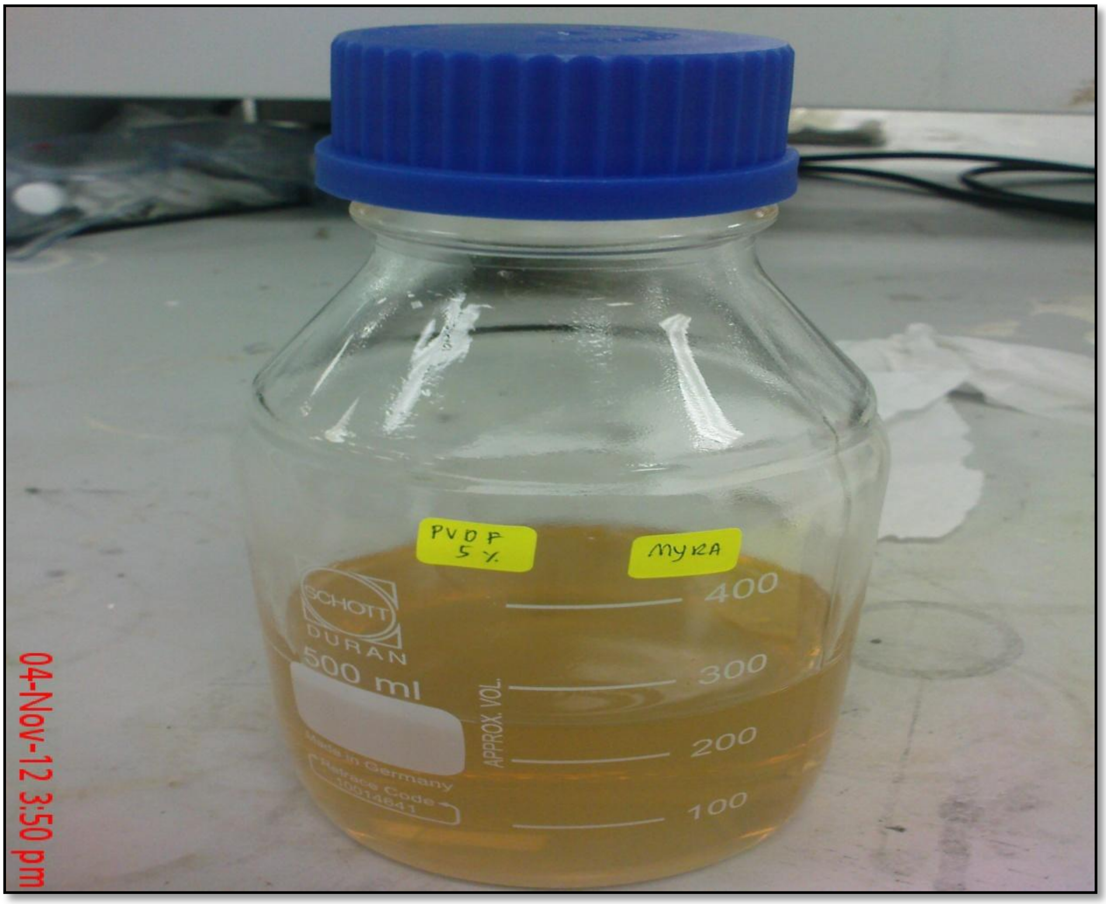
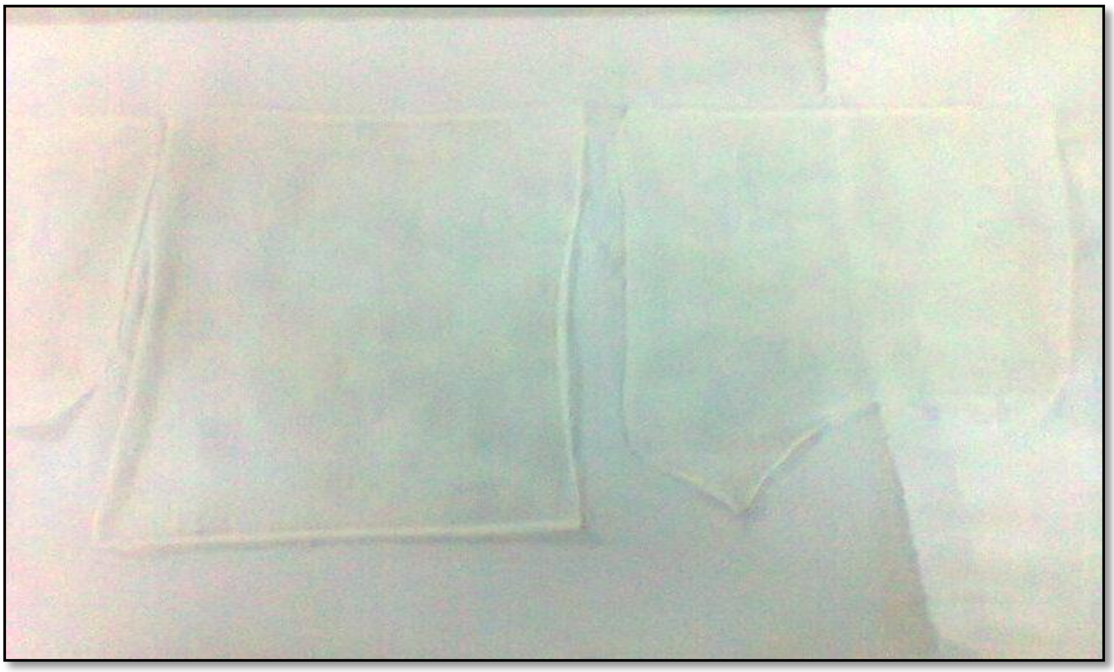
Appendix A (Permeation Cell)

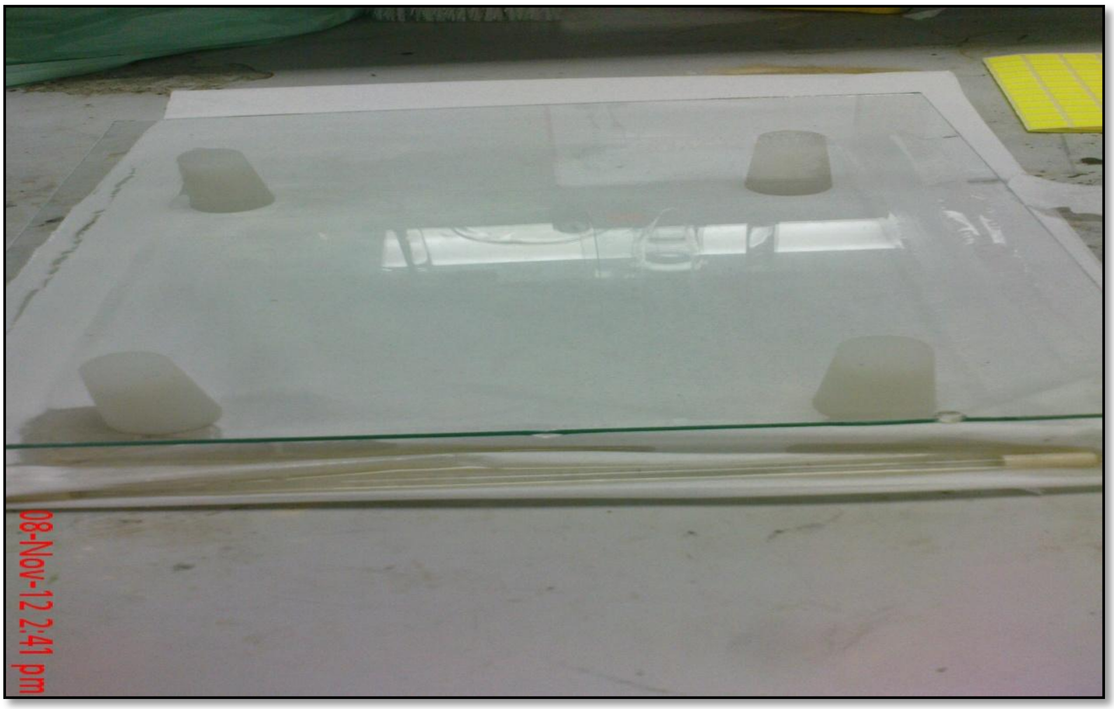


Appendix B (Dope Solution)

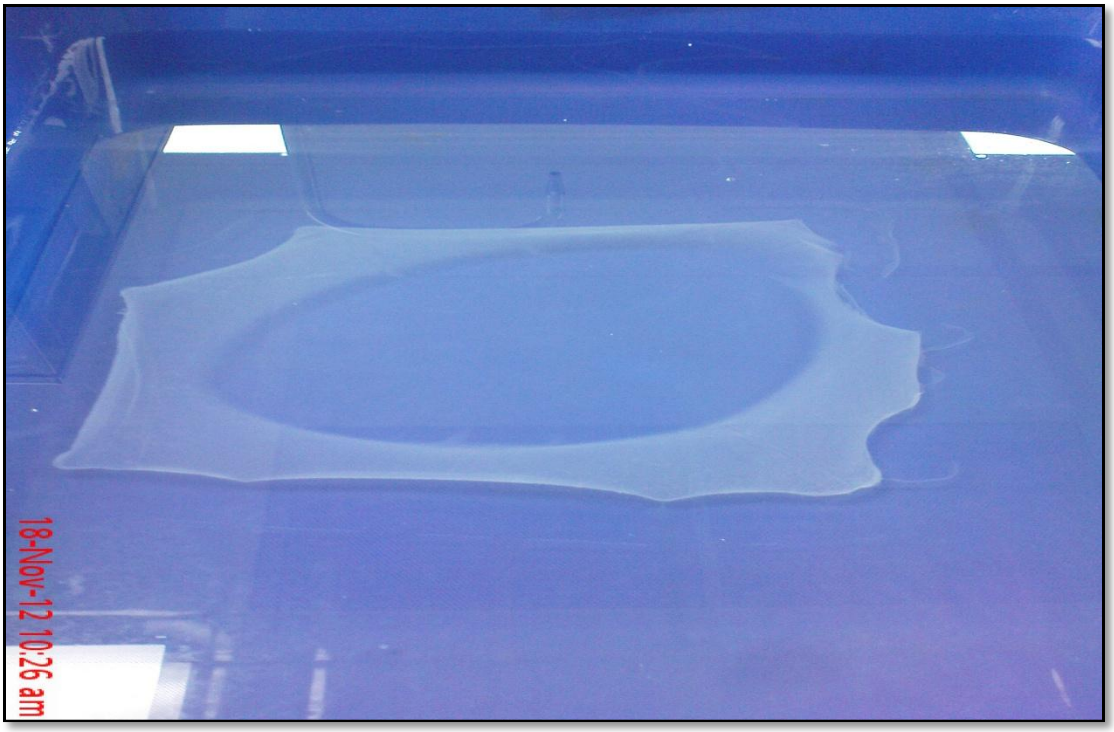


Appendix C (Membranes)

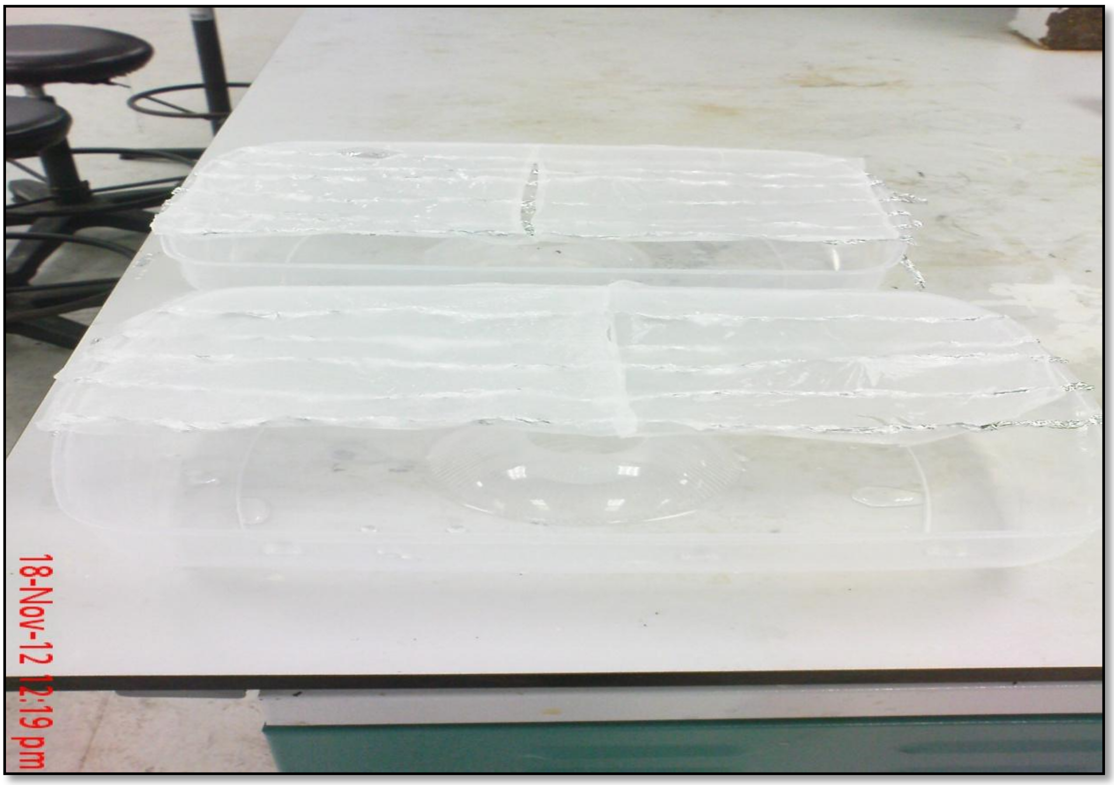
Appendix D (Membranes for Gas Permeation Test)



Appendix E (Dry Casting)



Appendix F (Phase Inversion)



Appendix G (Drying Membrane Process)

Appendix H (The summary result for FTIR analysis of membrane sample)

0.2wt% LiNO3			**1.8wt% LiNO$_3$**			**5wt% LiNO$_3$**		
materials	**wavenumbers (cm-1)**	**functional group**	**materials**	**wavenumbers (cm-1)**	**functional group**	**materials**	**wavenumbers (cm-1)**	**functional group**
PVDF	880.57	Alkenes (–CH2-)	PVDF	880.52	Alkenes (–CH2-)	PVDF	881.17	Alkenes (–CH2-)
	1174.47	Alkyl halide (-CF2-)		1403.31	Alkyl halide (-CF2-)		1175.12	Alkyl halide (-CF2-)
NMP	1403.68	Aromatic (C=C)	NMP	1430.72	Aromatic (C=C)	NMP	1403.37	Aromatic (C=C)
	1275.31	Amine (C-N)		1177.67	Amine (C-N)		1276.48	Amine (C-N)
LiNO$_3$	1403.68, 1508.43	Nitro (N=O)	LiNO$_3$	1508.81	Nitro (N=O)	LiNO$_3$	1457.7, 1509.88	Nitro (N=O)

15wt% PVDF		
materials	wavenumbers (cm-1)	functional group
PVDF	838.65	Alkenes (–CH2-)
	1068.21	Alkyl halide (-CF2-)
NMP	1403.7	Aromatic (C=C)