STUDY EFFECT OF ADDITIVE ON PVDF MEMBRANE FOR CO_2/N_2 GAS SEPARATION PROCESS

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ABSTRACT

Flat sheet asymmetric membranes were produced from homogenous solution of Poly(vinylideneflouride) (PVDF) via phase inversion method using N-methyl-2-pyrrolidone (NMP) as the solvent and Lithium Chloride (LiCl) as an additive. The effect of addition of different ratio of LiCl in the casting solution on the membrane properties and performance were studied. The morphology and cross section of the produced membranes were observed by Scanning Electron Microscope (SEM). Then, the membranes were tested for chemical analysis to define the presence of LiCl in the membrane by using Fourier Transform Infrared (FTIR) spectroscopy. The permeation performances of the membranes were evaluated in terms of permeability and selectivity of the membranes in separating the gaseous mixture by using single gas permeation test. The addition of LiCl into the casting solution definitely improved the morphology and structure of the membrane. The macrovoid formation was suppressed and very fine pores were formed at higher LiCl content. Increasing the LiCl content significantly increased the selectivity of the PVDF membrane to separate the CO_2/N_2 gases but decreased the amount of the gases that passed through the membrane.

ABSTRAK

Membran asimetrik yang rata dihasilkan dari larutan sebati Poly(vinyldeneflorida) (PVDF) melalui kaedah fasa penyongsangan menggunakan N-metil-2-pyrrolidone (NMP) sebagai pelarut dan Litium Klorida (LiCl) sebagai bahan penambah. Kesan penambahan nisbah LiCl yang berbeza dalam larutan membran terhadap ciri fizikal dan prestasi membran telah dikaji. Morfologi dan keratan rentas membran yang dihasilkan dianalisis di bawah Mikroskopi Elektron Imbasan (SEM). Kemudian, membran diuji untuk analisis kimia untuk menentukan kehadiran LiCl dalam membran dengan menggunakan Fourier Transform Infrared (FTIR) spektroskopi. Tahap kebolehan membran untuk mengasingkan campuran gas telah diuji dengan menjalankan ujian penyerapan gas tunggal. Penambahan LiCl ke dalam larutan membran telah menjadikan morfologi dan struktur membran lebih baik. Pembentukan macrovoid telah berkurang dan pembentukan liang yang sangat halus terhasil pada kandungan LiCl yang lebih tinggi. Peningkatan kandungan LiCl dalam larutan membran telah meningkatkan tahap kebolehan membran untuk mengasingkan campuran gas karbon dioxida dan nitrogen tetapi kadar amaun gas yang melalui membran menurun.

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LIST OF ABBREVIATIONS

α_{AB}	Selectivity of pure gas
^oC	Degrees celcius
μm	Micro meter
mm	Millimeter
A	Area
l	Thickness of membrane
P	Permeability
ΔP	Pressure change across membrane
V	Volume displaced in time(s)
Wt%	Weight percent

LIST OF ABBREVIATIONS

CA	Cellulosic esters
PS	Polysulfone
PA	Polyamide
PVDF	Poly (vinyldene fluoride)
RO	Reverse Osmosis
PV	Pervaporation
GP	Gas permeation
PTFE	Polytetrafluoroethylene
PP	Polypropylene
NMP	N-methyl-2-pyrolidone
LiCl	Lithium Chloride

CHAPTER 1

INTRODUCTION

1.1 Motivation

The major fossil fuels product that contributes to the greenhouse effect is carbon dioxide. Among all the industries emitting CO_2, fossil fuel power plants generate the largest amount of CO_2 emission with more than 30 billion tons of carbon dioxide emission in recent years. This has made the greenhouse gas as the main contributor to global warming. The release of CO_2 and N_2 gases from the combustion of fossil fuel is refer as post combustion. (Zhang et al, 2014; Renewables 2012 Global Status Report, REN 21; Brunetti et al, 2010).

By removing this carbon dioxide gas, the flue gas released to the atmosphere will have low CO_2 content and high in N_2. Mostly, in the petrochemical industry, the capability to separate gas will be the most essential. The separation of carbon dioxide is one of the energy intensive process where it has an important role in energy saving and carbon dioxide capture and storage implementation to reduce global warming. The captured CO_2 from membrane separation can be send to storage for the use in the carbonated beverage and food processing production, as the PH control in industrial processes and many others. These have increase the interest in the development of gas separation process by membrane based technology as membrane gas separation also provide a great performance due to the membrane interactions of high form of permeability with a huge selectivity to capture specific gaseous species (Zhang et al, 2014; Luis et al, 2012).

1.2 Statement of problem

The foremost important key for a good performance of a membrane in gas separation process are depend on the permeability and selectivity of the membrane. Polymeric membranes are material that chemically stable in a range of conditions and have the ability to make a stable solution in a suitable solvent (Scott & Hughes, 1996). However, previous study found out that pure polymers are materials with low selectivity (Hu et al, 2013). It has become a great challenge for producing membranes with high permeability and selectivity in gas separation process. Therefore, this study is conducted to overcome the problem by adding additive to the membrane casting solution to achieve high selectivity and permeability of the membrane.

1.3 Objectives

The following are the objectives of this research:

1) To produce PVDF membrane.
2) To characterize the membrane physically and chemically.
3) To investigate the performance of the membrane with additive.

1.4 Scope of this research

This study has focused on several scopes in order to achieve its objective. The scopes are as follows:

1) Phase separation method of phase inversion is used to produce a flat sheet PVDF membrane.
2) The PVDF membrane will be tested for chemical analysis using Fourier transform infrared (FTIR) spectroscopy.
3) Physical analysis will be tested using Scanning electron microscopic (SEM). This analyses will help to determine the characteristic of the PVDF membrane produced.
4) The membrane is then tested for its performance in separating CO_2/N_2 gaseous using Gas Permeation Test.

1.5 Organisation of this Thesis

This thesis is organized and structured into five chapters.
Chapter 1 is an introduction chapter for this thesis where the research objectives and outline of the thesis are presented.

The concept and fundamentals of polymeric membrane and gas separation process are introduced in chapter 2. In this chapter, a brief description on membrane transport process, membrane structure and module, membrane materials selection and the methods commonly used to produce membrane. Besides, this chapter also gives some description on the effect of modification of membrane.

Chapter 3 shows a review on the method of fabrication of membrane used for this research which is by using the dry/wet phase inversion method. The fabricated membrane with the modification is tested for its performance through single gas permeation test with CO2 and N2 gases. The selectivity and permeability of the membrane to separate the gases mixture is studied. Besides, the performance of the membrane also is defined from the physical and chemical properties by using SEM and FTIR instrument. Effect addition of different amount of additive into the membrane casting solution to the performance of the membrane to separate gases is studied.

Chapter 4 demonstrated the analysis of the performance of the produced membrane in comparison with the predicted result obtain from several researchers that have done similar research. The analysis includes the morphology of the membrane and the presence of functional group of the added additives through the FTIR analysis. The permeability and selectivity of the membrane is calculated and discussed according to the different ratio of additive composition in the membrane.

Chapter 5 displayed the conclusion of the research that ties together the physical properties of the membrane and its performance in separating gas by the effect of additive composition. The recommendations for future work also presented in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Definition of membrane

Generally, membranes are known as a thin layer which is in a permeable or semi-permeable phase that limit the movement of certain species. It also can be define as a selective barrier between the feed stream for separation and a product stream (Scott & Hughes, 1996).

2.1.2 History of membrane

In 1866, Graham was the earliest to indicate the membrane gas separation through the performance of natural rubber film that can enriched the oxygen content in the air. However, this technology has not yet lead in the commercial applications during that time because of the low permeation flux obtained by the thick polymer films. In 1960s, Loeb and Sourirajan have come up with the formation of high flux asymmetric membrane that is made up by cellulose in the reverse osmosis process. But pinholes occurred on the surface of the membrane as the membrane is dried. By using the concept of 'resistance model', Henis and Tripodi have developed a defect-free composite membrane in the 1980s where the surface of the asymmetric membrane is sealed with silicone rubber. With this membrane separation technology, Mosanto has developed the first hollow fiber membrane for hydrogen gas separation. The separation of gas mixture by membrane has attract the industry and become economically viable (Liu, 2008).

2.1.3 Principal of Membrane Separation

Membranes can be used for separation through their ability to prevent or regulate the permeation of certain species that flow through them. Therefore, the requirements for a good gas separation membranes include the selectivity of the membranes that depend on the structure of the membrane and the permeability of the membrane towards the desired component that depend highly on the appropriate selection of the membrane materials (Naylor, 1996). Selectivity is the measure of the ability of a membrane to separate two gases without any defect while permeability is the measurement of the quantity of the substance that passes through membrane per unit area of membrane and time (Baker, 2006).

2.1.4 Membrane Based Technology

Membrane based technology is in the process of focusing at advancing towards sustainable system that minimize carbon dioxide emission. Membrane gas separation is environmentally friendly as it does not need additional mass agent for separation and with that it will not generate secondary waste. Membrane technology has a technical breakthrough in the terms of selectivity and rate of separation because they are found to achieve higher efficiency of separation more frequent as membrane separation usually produce faster separation compared to other type of separations. Besides, this technology meets the needs of cost effectiveness and increment in the efficiency with simpler design and environmental compatibility. Technical advantages of membrane separation also results in the low capital investment as it offers a lower operating cost due to its energy saving, compactness and ease of operation and maintenance The operation with small or large plant is relatively simple as the membranes are modular in design and easy to scale up. Other benefit of membrane technology is that it comprise of higher recovery of the desired gaseous effluent which can be reused for various purposes. Currently, membrane technology is applied commercially to separate single components from mixtures of liquids and gases in the area of separation of mixtures. Thus, membrane process can be said to have almost ideal separation processes as they offer a possibility of selectively permeating single component from a mixture while rejecting others in a continuous steady state (Liu, 2008; Naylor, 1996; Abedini&Nezhadmoghadam, 2010).

2.2 Membrane Structure

2.2.1 Dense Membrane

Dense membranes are nonporous and consist of a dense film where permeants are transported by diffusion with the driving force of a pressure, concentration, or electrical potential gradient. In dense membranes, permeants with same size can be separated if their membrane materials have different concentrations. Therefore, the separation of mixture of components depend on the relative transport rate between the membrane that is determined by the diffusivity and solubility in the membrane materials. Dense membranes are applicable in gas separation, pervaporation and reverse osmosis process. (Baker, 2004)

2.2.2 Symmetric Membrane

Symmetric membranes can be define as a uniform structure as the membrane's properties do not change throughout the cross-section. Normally, symmetric membranes will have thickness ranges roughly around 10-200µm. In the term of principle of operation, microporous membranes are the most uncomplicated symmetric membranes. Microporous membranes have very small pores or holes and separation is reached by a sieving action. Track etching is a method for uniform cylindrical pores of microporous membranes. Other categories of symmetric membranes are microporous glass and ceramics which is an inorganic material. This type of material can be coated to form composites with a specific properties, improved rejection, structural improvements, increased flux and selectivity. The commonly produced symmetric membrane is by sintering or stretching for the manufacture of microporous membranes, casting process for the manufacture of ion-exchange and pervaporation membrane, etching and phase inversion for the manufacture of materials function as pore membrane and lastly by the method of extrusion where the materials work as diffusion membranes for gas permeation and pervaporation (Scott & Hughes, 1996; Ramakrishna et al, 2011).

2.2.3 Asymmetric Membrane

Asymmetric membranes consist of a thin selective layer and a strong supportive layer that provide mechanical strength to the membrane. They can be produced by two ways which are by phase inversion from single polymers or as composite structures. Precipitation from a homogeneous polymer solution will form a porous structure by phase inversion. The membranes produced will be classed as pore membranes that have a dense active 'skin' layer of less than 1 µm and have a thick porous support layer of 0.2 to 0.5 mm as shown in figure 2-1 whereas composite membranes are produced with the skin and support come from different materials. Generally, asymmetric membranes are superior compared to symmetric membranes due to their very thin top layer that made them rarely get "plugged" as rejection only occur at the surface and retained particles do not enter the membrane's main body. Mainly, asymmetric membranes are classed as diffusion membranes that are used for reverse osmosis process, gas permeation or separation process and pervaporation process. The membrane separation properties can be optimized to get a good membrane by varying the top skin layers preparation parameters. As for polymer membrane, the selective layer and supportive layer of the asymmetric membranes are produced in a single preparation step of phase separation method. (Scott & Hughes, 1996; Ramakrishna et al, 2011).

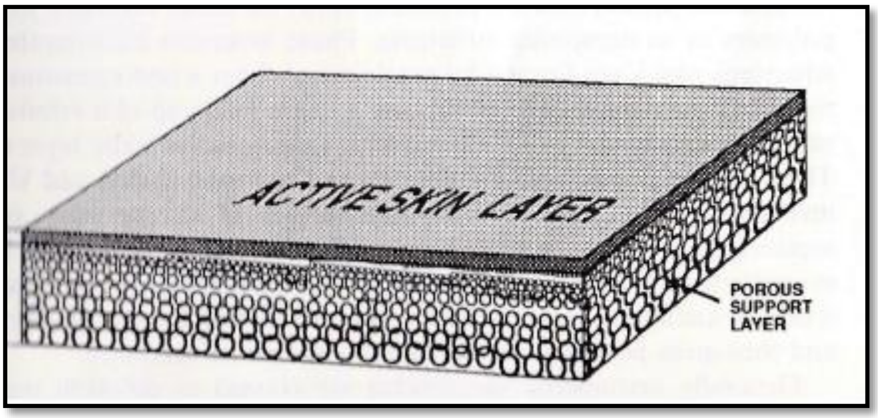

Figure 2-1: Asymmetric membrane structure (Scott & Hughes, 1996)

2.3 Membrane Formats and Modules

2.3.1 Hollow Fibre

Hollow fibre membranes are protected by stricter pre-treatment and they will go through backwash which requires to be cleaned more frequently mechanically and chemically. Hollow fibre configurations also designed to function at higher fluxes. However, they operate at lower concentrations compared to flat sheet configurations. Hollow fibre membranes are not like any other type of membrane as they do not have additional supporting layer, they are self-supporting and their diameter are usually less than 1 mm. Essentially, it is a fibre with a hollow space inside and packed in a bundle. The skin of the membrane can be on both side of the membranes or either one of them. There are two type of module to make this kind of membrane. Firstly is made by DuPont under the trade mark Permasep where the fibres are looped in U shape and potted in one resin block by their open end. This type of arrangement often used for reverse osmosis application due to its small diameter fibres that will produce great strength when under pressure. Another basic design of module is more common where the fibres are laid out parallel to each other in a bundle and the open ends are cast in two resin blocks that are bonded into shroud to form a cartridge. The process fluid (retenate) will flows through the centre of the hollow fibre and permeate passes through the fibre wall to the outside of the membrane fibre as shown in figure 2-2. Therefore, hollow fibre membranes are suitable for reverse osmosis, ultrafiltration and microfiltration applications. (Scott & Hughes, 1996; Bodik et al, 2008; Ramakrishna, 2011)

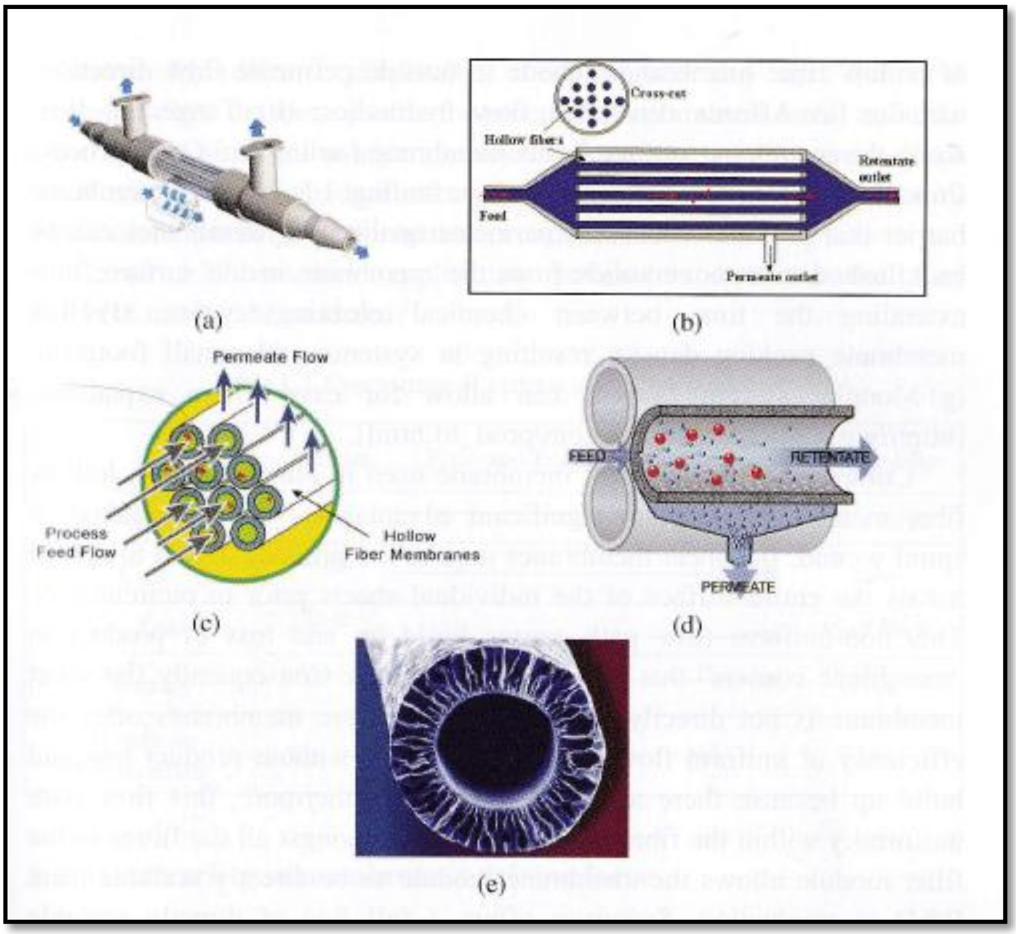

Figure 2-2: Hollow-fibre membrane module. Feed solution goes to inside of the hollow fibre and permeate goes outside of the fibre through the fibre wall. Magnification increase from (a) to (b), (c), (d) and (e) (Ramakrishna, 2011).

2.3.2 Plate and Frame

The design concept of plate and frame membrane module is very similar to the flat sheet membrane used in the laboratory. Basically, the modules are built from many layers of membranes, feed spacer plates and permeate spacer that contain sheets of material that are common to that in spirals. The feed spacer plate that is made of plastics contains channels moulded into it that lead the feed flow from the inlet of plate to the outlet (Figure 2-3). There are a lot of designs of plate and frame membranes that are established to enhance the performance of the membrane. One of the design is called the ‘Disk Tube’ module produced by RoChem RO Wasserbehandlung GmbH that consist of two sheets of membrane that are welded back to back to form an octagonal cushion that contains permeate space sheet in it. The advantages of plate and frame membranes are that they provide large membrane area per unit volume and they can be permeate by extracted out by gravity flow. When gravity flow is applied, energy will be saved in operating as the effluent pumps are saved. Besides, this type of membranes are mechanically easy for clean-up but also considered as more time consuming for cleaning compared to tubular systems. However, in term of operating cost they are much lower than tubular systems. (Scott & Hughes, 1996; Bodik, 2009; Ramakrishna et al, 2011)

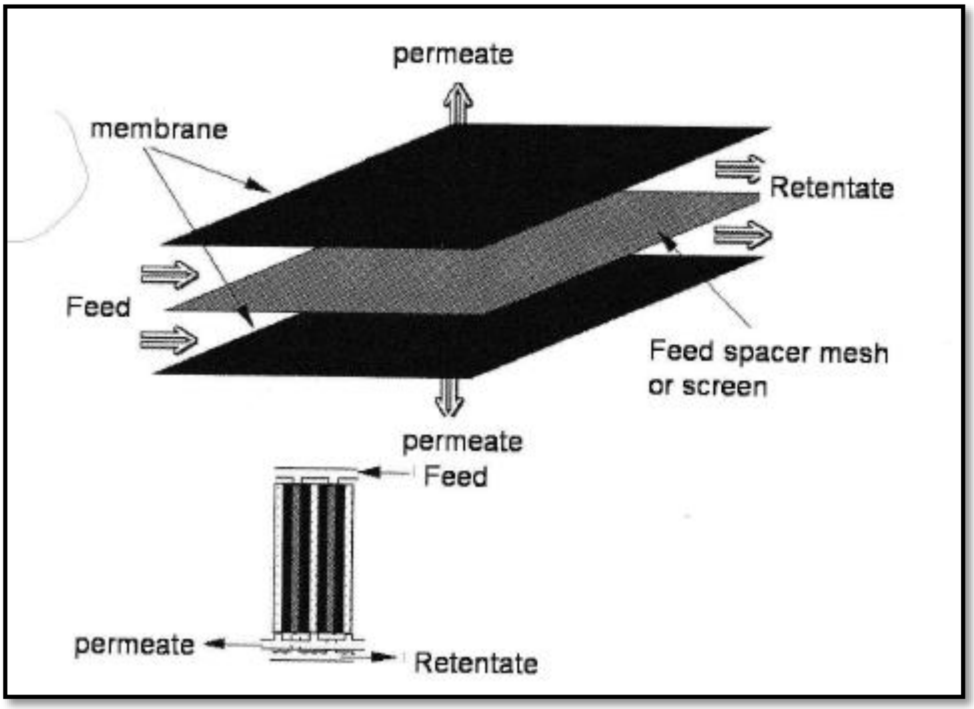

Figure 2-3: Plate-and-frame membrane module (Ramakrishna, 2011)

2.3.3 Spiral-Wound

This type of membrane module is the most inexpensive design of membrane used recently. Based on its principle, spiral-wound membrane is a plate-and-frame system that has been rolled up as shown in figure 2-4. The permeate spacer is in the middle between two membranes and a membrane envelope is formed from the glued edges. The permeate is forced towards the centre of the tube through the permeate channel and flows out from the centre tube. In these type of modules, the surface area are very large and have low operating costs (Ramakrishna et al, 2011).

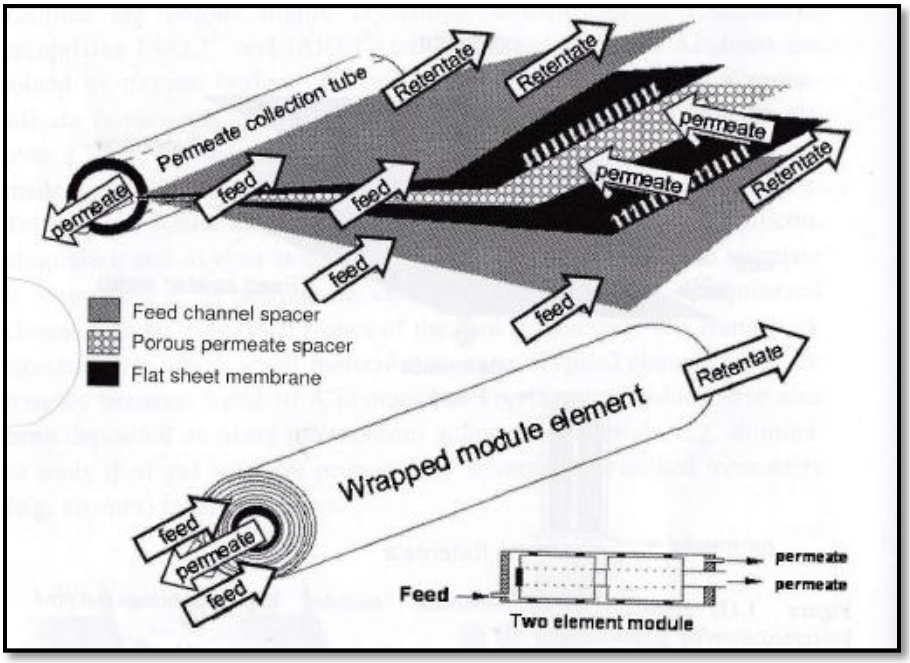

Figure 2-4: Spiral-wound membrane module (Ramakrishna, 2011)

2.3.4 Tubular Membrane

As shown in figure 2-5, the membranes are placed inside porous stainless steel or fibreglass reinforced plastic tube and supported by an outer tube with outlet ports for the filtrate. The feed flows inside the membrane tube while the permeate will flows across the membrane tube from the inside to the outside of the membrane. These type of membranes are easy for maintenance but high in operating cost and small surface area (Ramakrishna, 2011).

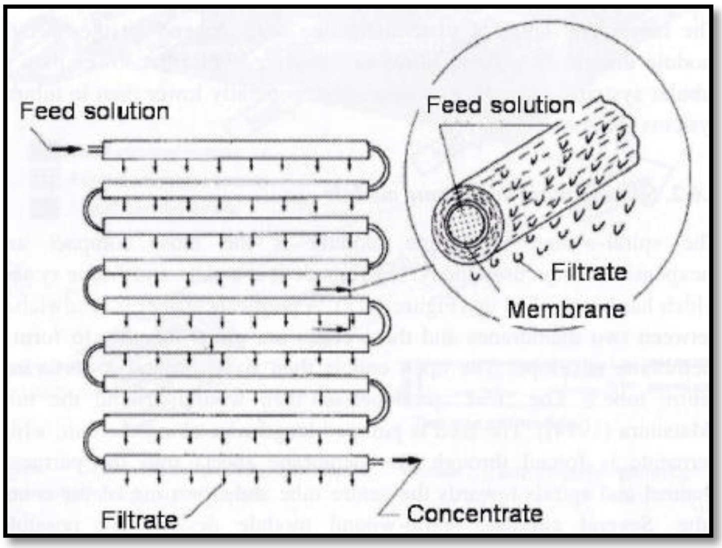

Figure 2-5: Tubular membrane module (Ramakrishna, 2011)

2.4 Membrane Separation Processes

The membrane separation processes are summarized in Table 2-1 and characterized based on membrane type, driving force and its application.

Table 2-1: Membrane separations (Scott & Hughes, 1996).

Membrane separation	Membrane type	Driving force	Applications
Microfiltration	Symmetric microporous	Hydrostatic pressure	Clarification, sterile filtration
Ultrafiltration	Asymmetric microporous	Hydrostatic pressure	Separation of macromolecular solutions
Nanofiltration	Asymmetric microporous	Hydrostatic pressure	Separation of small organic compounds and selected salts from solutions
Reverse Osmosis	Asymmetric, composite with homogenous skin	Hydrostatic pressure	Separation of microsolutes and salts from solutions
Gas permeation	Asymmetric or composite, homogenous or porous polymer	Hydrostatic pressure, concentration gradient	Separation of gas mixture
Dialysis	Symmetric microporous	Concentration gradient	Separation of microsolutes and salts from macromolecular solutions
Pervaporation	Asymmetric, composite	Concentration gradient, vapour pressure	Separation of mixtures of volatiles liquids
Vapor permeation	Composite	Concentration gradient	Separation of volatile vapours and gases
Membrane distillation	Microporous	Temperature	Separation of water from non-volatile solutes
Electrodialysis	Ion-exchange, homogenous or microporous polymer	Electrical potential	Separation of ions from water and non-ionic solutes
Electro-osmosis	Microporous changed membrane	Electrical potential	Dewatering of solutions of suspended solids
Electrophoresis	Microfiltration membranes	Electrical potential, hydrostatic pressure	Separation of water and ions from colloidal solutions
Liquid membrane	Microporous, liquid carrier	Concentration, reaction	Separation of ions and solutes from aqueous solutions

The first type of separation classification shows that separation is directly proportional to the transport rate of species inside the membranes where these membranes are usually in the form of composites of homogeneous film on a microporous support such as used in reverse osmosis and pervaporation to separate or remove water from concentrate solutions of ionic or organic solutes. Gas permeation is another type of classification that uses homogenous membranes to separate species in terms of diffusivity and concentration inside the membranes. The last classification of membranes is based on the electrical charge. The separation occur by the exclusion of ions that have same charges carried by the membrane either positive or negative charges (Scott & Hughes, 1996). Some of the membrane processes are explained in detailed below.

2.4.1 Reverse Osmosis

Reverse osmosis (RO) is widely known as the technology for desalination. More than 15 000 desalination plants in the world use this process. This process is very economical in producing portable water from saline water. The advantages of this process is that it has high permeation flux, easy to operate, minimal chemical addition and low requirement for energy (Zhao et al, 2014).

2.4.2 Pervaporation

Pervaporation (PV) is suitable for processing wastewater from the industrial that contain volatile organic compound (VOC). PV is the best technology for the removal of volatile organics. This process is an energy efficient process compared to distillation as it requires less heat requirements. For the case of hydrophobic pervaporation for the removal of VOC from water, the hydrophobic side of the membrane is bought to contact with the liquid stream that contain VOC and vacuum gas is applied on the other side as shown in figure 2-5. The membrane will sorbed the components of the liquid and permeate will evaporate to the permeate side (Kujawa et al, 2014).

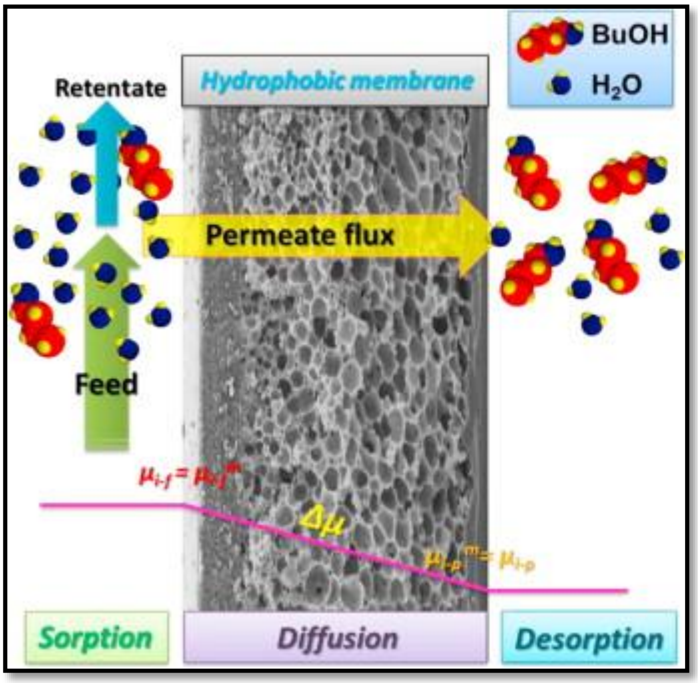

Figure 2-6 : The mechanism of mass transfer and separation through the membrane in a pervaporation process (Kujawa et al, 2014).

2.4.3 Gas Permeation

Gas permeation (GP) is one of the main approaches of membrane system for carbon dioxide recovery (Luis et al, 2008). GP means that membranes are used to separate gas mixture without changing phase. These have made the gas permeation competitive compared to other well developed gas separation process like cryogenic distillation, pressure swing adsorption and liquid absorption (Abedini&Nezhadmoghadam, 2010; Naylor, 1996). Gas separation is based on two factors which are permeability and selectivity. However, for the gases from vapours that have large differences in interaction, the permeability ratio will be large and a highly permeable material need to be used. The permeability is inversely proportional to the membrane thickness. Therefore, minimizing the membrane thickness will optimize the permeation properties. The driving force for this type of membrane will be pressure and the most suitable membrane structure is asymmetric membrane (Mulder, 1996).

2.5 Membrane Materials

2.5.1 Ceramic Membrane

Ceramic membranes are more tolerance to acid and alkali and also have long membrane life. The membranes are now applicable in the microfiltration and ultrafiltration format. Soon, this type of membrane is prove to be available in the coming years (Scott & Hughes, 1996).

2.5.2 Glass Membrane

The glass membranes usually in the form of hollow fibre with pore size of 10-90 nm. These membranes shows a clear reductions in products loss as they exhibit the resistance to adsorption (Scott & Hughes, 1996).

2.5.3 Steel Membrane

For steel membranes, they are made of sintered stainless steel and available in tubular formats. For this membrane, the pore size is large and suitable for aggressive environment and commonly used for high temperature membrane reactor applications (Scott & Hughes, 1996; Baker, 2004).

2.5.4 Polymer Membrane

There are various type of membrane used in the industry for gas separation. Polymeric membranes have been developed for various type of industrial applications including gas separation. The selectivity and permeability of the membrane's material effects the efficiency of the gas separation process. Polymeric membranes currently used by the industry due to their comparatively low in manufacturing cost and ability of processing into flat sheet or hollow fibre configuration and also well documented research studies. Polymers are considered as the most versatile group of materials for membrane synthesis. They meet certain requirements like mechanical, thermal, hydraulic, chemical stability and high biodegradability but the difference in physical and chemical properties have limit the use of these polymer in food, pharmaceutical and related industries. Table 2-2 shows some of the advantages and disadvantages of the commonly used polymer in the industry for the manufacturing of membranes and the summary