DEVELOPMENT OF PVDF MEMBRANE WITH PEG COATING FOR CO_2 AND CH_4 GAS SEPARATION

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DEVELOPMENT OF PVDF MEMBRANE WITH PEG COATING FOR CO2 AND CH4 GAS SEPARATION

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CHEMICAL ENGINEERING AND NATURAL RESOURCES

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Engineering Chemical (Gas Technology)

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STUDENT'S DECLARATION

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

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ABSTRACT

Thin film composite membranes were prepared for separation of carbon dioxide from methane using polyvinylidene fluoride (PVDF) as support and polyethylene glycol (PEG) as active layer at various concentrations. Permeance and the ideal selectivity were measured for all membranes under the feed pressure 1 and 2 bar. Influences of affecting parameters on membrane performance (permeances and selectivity) were investigated. For all coated membranes, the carbon dioxide permeance was higher compared to the methane permeances. The SEM study was carried out for investigation of membrane pore sizes. The membranes are coated with 2%, 4% and 6% PEG. For surface image of the membranes were identified by using scanning electron microscopy (SEM). The SEM images exhibited the best surface image with large pores was discovered at concentration 2% PEG. Membranes were also characterized using Fourier Transform Infrared Spectroscopy (FTIR) to detect the presence of PEG functional group in the membrane. The performance of the membrane was proven by conducting the gas permeation test. The selectivity of CO_2/CH_4 at 1 bar was 1.117 (2% PEG) and at 2 bar was 1.155 (6% PEG). Hence, coated membranes were discovered to affect the pore sizes which will consequently affect the permeability and selectivity of PVDF thin film composite membrane. As a conclusion, the increasing value of PEG coating concentration, the greater the feed pressure should be applied due to the resistance of membrane.

ABSTRAK

Membran komposit filem nipis telah disediakan untuk pemisahan karbon dioksida dari metana menggunakan fluorida polyvinylidene (PVDF) sebagai sokongan dan polietilena glikol (PEG) sebagai lapisan aktif pada pelbagai kepekatan. Permeance dan kepilihan yang ideal telah diukur bagi semua membran di bawah tekanan suapan 1 dan 2 bar. Pengaruh mempengaruhi parameter mengenai prestasi membran (permeances dan selektiviti) dengan telah disiasat. Bagi semua membran bersalut, permeance karbon dioksida adalah lebih tinggi berbanding permeances metana. Kajian SEM telah dijalankan untuk siasatan saiz liang membran. Membran disalut dengan 2%, 4% dan 6% PEG. Bagi imej permukaan membran telah dikenal pasti dengan menggunakan mikroskop imbasan elektron (SEM). Imej-imej SEM mempamerkan imej permukaan yang terbaik dengan liang roma yang besar telah ditemui di PEG kepekatan 2%. Membran telah juga dicirikan menggunakan Spektroskopi inframerah transformasi Fourier (FTIR) untuk mengesan kehadiran kumpulan PEG berfungsi dalam membran. Prestasi membran telah terbukti dengan menjalankan ujian penyerapan gas. Kepilihan CO2/CH4 pada 1 bar ialah 1,117 (2% PEG) dan pada 2 bar ialah 1,155 (6% PEG). Oleh itu, membran bersalut ditemui untuk menjejaskan saiz liang yang seterusnya akan menjejaskan kebolehtelapan dan selektiviti PVDF membran komposit filem nipis. Kesimpulannya, peningkatan nilai kepekatan salutan PEG, semakin besar tekanan suapan harus digunakan kerana rintangan membran.

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LIST OF ABBREVIATIONS

CO_2	-	Carbon Dioxide
PEG	-	Polyethylene Glycol
SEM	-	Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
RO	-	Reverse Osmosis
CH ₄	-	Methane
Р	-	Permeability
D	-	Diffusion Coefficient in Membrane
PVDF	-	Polyvinylidene Fluoride
Pi	-	Permeability for Gas component
Q	-	Gas Flowrate
А	-	Area
$\triangle P$	-	Pressure in System
Pj	-	Permeability of Another Gas Component
Pj	-	Permeability of Another Gas Component
α	-	Selectivity

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Various technologies exist that have been designed to remove CO_2 from natural gas and recovery CO_2 from landfill gas. Typically, raw natural gas contains 75–90% CH₄ and biogas contains 54–59% CH₄. Due to the high composition of contaminants these gases need to be treated. Separation of CO_2 becoming more important issues due to the most significant sources to pollution. So the upgrading CH₄ for use in the local gas distribution system is possible by applying a membrane system. Membrane processes have been proven to be technically and economically superior to the competing technologies in many industrial applications. This superiority is due to many advantages that membrane technology benefits from, including low capital investment, simplicity and ease of installation and operation, low maintenance requirements, low weight and space requirements, and high process flexibility.

1.2 PROBLEM STATEMENT

One of the most fundamental problems facing the earth today is global warming. The emissions of CO_2 , the most important greenhouse gas must be reduced. The burning of fossil fuels and biomass is the most significant source and also drilling from wellhead which come out with methane, CH_4 . In these cases, the similarities there are containing CO_2 and CH_4 .

Natural gas is the one that contributes major fuel for transportation after diesel. The composition of natural gas varies from one location to another and its quality highly depends on the concentration of the contaminants. After drilling from wellhead, the natural gas, CH_4 containing other contaminants which is the high acid gas CO_2 . CO_2 is corrosive and would normally require stainless steel equipment. Otherwise, the concentration of CO_2 must be minimizing to make sure the natural gas can be selling. To meet market requirements, this contaminant must comply with such concentration specifications as less than 2% CO_2 .

Available techniques for natural gas separation include membrane, absorption, adsorption, and cryogenic distillation. Among these separation technologies, research is directed towards high performance, efficient materials and processes to achieve cost effective CO_2 capture for the lowest energy penalty. Therefore it is important to develop a membrane can separate CO_2 and CH_4 efficiently.

1.3 OBJECTIVES

The aim of this study is to develop PVDF membrane with PEG coating for CO_2 and CH_4 gas separation. Hence, the objective is

- To produce Thin Film Composite (TFC) PEG-PVDF membrane.
- To investigate the effect of concentration of additives through permeability of PVDF membrane for CO₂ /CH₄ gas separation.

1.4 SCOPE OF RESEARCH

Based on the objective, the scopes of study are highlighted as follows:

- Study the preparation of PVDF-PEG membrane using dip coating method.
- Study the significant permeability of CO₂ and CH₄ through PVDF-PEG membrane.

1.5 RATIONALE AND SIGNIFICANCE

The purpose of this study is to develop a coated membrane that will result separating CO_2 and CH_4 efficiently. The coating technique, on the other hand, increased the separation factor by plugging the large pores and defects of the selective layer using materials such as silicone rubber. Besides that the most important thing is the developed membrane must be high pressure resistance and high permeable to CO_2 . Then the cost of separation of CO_2 and CH_4 will be decreased by using this separation technology.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE GAS SEPARATION

Membranes for natural gas processing were first commercialized in the 1980s for CO_2 removal (Schell, 1989) and have been the dominant membrane gas separation process since then. There are also other processing stages in natural gas treatment that can utilize membranes, and these are also now being commercially deployed. In particular, the removal and recovery of heavier hydrocarbons from the raw gas, dehydration, as well as separation of nitrogen and other inert gases is possible (Zolandz, 2001). These processes are undertaken to produce natural gas at the necessary composition for consumption, as well as to recover valuable components. A good example of this is the recovery of heavier hydrocarbons, such as butane.

In all of these situations, polymeric membranes are the focus of commercialization because of their ease of manufacture (Zolandz, 2001). Other materials, such as inorganic

membranes, demonstrate high performance under research conditions but module fabrication is still too expensive to compete against current polymeric modules. However, it is worthwhile noting that only a small number of polymers of the many hundreds developed in the research laboratory have themselves reached their commercial potential. In 2002, only nine polymeric materials made up 90% of the total gas separation membrane market (Baker, 2002).

Polymeric membranes are generally non-porous and gas permeation is described by the solution diffusion mechanism. This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Hence, separation is not just dependent upon molecular size but also relies on the chemical interaction between the gases and the polymer. Polymeric membranes are further classified as rubbery or glassy dependent on the value of their glass transition temperature relative to ambient. Rubbery membranes selectivity is generally solubility based while glassy membrane selectivity is generally diffusion based.

Here, the application of polymeric membranes to natural gas processing is on membranes applied to carbon dioxide gas separation. The review covers available membrane materials, additives properties, their performance and limitations and processing strategies.

2.1.1 Historical

The gas separation properties of membranes have been realized for more than a century. The early documented reports root back to the works of Mitchell, Fick, and Graham of the mid-nineteenth century. In 1831, Mitchell measured the rates of escape of ten gases through natural rubber balloons (Mears, 1986). At approximately the same time, Fick developed his famous laws of diffusion by studying gas transport across a nitrocellulose membrane (Paul, 1994).

A few decades later in 1866, Thomas Graham observed the separation of gases using natural rubber via Knudsen diffusion (Stanly, 1986). In 1920, H. A. Daynes recognized the relation between time lag and diffusion coefficient by studying the nonsteady state transport behavior of gases through a membrane (Paul, 1994).

Despite many experimental works, the progress of membrane separation techniques was very slow in the early stages. The major problem with the early membranes was their insufficient selectivity and low fluxes. The first breakthrough came about with the introduction of asymmetric membranes by Loeb and Sourirajan (Loeb and Sourirajan, 1960). They successfully produced a membrane with a very thin dense layer and a relatively thick porous sub layer. The dense layer was responsible for the separation, while the porous sub layer provided mechanical strength to the selective layer with minimum resistance to the permeation of components.

2.1.2 Asymmetric membranes

Among various types of membranes suitable for gas separation, the asymmetric membranes have revealed themselves to be exceptionally effective (Wang Onley, 1991). An asymmetric membrane may be defined as an entity composed of an ultrathin dense skin over a thick porous structure of the same or different material. Asymmetric membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure. Figure 2.1 shows asymmetric membrane structure.



Figure 2.1: Asymmetric membrane structure

The surface layer and its substructure may be formed in a single operation or separately. The surface layer performs the separation and is the principal barrier to flow through the membrane. The open support layer provides mechanical strength.

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; therefore, the membrane should be as thin as possible. Conventional film fabrication technology limits manufacture of mechanically strong, defect-free films to about 20 μ m thickness. In composite membranes, the layers are usually made from different polymers. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by asymmetric membranes are so great that almost all commercial processes use such membranes.

2.1.3 Module of membrane

2.1.3.1 Flat-Sheet membrane

Flat-Sheet membrane form can be made in very thin selective membrane layers. This means the permeances of flat sheet membranes is high. Also, flat sheet membranes did not require more pretreatment of the feed to remove particulates, oil mist and other fouling components. For practical application in gas separation membranes, the selective layer is usually made as thin as possible to have as high a flux as possible.

Figure 2.2 shows the flat sheet membranes, porous membrane support plates, and spacers forming the feed flow channel are clamped together and stacked between two endplates and placed in housing. Its design has its origin in the conventional filter press-concept. Membrane, feed spacers, and product spacers are layered together between two end plates.



Figure 2.2: Early plate-and-frame design developed by Stern et al. for the separation of helium from natural gas.

The feed mixture is forced across the surface of the membrane. A portion passes through the membrane, enters the permeate channel, and makes its way to a central permeate collection manifold. Plate-and-frame units have been developed for some small-scale applications these units are expensive compared to the alternatives, and leaks through the gaskets required for each plate are a serious problem. Plate-and-frame modules are now only used in electrodialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration.

Figure 2.3 shows a plate and frame modules which is provides good flow control on both permeate and feed side of the membrane, but the large number of spacer plates and seals lead to high module costs. The feed solution is directed across each plate in series. Permeate enters the membrane envelope and is collected through the central permeate collection channel.



Figure 2.3: Schematic of a plate and frame module

The same basic spinning process is used for the preparation of hollow fiber membranes, which have an outer diameter of 50 to 100 μ m. In hollow fiber membranes, the selective layer is on the outside of the fibers, which are installed as a bundle of several thousand fibers in a half loop with the free ends potted with an epoxy resin in a pressure tube as indicated in Figure 2.4. The filtrate passes through the fiber walls and flows up the bore to the open end of the fibers at the epoxy head.



Figure 2.4: Schematic drawing of a hollow fiber module

The hollow fiber membrane 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. When operated with liquid solutions the modules do not tolerate any particals, macromolecules or other materials that may easily precipitated at the membrane surface. 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. Both applications require high operating pressures and low cost membranes which have a long useful life. In reverse osmosis, of sea water an extensive pretreatment of the sea water is required.

Hollow fiber membrane modules are formed in two basic geometries. The first is the shell-side feed design illustrated in Figure 2.4 and used, for example, by Monsanto in their hydrogen separation systems and by Du Pont in their reverse osmosis systems. In such a module, a loop or a closed bundle of fibers is contained in a pressure vessel. The system is pressurized from the shell side; permeate passes through the fiber wall and exits through the open fiber ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fiber wall must support considerable hydrostatic pressure, the fibers usually have small diameters and thick walls, typically 50µm internal diameter and 100 to 200µm outer diameter.

2.1.3.3 Spiral Wound membrane

In spiral-wound modules, two flat-sheet membranes are sealed together to form an envelope enclosing a separator in between. The separator prevents the two membranes from collapsing and provides mechanical strength, while exhibiting minimum resistance toward the flow of permeates. One or more of these envelopes are wound around a cylindrical collector.

The spiral-wound module is widely used today in reverse osmosis, ultrafiltration, and gas separation. Figure 2.5 shows a spiral-wound module installed in a multimodule pressure vessel. Typically four to six modules are installed in a single pressure vessel.



Figure 2.5: Schematic of a spiral-wound module installed in a multimodule pressure vessel.

In this configuration, feed flows outside the envelopes and permeate is collected inside and is removed through the central collector. The feed solution passes in axial direction through the feed channel across the membrane surface. The filtrate is moved along the permeate channel and is collected in a perforated tube in the center of the roll. 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 m². The main reason for the limitation of the surface area which can be installed in a module containing one single envelope is the pressure drop encountered by permeate moving down the permeate channel to the central collection tube. Because the channel in a practical unit is very narrow its length is limited to 2 to 5 m.

2.2 MECHANISM FOR GAS SEPARATION

Membranes act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate. Two characteristics dictate membrane performance, permeability; that is the flux of a specific gas through the membrane, and selectivity; the membrane's preference to pass one gas species and not another.

There are five possible mechanisms for membrane separation (Paul, 1994); Knudsen diffusion, molecular sieving, solution-diffusion separation, surface diffusion and capillary condensation. Molecular sieving and solution diffusion are the main mechanisms for nearly all gas separating membranes. Knudsen separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Figure 2.6 shows first three possible mechanisms for gas separation.



Figure 2.6: Schematic representation of three of the different possible mechanisms for membrane gas separation, Knudsen diffusion, molecular sieving and solution-diffusion

2.2.1 Knudsen Diffusion

Diffusing gas molecules then have more collisions with the pore walls than with other gas molecules. Gas permeation in this region is called Knudsen diffusion. At every collision with the pore walls, the gas molecules are momentarily adsorbed and then reflected in a random direction. Molecule–molecule collisions are rare, so each gas molecule moves independently of all others. Hence with gas mixtures in which the different species move at different average velocities, a separation is possible.

Knudsen diffusion membranes have been used to separate gas isotopes that are difficult to separate by other methods, for example tritium from hydrogen, $C_{12}H_4$ from $C_{14}H_4$ and most importantly $U_{235}F_6$ from $U_{238}F_6$. The membrane selectivity for

 $U_{235}F6/U_{238}F_6$ mixtures is only 1.0043, so hundreds of separation stages are required to produce a complete separation. Nevertheless, at the height of the Cold War, the US Atomic Energy Commission operated three plants fitted with microporous metal membranes that processed almost 20 000 tons/year of uranium.

For CO_2/N_2 and CO_2/H_2 separation, Knudsen diffusion predicts a selectivity of less than unity. Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules. In this case, the CO_2/N_2 , selectivity is greater than unity, as CO_2 has a smaller kinetic diameter than N_2 . Surface diffusion is the migration of adsorbed gases along the pore walls of porous membranes. (. Hwang, Kammermeyer, 1975)

2.2.2 Solution-Diffusion Mechanism

Second property of membranes is their ability to control the rate of permeation of different species. It is solution-diffusion model. Permeates dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. These permeates are separated because of the differences in the solubility of the materials in the membrane and the differences in the rates at which the materials diffuse through the membrane. The other model is the pore-flow model, in which permeates are transported by pressure-driven convective flow through tiny pores. Separation occurs because one of these permeate is excluded (filtered) from some of the pores in the membrane through which other permeates move.

Diffusion, the basis of the solution-diffusion model, is the process by which matter is transported from one part of a system to another by a concentration gradient. The individual molecules in the membrane medium are in constant random molecular motion, but in an isotropic medium, individual molecules have no preferred direction of motion. For membranes in which transport is best described by the solution-diffusion model and Fick's law, the free-volume elements (pores) in the membrane are tiny spaces between polymer chains caused by thermal motion of the polymer molecules. These volume elements appear and disappear on about the same timescale as the motions of the permeate traversing the membrane.

The solution-diffusion model applies to reverse osmosis, pervaporation and gas permeation in polymer films. At first glance these processes appear to be very different. Reverse osmosis uses a large pressure difference across the membrane to separate water from salt solutions. In pervaporation, the pressure difference across the membrane is small, and the process is driven by the vapor pressure difference between the feed liquid and the low partial pressure of the permeate vapor. Gas permeation involves transport of gases down a pressure or concentration gradient. However, all three processes involve diffusion of molecules in a dense polymer. The pressure, temperature, and composition of the fluids on either side of the membrane determine the concentration of the diffusing species at the membrane surface in equilibrium with the fluid. Once dissolved in the membrane, individual permeating molecules move by the same random process of molecular diffusion no matter whether the membrane is being used in reverse osmosis, pervaporation, or gas permeation. Often, similar membranes are used in very different processes. For example, cellulose acetate membranes were developed for desalination of water by reverse osmosis, but essentially identical membranes have been used in pervaporation to dehydrate alcohol and are widely used in gas permeation to separate carbon dioxide from natural gas. Similarly, silicone rubber membranes are too hydrophobic to be useful in reverse osmosis but are used to separate volatile organics from water by pervaporation and organic vapors from air in gas permeation.

2.2.3 Molecular Sieving

Finally, if the membrane pores are extremely small, of the order $5-20 \text{ A}^{\circ}$, then gases are separated by molecular sieving. Transport through this type of membrane is complex and includes both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores (surface diffusion). These very small-pore membranes have not been used on a large scale, but ceramic and ultra microporous glass membranes with extraordinarily high selectivity for similar molecules have been prepared in the laboratory.

2.3 DRIVING FORCES IN MEMBRANE GAS SEPARATION

The driving forces applied for the transport of the various components through the membrane are hydrostatic pressure differences and chemical or electrochemical potential gradients across the membrane which may be expressed in concentration differences, partial pressure differences or electrical potential differences between two solutions separated by a membrane. The efficiency of a separation in a given membrane process, however, is not only determined by the membrane properties, it also depends on the applied driving force or forces. In membrane separation processes components are generally concentrated in the so-called retentate and depleted in the permeances. Table 2.1 gives a summary of technically relevant membrane separation processes, the membrane type used in these processes, their operating principles, and their main areas of application.

separation process	membrane type used	applied driving force	mode of separation	applications
microfiltration	symmetric porous structure, pore radius 0.05-5 µm	hydrostatic pressure 0.5-4 bar	filtration (size exclusion)	water purification, sterilization
ultrafiltration	asymmetric porous structure,pore radius 2-10 nm	hydrostatic pressure 1-10 bar	filtration (size exclusion)	Separation & fractionation of molecular mixtures
diafiltration	asymmetric porous structure,pore radius 2-10 nm	hydrostatic pressure 1-10 bar	filtration & dialysation (size exclusion)	purification of molecular mixtures artificial kidney
reverse osmosis	asymmetric skin-type solution- diffusion structure	hydrostatic pressure 10-100 bar	solution- diffusion mechanism	sea & brackish water desalination
gas separation	homogeneous symmetric structure	vapor pressure gradient	solution- diffusion	oxygen/nitrogen separation
pervaporation	homogeneous symmetric structure	vapor pressure gradient	solution- diffusion	separation of azeotropic mixtures
vapor permeation	homogeneous symmetric structure	vapor pressure gradient	solution- diffusion	recovering of organic vapors from air
membrane distillation	symmetric porous hydrophobic	vapor pressure	diffusion	liquid/solid separation

Table 2.1: Technically relevant membrane separation processes, their operating principles,

 and their application

2.4 THIN FILM COMPOSITE MEMBRANE

A thin film composite reverse osmosis membrane can be defined as a multilayer membrane in which an ultrathin semipermeable membrane layer is deposited on a preformed, finely microporous support structure. This contrasts with asymmetric reverse osmosis membranes in which both the barrier layer and the porous substructure are formed in a single-step phase inversion process and are integrally bonded. Figure 2.7 contains a schematic diagram illustrating the concept of a thin film composite reverse osmosis membrane.



Figure 2.7: Schematic diagram concept of a thin film composite reverse osmosis membrane.

The term "thin film composite" has the connotation that the barrier layer is extremely thin, and hence quite fragile. Indeed, the barrier layer may be quite thin, varying to as low as 200 angstroms depending on the nature of the particular reverse osmosis membrane and its method of manufacture. But this does not necessarily result in fragility. Some of these membranes may be considerably more rugged and chemically resistant than the typical asymmetric cellulose acetate membrane in field service.

2.5 POLYMERIC MEMBRANE

The most desirable gas separation membrane materials should have high permeability and high perm selectivity as well as high mechanical and thermal stability. However, structural modifications which lead to increases in polymer permeability usually cause losses in perm selectivity and vice versa. This so-called `trade-off' relationship is well described in the literature (Stem, 1994).

The first carbon dioxide separating membranes were based on cellulose acetate and derivatives thereof, originally designed for reverse osmosis (Hwang, 1975). These polymeric membranes are characterized by a thin, dense selective surface 'skin' on a less dense porous support that is nonselective. This is the basis of all asymmetric membrane materials that are readily used in industry. However, the carbon dioxide flux of cellulose acetate based membranes decreases substantially with time, due to the material being susceptible to plasticization and compaction under feed stream conditions. Therefore, later polymeric membrane patents focus on more robust polymers that achieve greater selectivity and/or permeability. Improving the performance of the CO_2 selective polymeric membrane
through changes in polymeric composition, and increasing the diffusion of carbon dioxide by altering the polymer packing within the membrane. Diffusion is generally enhanced by increasing the volume of free space within the membrane and this can sometimes be achieved through the addition of bulk substituent groups (Powell, 2006). The polymer packing in glassy membranes and thus the free volume is also influenced by the casting method and annealing conditions. Therefore, along with the polymeric materials, casting methods have also been patented (Lee, 2003). The combination of these approaches has produced a wide range of polymeric membranes with reasonable permeability and selectivity to provide good carbon dioxide separation. Some patented polymeric membranes are based on polyamides, polysemicarbazides, polycarbonates, polyarylates, poly (phenyleneoxide), polyaniline and polypyrrolones. These all have reasonable permeability and selectivity, with some achieving performance around Robeson's upper bound. The difference between individual patents for each polymeric system is through the addition of bulky substituent and functional groups to the polymer, as well as cast history.

One of the most widely patented polymeric materials is polysulfone. They are regarded as among the most chemically and thermally durable thermoplastic polymers available; and polysulfone have been extensively applied to gas separation. More recently, polyimides based membranes have outperformed polysulfone, displaying some of the best permeability and selectivity properties for purely polymeric membranes. This coupled with their thermal, chemical and plasticization resilience, as well as considerable mechanical strength makes them an attractive material for gas separation membranes. The performance of these two polymers has resulted in a large number of patents. Differences between patents deal with substituent groups to change the carbon dioxide solubility, membrane packing density and free volume, as well as improving the membrane resistance to harsh environments.

More recent patents on purely polymeric membranes have focused on combining different polymers to produce composite polymeric membranes. The copolymers used generally have a glassy (hard) polymer segment and a rubbery (soft) polymer segment. The hard segment forms the structural frame and provides the mechanical support. The rubbery segment generally forms continuous micro domains within the membrane and the flexible nature of the structure allows the transportation of gas, hence greater permeability. The idea is to combine the selectivity of one polymer with the permeability of the other to provide a better performance membrane. Again, a considerable number of patents have been awarded for copolymer membranes, with the best performance based on blends of polyimide.

2.6 MEMBRANE PERMEATION

The membranes used for CO_2 removal do not operate as filters, where small molecules are separated from larger ones through a medium with pores. Instead, they operate on the principle of solution-diffusion through a nonporous membrane. The CO_2 first dissolves into the membrane and then diffuses through it. Because the membrane does not have pores, it does not separate on the basis of molecular size. Rather, it separates based on how well different compounds dissolve into the membrane and then diffuse through it.

Because carbon dioxide, hydrogen, helium, hydrogen sulfide, and water vapor, for example, permeate quickly, they are called "fast" gases. Carbon monoxide, nitrogen, methane, ethane and other hydrocarbons permeate less quickly and so are called "slow" gases. The membranes allow selective removal of fast gases from slow gases. For example, as CO_2 is removed from a natural gas stream, water and H_2S are removed at the same time; but methane, ethane, and higher hydrocarbons are removed at a much lower rate.

Fick's law, shown below, is widely used to approximate the solution-diffusion process:

$$J = \frac{k \times D \times \Delta \rho}{\ell}$$

J = the membrane flux of CO₂, that is, the molar flow of CO₂ through the membrane per unit area of membrane.

k = the solubility of CO₂ in the membrane.

D = the diffusion coefficient of CO₂ through the membrane.

 $\Delta \rho$ = the partial pressure difference of CO₂ between the feed (high pressure) and permeate (low pressure) side of the membrane.

 ℓ = the membrane thickness.

To simplify matters further, the solubility and diffusion coefficients are usually combined into a new variable called permeability (P). Fick's law can therefore be split into two portions: a membrane- dependent portion (P/ ℓ) and a process-dependent portion (Δ p). To achieve a high flux, the correct membrane material and the correct processing conditions are needed. P/ ℓ is not a constant; it is sensitive to a variety of operating conditions such as temperature and pressure.

The Fick's law equation can be equally written for methane or any other component in the stream. This set of equations leads to the definition of a second important variable called selectivity (\propto). Selectivity is the ratio of the permeability of CO₂ to other components in the stream and is a measure of how much better the membrane permeates CO₂ compared to the compound in question. For example, most CO₂ membranes provide a CO₂ to methane selectivity anywhere between 5 and 30, meaning that CO₂ permeates the membrane 5 to 30 times faster than methane.

Both permeability and selectivity are important considerations when selecting a membrane. The higher the permeability, the less membrane area is required for a given separation and therefore the lower the system cost.

Unfortunately, high CO_2 permeability does not correspond to high selectivity, though achieving this combination is a constant goal for membrane scientists. Instead, they have to settle for a highly selective or permeable membrane or somewhere in-between on both parameters. The usual choice is to use a highly selective material then make it as thin

as possible to increase the permeability. However, this reduced thickness makes the membrane extremely fragile and therefore unusable. For many years, membrane systems were not a viable process because the membrane thickness required to provide the necessary mechanical strength was so high that the permeability was minimal. An ingenious solution to this problem allowed membranes to break this limitation.

2.6.1 Permeate Pressure

The effect of permeate pressure is the opposite of the effect of feed pressure. The lower the permeate pressure, the higher the driving force and therefore the lower the membrane area requirement. Unlike feed pressure, however, permeate pressure has a strong effect on hydrocarbon losses. Figure 2.8 shows the effect of permeate pressure on hydrocarbon losses.



Figure 2.8: Effect of Permeate Pressure on hydrocarbon losses

The pressure difference across the membrane is not the only consideration. Detailed analysis shows that an equally important factor in system design is the pressure ratio across the membrane. This ratio is strongly affected by the permeate pressure. For example, a feed pressure of 90 bar and a permeate pressure of 3 bar produce a pressure ratio of 30. Decreasing the permeate pressure to 1 bar increases the pressure ratio to 90 and has a dramatic effect on system performance.

For this reason, membrane design engineers try to achieve the lowest-possible permeate pressure. This need is an important consideration in deciding how to further process the permeate stream. For example, if it must be flared, then flare design must be optimized for low pressure drop. If the permeate gas is to be compressed, for example, to feed it to a second membrane stage or reinjection it into a well, the increased compressor power and size at low permeate pressures must be balanced against the reduced membrane area requirements.

2.7 PEG ADDITIVES

Polyethylene glycol (PEG) is one of the additives used to promote pore formation in the polymeric membranes. PEG is a linear polyether compound available in a variety of molecular weight, which is indicated by a numeric suffix, followed the abbreviation (PEG). Its general formula is expressed as H(OCH₂CH₂)nOH, where n is the average number of repeating oxyethylene groups. PEG is water-soluble. It is also soluble in many organic solvents including aromatic hydrocarbons. Thus PEG has been reported as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic membrane preparation. For instance, Arthanareeswaran et al. observed that the ultrafiltration membrane made from cellulose acetate (CA) and silica (SiO₂) blended solution containing PEG-600 (the molecular weight of PEG is 600 Da) possessed a high

average pore size and porosity; the membrane made of polysulfone (PSf) blended with sulfonated poly(ether ketone) (SPEEK) showed improved pure water flux with the addition of PEG-600 in the dope solution, PVDF-HFP flat-sheet membranes presented higher pure water permeation flux and higher permeate flux in the direct contact membrane distillation when the PEG concentration in the polymer solution was increased, the addition of PEG-600 in the PVDF dope solution resulted in increases of the inner and surface porosities of final hollow fiber membranes. PEG-600 is a commonly used additive. Other types of PEG with different molecular weights are also used for membrane formation. Examples include PEG-6000 as an additive for preparing PVDF-HFP hollow fibers used in membrane distillation by García-Payo et al. Xu and Xu prepared polyvinyl chloride (PVC) hollow fiber ultrafiltration membranes using PEG with different molecular weights of PEG-600, PEG-800 and PEG-1000 as additives. Their results showed that membrane porosity and permeation flux increased with increasing PEG molecular weight, but protein rejections and mechanical strength decreased. When the molecular weight of PEG additive increased from 600 to 2000 and 6000 Da, pure water flux of resultant polysulfone (PSf) membranes increased and solute rejection decreased.

Moreover, with an increase in the ratio of PEG-600 additive to NMP, water flux increased and solute rejection decreased. Chakrabarty et al. also studied the effect of PEG molecular weight on polysulfone flat-sheet membrane. They used PEG-400, PEG-6000 and PEG-20000 as additives. It was found that the porosity remained almost unchanged when the PEG molecular weight increased from 400 to 6000 Da while it increased significantly with increasing PEG molecular weight from 6000 to 20,000 Da.

The poor miscibility of the casting solution with water due to the addition of PEG-20000 was attributed to this result. From the above, it can be seen that there are many works involving PEG as an additive for various membrane preparation via nonsolvent-induced phase separation (NIPS), and PEG with different molecular weights might present different impacts on membrane structure.

However, no systematic report was found with respect to the behavior of PEG additives during the formation of PVDF-HFP hollow fibers. From the polymer chemistry point of view, the interaction of PEG additive with a polymer solution depends on not only the polymer and solvent, but also PEG molecular weight and concentration, which may couple with the condition of phase inversion to affect the thermodynamics and kinetics of membrane formation process, resulting in different structures and performances of final membranes.

2.8 CARBON DIOXIDE REMOVAL MEMBRANE

Carbon dioxide membranes operate on the principle of selective permeation. Each gas component has a specific permeation rate. The rate of permeation is determined by the rate which a component dissolves into the membrane surface and the rate at which it diffuses through the membrane.

The components with higher permeation rates (such as CO_2 , H_2 , and H_2S) will permeate faster through the membrane module than components with lower permeation rates (such as N_2 , C_1 , C_2 and heavier hydrocarbons). For example, carbon dioxide is a "fast," more permeable, gas than methane. When a stream consisting of these two gases contacts the membrane, the carbon dioxide will permeate through the fiber at a faster rate than the methane. Thus, the feed stream is separated into a methane-rich (residual) stream on the exterior of the membrane fiber and a carbon dioxide-rich (permeate) stream on the interior of the membrane fiber.

The primary driving force of the separation is the differential partial pressure of the permeating component. Therefore, the pressure difference between the feed gas and permeate gas and the concentration of the permeating component determine the product purity and the amount of carbon dioxide membrane surface required.

2.9 GAS CARBON DIOXIDE METHANE SEPARATION APPLICATIONS

In recent years, membrane technology has impacted the market by its many advantages over amine processes, including:

- Smaller and lighter systems, especially for offshore platforms.
- Simultaneous removal of carbon dioxide, hydrogen sulfide, and water vapor.
- Small or no need for human supervision and maintenance.
- Reduced energy consumption.
- No fire or explosion hazards.
- Lower capital and operating costs.
- Ability to treat gas at the wellhead. The high gas pressure at the wellhead is ideal for membrane processes

2.9.1 Removal of Acid Gases

Carbon dioxide can be found in natural gas in various concentrations, typically between 7 and 40%. In case of enhanced oil recovery this concentration can rise up to 80%. Removal of carbon dioxide to less than 2% is essential for reducing the risk of pipeline corrosion. Most commercial membranes offer a separation factor of 20 or higher for CO_2 over methane. However, a number of

laboratory-scale experiments report significantly higher separation factors, which are indicative of a great potential for improving the CO_2 removal membranes.

Table 2.2 compares the separation factor of some membranes toward carbon dioxide over methane found in laboratory-scale experiments. Membrane modules are of hollow fiber or spiral wound designs. CO_2 preferentially concentrates in the permeate side, leaving the methane-rich residue at approximately the same pressure as the feed.

Table 2.2: Separation Factor of Selected Membranes toward Carbon Dioxide over

 Methane

Polymer	Separation factor		
Polyimide	67		
Polyimide	50		
Polycarbonate	30		
Polyimide (film)	50-70		
Polyethersulfone	50 32.3		
Radel A PSF			
Polyaniline	336		
Ultem (polyetherimide)	45		
Polyimide	70		

Cook and Losin (Cook, 1995) reported the installation of a membrane system to treat 30 MMscfd of natural gas containing 11% carbon dioxide. They compared a membrane system with an amine/glycol system and concluded that the total operating costs for both systems were the same at 0.13 MMscf. They also recognized the advantages of the membrane system such as flexibility for expansion and turndown, and space savings. Because CO₂ removal membranes are also

selective to hydrogen sulfide, there is no need for an additional membrane stage to separate the latter gas.

Hydrogen sulfide is both corrosive and toxic, and it would be advantageous to remove it at the wellhead. Commercial membranes such as cellulose acetate show relative selectivity of around 50 for H₂S with respect to methane, and with respect to carbon dioxide. Membrane units can reduce the H₂S content of natural gas to around 100 ppm. Final polishing can then be achieved with a zinc oxide bed. Because of the toxicity of hydrogen sulfide the concentrated gas must be treated before releasing it into the atmosphere. In a study conducted by Alexander and Winnick (Alexander, 1994), a novel membrane system is introduced for removal of hydrogen sulfide from natural gas, and recovery of elemental sulfide and hydrogen, using an electrochemical membrane separator.

In an economic comparison with available technologies they showed that the treating cost for 1000 m³ of feed is \$5.38 for the membrane system versus \$9.25 for the conventional technology. While membranes are good for bulk removal of acid gases, they are inferior to, or must be combined with, other processes when the acid gases are present at low concentration. That is because, at small concentrations, the partial pressure of acid gases, and therefore the driving force of the process, decreases. A number of membrane hybrid systems have received attention in the literature for acid gas removal from natural gas. The membrane/potassium carbonate system at the SACROC installation discussed earlier is an example of such hybrids (Parro, 1984). PRISM, from Permea, has also been combined with traditional amine and cryogenic processing units (BackHouse, 1986). Baldus and Tillmann (Baldus, 1991) also show that a membrane/cryogenic hybrid with a membrane separation factor of 20 is advantageous over a membrane alone system. They show that a membrane system alone is economical and efficient if the separation factor of the membrane is 50 or greater.

2.9.2 Enhanced Oil Recovery (EOR)

In addition to natural gas treatment, membranes have found a variety of applications in enhanced oil recovery. In EOR, CO₂ is injected into an oil-bearing reservoir at high pressure. The carbon dioxide dissolves the oil and carries it to the production well. The produced gas contains CO_2 , CH_4 , and other hydrocarbons. It is desired to recover both the natural gas and carbon dioxide contents of this stream. The volume of produced gas and it CO_2 content increasing with time, making it a difficult application for conventional amine processes. The modularity of membranes allows for capacity expansion as needed, flexibility not available with other technologies. In a typical application of membrane systems to enhanced oil recovery, the carbon dioxide concentration in the product is reduced from 70 to 10%. Permeate is then enriched in CO₂ to around 95%. A membrane/DEA hybrid is a well-established design for enhanced oil recovery applications at optimum cost. In this design a membrane is used to remove the bulk of the carbon dioxide before feeding the stream into a conventional DEA system for final polishing. According to a study conducted by Ryan (Ryan, 1988), a combination of these two processes is more economical than each process alone. Presently, membranes and membrane hybrids are showing significant growth and attract more attention in both natural gas and enhanced oil recovery applications. In addition, removal of carbon dioxide from Natural Gas Liquid using membranes resulted in commercial adoption of this process. All of the above applications have proven to be economically more justifiable than competing techniques.

2.9.3 Carbon Dioxide Recovery from Landfill Gas

Landfill gas is produced at atmospheric pressures from the decomposition of organic materials under anaerobic conditions. This biogas contains 40–45% CO₂, 54–59% CH₄, 4% nitrogen, 1% oxygen, 1% water vapor, and traces of hydrogen sulfide and halogenated hydrocarbon (CFC). This biogas can be recovered for potential use when the landfill is covered. The upgrading of CH₄ for use in the local gas distribution system is possible by applying a membrane system. For this application, the toxic trace gases of H₂S and CFC are removed first by an adsorption process. The remaining gas stream is fed to a membrane system and is often compressed to higher pressure, up to 500 psig, to enhance membrane efficiency.

2.10 ADVANTAGES OF MEMBRANE PROCESSES

Membrane systems have major advantages over more traditional methods of CO₂ removal:

• Lower capital cost: Membrane systems are skid mounted, except for the larger pretreatment vessels, and so the scope, cost, and time taken for site preparation are minimal. Therefore, installation costs are significantly lower than alternative technologies, especially for remote areas. Furthermore, membrane units do not require the additional facilities, such as solvent storage and water treatment, needed by other processes.

- Lower operating costs: The only major operating cost for single-stage membrane systems is membrane replacement. This cost is significantly lower than the solvent replacement and energy costs associated with traditional technologies. The improvements in membrane and pretreatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors are usually comparable to those for traditional technologies.
- **Deferred capital investment**: Often, contracted sales-gas flow rates increase over time, as more wells are brought on-line. With traditional technologies, the system design needs to take this later production into account immediately, and so the majority of the equipment is installed before it is even needed. The modular nature of membrane systems means that only the membranes that are needed at start-up need be installed. The rest can be added, either into existing tubes or in new skids, only when they are required.
- Operational simplicity and high reliability: Because single-stage membrane systems have no moving parts, they have almost no unscheduled downtime and are extremely simple to operate. They can operate unattended for long periods, provided that external upsets, such as well shutdowns, do not occur. Items in the pretreatment system that could cause downtime, such as filter coalesces are usually spared so that production can continue while the item is under maintenance. The addition of a recycle compressor adds some complexity to the system but still much less than with a solvent or adsorbent-based technology. Multistage systems can be operated at full capacity as single-stage systems when the recycle compressor is down, although hydrocarbon losses will increase. The start-up, operation, and shutdown of a complex multistage membrane system can be automated so that all important functions are initiated from a control room with minimal staffing.

- **Power generation**: The permeate gas from membrane systems can be used to provide fuel gas for power generation, either for a recycle compressor or other equipment.
- Environmentally friendly: Membrane systems do not involve the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or reinjected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated.

CHAPTER 3

METHODOLOGY

3.1 MATERIAL

3.1.1 Polyethylene glycol

Polyethylene glycol was chose to be a polymer due to it characteristics which were tough and rigid resin same to conventional engineering plastics such as polycarbonate at room temperature. Polyethylene glycol has better high temperature properties compare to conventional engineering plastics. It remains in satisfactory condition in long term continuous use without having any dimensional change or physical deterioration at temperature as high as 200 °C. Polyethylene glycol has glass transition temperature which is at 140°C. Molecular weight of repeat unit for Polyethylene glycol is 2000 g/mol.

3.1.2 Methanol (CH₃OH)

In this research, methanol was used as solvent due to the high solvent power for PEG. Table 3.1 is shown properties for methanol.

Properties		
Component	Methanol	
Molecular Weight	32.04 g/mol	
Boiling Point	64.7°C	
Melting Point	-98°C	
Density	0.791 g/mL	

Table 3.1: Properties of coagulation medium

3.1.3 Polyvinylidene Fluoride Microfiltration membrane

PVDF hydrophobic microfiltration membranes with reported nominal pore sizes of 0.01 μm purchased from Millipore were used in the studies reported here.

3.2 RESEARCH DESIGN



Figure 3.1: Research Design

3.3 PREPARE COMMERCIAL MEMBRANE

3.4 MEMBRANE COATING

The objective of coating the membrane was to prepare defect free high performance membranes (Ismail et al., 2011). Membrane coating was filled the pinholes on the membrane outer dense skin layer. The membrane was coated by using coating agent which is polyethylene glycol (PEG). Coating solution was prepared by dissolve 2% PEG in 98% methanol, 4% PEG in 96% methanol and 6% PEG in 94% methanol. Then the coating membrane was placed in an oven at temperature 40°C- 60°C for 60 minutes.

3.5 GAS PERMEATION TEST

Gas permeation system was used to measure pure gas permeation rate of membrane. The test was carried out at the ambient temperature which is about 25 °C. The permeate side was open to atmosphere. The gas permeation rate was measured by using a soap bubble flow meter. Figure 3.3 shows gas permeation unit.



Figure 3.3: Gas Permeation Unit

The permeation rate can be calculated by using:

$$Pi = Q/A.\Delta P = Pi/l$$

Where:

Q= Gas Flowrate (cm³/s)

 $A = Area (cm^2)$

 ΔP = Pressure in System (cm Hg)

Pi = Permeability for Gas Component (cm³/s.cm².cm Hg)

 $1 \text{ GPU} = 1 \text{x} 10\text{-}6 \text{ cm}^3\text{/s.cm}^2\text{.cm Hg}$

The selectivity can be calculated by using:

Selectivity,
$$\alpha = Pi/Pj$$

Where:

- Pi = Permeability of one gas component
- Pj =Permeability of another gas component

3.6 MEMBRANE CHARACTERIZATION

3.6.1 Scanning Electron Microscopic (SEM)

Scanning Electron Microscopic (SEM) was used to study the membrane morphology. The model that was used is Philips SEM Model XL-40. The membrane was cut into small pieces, then immerse in liquid nitrogen. The membrane was coated with a thin gold layer under vacuum. Lastly SEM was analyzing the surface morphology of the membrane. Figure 3.2 shows SEM unit.



Figure 3.2: Scanning Electron Microscopic (SEM)

3.6.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out on each of composite membrane fabricated. Through this analysis, infrared spectrum measurement based on the transmission band changes of functional groups in membrane was used to identify (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. The FTIR results can display changes of the functional groups and elements in the membranes when they are heated from room temperature to high temperature, which is up to 250°C. With modern software algorithms, infrared is an excellent tool for quantitative analysis. Therefore, this analysis was primarily used to identify the quality or consistency of a sample.

CHAPTER 4

RESULT & DISCUSSIONS

4.1 Effect of Coating on the Structure of Membrane

Coating for thin film composite membrane usually is for improving the performance of membrane so as to get desired membrane performance. In this research, for coating the membrane, Polyethylene Glycol 200 was used with differently of concentration. The solvents physical properties are tabulated in Table 4.1.

Table 4.1: Physical Properties of Polyethylene Glycol

Physical Properties	Polyethylene Glycol
Boiling Point	260°C
Melting Point	-65°C

The SEM images of membrane surface of the prepared membranes are depicted in Figure 4.1 to 4.4. The images clearly demonstrate the differences of surface image for the membranes.



Figure 4.1: Structure of TFC membrane of PVDF without % PEG Magnification 150X



Figure 4.2: Structure of TFC membrane of PVDF with 2% PEG at Magnification 350X



Figure 4.3: Structure of TFC membrane of PVDF with 4% PEG at Magnification 350X



Figure 4.4: Structure of TFC membrane of PVDF with 6% PEG at Magnification 350X

Figure 4.2 displays the best structure as compared to Figure 4.1, Figure 4.3 and Figure 4.4. The large pores size is the most important criteria for causing a good separation. From observation, the membrane structure with coating 2% PEG has pore sizes between 558.2 nm to $1.1 \mu m$.

The prepared membranes were examined with scanning electron microscope. The membranes were cut into pieces of various sizes. These pieces were immersed in liquid nitrogen for 20–30 s and were frozen. Frozen segments of the membranes were broken. The samples were gold sputtered for producing electric conductivity. The micrographs were obtained at 10 kV.

4.2 Effect of Coating on the Membrane Performance

In this study, the performance of the membrane produced is evaluated by conducting gas permeation test. The permeation rate can be calculated by using:

$$P_i = Q/A.\Delta P = P_i/l$$

Where:

Q = Gas Flow rate (cm³/s)

 $A = Area (cm^2)$

 ΔP = Pressure in System (cm Hg)

Pi = Permeability for Gas Component (cm³/s.cm².cm Hg)

1 GPU = 1×10^{-6} cm³/s.cm².cm Hg (The calculated permeability should be converted in GPU unit).

The selectivity can be calculated by using:

Selectivity, $\alpha = P_i / P_j$

Where:

 P_i = Permeability of one gas component

P_i=Permeability of another gas component

The permeation test was performed using a permeation unit with an effective permeation area of 24.63cm². To elucidate the membrane performance, they were tested with CH₄ and CO₂ under the applied pressures of 1 and 2 bar. The permeance results are presented in Figure 4.5 (for applied pressure 1 bar) and Figure 4.6 (for applied pressure 2 bar) membranes. Table 4.1 exhibits the selectivity of the prepared membranes.

PEG Concentrations	Pressure (bar)	Permeability		Selectivity,
		CH ₄	CO ₂	α (CO ₂ /CH ₄)
0%	1	1388.0	1546.6	1.114
	2	1640.3	1866.6	1.138
2%	1	1424.8	1592.1	1.117
	2	1546.6	1746.4	1.129
4%	1	1288.9	1413.5	1.097
	2	1503.9	1655.4	1.100
6%	1	1353.4	1503.9	1.111
	2	1546.6	1786.4	1.155

Table 4.1: Tabulated Calculation Result of Permeability and Selectivity of Membrane

 $GPU= 1 \times 10^{-6} \text{ cm}^2 (\text{STP}) / (\text{cm}^2.\text{s.cmHg})$

The gas separation performance is determined by plotting the permeances of CO_2 , CH_4 and CO_2/CH_4 selectivity against the PEG concentrations.



Figure 4.5: Graph of CO₂/CH₄ Permeability versus PEG Concentration



Figure 4.6: Graph of CO₂/CH₄ Permeability versus PEG Concentration

According to Figure 4.5 and 4.6, CO_2 and CH_4 permeances values increase at 2% PEG concentration and decrease at 4% PEG concentration. Here, CO_2 is the fast gas component, permeating at a greater rate through the membrane and becoming enriched in permeate (or downstream) due to the graph plotted CO_2 higher than CH_4 permeances value therefore CH_4 becomes enriched in the residue (or retentate) stream.

The results for PVDF membrane with 2% PEG are interesting. The permeances are very close and therefore the selectivity is low. However the selectivity of this membrane was higher at 2% PEG at 1 bar and at 6% PEG at 2 bars. In other words this membrane is more permeable to carbon dioxide than to nitrogen for these two different pressures. This behavior may be explained on the basis of membrane surface morphology.



Figure 4.7: Graph of Selectivity CO₂/CH₄ versus PEG Concentration

Figure 4.7, selectivity CO_2 increase with the increasing of applied pressure. The produced membrane shows coating with PEG provide surface resistance towards the

pressure. The polymer concentration is a significant parameter for tailoring a membrane in terms of its structure and separation properties. Four sets of membranes with 2%, 4% and 6% PEG as coating layer and PVDF as coating layer were prepared. The lower concentration of the coating polymer leads to the formation of wider pores. This is due to the compactness of the support for highly concentrated polymer. The lower concentration results in less tight membrane. The membrane performance is in agreement with the membrane morphology. The selectivity are in an acceptable range (Figure 4.7). The permeances are higher for less concentrated membrane with larges voids (Figure 4.5). In summary the results indicate that the support concentration play a major role in membrane performance.

4.3 Effect of Coating on the FTIR Analysis of Membrane

FT-IR stands for Fourier Transform Infra-Red, 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 fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. During FTIR analysis a spot on the membrane is subjected to a modulated infrared (IR) beam. The membrane's transmittance and reflectance of the infrared rays at different frequencies is translated into an infrared (IR) absorption plot consisting of reverse peaks. Those four figures are comparison of FTIR analysis for asymmetric thin film composite membrane that produced using different coating concentrations. Figure 4.7 shows the FTIR Transmittance Peak with 2% PEG, Figure 4.9 shows the FTIR Transmittance Peak with 4% PEG and Figure 4.10 shows the FTIR Transmittance Peak with 6% PEG.



Figure 4.8: FTIR Transmittance Peak without % PEG.



Figure 4.9: FTIR Transmittance Peak with 2% PEG.



Figure 4.10: FTIR Transmittance Peak with 4% PEG.



Figure 4.11: FTIR Transmittance Peak with 6% PEG.

CHAPTER 5

CONCLUSIONS & RECOMMENDATINS

5.1 Conclusion

The effect of PEG concentration on CO_2 and CH_4 permeability and selectivity of PVDF membrane were investigated in detail. The selectivity of CO_2/CH_4 improved remarkably while their permeability decreased. At 1 bar, selectivity of CO_2 was higher with coated 2% PEG and for 2 bar applied pressure; the selectivity was higher coated with 6% PEG. The results suggested the addition of PEG with different concentration could change the PVDF structure and properties. When PEG concentration increased from 2% to 6%, the CO_2 selectivity not increases constantly because the feed pressure was a leading factor.

5.2 Recommendation

Based on the study conducted, some recommendations are given for future work. Polyvinylidene Fluoride membrane should be coated with variety of PEG molecular weight and gas permeation testing need to be test with a large range of feed pressure to know the best concentration which will give good permeability and high selectivity of CO_2 . Further study will focus on enhancing permeances without loss of selectivity.

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