PERMEABILITY AND SELECTIVITY STUDY OF NATURAL GAS WITH CO₂, N₂, AND O₂ USING POLYACRYLONITRILE (PAN) MEMBRANE

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PERMEABILITY AND SELECTIVITY STUDY OF NATURAL GAS WITH CO₂, N₂, AND O₂ USING POLYACRYLONITRILE (PAN) MEMBRANE

MAHATHIR KADDIR

A thesis submitted in fulfillment for the award of the Degree of Bachelor in Chemical Engineering (Gas Technology)

> Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang

> > **APRIL 2009**

DECLARATION

I declare that this thesis entitled "Permeability and Selectivity Study of Natural Gas with CO_2 , N_2 , and O_2 using Polyacrylonitrile (PAN) Membrane" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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| Date | : 30 April 2009 |

Special dedication to my mother, father and family members that always love me, my supervisor, my beloved friends, my fellow colleague, and all faculty members

For all your love, care, support, and believe in me

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ABSTRACT

The permeability and the selectivity of CH₄, CO₂, N₂, and O₂ were determined in a polymer membrane prepared from 8% weight ratio PAN powder and 92% weight ratio of dimethylformamide (DMF) as a solvent, commercially known as Polyacrylonitrile (PAN) membrane. Flat sheet membrane with an average thickness of 0.025cm was produced manually using casting knife. Permeability test was conducted with a permeability/permeation unit where the volumetric flow rates of the effluent were measured by a bubble soap flow meter. This polymer exhibits higher permeability of CH₄ compare with CO₂, N₂, and O₂. Higher selectivity also achieved for CH₄ compare with CO₂, N₂, and O₂ under low pressure and high volumetric flow rates. On the basis of a best fit of the natural logarithm of permeability versus inlet flow rate, PAN membrane should have much higher permeability of CH₄ when it is applied with higher inlet flow rate under low feed pressure. For this experiment, the prepared membrane gave the best permeability and selectivity reading at 0.5bar and 0.3 liter per minute of flow rate. Pure gas CO₂/CH₄ separation properties of this polymer are comparable with those of some other polymers considered for natural gas purification. When exposed to a feed stream with higher pressure, the permeability of CO₂, N₂, and O₂ were high indicates the separation process was not that successful. Successful separation process was achieved at low feed stream pressure and high inlet flow rates.

ABSTRAK

Kadar ketertelapan dan kadar pemilihan bagi CH4, CO2, N2, dan O2 telah ditentukan dengan mengalirkan ia melalui membran separa telap yang telah disediakan daripada 8% nisbah berat serbuk PAN dan 92% nisbah berat larutan dimethylformamide (DMF) dengan panggilan komersial membran Polyacrylonitrile (PAN). Kepingan membran dengan ketebalan purata 0.025cm telah disediakan secara manual dengan menggunakan pisau lempar. Ujian untuk kadar keterlelapan telah dijalankan dengan menggunakan unit kadar keterlelapan dimana aliran gas yang keluar disukat dengan menggunakan meter buih sabun. Polimer ini memberi kadar keterlelapan yang tinggi untuk CH4 berbanding dengan CO2, N2, dan O2. Kadar pemilihan yang tinggi juga dicapai untuk CH4 berbanding dengan CO2, N2, dan O2 keseluruhannya pada tekanan yang rendah disertai dengan kadar aliran yang tinggi. Daripada ujian yang telah dijalani, graf kadar ketertelapan melawan kadar aliran masuk yang terbaik menunjukkan bahawa membran PAN akan mempunyai kadar ketertelapan yang lebih tinggi bila dibekalkan dengan kadar aliran masuk yang lebih tinggi pada tekanan yang rendah. Daripada eksperimen yang telah dijalankan, membran yang telah disediakan memberi kadar ketertelapan dan kadar pemilihan yang terbaik pada tekanan 0.5bar dan 0.3 liter per minit kadar aliran. Pada tekanan tinggi, kadar ketertelapan untuk CO₂, N₂, dan O₂ menunjukkan jumlah yang tinggi dimana ianya membawa maksud bahawa proses penyingkiran CO₂ daripada gas asli kurang berkesan. Keberkesanan di dalam proses penyingkiran CO₂ daripada gas asli boleh dicapai pada tekanan aliran masuk yang rendah dan pada kadar aliran yang tinggi.

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LIST OF SYMBOLS

| cm | - | Centimeter | |
|-----------------|---|--|--|
| Mcf | - | Thousand of cubic feet | |
| MMcf | - | Millions of cubic feet | |
| Bcf | - | Billion of cubic feet | |
| Tcf | - | Trillion of cubic feet | |
| Btu | - | British thermal unit | |
| CH_4 | - | Methane | |
| C_2H_6 | - | Ethane | |
| C_3H_8 | - | Propane | |
| $C_4 H_{10}$ | - | Butane | |
| CO_2 | - | Carbon Dioxide | |
| O_2 | - | Oxygen | |
| N_2 | - | Nitrogen | |
| H_2S | - | Hydrogen sulfide | |
| NF | - | Nanofiltration | |
| RO | - | Reverse Osmosis | |
| EOR | - | Enhanced Oil Recovery | |
| LPG | - | Liquefied Petroleum Gas | |
| TTD | - | 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole | |

| TFE | - | Tetrafluoroethylene |
|-----------------|---|---|
| μm | - | Micrometer |
| g | - | Gram |
| cm ³ | - | Centimeter cube |
| % (w/v) | - | Weight over volume percentage |
| ppm | - | Part per million |
| atm | - | Atmosphere |
| cm^2 | - | Centimeter square |
| °C | - | Celsius |
| cmHg | - | Centimeter mercury |
| K | - | Kelvin |
| R | - | Universal gas constant (6236.56 cm ³ cmHg/(mol K)) |
| mmHg | - | Millimeter mercury |
| Si | - | Solubility |
| Di | - | Diffusivity |
| Pi | - | Permeability |
| bar | - | Pressure (in bar unit) |
| DMF | - | Dimethylformamide |
| rpm | - | Revolution per minute |
| ml | - | Milliliter |
| mm | - | Millimeter |
| GPU | - | Gas permeability unit |
| P/l | - | Pressure-normalized flux |
| Qi | - | Volumetric flow rate |

- Δp Pressure difference
 - *A* Effective surface area
 - *l* Membrane skin thickness
- L/min Liter per minute

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CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Natural Gas

The annual demand for natural gas has been steadily increasing over the past decade and is expected to increase further. Natural gas is combustible mixture hydrocarbon gases with colourless, shapeless, and odorless characteristics. Natural gas deals with a lot of energy when burned and it is a clean burning together with lower level emission of harmful byproduct to air. Natural gas is considered 'dry' when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is considered 'wet' [1]. Wet gas is a geological term for a mixture of hydrocarbons that contain a significant amount of liquid or condensable compounds heavier than ethane. These compounds may include propane or butane. Wet gas produced from a reservoir will always contain some amounts of water. This is the ground water/formation water vapour in equilibrium with the gas under the pressure and temperature in the reservoir. It must be emphasized however that the term wet refers to the presence of hydrocarbon components which are heavier than ethane and not water. It should also be noted that the presence of water is not exclusive to wet gas but may be present in each of the other four main types of reservoir in varying percentages.

Natural gas is composed of almost purely methane. The composition of natural gas can vary widely according to each reservoir. Every reservoir has its own

| Composition | Symbol | Percentage (%) |
|------------------|--------------------------------|----------------|
| Methane | CH_4 | $70 \sim 90$ |
| Ethane | C_2H_6 | |
| Propane | C_3H_8 | $0 \sim 20$ |
| Butane | C ₄ H ₁₀ | |
| Carbon Dioxide | CO_2 | $0 \sim 8$ |
| Oxygen | O ₂ | $0 \sim 0.2$ |
| Nitrogen | N ₂ | 0 ~ 5 |
| Hydrogen sulfide | H_2S | 0 ~ 5 |

Table 1.1: Typical composition of natural gas in reservoir.

Natural gas is a fossil fuel like oil and coal. They are the remains of plants, animals and microorganisms that lived millions and millions of years ago. Fossil fuels are formed when organic matter which is the remains of plant or animal is compressed under the earth at a very high pressure for a very long time [1]. This referred to as Thermogenic methane. Thermogenic methane is formed from organic particles that are covered in mud and other sediment which are piled on top of the organic matter. It puts a great deal of pressure on the organic matter which compress it. Compression combined with high temperature under the earth break down the carbon bonds in the organic matter. The deeper under the earth's crust, the higher the temperature. At lower temperature, more oil is produced compare to natural gas whereas at higher temperature, more natural gas is created. Deeper underground, it is usually contain primarily natural gas and in many cases it is pure methane [1].

Natural gas has a low density and once formed it will rise towards the surface of the earth through looses, shale type rock and other material. Impermeable rock traps the natural gas under the ground and if these formations are large enough, they can trap a great deal of natural gas in what is known as reservoir. Most common impermeable rock forms a 'dome' shape, like and umbrella that catches all of the natural gas that is floating to the surface. Natural gas comes from three types of well which are oil wells, gas wells, and condensate wells. From the oil wells, natural gas is term as 'associated gas' and exist as free gas where it exist separately from the oil and exist as dissolve gas where it is dissolve in oil. From gas and condensate wells, there is little or no crude oil it is term as 'nonassociated gas'. In gas well, natural gas exist by itself while from the condensate well, free natural gas together with semi liquid hydrocarbon condensate exist. Natural gas in the reservoir is typically under pressure which allowing it to escape from the reservoir on its own when it is drilled [1].

Natural gas users commonly come from residential areas, commercial, and industrial. Raw natural gas drilled from underground from three types of well which is oil wells, gas wells, or condensate wells with a lot of impurities that need to be remove. Refinery is the process in removing the impurities such as water, other gases (CO₂, O₂, N₂, and H₂S), sand and other compounds. After refinery process, natural gas is transported through a network of pipeline [1].

Natural gas commonly measured in thousand of cubic feet (Mcf), millions of cubic feet (MMcf), billion of cubic feet (Bcf), trillion of cubic feet (Tcf), and also as source of energy, British thermal unit (Btu). 1Btu equivalent to the energy required to heat up 1 pound of water by one degree at normal pressure. For billing purpose to residential area, it commonly measured as 'therms' which equivalent to 100000Btu or over 97 cubic feet of natural gas [1].

1.1.2 Acid Gas

As we may know, the composition of raw natural gas consists of impurities and other hydrocarbons. Main acid gases are hydrogen sulfide and carbon dioxide. Hydrogen sulfide removal is term as natural gas sweetening. Acid gas removal is very important in safety requirement where it is very high toxicity and for transport requirement which to avoid corrosion and crystallization. Each of these impurities and other hydrocarbons has its own properties and ways in separating them in order to purify the natural gas with almost purely methane.

Carbon dioxide and oxygen is one of the compositions in raw natural gas that is also considered as acid gas. It can cause corrosion to the pipeline if they are not separated from the natural gas. We need to separate carbon dioxide and oxygen from natural gas to prevent these pipelines from corrosion where it can cause leakage in pipelines which then need to be replaced with new ones with high purchasing and installing cost. Carbon dioxide also can form a weak acid, carbonic acid (H_2CO_3) in water, a relatively slow reaction which also can cause corrosion to the pipeline. However, carbon dioxide corrosion rates are greater then the effect of carbonic acid alone [3]. While for oxygen, it is considered as a strong oxidant and it can react quickly with metal in forming oxide [4].

Nitrogen in a different perspective is also referred as acid gas in natural gas. It's found in small quantities which are less than 2%. This small quantity actually does not have any major influence on the gas properties. Large concentration of nitrogen at 10% or higher, it have to be separated in order to maintain the calorific value of natural gas combustion. With high concentration nitrogen present, the calorific value of the natural gas will be lower and hence will give a small amount of energy of combustion [5].

1.1.3 Natural Gas Processing

Eventhough that natural gas has a wide range of compositions, the composition of gas delivered to consumers is tightly controlled. All natural gas

requires treatment to meet the specifications, and approximately 20% requires extensive treatment before it can be delivered to the pipeline. Before this, removal of acid gas components and water has been achieved by absorption-type processes in example the amine and glycol-based systems. However, nowadays, membrane processes have been shown to be very effective for performing some of these separations, especially for treating small to moderate size gas streams [6].

Membranes separation process has several advantages over the absorptiontype processes for natural gas treatment [6];

- i. Membrane-based separations are less energy intensive than traditional processing methods.
- Glassy, size-selective polymer membranes are more permeable to CO₂, H₂S and water vapor than to CH₄ and higher hydrocarbons. Thus, the desired methane product is obtained in the high-pressure retentate stream without significant loss in pressure, as desired for transport through pipelines.
- iii. Membrane units are modular and, hence, flexible with respect to the capacity they can handle. Additional membrane units can be easily added to handle higher capacities.
- iv. Membrane units are compact and, hence, they can be installed on offshore platforms. Thus, natural gas from the well can be processed on the platform before being transported. This on-site processing capability eliminates the need to use expensive materials of construction for the pipelines to carry corrosive gases like CO_2 and H_2S . Also, smaller pipelines can be used because contaminants in the stream no longer have to be transported to on-shore processing plants for removal, thereby reducing material and pumping costs.

Due to these significant advantages, membranes have generated interest in the natural gas processing industry, especially for the removal of CO₂. Currently, more than 200 membrane plants have been installed to perform this separation [6].

1.1.4 Polymer Membranes for Acid Gas Removal in Natural Gas

As energy costs rise, membrane technology for separating gases is likely to play an increasingly important role in reducing the environmental impact and costs of industrial processes. Gas separation membranes offer a number of benefits over other gas separation technologies where the phase change adds a significant energy cost to the separation cost while for membrane gas separation on the other hand, does not require a phase change. In addition, gas separation membrane units are smaller than other types of plants, like amine stripping plants, and therefore have relatively small footprints. A small footprint is important in environments such as offshore gasprocessing platforms. The lack of mechanical complexity in membrane systems is another advantage. Currently, gas separation membranes are most widely used in industry for [7];

- i. Hydrogen separation, for example, hydrogen/nitrogen separation in ammonia plants and hydrogen/hydrocarbon separations in petrochemical applications
- ii. Separating nitrogen from air
- iii. CO₂ and water removal from natural gas
- iv. Organic vapor removal from air or nitrogen streams

Membranes in detail definition are defined as a thin semipermeable barrier that selectively separate some compounds from others [8]. This definition is necessarily broad because of the large variety of membrane materials separating an equally vast number of compounds in all phases. Applications include [8];

- i. Ceramic membranes for gas purification in the semiconductor industry
- ii. Palladium-based metallic membranes for hydrogen extraction
- iii. Silicon rubber membranes for organic vapor recovery from air
- iv. Polyvinyl alcohol-based membranes for ethanol dehydration

At the moment, the most widely used membrane materials for gas separation are polymers. They are attractive as membranes because they can be processed into hollow fibers with high surface areas. The relatively low cost of manufacturing the fibers makes them of interest for large-scale industrial applications. Examples of such membranes are the MEDAL and PRISM membranes produced, respectively, by Air Liquide and Air Products for wide-ranging gas separation applications [7].

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 [8].

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 [8].

In membrane, gas transport through a non-porous polymeric membrane and it is known to follow the solution-diffusion mechanism. The gas first sorbs into the membrane on the high-pressure side, then diffuses across the membrane under a partial pressure driving force and finally desorbs from the low pressure side of the membrane. Therefore, gas permeability in the membrane is dependent both on the solubility of the gas in the polymer as well as its diffusion coefficient in the polymer.

Gas solubility in polymers typically increases with an increase in gas condensability together with the absence of specific interactions between the gas molecules and polymer chains [9]. Differences in molecular size and/or gas condensability can result in different gas permeation rates through a polymer. Differential permeation rates result in an increase in the concentration of the faster permeating species on the downstream side of the membrane as compared to its concentration in the feed stream, thus effecting a separation of the gases in the mixture [9]. The deterioration in membrane separation performance is primarily due to the action of higher hydrocarbon impurities present in natural gas. Large hydrocarbons are highly condensable and have high solubilities in the hydrocarbon polymers. Upon sorbing into a polymer, these higher hydrocarbons can act as plasticizers, increasing polymer chain mobility and decreasing the size-sieving ability of the polymer [9].

1.2 Problem Statement

Acid gases which are carbon dioxide, nitrogen, and oxygen must be separated from raw natural gas in order to meet the requirement of the users in term of energy burning and pipeline specification. There are several ways in separating those impurities in natural gas such as by amine treating, scavenger for hydrogen sulfide (H₂S), and membrane separation. This research is focus on separating the impurities by using membrane separation, Polyacrylonitrile (PAN). In membrane separation process, the main objectives are to familiarize ourselves about the selectivity and the permeability of a membrane.

In order to separate impurities from the natural gas, permeability of each compound is the most important aspect in the separation process. Compound with high permeation rates will diffuse through the membrane rapidly compare to the compound with lower permeation rates. Methane permeation rates are much smaller compare to the impurities and thus they will not desorb easily in a polymer membrane. Polyacrylonitrile membrane has long been used as flat or hollow fiber and it is also used as layers of composite membrane because of its excellent capability to resist pollution and chemical reactions. It has been used as a substrate for nanofiltration (NF) and reverse osmosis (RO). There are numerous PAN fibers advantages including a high degree of molecular orientation, higher melting point and a greater yield of the carbon fiber.

In carbon dioxide removal from natural gas processing, the existing membranes which are commonly used and suitable for this purpose are the polydimethylsiloxane and asymmetric cellulose acetate membrane [14]. Although other processes such as chemical absorption have been used extensively, membranes have a number of advantages for this application on offshore production platform where lightweight and minimal maintenance favors their adoption [14].

1.3 Objectives

As describe in the research background and problem statement section, the objective of this research is to develop Polyacrylonitrile (PAN) membrane for CO_2 gas separation in natural gas application.

1.4 Scope of study

In order to accomplish the set objectives, the following scope of works has been drawn;

- i. Identification of a suitable method to produced a flat sheet Polyacrylonitrile (PAN) membrane.
- ii. Permeability and selectivity determination from each component through the PAN membrane.
- iii. Introduce PAN membrane as one of the separation method in natural gas processing.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Definition

A membrane is a layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, molecules, or substances when exposed to the action of a driving force. Some components are allowed passage by the membrane into a permeate stream, whereas others are retained by it and accumulate in the retentate stream.

Membranes can be of various thicknesses with homogeneous or heterogeneous structure. Membrane can also be classified according to their pore diameter. According to International Union of Pure and Applied Chemistry (IUPAC), there are three different types of pore size classifications which are microporous, mesoporous and macroporous. Membranes can be neutral or charged, and particles transport can be active or passive. The latter can be facilitated by pressure, concentration, chemical or electrical gradients of the membrane process. Membranes can be generally classified into three groups which are inorganic, polymeric or biological membranes. These three types of membranes differ significantly in their structure and functionality.

A biological membrane or biomembrane is an enclosing or separating amphipathic layer that acts as a barrier within or around a cell. It is almost invariably, a lipid bilayer, composed of a double layer of lipid which is usually phospholipid molecules and proteins that may constitute close to 50% of membrane content. Such membranes typically define enclosed spaces or compartments in which cells may maintain a chemical or biochemical environment that differs from the outside. For example, the membrane around peroxisomes shields the rest of the cell from peroxides, and the plasma membrane separates a cell from its surrounding medium. Most organelles are defined by such membranes, and are called membrane-bound organelles.

Artificial membrane also known as synthetic membrane is a syntheticly created membrane which is usually intended for separation purposes in laboratory or in industry. Synthetic membranes have been successfully used for small and largescale industrial processes since the middle of twentieth century. A wide variety of synthetic membranes is known. They can be produced from organic materials such as polymers and liquids, as well as inorganic materials. The most of commercially utilized synthetic membranes in separation industry are made of polymeric structures. They can be classified based on their surface chemistry, bulk structure, morphology, and production method. The chemical and physical properties of synthetic membranes and separated particles as well as a choice of driving force define a particular membrane separation process. The most commonly used driving forces of a membrane process in industry are pressure and concentration gradients. The respective membrane process is therefore known as filtration. Synthetic membranes utilized in a separation process can be of different geometry and the respective flow configuration. They can be also categorized based on their application and separation regime. The most known synthetic membranes separation processes include water purification, reverse osmosis, dehydrogenation of natural gas, removal of cell particles by microfiltration and ultrafiltration, removal of microorganisms from dairy products, and dialysis.

Polymeric membranes are membranes that take the form of polymeric interphases, which can selectively transfer certain chemical species over others. There are several mechanisms that could be deployed in their functioning. Knudsen diffusion and solution diffusion are prominent mechanisms. Polymeric membranes are of particular importance in gas separation applications. Key industrial applications include the oxygen-nitrogen separation, removal of organics and natural gas enrichment.

2.2 Gas Separation by Membrane

Gas mixtures can be effectively separated by synthetic membranes. Membranes are employed in;

- i. Separation of hydrogen from gases like nitrogen and methane
- ii. Recovery of hydrogen from product streams of ammonia plants
- iii. Recovery of hydrogen in oil refinery processes
- iv. Separation of methane from biogas
- v. Enrichment of air by oxygen for medical or metallurgical purposes
- vi. Removal of water vapor from natural gas
- vii. Removal of CO₂ from natural gas
- viii. Removal of H₂S from natural gas
 - ix. Removal of volatile organic liquids (VOL) from air of exhaust streams
 - x. Desiccation

Usually nonporous polymeric membranes are utilized. Vapours and gases are separated due to their different solubility and diffusivity in polymers. Polymers in glassy state, generally more effective for separation, predominantly differentiate in diffusivity. Small molecules of penetrants move among polymer chains according to the formation of local gaps by thermal motion of polymer segments. Free volume of the polymer, its distribution and local changes of distribution are of the utmost importance. Then diffusivity of a penetrant depends mainly on the size of its molecule.

Porous membranes can also be utilized for the gas separation. The pores diameter must be smaller than the mean free path of gas molecules. Under normal condition (100kPa, 300K) it is about 50nm. Then the gas flux through the pore is proportional to molecules velocity i.e. inversely proportional to square root of the molecule mass. It is known as Knudsen diffusion. Gas flux through a porous membrane is much higher than through nonporous one three to five orders of magnitude. Separation efficiency is moderate hydrogen passes four times faster than oxygen. Porous polymeric or ceramic membranes for ultrafiltration serve the purpose. Note, in case the pores are larger than the limit then viscous flow occurs, hence no separation.

2.3 Review of Carbon Dioxide Removal from Natural Gas

Some gas fields contain high levels of carbon dioxide. Carbon dioxide has no calorific value and as a pure substance has limited industrial use. Such uses are mainly as an inert gas or carbonating agent, and in certain enhanced oil recovery (EOR) schemes. The principal source of pure carbon dioxide in the industrialized world is as a by-product in hydrogen and ammonia manufacture. Substantial quantities of the gas are produced, much of which is discharged to atmosphere. However, where demand is high, for instance in EOR schemes, gas fields can be developed for their carbon dioxide content [5].

Because of CO_2 inert nature, it can be a hindrance in the use of some natural gases by lowering the calorific value. It can also promote the corrosion of pipelines. CO_2 also must be removed to prevent freezing in the low-temperature chillers which can cause plugging in a pipeline. If the gas contains substantial amounts of carbon dioxide, the cost of removal becomes significant [5].

If LPG is extracted from natural gas, the carbon dioxide content is generally reduced to about 2% in the process, thus raising the calorific value of the product. For certain uses, especially in methanol production, the presence of some carbon dioxide can be an advantage. It can help bring into balance the hydrogen/carbon (H/C) ratio of the feedstock and product. Thus fields with poor marketability as fuel due to carbon dioxide content may be suitable for methanol production [5].

There a wide variety of approaches to the removal of carbon dioxide. One common approach is through the acid gas plant. Provided the presence of sulfur does not present a problem, carbon dioxide can also be removed using membrane separators and molecular sieve separators. These technologies have the advantages of being small and compact. They are particularly useful for smaller gas field developments or offshore operation where size is premium [5].

2.3.1 Low-Sulfur, Low Carbon Dioxide Removal from Natural Gas

Figure 2.1 below illustrates a typical flow sheet for gas treatment of a lowsulfur, low-carbon dioxide gas which sometime referred to as a sweet gas [5].



Figure 2.1: Gas treatment for low-sulfur, low-carbon dioxide gas schematic diagram.

Such a scheme is simple, and the capital cost is low. This type of scheme can be used on low-sulfur and low-carbon dioxide gases where gas is supplied to a limited number on users and the specification can be somewhat relaxed [5].

2.3.2 High-Sulfur, High-Carbon Dioxide Removal from Natural Gas

For high-sulfur, high-carbon dioxide gas, this type of gas is sometimes referred to as sour or acid gas. For this case, gas processing involves many steps and there are several alternatives to the order of unit operation. There are a large number of proprietary technologies available. An absorber is central to the treatment for the majority of technologies available. This is where the acidic hydrogen sulfide and carbon dioxide are absorbed into a solvent. There are many variations on type of solvent in use. Figure 2.2 below illustrates a typical flow sheet for treatment of a gas with a high-sulfur and high-carbon dioxide content [5].



Figure 2.2: Gas treatment for high-sulfur, high carbon dioxide gas schematic diagram.

The flow sheet shown in Figure 2.2 has the following steps [5];

i. An acid gas treatment plant is to remove hydrogen sulfide and carbon dioxide. This comprises two towers. Gas enters the bottom of the first tower, where it contacts a solvent that strips the acid gases out of the system. The solvent passes to the stripping tower, where it is recovered by boiling or sometimes by pressure swing.
ii. The treated gas passes out of the top of the first tower and is dried before transmission. The off gas from the stripping tower is passed to a Claus plant where several steps separate the sulfur. The residual vent gases are then principally carbon dioxide.

2.4 Basic Membrane Separators Structure

Membrane technology works on the principle that different gases diffuse at different rates through different types of polymer membranes. Carbon dioxide, water, and hydrogen are particularly fast and can be easily separated from slow diffusing molecules such as hydrocarbons or nitrogen. There are numbers of application of membrane technology and many proprietary technologies [5].

The basic method is illustrated in Figure 2.3. For carbon dioxide separation, gas is passed at pressure through one side of the membrane, and carbon dioxide and water preferentially diffuse through the membrane and are exhausted from the low-pressure side [5].



Figure 2.3: Schematic diagram of basic membrane separation for carbon dioxide removal in natural gas application.

Single stage systems as illustrated above are not very effective in the sense that a certain amount of hydrocarbon gas also passes through the membrane. To overcome this problem, membrane systems are normally operated with multiple separators using interstage compression as necessary. Membrane systems are claimed to offer significant cost advantages over acid gas plant technology [5].

Materials science research in this area has concentrated on the modification of hydrocarbon-based polymers to increase gas diffusion coefficients and diffusivity selectivity and to achieve higher CO_2 permeability and CO_2/CH_4 selectivity simultaneously. Natural gas typically contains a wide variety of aliphatic and aromatic hydrocarbon compounds and these hydrocarbons usually have high solubilities in hydrocarbon based polymers. Those components will sorbs into polymers in significant amounts. Loss in CO_2/CH_4 selectivity results in a loss of the product, methane. This requires either a second membrane module to recover the lost product or simply accepting the loss. Both are expensive method and inefficient options [9]. Efforts have been made in reducing the plasticization effect of hydrocarbon polymers by blending with other polymers, thermal treatment, and cross-linking. An alternative approach is to address the high solubility of higher hydrocarbon compounds in membrane materials by considering polymeric materials with low solubility for these compounds. Gas solubility in liquids and polymers generally increases with gas condensability in the absence of the specific interaction between the gas and the membrane [9].

Hydrocarbon and fluorocarbon gas solubility measurements in hydrocarbon polymers and fluoropolymers reveal that interactions between hydrocarbon and fluorocarbon species result in lower solubility of hydrocarbons in fluorocarbon polymers, and vice versa. The influence of these interactions on gas permeability is greater in lower free volume materials. Hydrocarbon solubility in fluoropolymers increases with the increasing penetrant condensability in hydrocarbon polymers, meaning that large hydrocarbon compounds will exhibit lower solubility in fluoropolymers than in hydrocarbon polymers. When there is an interaction between penetrant and membranes, there will be a significant reduction in solubility [9].

Lower hydrocarbon solubility may result in greater resistance of fluoropolymers to plasticization by hydrocarbon compounds and thus making them more attractive as a membrane material for separating gas streams. Gas molecules sorbing into a lower free volume membrane may experience stronger interactions with the surrounding polymer than they would in a high free volume material and therefore experience stronger interaction. It is of interest to study hydrocarbon solubility in a lower free volume fluoropolymer and compare it with that in higher free volume fluoropolymers and in hydrocarbon polymers [9].

In this reviewed research, they used a low free volume, glassy, amorphous copolymer composed of 80 mol% 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) and 20 mol% tetrafluoroethylene (TFE), commercially well known as Hyflon AD 80. Figure 2.4 on the next page shows the chemical structure of the Hyflon AD 80 in detail.



Figure 2.4: Chemical Structure of Hyflon AD 80 membrane.

2.5 Membrane Material

Recently, the only commercially viable membranes used for CO_2 removal are polymer based, for example, cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide. The most widely used and tested material is cellulose acetate as used in Universal Oil Product's membrane systems. Polyimide has some potential in certain CO_2 removal applications, but it has not received sufficient testing to be used in large applications [8].

The properties of polyimides and other polymers can be modified to enhance their performance. For example, polyimide membranes which are initially being used for hydrogen recovery but then it were modified for CO_2 removal. Cellulose acetate membranes were initially developed for reverse osmosis but are now the most rugged CO_2 removal membrane available [8].

In this research, Hyflon AD 80 was purchased from the Ausimont Co. (Thorofare, NJ), now Solvay Solexis. Uniform isotropic films with thicknesses ranging from 35μ m to 90μ m were cast from 2% (w/v) solution in example, 2g of polymer per 100cm³ of solvent in PF 5060, a perfluorinated volatile solvent from 3M (St. Paul, MN). The films were dried at ambient conditions for two to three days and then utilized for sorption and permeation measurements. The pure gases and vapors used in the experiments had a purity of at least 99.5%. N₂, O₂, CO₂, CH₄, and C₂H₆

were obtained from National Specialty Gases (Durham, NC). C_3H_8 and C_3F_8 were purchased from Machine and Welding (Raleigh, NC). A gas mixture containing 20% CO_2 in CH_4 and another containing 10% CO_2 , 50ppm toluene, and 500ppm n-hexane in CH_4 with primary standards with analyses provided were purchased from MG Industries (Wilmington, DE) for the mixed-gas permeation experiments. All gases were used as received [9].

Solubility coefficients were determined using a high-pressure barometric apparatus. Initially, a polymer film was placed in the sample chamber and exposed to vacuum overnight to degas it. A known amount of penetrant gas was introduced into the chamber, and the pressure was allowed to equilibrate. Once the chamber pressure was constant, the amount of gas sorbed by the polymer was determined by performing a mass balance. Additional penetrant was introduced, and the procedure was repeated. In this incremental manner, penetrant uptake was determined as a function of pressure. The maximum pressure was 7atm to 25atm, depending on the penetrant. After measuring each isotherm, the polymer samples were degassed under vacuum overnight. The system temperature was controlled to $\pm 0.1^{\circ}$ C using a constant temperature water bath. The sorption experiments were performed in the following order, N₂, CO₂, CH₄, C₂H₆, C₃H₈, and C₃F₈. N₂ sorption experiment was also performed after each of the other penetrants to ensure that the polymer film had not undergone significant sorption hysteresis during the experiments. Isotherms for subsequent penetrants were measured only after the N2 isotherm matched the initially measured isotherm [9].

Pure gas permeability coefficients for N₂, O₂, and CO₂ were determined using a constant pressure/variable volume apparatus. The membrane area was 13.8 cm^2 . The upstream pressure was varied from 2.7atm to 21.4atm. The downstream pressure was atmospheric. Prior to each experiment, the upstream and downstream sides of the permeation cell were purged with penetrant gas. The system temperature was controlled to ± 0.5 °C using a DYNA-SENSE temperature control system. Gas flow rates were measured with a soapfilm bubble flowmeter. When steady-state conditions were attained, the following expression was used to evaluate permeability (cm³ (STP) cm/(cm² s cmHg)) [9];

$$P = \frac{22414}{A} \frac{1}{p_2 - p_1} \frac{p_1}{RT} \frac{dV}{dt}$$
(2.1)

where p_2 is the upstream pressure (cmHg), p_1 is the downstream pressure (atmospheric pressure in this case, in example, 76cmHg), 1 is the membrane thickness (cm), A is the membrane area (cm²), T is the absolute temperature (K), R is the universal gas constant (6236.56 cm^3 cmHg/(mol K)), and dV/dt is the volumetric displacement rate of the soap film in the bubble flowmeter (cm^3/s) . Pure gas permeability coefficients of the hydrocarbons, CH₄, C₂H₆, and C₃H₈, were measured in a constant volume/variable pressure apparatus. The membrane area was 13.8cm². The upstream pressure was varied from 2.7atm to 18atm. The downstream side was maintained below 10mmHg. Prior to each experiment, the upstream and downstream sides of the permeation cell were evacuated to below 0.5mmHg. The system temperature was controlled to ±0.5 °C using an Omega CN76000 temperature controller. The increase in pressure on the downstream side was recorded using a data acquisition system employing Labtech software. When the rate of pressure increase on the downstream side, dp/dt (cmHg/s), attained its pseudo-steady-state value, the permeability (cm³ (STP) cm/(cm² s cmHg)) was calculated using the expression [9];

$$P = \frac{22414}{A} \frac{1}{p_{abs}} \frac{V}{RT} \frac{dp}{dt}$$
(2.2)

where p_{abs} is the upstream pressure (cmHg) and V is the downstream volume (cm³).

2.6 Theory of Operation

2.6.1 Permeability

Figure 2.5 below shows the permeability of Hyflon AD 80 to N_2 , O_2 , CO_2 , CH_4 , and C_2H_6 as a function of pressure difference across the membrane up to 20atm at 35°C [9].



Figure 2.5: Permeability of N₂, O₂, CO₂, CH₄, and C₂H₆ in Hyflon AD 80 at 35°C as a function or pressure difference across the membrane.

The penetrant permeabilities decrease as size increases [9];

$$CO_2 > O_2 > N_2 > CH_4 > C_2H_6$$

These permeability coefficients, measured in dense films, are two to three times lower than those reported by Arcella et al. in a composite membrane of this polymer on a PVDF support. The source of this discrepancy is not known, although it can be challenging to measure the effective thickness in a composite membrane, and the influence of substructure resistance in Arcella et al.'s data was not reported. From Figure 2.5, the permeabilities of N_2 and O_2 are independent of pressure while CH_4 permeability decreases with increasing pressure. In contrast, the permeabilities of CO_2 and C_2H_6 increase somewhat at higher pressures. Permanent gases and lowcondensability penetrants typically exhibit constant or decreasing permeabilities with increasing penetrant pressure in glassy polymers due to the dual modes of sorption and transport available in these materials. Also, at high gas pressures or penetrant activities, penetrants can plasticize the polymer matrix, which increases their permeabilities at higher pressures [9].

2.6.2 Selectivity

The ideal selectivity, $\alpha_{A/B}$, of component A over B is a measure of the potential separation characteristics of the membrane material. The ideal selectivity can be written as the ratio of the pure gas permeabilities [9];

$$\alpha_{\underline{a}} \equiv \frac{P_{\underline{A}}}{P_{\underline{B}}}$$
(2.3)
or
$$\alpha_{\underline{a}} \equiv \frac{S_{\underline{A}}}{D_{\underline{B}}} \frac{D_{\underline{A}}}{D_{\underline{B}}}$$
(2.4)

where the first term on the right-hand side of equation 2.4 is the solubility selectivity and the second is the diffusivity selectivity. In equation 2.3 and 2.4, *Si*, *Di*, and *Pi* are the solubility, diffusivity, and permeability of gas *i* in the polymer [9].

2.7 Design Considerations

Many process parameters in this field can be adjusted to optimize the performance depending on the customer and application needs. Optimization is the most critical for larger systems where small improvements can bring very large rewards. Some typical requirements are [8];

- i. Low cost
- ii. High reliability
- iii. High on-stream time
- iv. Easy operation
- v. High hydrocarbon recovery
- vi. Low maintenance
- vii. Low energy consumption
- viii. Low weight and space requirement

Many of these requirements work against one another for example a highrecovery system usually requires a compressor, which increases maintenance costs. The design engineer therefore has to balance the requirements against one another to achieve an overall optimum system [8].

2.7.1 Operating Temperature

As the feed temperature increase, the membrane permeability increase and its selectivity decrease. The membrane area requirement is therefore decreased, but hydrocarbon losses and the recycle compressor power for multistage systems are increased, as shown in Figure 2.6 on the next page [8].



Figure 2.6: Effect of operating temperature on the membrane relative area losses.

2.7.2 Feed Pressure

An increase in feed pressure decreases both membrane permeability and selectivity. However, the increased pressure creates a greater driving force across the membrane. A net increase in permeation through the membrane results and the membrane area requirement therefore drops. Compressor power increases slightly, and hydrocarbon losses decrease slightly [8]. Figure 2.7 on the next page shows the relationship between the relative area or losses with the feed pressure.



Figure 2.7: Effect of feed pressure on the membrane relative area losses.

2.7.3 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 [8]. Figure 2.8 below shows the relationship between the relative area losses with the permeate pressure.



Figure 2.8: Effect of permeate pressure on the membrane relative area 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 90bar and a permeate pressure of 3bar produce a pressure ratio of 30. Decreasing the permeate pressure to 1bar 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 reinject it into a well, the

increased compressor power and size at low permeate pressures must be balanced against the reduced membrane area requirements [8].

CHAPTER 3

RESEARCH METHODOLOGY

Currently there is a lot of polymer membrane being researched especially for carbon dioxide separation in natural gas application. Membranes for gas separation are either one of two types, elastonomer in example polydimethylsilcone, or glassy polymer, in example polyimide or polysulphone. Elastonomers generally show low selectivities for some separations whereas glassy polymers exhibit higher selectivities but lower permeabilities. The relatively low cost of manufacturing the polymer gives it an advantage among other separation methods in CO₂ removal from natural gas. The ease in mechanical handling in membrane system is also another advantage for membrane separation process.

This chapter describes all the experimental methods and procedures which were applied in the development of the Polyacrylonitrile (PAN) membrane.

3.1 Material Selection

Gas separation membranes are manufactured in two forms either flat sheet or hollow fiber. The flat sheets are typically combined into a spiral-wound element, and the hollow fibers are combined into a bundle similar to a shell and tube heat exchanger. Figures 3.1 and Figure 3.2 illustrate the spiral-wound element and the hollow fibers membrane [8]. In the spiral-wound arrangement, two flat sheets of membrane with a permeate spacer in between are glued along three of their sides to form an envelope that is open at one end. Many of these envelopes are separated by feed spacers and wrapped around a permeate tube with their open ends facing the permeate tube.

Feed gas enters along the side of the membrane and passes through the feed spacers separating the envelopes. As the gas travels between the envelopes, CO_2 , H_2S , and other highly permeable compounds permeate into the envelope. These permeated components have only one outlet where they must travel within the envelope to the permeate tube. The driving force for transport is the low permeate and high feed pressures. The permeate gas enters the permeate tube through holes drilled in the tube. From there, it travels down the tube to join the permeate from other tubes. Any gas on the feed side that does not get a chance to permeate leaves through the side of the element opposite the feed position.

In hollow-fiber elements, very fine hollow fibers are wrapped around a central tube in a highly dense pattern. In this wrapping pattern, both open ends of the fiber end up at a permeate pot on one side of the element. Feed gas flows over and between the fibers, and some components permeate into them. The permeated gas then travels within the fibers until it reaches the permeate pot, where it mixes with the permeates from other fibers. The total permeate exits the element through a permeate pipe.

The gas that does not permeate eventually reaches the element's center tube, which is perforated in a way similar to that of the spiral-wound permeates tube. In this case, however, the central tube is for residual collection, not permeate collection.

Each element type has its own advantages. Spiral-wound elements can handle higher pressure, are more resistant to fouling, and have a long history of service in natural gas sweetening. Hollow-fiber elements have a higher packing density, and so hollow fiber-based plants are typically smaller than spiral wound-based plants. Those vendors that supply both types of elements can provide objective reasons for choosing one type over the other.



Figure 3.1: Spiral wound membrane element which consist of series of flat sheet membrane combined together.



Figure 3.2: Hollow-fiber membrane element wrapped around a central tube in a highly dense pattern.

In this research, it was only focus on the development of a flat sheet polyacrylonitrile (PAN) membrane for CO_2 removal in natural gas application.

3.1.1 Polyacrylonitrile (PAN)

Polyacrylonitrile is one of the versatile polymers that are widely used for making membranes due to its good solvent resistance property [12]. It has been used as a substrate for nanofiltration (NF) and reverse osmosis (RO). The thermosetting characteristic offered by PAN makes it suitable as a carbon membrane precursor. The general molecular structure of PAN is shown in Figure 3.1 [12].



Figure 3.3: Molecular structure of Polyacrylonitrile (PAN) membrane.

In addition, its chemical modification can be done easily to modify its properties. Its nitrile group can be converted into various functionalities to offer membranes with better antifouling and flux performance due to increased hydrophilicity.

3.1.2 Solvent

The solvents used in the preparation of polyacrylonitrile (PAN) must have the ability to dissolve the base polymer. The preferred solvent was dimethylformamide (DMF). DMF is a common solvent for chemical reactions [13]. Figure 3.4 below shows the molecular structure of dimethylformamide (DMF).



Figure 3.4: Molecular structure of dimethylformamide (DMF) which was used as the solvent in preparing the PAN membrane.

Dimethylformamide is a polar solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as S_N2 reactions. The primary use of dimethylformamide is as a solvent with low evaporation rate. Dimethylformamide is used in the production of acrylic fibers and plastics. It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings. DMF penetrates most plastics and makes them swell. It therefore frequently occurs as a component of paint strippers.

DMF has been linked to cancer in humans, and it can cause birth defects. In some sectors, women are banned from working with DMF. For many reactions, it can be replaced with dimethyl sulfoxide. Most manufacturers list DMF as a health hazard since it is not readily disposed of by the body.

3.2 Experimental Stages

Figure 3.5 shows the experimental stages in this research. The solution was prepared in the fume cupboard and it was then proceed to the membrane fabrication procedure. The membrane was selected according to the physical appearance of the membrane. Smooth flat sheet membranes are preferable over a defect membrane. Defect membranes produced need to be disposed and the procedure is repeated from the beginning of the solution preparation. After the satisfactory flat sheet membranes achieved, the procedure continues to the permeability test conducted using the bubble flow meter. From the permeability test, permeability and selectivity calculation may then be performed. Permeability comparison between all gasses was then discussed in Chapter 4 in detailed. Detail procedure of the experimental procedure will be explained briefly on the next section.



Figure 3.5: Experimental flow diagram the PAN membrane preparation and experimental procedures.

3.2.1 Solution Preparation

Preparation of binary polymeric dope solution was prepared by dissolving an amount of 8% weight ratio of polyacrylonitrile (PAN) white powder with 92% weight ratio of the liquid solvent which was dimethylformamide (DMF). 450g of dope solution was prepared and it was conducted in a fume cupboard. For this experiment, dimethylformamide (DMF) is a polar liquid with a faint odor typical of amines. The mixing was carried out at a temperature of 60°C. The solution was mixed and stirred with the agitator at 400rpm. Figure 3.6 below shows the typical setup for the preparation of the PAN membrane solution.



Figure 3.6: Typical apparatus setup for the preparation of the PAN membrane solution.

All of those apparatus as illustrated in Figure 3.6 were prepared in the fume hood. The thermometer was attached to the mixer to maintain the temperature during the mixing process. The condenser duty was to condense the vapor back to its initial state liquid. Heating mantle was used in providing continuously heat for the mixing process.

The mixing was carried out for six hours to ensure that all of the polymers were dissolved. As the polymers were completely dissolved, the solution shows a yellowish in color. The membrane solution was then transferred into a 500ml Schott bottle. Figure 3.7 below shows the yellowish PAN membrane solution that has been transferred into a 500ml Schott bottle.



Figure 3.7: Yellowish PAN membrane solution that has been transferred into a 500ml Schott bottle.

For safety procedure, the flask bottom of the mixer is hot and the transfer progress into the Schott bottle should be done carefully with appropriate protection equipments. The formed dope solution was then degassed for three hours by using the Ultrasonic Cleaner with 70% wavelength. Figure 3.8 below illustrates the Ultrasonic Cleaner which is located at the FKKSA Clean Lab. Ultrasonic Cleaner is a cleaning device that uses ultrasound usually from 15kHz to 400kHz and an appropriate cleaning solution to clean delicate items. In this research, the purpose of the Ultrasonic Cleaner was to degas any bubbles which exist in the concentrated dope solution. This procedure is important in avoiding any bubbles exist in the membrane. Bubbles in membrane can cause membrane to ruptured when a small amount of pressure applied to them.



Figure 3.8: Ultrasonic cleaner which was used for degassing the Polyacrylonitrile dope solution.

3.2.2 Membrane Fabrication

Flat sheet PAN membranes were then produced by using a manually controlled membrane-casting knife. Figure 3.9 on the next page illustrates the casting knife which has been used in the PAN membranes fabrication.



Figure 3.9: Casting knife for the preparation of the flat sheet membrane.

Casting solution was casted with a casting knife on a glass plate with gap setting of $150\mu m$ at an appropriate casting shear. The overall casting knife geometry was 265mm length and 60mm width.

Casting was carried out at ambient atmosphere at 30°C and 84% relative humidity. The membrane was then submerged into the coagulation bath for one hour. The submersion of the solution into the coagulation bath has to be done efficiently in avoiding any defects to the membrane. The glass plate needs to be 45 degree incline in angle to the water surface during the submersion process and the velocity of the submersion need to be constant during the procedure. A defect membrane will be produced if the PAN membrane solutions were not being carefully submerged, where it can be easily torn when a certain amount of stress is applied. The membrane was then finally stored in aqueous bath until further use. Figure 3.10 on the next page illustrates the coagulation bath of the PAN membrane solution in detail.



Figure 3.10: Coagulation bath for the phase inversion process of the PAN membrane.

3.2.3 Membrane Selection

Smooth flat sheet membrane with no defects was the priority for the membrane to be selected. Physical appearance of the membranes were observed in term of smoothness of the membrane in avoiding the membrane from easily ruptured during the permeability test. Defect membrane can easily rupture when it is applied by certain amount of pressure. If defect membranes were majority produced, the procedure could not proceed to the next one. New solution need to be prepared starting from the beginning of the procedure in order to produce a smooth membrane.

Flat sheet membranes that have been produced were then been cut in a certain size accordingly to the permeability test unit which was 4.72cm in diameter. Figure 3.11 and Figure 3.12 on the next page show the cutting procedure of the flat sheet

PAN membranes which were produced into a circular flat sheet membrane with 4.72cm in diameter.



Figure 3.11: Photo of a smooth flat sheet PAN membrane selected.



Figure 3.12: Photo of well cut membrane with 4.72cm diameter.

3.2.4 Permeability Test

Flat sheet membranes that had been finely cut were then tested by using the Permeability Unit. The permeability unit is a device which allows any gases to flow or permeate through a certain area of the membrane. Circular membrane discs with an effective permeation diameter of 4.72cm were used. Figure 3.13 below shows the membrane permeation unit which is located at the FKKSA Gas Lab.



Figure 3.13: Membrane permeability/permeation unit which was used in the permeability determination of each gas.

In this research, the feed pressure for the permeability test was controlled at 0.5bar, 1.0bar, and 1.5bar of pressure. Experiment was carried out at ambient temperature of 30°C. The thickness of each membrane which to be tested was determined by using the Vernier Caliper. Gas permeation rates through the membrane were measured by a soap bubble flow meter. An amount of 20ml of volume was taken and the timing of the bubble soap travelled within the 20ml of volume was taken. Figure 3.14 on the next page shows the schematic diagram of the

permeability unit. Gas inlet was at the bottom of the circular disc. Each gas passed through the PAN membrane at certain pressure and it was then travelled out through the gas outlet on the top. From the gas outlet, it was then flows into the burette through the hose. There was an amount of soap water in the burette so that bubbles can be induced when a certain amount of gas flows through them. Time duration for the bubbles travelled up within the 20ml was taken in determining the volumetric flow rates of the effluent gas.



Figure 3.14: Schematic diagram of the PAN membrane permeability test.

Each set of data was determined as an average of three replicates. Gas permeation rate was then calculated by [11];

$$\left(\frac{p}{l}\right)_{i} = \frac{Q_{i}}{A\Delta p} \tag{3.1}$$

where (P/l) defined as pressure-normalized flux or permeability for gas *i*. The common unit of pressure-normalized gas flux is GPU (1 GPU = $1 \times 10-6$ cm³ (STP)

cm/cm² s cmHg). Q*i* is volumetric flow rate of gas *i*, Δp the pressure difference across membrane, *A* the membrane effective surface area and *l* the membrane skin thickness [11]. Selectivity of asymmetric membrane which is dimensionless can be determined by [11];

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{(P/l)_i}{(P/l)_j}$$
(3.2)

Pure gas of methane (CH₄), nitrogen (N₂), carbon dioxide (CO₂), and oxygen (O₂) were flowed through the PAN membrane attached in the circular disc of the permeability unit. Each of the gases gave a certain amount of volumetric flow rates through the bubble flow meter readings and thus permeability of each gas through the PAN membrane was then determined from equation 3.3 above. The selectivity was then finally determined by using equation 3.4 as shown above.

CHAPTER 4

RESULT AND DISCUSSION

Permeability of the penetrant of the feed gas molecular size through the Hyflon AD 80 polymer membrane increased in the following manner [9];

$$CO_2 > O_2 > N_2 > CH_4 > C_2H_6$$

From the relationship above, it shows that on the left side were all the contaminants CO_2 , O_2 and N_2 which are exist in raw natural gas composition while for methane (CH₄) and ethane (C₂H₆), there were all on the right side. From the trend, separation process can be successfully achieved where the membrane can act as a barrier between the contaminants and the hydrocarbon composition.

4.1 Permeability

The permeability of each gas decreased as the molecular size of each gas increased [9]. From this research, the impurities which were CO_2 , N_2 and O_2 were successfully removed from the natural gas. The permeability of each gas in PAN membrane shows a similar permeation trend as the permeability of the gases through the Hyflon AD 80 but in different permeation rates.

There were two parameters chosen in determining the permeability of each gas which are feed pressure and inlet flow rates. These are the most important parameters at which their significances can greatly affect the permeability of each gas.

4.1.1 Pressure Effect

Three values of pressure have been applied in the determination of the permeability of each gas CH_4 , CO_2 , O_2 and N_2 . The thickness of the flat sheet membrane is only 0.02cm to 0.03cm. A highly pressure of gas stream flowing through the membrane are not recommended to avoid the membrane from rupture. At this thickness, the membrane can be easily broken if there were any defect exists during the membrane preparations. Through all three pressures applied, the timing of the soup bubbles to travel within the 20ml of volumes of the bubble flow meter was taken and the permeability was determined by performing a specific calculation from the permeability equation;

$$\left(\frac{P}{l}\right)_{i} = \frac{Q_{i}}{A\Delta p} \tag{4.1}$$

Table 4.1 shows the result from the experiment that was conducted at 0.5bar of pressure at ambient temperature. Meanwhile, Table 4.2 shows the result from the experiment that was conducted at 1.0bar of pressure and Table 4.3 shows the result from the experiment that was conducted at 1.5bar of pressure. The effective area of the membrane is 17.5cm² in average and the pressure was maintained during the test. The inlet flow rate was in liter per minute.

| Q in (L/min) | Permeability [cm ³ (STP)cm/(cm ² *s*Pa)] | | | | |
|--------------|--|-----------------|-------------|-------------|--|
| | CH ₄ | CO ₂ | O_2 | N_2 | |
| 0.1 | 8.06727E-08 | 5.29725E-08 | 4.30969E-08 | 4.7085E-08 | |
| 0.2 | 1.26711E-07 | 8.10264E-08 | 6.83541E-08 | 7.82079E-08 | |
| 0.3 | 2.7385E-07 | 1.47549E-07 | 1.22453E-07 | 1.41799E-07 | |

Table 4.1: Permeability test conducted at 0.5bar with different flow rates.

Table 4.2: Permeability test conducted at 1.0bar with different flow rates.

| Q in (L/min) | Permeability [cm ³ (STP)cm/(cm ² *s*Pa)] | | | | |
|-----------------|--|-----------------|-----------------------|-------------|--|
| | CH ₄ | CO ₂ | O ₂ | N_2 | |
| 0.1 | 3.86984E-08 | 2.63984E-08 | 2.18884E-08 | 2.55941E-08 | |
| 0.2 | 6.03315E-08 | 4.08561E-08 | 2.96189E-08 | 3.77447E-08 | |
| 0.3 | 1.03668E-07 | 6.77071E-08 | 6.29369E-08 | 7.23392E-08 | |

Table 4.3: Permeability test conducted at 1.5bar with different flow rates.

| Q in (L/min) | Permeability [cm ³ (STP)cm/(cm ² *s*Pa)] | | | | |
|-----------------|--|-----------------|-------------|-------------|--|
| | CH ₄ | CO ₂ | O_2 | N_2 | |
| 0.1 | 2.1767E-08 | 1.64542E-08 | 1.33748E-08 | 1.53151E-08 | |
| 0.2 | 3.83967E-08 | 2.79924E-08 | 2.23307E-08 | 2.52339E-08 | |
| 0.3 | 6.76066E-08 | 5.50113E-08 | 5.51179E-08 | 4.41609E-08 | |



Figure 4.1: Permeability of CH₄, CO₂, O₂, and N₂ in PAN membrane at 0.5bar as a function of inlet flow rate across the membrane



Figure 4.2: Permeability of CH₄, CO₂, O₂, and N₂ in PAN membrane at 1.0bar as a function of inlet flow rate across the membrane.



Figure 4.3: Permeability of CH₄, CO₂, O₂, and N₂ in PAN membrane at 1.5bar as a function of inlet flow rate across the membrane.

Figure 4.1, Figure 4.2 and Figure 4.3 show the relationship between the permeability and the inlet flow rate of each gas under different feed pressure. From each figure, it shows that the trends of the graphs for all gasses were all the same where as the inlet flows increased, the permeability of each gas at different feed pressures which were 0.5bar, 1.0bar and 1.5bar were also increased. The permeability of CH₄ was way higher compare to the other gasses while for the other three gasses which were CO_2 , O_2 and N_2 , their permeability readings were all quite the same. From the calculated data on each feed pressure, it was shown that the permeability of each gas was decreased as the feed pressure increased.

From the figures shown, it also shown that as the flow rate increased, the gap between CH_4 and CO_2 were also increased. Figure 4.1 show the highest gap achieved which was at 0.5bar pressure and at 0.3 liter per minutes of flow rate. The gap between those two gasses indicates that the separation process between CH_4 and CO_2 was successfully achieved. In comparison from Figure 4.2 and Figure 4.3, their graphs show a narrower gap between CH_4 and CO_2 . As pressure increased, the gap became narrower. A narrow gap indicates that the separations are poor. A highly pressure applied to the gas was the reason why the separation process was poor. The permeability of the gas was crucially depending to their molecular size. Larger entities were excluded and smaller ones were allowed to pass through. Among all four gasses, CH_4 have the smallest molecular size. Their molecular size increased in the following manner;

$$CH_4 < CO_2 < N_2 < O_2$$

At higher feed pressure, the larger entities which were N_2 , CO_2 , and O_2 were forced to permeate through the membrane since this high pressure act as their driving force for the entities to flow through the membrane. For lower pressure, the driving force for the gas were low and as a result, gas with higher molecular size was trap in the membrane as it could not pass the membrane pores with a low quantity of driving force act upon them. This explains why the gap between CH_4 and those other three gasses became narrower as their feed pressure increases.

4.1.2 Flow Rates Effect

In the permeability testing, three inlet flow rates have been taken into account in the determination of the permeability of each gas stream flowing through the PAN membrane. There were 0.1 liter per minutes followed by 0.2 liter per minutes and 0.3 liter per minutes. Those three flow rates were chosen in order to analyze and differentiate the performance of the PAN membrane under different flow rates. For all three flow rates, each data which was the timing of the soup bubble travelled within the 20ml of volumes were taken and the permeability were then determined by performing calculation from the permeability. Figure 4.4, Figure 4.5 and Figure 4.6 show the relationship of the permeability under inlet flow rates effect.



Figure 4.4: Permeability of CH₄, CO₂, O₂, and N₂ in PAN membrane at 0.1 liter per minutes as a function of inlet pressure into the membrane.



Figure 4.5: Permeability of CH₄, CO₂, O₂, and N₂ in PAN membrane at 0.2 liter per minutes as a function of inlet pressure into the membrane.



Figure 4.6: Permeability of CH₄, CO₂, O₂, and N₂ in PAN membrane at 0.3 liter per minutes as a function of inlet pressure into the membrane.

Figure 4.4, Figure 4.5 and Figure 4.6 as shown shows the relationship between the permeability of four gasses which were CH_4 , CO_2 , O_2 and N_2 under 0.1 liter per minutes, 0.2 liter per minutes and 0.3 liter per minutes of flow rates respectively. From the relationships, it was clearly shown that the permeability decreased as the pressure increased. Through all three flow rates, CH_4 gave the highest permeability reading and O_2 gave the lowest permeability reading. From the calculated data, the permeability of each gas increased as the inlet flow rate of the gasses increased.

From the graph, it was also shown that as the feed pressure increased, gap between CH_4 and CO_2 also decreased. Those gaps which was between CH_4 and CO_2 indicates that separation process between those gases was succeed. Large gap indicates an efficient separation process while narrower gap indicates poor separation process. Flow rates of 0.3 liter per minutes gave the highest gap between those two gasses compared to the other flow rates. Higher flow rate indicates higher volume of gas passes through the membrane per unit of time. CH_4 which have the smallest
molecular size was allowed to pass through the membrane in a high quantity of volume. Effluent with higher volume of flow rate was then resulting a higher permeability reading.

Smaller flow rates in the other hand gave a smaller reading in permeability. Due to the lower volume of flowing gasses through the membrane per unit of time, a lower effluent of CH_4 gas was then resulted. Low volumetric flow rate of the membrane effluents gave lower permeability reading.

4.2 Selectivity

Selectivity is a measure of the potential separation characteristics of the membrane material. The selectivity of the mixed gas of CO_2 , O_2 , and N_2 with CH_4 were determined from a specific calculation of the permeability ratio of each pure gas.

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{(P/l)_i}{(P/l)_j} \tag{4.2}$$

In this research, it deals with a flat sheet type of membrane. Industrial usage of membrane on the other hand regularly applies the hollow-fiber type of membrane where low selectivity of hydrocarbon and higher selectivity of contaminants are preferable. Figure 4.7 shows the schematic diagram of the hollow-fiber type of membrane which usually applies in the natural gas purification.



Figure 4.7: Schematic diagram of a hollow-fiber membrane used in the natural gas purification.

From the schematic diagram of Figure 4.7 above, CH_4 with low selectivity will permeate through the membrane in a small quantity whereas for CO_2 , O_2 and N_2 with high selectivity are allowed to permeate more through the membrane under the pressure differences which acts as their driving force. Two effluents will then be resulted where one of it with purified CH_4 and the other one are high in contaminants CO_2 , O_2 and N_2 .

In a flat sheet type of membrane, the concept applied is totally different from the hollow-fiber type membrane. Higher selectivity of CH_4 in a flat sheet membrane is preferable compare the hollow-fiber membrane which prefers low selectivity of CH_4 . While for the contaminants CO_2 , N_2 , and O_2 , lower selectivity is much more preferable. Figure 4.8 shows the schematic diagram of a flat sheet membrane.



Figure 4.8: Schematic diagram of a flat sheet membrane separating the contaminants from natural gas.

All of the gasses CH_4 , CO_2 , O_2 and N_2 are applied with a certain amount of pressure and gasses with small molecular size are allowed to pass through the membrane while those with large molecular size will trap on the membrane. Smaller selectivity of the CO_2 , O_2 and N_2 and higher selectivity of CH_4 are thus preferable for the flat sheet membranes. In this research, the selectivity of the contaminant over CH_4 will never exceed one (<1). Higher selectivity of CH_4 and smaller selectivity of CO_2 , O_2 and N_2 over CH_4 indicates a successful separation.

4.2.1 Pressure Effect

Table 4.5, Table 4.6 and Table 4.7 below shows the result of the calculated selectivity under 0.5bar, 1.0bar and 1.5bar of pressure respectively at ambient temperature. The effective area of the membrane is 17.5cm² in average and the pressure was maintained during the test. The inlet flow rate was in liter per minutes. Four gasses were tested and below is their detailed result from the test.

| 0 | Selectivity | | | | | | |
|-----------------|----------------------------------|---------------------------------|---------------------------------|--|--|--|--|
| Q in (L/min) | CO ₂ /CH ₄ | O ₂ /CH ₄ | N ₂ /CH ₄ | | | | |
| 0.1 | 0.656634425 | 0.534218995 | 0.583653906 | | | | |
| 0.2 | 0.639456713 | 0.539447493 | 0.617213191 | | | | |
| 0.3 | 0.538795535 | 0.44715373 | 0.517798575 | | | | |

Table 4.4: Selectivity at 0.5bar conducted with different flow rates.

Table 4.5: Selectivity at 1.0bar conducted with different flow rates.

| 0 | Selectivity | | | | | | |
|-----------------|----------------------------------|---------------------------------|---------------------------------|--|--|--|--|
| Q in (L/min) | CO ₂ /CH ₄ | O ₂ /CH ₄ | N ₂ /CH ₄ | | | | |
| 0.1 | 0.682156447 | 0.565614973 | 0.661372099 | | | | |
| 0.2 | 0.677194712 | 0.490935727 | 0.625622048 | | | | |
| 0.3 | 0.653115874 | 0.607101929 | 0.697798117 | | | | |

Table 4.6: Selectivity at 1.5bar conducted with different flow rates.

| 0 | Selectivity | | | | | | |
|-----------------|----------------------------------|---------------------------------|---------------------------------|--|--|--|--|
| Q in (L/min) | CO ₂ /CH ₄ | O ₂ /CH ₄ | N ₂ /CH ₄ | | | | |
| 0.1 | 0.755923868 | 0.614453602 | 0.703591445 | | | | |
| 0.2 | 0.729031813 | 0.581578402 | 0.65718912 | | | | |
| 0.3 | 0.813696042 | 0.815273739 | 0.653203001 | | | | |



Figure 4.9: Selectivity of CO₂/CH₄, O₂/CH₄, and N₂/CH₄ at 0.5bar as a function of different inlet flow rates across the membrane.



Figure 4.10: Selectivity of CO₂/CH₄, O₂/CH₄, and N₂/CH₄ at 1.0bar as a function of different inlet flow rates across the membrane.



Figure 4.11: Selectivity of CO₂/CH₄, O₂/CH₄, and N₂/CH₄ at 1.5bar as a function of different inlet flow rates across the membrane.

Figure 4.9, Figure 4.10 and Figure 4.11 shows the CO_2/CH_4 , O_2/CH_4 , and N_2/CH_4 separation performance based on pure gas permeation experiments of PAN membrane at 0.5bar, 1.0bar and 1.5bar of pressure respectively at ambient temperature. From the graph, it shows that all of the figure number was less than one in reading meaning at selectivity reading of one, CH_4 gas is much more favors to permeate through the PAN membrane compare to the other three gases. In Figure 4.9, as the inlet flow rate increased, the selectivity of the CO_2 , O_2 and N_2 gasses over CH_4 gas decreased while for Figure 4.10 and Figure 4.11, the trend of the graph were different where the pattern was up and down in manner. This was due to the differential thickness of the PAN membrane. Gasses were allowed to permeate more on the thinner thickness compare to the thicker one.

In selectivity, lower selectivity of the PAN membrane for CO_2 , O_2 , and N_2 are much more preferable while for CH_4 , highly selectivity of the PAN membrane for CH_4 are much more preferable. Lower selectivity indicates restriction for a certain entity to flow through the membrane. Higher selectivity on the other hand

indicates favorable entity to flow through the membrane which in this case was the CH_4 gas. Figure 4.7 shows the lowest selectivity of CO_2 , N_2 and O_2 at 0.5bar of pressure and 0.3 liter per minutes of flow rate. Low selectivity indicates that the separation process was successfully achieved.

4.2.2 Flow Rate Effect

In selectivity, three inlet flow rates have been chosen in the determination of the permeability of each gas stream flowing through the PAN membrane. There were 0.1 liter per minutes followed by 0.2 liter per minutes and 0.3 liter per minutes. Those three flow rates were chosen in order to analyze and differentiate the performance of the PAN membrane under different flow rates which were applied on them. For all three flow rate values, the permeability was determined first and from the calculated permeability, selectivity was then determined as the ratio of the CO_2 , N_2 and O_2 permeability to the permeability of CH_4 .



Figure 4.12: Selectivity of CO₂/CH₄, O₂/CH₄, and N₂/CH₄ at 0.1 liter per minutes as a function of different inlet pressure into the membrane.



Figure 4.13: Selectivity of CO₂/CH₄, O₂/CH₄, and N₂/CH₄ at 0.2 liter per minutes as a function of different inlet pressure into the membrane.



Figure 4.14: Selectivity of CO₂/CH₄, O₂/CH₄, and N₂/CH₄ at 0.3 liter per minutes as a function of different inlet pressure into the membrane.

Figure 4.12, Figure 4.13 and Figure 4.14 show the relationships of the selectivity under different pressure at certain flow rates which were 0.1 liter per minutes, 0.2 liter per minutes and 0.3 liter per minutes. As discussed earlier in section 4.2.1, low selectivity was favorable as it's indicates a successful separation process. In comparison of Figure 4.12, Figure 4.13 and Figure 4.14, the selectivity for CO_2 , O_2 and N_2 in Figure 4.14 which was at 0.3 liter per minutes of flow rates shows the lowest selectivity reading under 0.5bar of pressure. Hence, separation process was successfully achieved at low pressure together with high flow rates.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

PAN membrane is suitable for natural gas separation process where its characteristic suits the requirement in separating the natural gas contaminants which are CO_2 , N_2 and O_2 . From the experiment which has been conducted, it shows that CH_4 has the smallest molecular size compare to the other three gasses while O_2 has the biggest molecular size since permeation process was crucially depends on the molecular size of a molecule. The smaller particle molecular sizes, the smaller pores of the membrane were needed in order to separate them from a certain mixture either in gaseous form or liquid form. The result also shows that CH_4 has the smallest molecular size since it permeate more through the PAN membrane compared to the other three gasses and thus, the other three gasses which having a relatively larger molecular size may be separated from the mixture of CH_4 , CO_2 , O_2 and N_2 or in other words natural gas purification. The feed gas molecular size through the PAN membrane increased in the following manner;

$$CH_4 < CO_2 < N_2 < O_2$$

The dimension of the molecule's electron cloud defines the size and shape for a given type of molecule. When one molecule bumps into another molecule, the outer most extent of the electron clouds of each molecule repel each other in that local vicinity of the contact between the molecules. Each colliding molecule's electron cloud experiences a repulsion, due to the proximity to the like electrical charge of electrons around the other molecule in the collision. Since like electrical charges repel each other, the electrostatic interaction between the electron clouds of the colliding molecules is repulsive. That repulsion effectively defines the size of the molecules.

The objective of this research which was to develop Polyacrylonitrile (PAN) membrane for CO_2 separation from natural gas application has been successfully achieved. From the relationship of the molecular size above, the contaminants which are CO_2 , N_2 and O_2 can be separate from the mixture where PAN membrane can act as a barrier between the contaminants and hydrocarbon methane CH_4 . The results have shown that CH_4 permeability was much way higher compare to CO_2 permeability meaning that CO_2 can be separated from natural gas by using PAN membrane. By introducing this new type of membrane, it manages the industries to gain more benefits from the usage of this membrane in term of cost and thus can substitute the previous type of membrane. Other benefit is, it is environmental friendly and ease of operation. However, a lot of research and development effort need to be emphasized to enhance the current performance of PAN membrane since it is too brittle in order to commercialize the Polyacrylonitrile (PAN) membrane widely in the international market.

5.2 Recommendations

Flow rate and the feed pressure of each feed gas play a big role in the membrane testing where when there are too much pressures applied, the PAN membrane may burst up since it is thin and a brittle type of membrane. Pressure more than 2.0bar is not recommended since it may cause the membrane to broken. For flow rate, too much of flow rate may cause difficulty in determine the duration of time for the gas to travels within the 20ml volume of the bubble soap flow meter. In this experiment, CH_4 gas took an average of two second of time duration to travel within the 20ml of volume under 0.3 liters per minutes of flow rate. Hence, any higher flow rates are not recommended. On the other hand, during the preparation of the membrane, the speed and the angle during submerging the liquid dope solution into the coagulation bath also plays a major role in producing a smooth membrane. Angle need to be 45 degree incline and the submerging speed need to be constant to avoid defects where it can cause the membrane easily torn. Do not air dried PAN membrane since it is a brittle type of membrane. PAN membrane need to be store in aqueous bath until further use.

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APPENDIX A

Membrane Area = 17.5 cm^2 Temperature = 30°C Pressure = 0.5bar = 50000 Pa

| 0 | Q _{out} (L/min) | | | | | | | | | | | |
|---------------------|--------------------------|-----------------|---------|---------|-----------------|---------|---------|---------|---------|---------|---------|---------|
| Q in (L/m in) | | CH ₄ | | | CO ₂ | | | O_2 | | | N_2 | |
| , | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 |
| 0.1 | 0.16925 | 0.16997 | 0.16901 | 0.10938 | 0.11363 | 0.11070 | 0.09097 | 0.08948 | 0.09104 | 0.09795 | 0.09950 | 0.09917 |
| 0.2 | 0.26666 | 0.26845 | 0.26315 | 0.17241 | 0.17045 | 0.16759 | 0.14336 | 0.14440 | 0.14285 | 0.16460 | 0.16326 | 0.16483 |
| 0.3 | 0.54298 | 0.59113 | 0.59113 | 0.31496 | 0.30690 | 0.30769 | 0.25917 | 0.25586 | 0.25641 | 0.3 | 0.29556 | 0.29776 |

Table A1: Flow rates of each gas effluent conducted three times in liter per minutes.

Table A2: Flow rates of each gas effluent as an average of three replicates in liter per minutes.

| 0. | Q _{out} (L/min) | | | | | | | |
|---------|--------------------------|-----------------|-------------|-------------|--|--|--|--|
| (L/min) | CH ₄ | CO ₂ | O_2 | N_2 | | | | |
| 0.1 | 0.169412741 | 0.111242238 | 0.090503504 | 0.098878408 | | | | |
| 0.2 | 0.266093646 | 0.170155368 | 0.14354355 | 0.164236508 | | | | |
| 0.3 | 0.575084145 | 0.309852769 | 0.257151021 | 0.297777751 | | | | |

| 0. | Q_{out} (cm ³ /s) | | | | | | | |
|---------|--------------------------------|-----------------|-------------|-------------|--|--|--|--|
| (L/min) | CH ₄ | CO ₂ | O_2 | N_2 | | | | |
| 0.1 | 2.82354569 | 1.854037301 | 1.50839174 | 1.647973472 | | | | |
| 0.2 | 4.434894097 | 2.8359228 | 2.392392504 | 2.737275136 | | | | |
| 0.3 | 9.584735753 | 5.164212826 | 4.285850343 | 4.962962511 | | | | |

Table A3: Flow rates of each gas effluent in centimeter cube per second.

Table A4: Permeability of each gas calculated from the permeability equation.

| 0 | Permeability [cm ³ (STP)cm/(cm ² *s*Pa)] | | | | | | | |
|-----------------|--|-----------------|-----------------------|-------------|--|--|--|--|
| Q in (L/min) | CH ₄ | CO ₂ | O ₂ | N_2 | | | | |
| 0.1 | 8.06727E-08 | 5.29725E-08 | 4.30969E-08 | 4.7085E-08 | | | | |
| 0.2 | 1.26711E-07 | 8.10264E-08 | 6.83541E-08 | 7.82079E-08 | | | | |
| 0.3 | 2.7385E-07 | 1.47549E-07 | 1.22453E-07 | 1.41799E-07 | | | | |

Table A5: Selectivity of CO₂, O₂, and N₂ over CH₄ calculated from the permeability ratio of each gas.

| 0 | Selectivity | | | | | | |
|-----------------|----------------------------------|---------------------------------|---------------------------------|--|--|--|--|
| Q in (L/min) | CO ₂ /CH ₄ | O ₂ /CH ₄ | N ₂ /CH ₄ | | | | |
| 0.1 | 0.656634425 | 0.534218995 | 0.583653906 | | | | |
| 0.2 | 0.639456713 | 0.539447493 | 0.617213191 | | | | |
| 0.3 | 0.538795535 | 0.44715373 | 0.517798575 | | | | |

APPENDIX B

Membrane Area = 17.5 cm^2 Temperature = 30°C Pressure = 1.0bar = 100000Pa

| | | | | | , , | | | | | 1 | | |
|---------------------|---------|-----------------|---------|---------|-----------------|---------------------|---------|---------|---------|---------|---------|---------|
| _ | | | | | | Q _{out} (1 | L/min) | | | | | |
| Q in (L/min) | | CH ₄ | | | CO ₂ | | | O_2 | | | N_2 | |
| | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 |
| 0.1 | 0.16282 | 0.16348 | 0.16129 | 0.11131 | 0.11100 | 0.11029 | 0.09230 | 0.09181 | 0.09167 | 0.10762 | 0.10762 | 0.10723 |
| 0.2 | 0.25263 | 0.25806 | 0.24948 | 0.17216 | 0.17216 | 0.17045 | 0.12513 | 0.12461 | 0.12345 | 0.16 | 0.15748 | 0.15810 |
| 0.3 | 0.44280 | 0.42704 | 0.43636 | 0.28235 | 0.28436 | 0.28639 | 0.26490 | 0.26143 | 0.26666 | 0.3 | 0.30456 | 0.30690 |

Table B1: Flow rates of each gas effluent conducted three times in liter per minutes.

Table B2: Flow rates of each gas effluent as an average of three replicates in liter per minutes.

| Q in (L/min) | Q _{out} (L/min) | | | | | | | |
|-----------------|--------------------------|-----------------|-------------|-------------|--|--|--|--|
| | CH ₄ | CO ₂ | O_2 | N_2 | | | | |
| 0.1 | 0.162533438 | 0.110873232 | 0.091931346 | 0.107495081 | | | | |
| 0.2 | 0.253392115 | 0.1715958 | 0.124399242 | 0.158527694 | | | | |
| 0.3 | 0.435404776 | 0.284369771 | 0.264335079 | 0.303824633 | | | | |

| 0. | Q_{out} (cm ³ /s) | | | | | | | |
|---------|--------------------------------|-----------------|-----------------------|-------------|--|--|--|--|
| (L/min) | CH ₄ | CO ₂ | O ₂ | N_2 | | | | |
| 0.1 | 2.70889063 | 1.847887208 | 1.532189101 | 1.791584682 | | | | |
| 0.2 | 4.223201915 | 2.859930004 | 2.073320701 | 2.642128233 | | | | |
| 0.3 | 7.256746267 | 4.739496179 | 4.405584653 | 5.063743883 | | | | |

Table B3: Flow rates of each gas effluent in centimeter cube per second.

Table B4: Permeability of each gas calculated from the permeability equation.

| 0 | Permeability [cm ³ (STP)cm/(cm ² *s*Pa)] | | | | | | | |
|-----------------|--|-----------------|-------------|-------------|--|--|--|--|
| Q in (L/min) | CH ₄ | CO ₂ | O_2 | N_2 | | | | |
| 0.1 | 3.86984E-08 | 2.63984E-08 | 2.18884E-08 | 2.55941E-08 | | | | |
| 0.2 | 6.03315E-08 | 4.08561E-08 | 2.96189E-08 | 3.77447E-08 | | | | |
| 0.3 | 1.03668E-07 | 6.77071E-08 | 6.29369E-08 | 7.23392E-08 | | | | |

Table B5: Selectivity of CO₂, O₂, and N₂ over CH₄ calculated from the permeability ratio of each gas.

| Q in (L/min) | Selectivity | | | | | |
|-----------------|----------------------------------|---------------------------------|---------------------------------|--|--|--|
| | CO ₂ /CH ₄ | O ₂ /CH ₄ | N ₂ /CH ₄ | | | |
| 0.1 | 0.682156447 | 0.565614973 | 0.661372099 | | | |
| 0.2 | 0.677194712 | 0.490935727 | 0.625622048 | | | |
| 0.3 | 0.653115874 | 0.607101929 | 0.697798117 | | | |

APPENDIX C

Membrane Area = 17.5 cm^2 Temperature = 30°C Pressure = 1.5bar = 150000Pa

| 0 | Q _{out} (L/min) | | | | | | | | | | | |
|---------------------|--------------------------|-----------------|---------|---------|-----------------|---------|---------|---------|---------|---------|---------|---------|
| Q in (L/m in) | | CH ₄ | | | CO ₂ | | | O_2 | | | N_2 | |
| , | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 | Test 1 | Test 2 | Test 3 |
| 0.1 | 0.138568 | 0.13377 | 0.13905 | 0.10462 | 0.10344 | 0.10291 | 0.08135 | 0.08571 | 0.08571 | 0.10462 | 0.09188 | 0.09295 |
| 0.2 | 0.261437 | 0.22988 | 0.23437 | 0.18209 | 0.16997 | 0.17699 | 0.1411 | 0.13969 | 0.14117 | 0.16415 | 0.15424 | 0.15852 |
| 0.3 | 0.436363 | 0.45801 | 0.38338 | 0.3125 | 0.34985 | 0.37735 | 0.33057 | 0.35820 | 0.35294 | 0.27842 | 0.27649 | 0.27972 |

Table C1: Flow rates of each gas effluent conducted three times in liter per minutes.

Table C2: Flow rates of each gas effluent as an average of three replicates in liter per minutes.

| 0. | Q _{out} (L/min) | | | | | |
|---------|--------------------------|-----------------|-------------|-------------|--|--|
| (L/min) | CH ₄ | CO ₂ | O_2 | N_2 | | |
| 0.1 | 0.137132407 | 0.103661659 | 0.084261501 | 0.096485188 | | |
| 0.2 | 0.241899322 | 0.176352301 | 0.140683421 | 0.158973603 | | |
| 0.3 | 0.425921828 | 0.346570906 | 0.347242881 | 0.278213416 | | |

| 0. | Q _{out} (cm ³ /s) | | | | | |
|---------|---------------------------------------|-----------------|-------------|-------------|--|--|
| (L/min) | CH ₄ | CO ₂ | O_2 | N_2 | | |
| 0.1 | 2.28554011 | 1.72769432 | 1.404358354 | 1.60808647 | | |
| 0.2 | 4.031655367 | 2.939205022 | 2.344723687 | 2.649560042 | | |
| 0.3 | 7.09869714 | 5.776181768 | 5.787381357 | 4.636890275 | | |

Table C3: Flow rates of each gas effluent in centimeter cube per second.

Table C4: Permeability of each gas calculated from the permeability equation.

| 0 | Permeability [cm ³ (STP)cm/(cm ² *s*Pa)] | | | | | |
|-----------------|--|-----------------|-------------|-------------|--|--|
| Q in (L/min) | CH ₄ | CO ₂ | O_2 | N_2 | | |
| 0.1 | 2.1767E-08 | 1.64542E-08 | 1.33748E-08 | 1.53151E-08 | | |
| 0.2 | 3.83967E-08 | 2.79924E-08 | 2.23307E-08 | 2.52339E-08 | | |
| 0.3 | 6.76066E-08 | 5.50113E-08 | 5.51179E-08 | 4.41609E-08 | | |

Table C5: Selectivity of CO₂, O₂, and N₂ over CH₄ calculated from the permeability ratio of each gas.

| Q in (L/min) | Selectivity | | | | | |
|-----------------|---|---------------------------------|---------------------------------|--|--|--|
| | CO ₂ /CH ₄ | O ₂ /CH ₄ | N ₂ /CH ₄ | | | |
| 0.1 | 0.755923868 | 0.614453602 | 0.703591445 | | | |
| 0.2 | 0.729031813 | 0.581578402 | 0.65718912 | | | |
| 0.3 | 0.813696042 | 0.815273739 | 0.653203001 | | | |