Removal of CO_2 from Natural Gas by Polyimide Membrane In the Presence of Heavy Hydrocarbon

by

Wong Kin Fai

Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Lau Kok Keong)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken by unspecified sources or persons.

WONG KIN FAI

ABSTRACT

Carbon dioxide, heavy hydrocarbon, hydrogen sulfide, water vapor and toluene are the common impurities found in raw natural gas that can bring detrimental effects on the performance of membrane. The heavy hydrocarbon contamination can cause the loss of flux and membrane performance and thus it is imperative for pretreatment of the natural gas feed stream to remove the contaminants. This project is to study the effect of heavy hydrocarbon on the polyimide membrane performance in separating gas CO_2 from natural gas feed stream at designed operating parameters, i.e. feed pressure, temperature and CO_2 concentration in feed. Liquid Pentane (C_5H_{12}) is used as a basis to simulate the presence of heavy hydrocarbon in the experiments. Gas permeation experiments have been conducted in laboratory to study the effect of pentane on Polyimide membrane performance. It is proven that permeance of CO_2 and CH_4 will decrease with an increase in operating pressure at feed side in both dry and wet condition. The CO_2/CH_4 selectivity increases with an increase in feed pressure. Higher operating temperatures increased CO_2 and CH_4 permeance but decreased CO_2/CH_4 selectivity of polyimide membrane. An increase in CO_2 concentration in feed composition increases the losses of hydrocarbon but reduced CO_2, CH_4 permeance and CO_2/CH_4 selectivity. The decrease of membrane permeance and selectivity with an increase in CO_2 concentration in the feed composition is due to the plasticization and coupling effect. The pentane presence in the feed gas caused swelling or plasticization of polyimide membrane and lead to the reduction in membrane selectivity. It was concluded that the presence of pentane as heavy hydrocarbon in natural gas stream contributed to the loss of membrane selectivity and caused the separation performance of the membrane system become less efficient.

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Natural gas is a fuel that burns cleaner and more environmentally attractive than other traditional fossil fuels as it emits lower quantities of greenhouse gases during combustion. Raw natural gas contains typically 75% to 90% of methane from the total composition and significant amounts of ethane, propane, butane, and 1% to 3% of other higher hydrocarbons (Baker & Lokhandwala, 2008). In addition, the raw natural gas contains undesirable impurities, such as water, carbon dioxide, nitrogen, and hydrogen sulfide. The composition of Carbon dioxide, CO_2 found in the natural gas streams can reach as high as 80% from the total composition. Carbon dioxide, a type of acid gases, is highly corrosive when mixed with water and it will rapidly destroy pipelines and equipment (Dortmundt & Doshi, 1999). In addition, carbon dioxide reduces the heating value of natural gas and freezes at a relatively high temperature, forming blocks of dry ice that can clog equipment lines and damage pumps (Bernardo, Drioli, & Golemme, 2009). Therefore, it is very important to control the composition of gas delivered to the pipeline grids although the composition of raw gas varies widely (Baker & Lokhandwala, 2008).

Carbon dioxide removal from natural gas, also known as natural gas sweetening, is mandatory to meet pipeline specifications limit the CO_2 concentration to 2 mole percent, the H_2S concentration to 4 ppm and water vapour concentration to 0.1 g/m^3 (Lee et al., 1995). There are many types of acid gas removal technologies are available for natural gas sweetening in the market. Each process has its own advantages and disadvantages. Acid gas removal technologies include absorption processes, such as the Benfield^{TM} process (hot potassium carbonate solutions) and Amine Guard-FS^{TM} process (formulated solvents); cryogenic processes; adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA) and membranes processes (Dortmundt & Doshi, 1999). Conventional natural gas processing has included absorption type processes, using either chemical or physical type solvents (amines or glycol-based systems) to remove CO_2, H_2S and H_2O (Lee, et al., 1995). Cryogenic distillation is essentially a fractional distillation of gaseous mixture by exploiting the difference of relative volatilities of CO_2 and CH_4 (Rahman, Aizan, & Ismail, 2005). Adsorption processes operate as an equilibrium or kinetic process depending on the desire product and adsorbent (Y. Yampolskii, 2012).

Membrane gas separation is a pressure-driven process that consists of thin barriers that allow selective permeation of certain gases. A synthetic membrane is a thin barrier between two phases through which differential transport can occur under a variety of driving forces including pressure, concentration and electrical potential across the membranes (Koros, Ma, & Shimidzu, 1996). Membrane gas separation does not require a phase change and presents significant advantages for remote application such as offshore gas-processing platform (Bernardo, et al., 2009). With the flexible design, the compactness and the efficiency of membrane units, membrane gas separation by polymer membranes is a proven technology that is more attractive compared to conventional gas separation methods like cryogenic distillation, absorption or adsorption. (Staudt-Bickel & J Koros, 1999). Membrane plants are generally preferred when processing small gas flows and able to treat high-concentration gas streams much more efficiently than low concentration gas streams. Membrane plant is less complex than amine (Baker & Lokhandwala, 2008). Membranes are predominately based on polymeric materials (Wong & Bioletti, 2002). In an industrial process, the purification of natural gas can be accomplished with membrane systems where it requires a membrane with high selectivity for carbon dioxide to methane (White, Blinka, Kloczewski, & Wang, 1995). Polyimides have been identified as materials with high selectivity for CO_2/CH_4 (White, et al., 1995).

1.2 PROBLEM STATEMENT

One of the most important emerging applications of membrane technology is the usage of membrane systems in the natural gas sweetening processes. Membrane technology for separating gases helps in reducing the environmental impact and costs of industrial processes. Natural gas contains a wide variety of contaminants that can reduce the membrane effectiveness and force premature replacement of the elements. The membrane performance can be easily affected by the presence of heavy hydrocarbon and impurities such as CO_2. Membrane may undergo plasticization or swelling effects when exposed to heavy hydrocarbons or CO_2 with high partial pressure, even in low concentration. Polymeric asymmetric membrane performance can be dramatically reduced by the presence of heavy and condensable hydrocarbons in natural gas streams (Vu, Koros, & Miller, 2003a). Therefore, it is very important to perform pretreatment of the natural gas in feed stream to remove the contaminants such as CO_2, liquids, heavy hydrocarbons and particulate material. There are two situations where liquid hydrocarbons can form within the membrane surface and cause loss of flux and selectivity of membrane. The first one is Joule-Thomson effect results in the gas cools down and the formation of heavy hydrocarbon within the membrane. The second case is when the CO_2 permeates and the gas becomes heavier in hydrocarbons and its dew point therefore increases through the membrane (Paul, Lloyd, & Eldridge, 2004).

Generally, polymeric membranes cannot withstand high temperatures and aggressive chemical environments. The presence of heavy hydrocarbon in feed gas streams can bring detrimental effects to the membrane, particularly in polyimide flat sheet membrane, when applied in petrochemical plants, refineries, off-shore gas processing platform, and natural gas treatment plants. As a result, it is important to evaluate separation performance of membrane material under adverse conditions. The study of the effect of heavy hydrocarbon in natural gas sweetening processes is important to evaluate the performance of membrane systems. The present research works only demonstrated limited studies on this potential problem for the polyimide membrane material. Due to the complexity of heavy hydrocarbon and other impurities in natural gas, the impact of these components on the membrane system has remained poorly understood until today. Also, previous research works showed that it is difficult to characterize the effects of heavy hydrocarbon and impurities experimentally. It is often a challenge to truly simulate the real working environment of a membrane in the laboratory due to the difficulties in identifying the environmental conditions and constraints. Generally, the membrane device in the field has to be robust enough to withstand deterioration due to the wet conditions found with natural gas streams.

In addition, the conventional membrane separation research works for the natural gas sweetening are mainly focused on low feed CO_2 composition and low feed pressure. There are scarce works on the performance of membrane materials in high concentration of carbon dioxide and high pressure operating conditions. It is important to study the maximum limit pressure and feed CO_2 composition for the membrane elements to achieve a cheaper and more effective membrane system. Experimental works in laboratory that simulates field conditions assist in the study of limitations to the polymer and membrane in natural gas sweetening process. Therefore, it is imperative to conduct researches on adverse conditions, particularly on high CO_2 composition in feed stream and high feed pressure, and to study the polymeric membrane performance.

There is a significant interest in research of the effects of heavy hydrocarbons on the membrane performance since these components contribute to loss in permeability and selectivity. Also, it is important to evaluate separation performance of polyimide membrane material in natural gas sweetening under adverse conditions for membrane development in the future.

1.3 OBJECTIVE AND SCOPE OF STUDY

1.3.1 Objective

The main objective of this work is to study the effect of heavy hydrocarbon on the polyimide membrane performance in removing gas CO_2 from natural gas feed stream at designed operating parameters, i.e. feed pressure, operating temperature and CO_2 concentration in feed. Liquid Pentane, C_5H_{12}, is used as a basis to simulate the presence of heavy hydrocarbon in the experiments.

1.3.2 Scope of Works

In order to achieve the objective stated above, the following scope of works has to be conducted:

- To perform preliminary literature research on the commercial membrane, particularly on polyimide membrane.
- To conduct parametric studies for polyimide membrane separation under different operating parameters and conditions in experimental lab for two consecutive semesters. Feed pressure, operating temperature and feed composition (%CO_2 concentration) are the important parameters to be studied in the project.
- To compare the performance of the polyimide membrane in separating CO_2 from natural gas in two different conditions, namely Dry Condition (Without the presence of Pentane as hydrocarbon impurities) and Wet Conditions (with Pentane).
- To discuss and analyze the possible effect of heavy hydrocarbon on the performance of polyimide membrane.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE TECHNOLOGY

Membranes which are thin semipermeable barriers between feed and permeate gas streams have been used to selectively separate some compounds from others (Dortmundt & Doshi, 1999). The widest application for gas separation membranes is the removal of acidic gases, CO_2 and H_2S from raw natural gas. For natural gas sweetening, CO_2 is collected in the low pressure permeate stream whereas CH_4 is enriched in the high pressure retentate stream. The advantages of membranes are cost effectiveness, low capital investment, ease of operation, low energy consumption, space efficiency, good weight and suitable to be used in remote locations, particularly offshore gas processing platform (Dortmundt & Doshi, 1999).

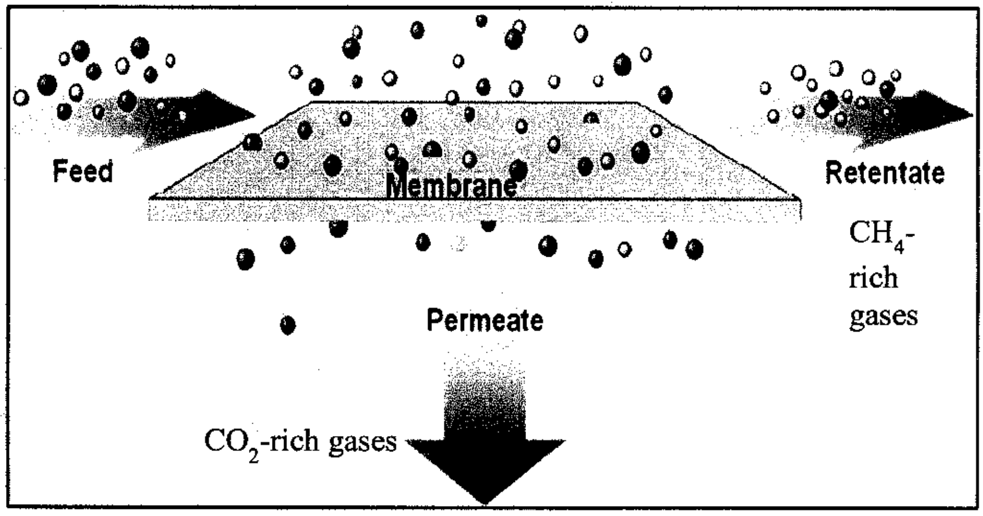


Figure 2.1: Membrane unit for natural gas sweetening. Adapted from (Schmeling, Konietzny, Sieffert, Rölling, & Staudt, 2010)

2.2 MEMBRANE PERMEATION

In petrochemical processing polymer membranes are used commercially to separate air, to remove carbon dioxide from natural gas and to remove hydrogen from mixtures with nitrogen or hydrocarbons. The fundamental parameters characterizing membrane separation performance are the permeability coefficient, P_A, and the selectivity, $\alpha_{A/B}$. In one-dimensional diffusion through a flat membrane, the local flux, N of a penetrant can be described by Fick's law as shown in the following equation:

$$N = -D\left[\frac{\partial C}{\partial x}\right] \qquad (1)$$

where the diffusion coefficient, D, may be a function of local concentration, C (Fick, 1995).

The permeability coefficient, P is generally defined as the flux, N normalized by pressure and membrane thickness.

$$P = \frac{N}{(p_2 - p_1)/l} \qquad (2)$$

Thereby, p_2 and p_1 are upstream and downstream pressures of the penetrants and l is the membrane thickness. Permeation is a solution-diffusion process. Permeability is the rate at which any compound permeates through a membrane; it depends upon a thermodynamic factor and kinetic factor (Bernardo, et al., 2009). Therefore, the permeability coefficient can be expressed as a product of an average diffusion coefficient, D and a solubility coefficient, S (Koros, Flemming, Jordan, Kim, & Hoehn, 1988).

$$P = S.D \qquad (3)$$

The solubility coefficient is determined by the condensability of the penetrants, by the polymer-penetrant interactions and by the amount of excess volume existing in the glassy polymer. The diffusion coefficient, D, is a measure of mobility of the penetrants between the upstream and downstream conditions of the membrane (Staudt-Bickel & J Koros, 1999).

The permselectivity of a membrane for gas separations is characterized by a separation factor, $\propto_{A/B}$ defined in terms of the downstream (y) and upstream (x) mole fractions of two components A and B is given in the following equation:

$$\propto_{A/B} = \left(\frac{y_A}{y_B}\right)\left(\frac{x_B}{x_A}\right) \tag{4}$$

In cases where the downstream pressure is negligible, the separation factor $\propto_{A/B}$ is equal to the ratio of permeabilities of the two gases A and B under mixed gas feed conditions as show in the following equation:

$$\propto^*_{A/B} = \frac{P_A}{P_B} \tag{5}$$

The ideal separation factor, $\propto^*_{A/B}$ is a measure of the intrinsic permselectivity of a membrane material for mixtures of A and B.

The ideal separation factor can be split into two parts:

$$\propto^*_{A/B} = \left(\frac{D_A}{D_B}\right) \cdot \left(\frac{S_A}{S_B}\right) \tag{6}$$

where $\frac{D_A}{D_B}$ is the diffusivity selectivity and $\frac{S_A}{S_B}$ is the solubility selectivity.

Membranes used for CO_2 removal operate on the principle of solution-diffusion through a nonporous membrane. Gas separation membrane processes are mostly based on the sorption of the permeant into the membrane, permeation by diffusion through the membrane, desorption at the low pressure side of the membrane (Bernardo, et al., 2009).

Polymeric membranes are further classified as glassy or rubbery dependent on the value of their glass transition temperature relative to ambient (Scholes, Stevens, & Kentish). Glassy polymers (mainly cellulose acetate and polyimides) dominate industrial carbon dioxide separation applications such as the separation of carbon dioxide from methane, carbon monoxide, nitrogen or other hydrocarbons (Morisato & Pinnau, 1996). Glassy polymeric membranes are based on diffusivity selectivity (Scholes, et al.). The gas CO_2 first dissolves into the membrane and then diffuses through it. The membrane separates based on how well different compounds dissolve into the membrane and then diffuse through it. Fast gases are gases that permeate quickly such as carbon dioxide, hydrogen, helium, hydrogen sulfide and water vapor. Slow gases are the gases that permeate less quickly, for example, carbon monoxide, nitrogen, methane, ethane and other hydrocarbons. The membranes allow selective removal of fast gases from slow gases (Dortmundt & Doshi, 1999).

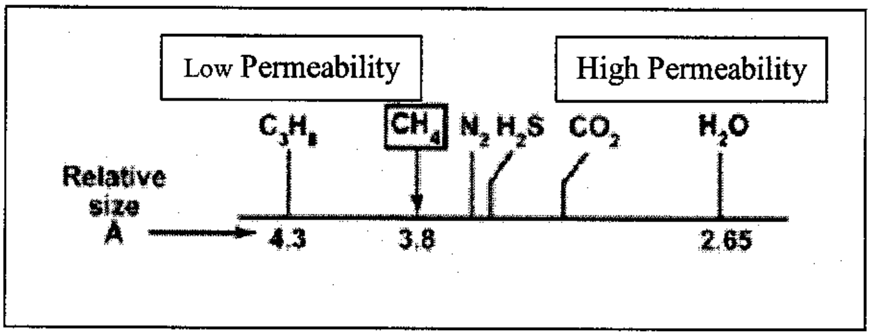


Figure 2.2: Glassy polymers separate gases principally by size.
Adapted from Baker & Lokhandwala (2008).

Rubbery polymeric membranes are the focus due to their ability to separate based on gas condensability. Heavy hydrocarbons are able to permeate at a greater flux than methane (Scholes, et al.). Rubbery polymers have attracted greater interest for the separation of carbon dioxide from hydrogen due to higher flux rates and high selectivity.

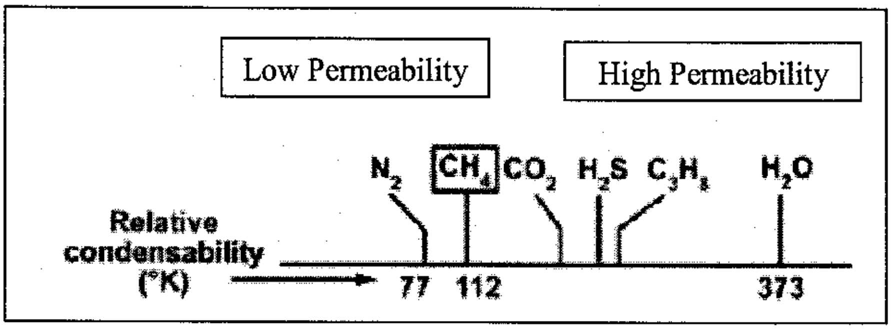


Figure 2.3: Rubbery polymers separate gases principally by condensability.
Adapted from Baker & Lokhandwala (2008).

Rubbery and glassy polymers can also separate carbon dioxide and hydrogen sulfide from natural gas. However, in practice, CO_2 is best separated by glassy polymer membranes that maximizing size selectivity whereas H_2S is best separated by rubbery polymer membranes that maximizing sorption selectivity (Baker & Lokhandwala, 2008).

Despite of the large number of polymeric materials investigated and developed for gas separation applications, the number of polymers used in commercial system is still limited. The main rubbery and glassy polymers employed for gas separation membranes are listed in **Table 2.1** (Bernardo, et al., 2009).

Table 2.1: Most Important Glassy and Rubbery Polymers Used in Industrial Membrane Gas Separation. Adapted from Bernardo, et al. (2009).

Rubbery Polymer	**Glassy Polymers**
Poly(dimethlsiloxane)	Cellulose acetate
Ethylene oxide/propylene oxide – amide Copolymers	Polyperfluorodioxoles
	Polycarbonates
	Polyimides
	Poly(phenylene oxide)
	Polysulfone

2.3 POLYIMIDES

Polyimides are rigid, high-melting point, and thermally stable polymers obtained by polycondensation reactions of dianhydrides with diamines (Bernardo, et al., 2009). Polyimides are a class of polymer that display high permeability for carbon dioxide and good selectivity again methane. They are easy to prepare as asymmetric membranes while demonstrating good thermal and chemical stability and they are viewed as an alternative to cellulose acetate (Tanaka, Taguchi, Hao, Kita, & Okamoto, 1996). Polyimides exhibit an exceptional combination of thermal stability (>500 °C), mechanical toughness and chemical resistance (Rahman, et al., 2005). In addition to high selectivities, polyimide possess high glass transition temperatures, ($T_g > 200^{\circ}C$). A polyimide that is available in the market is Matrimid® 5218. Its permeation properties, combined with its process ability make it an attractive candidate for gas separation application. Furthermore, its mechanical strength and high glass transition temperature, better suit it for more rigorous working environments than other non-cellulosics such as polysulfone (Al-Juaied & Koros, 2006).

2.4 MEMBRANE STRUCTURE

For industrial applications, polymeric membranes can be classified broadly into three classes based on flux density and selectivity: porous, non-porous and asymmetric (Pandey & Chauhan, 2001). According to Pandey & Chauhan (2001), a porous membrane is a rigid, highly voided structure with randomly distributed inter-connected pores whereas non-porous or dense membranes provide high selectivity or separation of gases from their mixtures but the rate of transport of the gases are usually slow.

Asymmetric membranes consist of two structurally distinct layers, one of which is an extremely thin nonporous layer mounted on a much thicker and highly porous layer of the same material as shown in **Figure 2.4**. The nonporous layer is highly selective and thin whereas the porous layer provides mechanical support and allows the free flow of compounds that permeate through the nonporous layer. The drawback for asymmetric membranes are they are costly to make out of exotic, highly customized polymers, which often can be produced only in small amounts (Dortmundt & Doshi, 1999).

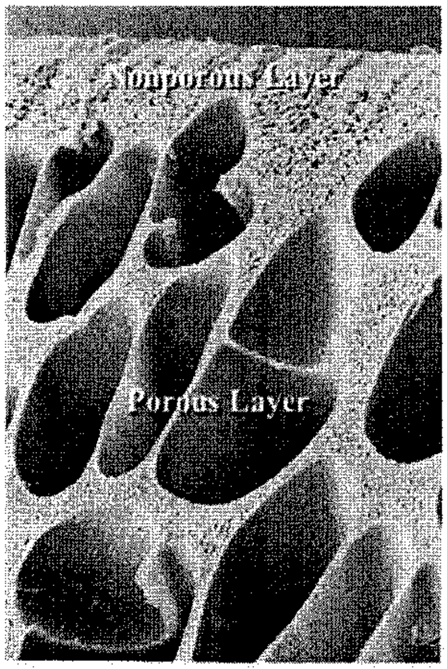


Figure 2.4: Asymmetric membrane structure.

Adapted from Dortmundt & Doshi (1999).

2.5 MEMBRANE ELEMENTS

There are three main types of membranes commercially available for CO_2 removal: cellulose acetate, polyimides and perfluoropolymers (Sridhar, Smitha, & Aminabhavi, 2007). In addition to their gas permeation properties, these polymers are all easy to process through to membrane modules, are mechanically strong and have thermal and chemical resistance to ensure long term viability (Sridhar, et al., 2007). The first membrane systems to separate carbon dioxide from natural gas were introduced by Grace Membrane Systems, Separex, and Cynara. These companies used anisotropic cellulose acetate membrane that was produced using the Loeb-Sourirajan technique (Kohl & Nielsen, 1997).

Cellulose acetate membranes are still widely used. In the last 10 years, they have begun to be challenged by newer membranes, such as the polyimide membranes (made by Medal a division of Air Liquide) (Simmons, Kulkarni, & Ekiner, 2006) and perfluoropolymer membranes (made by ABB/MTR) (Y. P. Yampolskii, Pinnau, & Freeman, 2006).

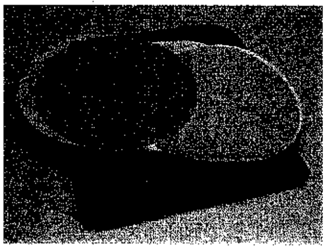


Figure 2.5: Cellulose Acetate

Figure 2.6: Polyimides

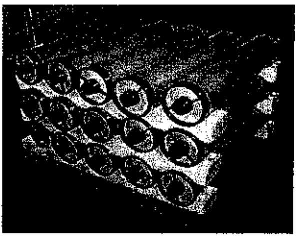


Figure 2.7: Perfluoropolymers

Good membrane module designs consist of the following attributes: high packing density, cost-effective manufacturing, low pressure drops on feed and permeate sides, minimal concentration polarization and have good flow pattern and flow distribution (Rahman, et al., 2005). There are six type of membrane module available and used today on a large industrial scale such as plate and frame module, spiral wound module, capillary membrane module, hollow fiber module and tubular membrane module (Paul, et al., 2004). Gas separation membranes are manufactured in one of two forms: flat sheet or hollow fiber (Dortmundt & Doshi, 1999).

Membranes for gas separation are usually formed as hollow fibers arranged in the tube-and-shell configuration and the flat sheets are typically packaged as spiral-wound modules (Wong & Bioletti, 2002). 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 in the spiral wound module arrangement (Dortmundt & Doshi, 1999).

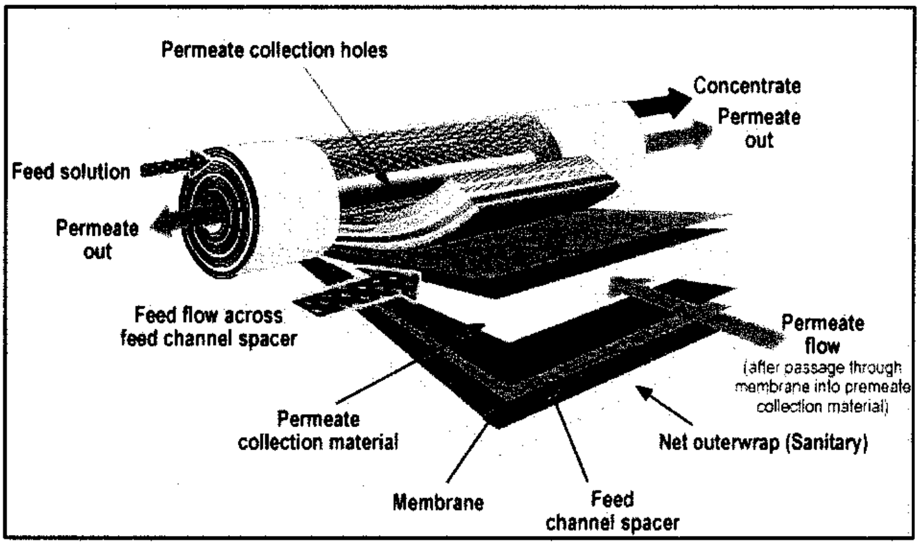


Figure 2.8: Spiral wound membrane element. Adapted from Paul, et al. (2004).

Most of the gas separation membranes today are formed into hollow-fiber modules, with perhaps fewer than 20% being formed into spiral-wound modules (Baker, 2002). In hollow-fiber elements, very fine hollow fibers are wrapped around a central tube in a highly dense pattern. Feed gas flows over and between the fibers and some components permeate into them. The permeated gas travels within the fibers until it reaches the permeate pot and exits the element through a permeate pipe (Dortmundt & Doshi, 1999).

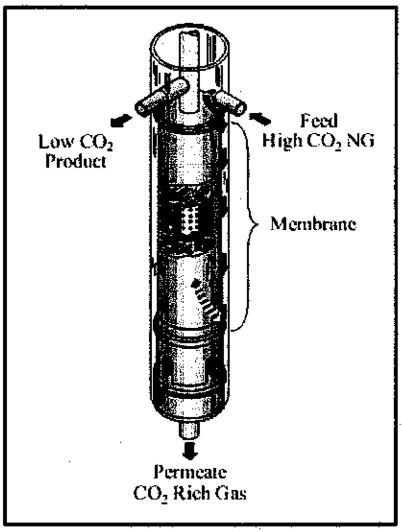


Figure 2.9: Hollow-fiber membrane element. Adapted from Dortmundt & Doshi (1999).

2.6 EFFECT OF IMPURITIES ON THE MEMBRANES PERFORMANCE

The presence of heavy hydrocarbons in the natural gas feed streams can lead to a great impact to the membrane systems. The membrane systems may loss in performance or failure due to the present of very heavy hydrocarbons in the natural gas streams. Loss of flux and/or selectivity due to heavy hydrocarbon exposure can be detrimental to membrane performance in the field. Therefore, it is very important to carefully consider the required pretreatment requirements for membrane systems. Previous work on membrane formation has led to successful formation and modeling of reliable membrane structures for CO_2 removal from natural gas feeds (Clausi & Koros, 2000).

According to Staudt-Bickel and J. Koros (1999), the gaseous feed stream can be composed of over 50% CO_2 at elevated temperature and up to a feed pressure of 60 atm in extreme cases. The CO_2 present in the feed stream can result in the swelling and plasticization of most membrane materials under extreme operation conditions. In enhanced oil recovery applications (EOR), fractured wells and in landfill gas recovery processes are some of the interest areas of CO_2/CH_4 separation with the use of polymeric membrane. The membranes are exposed to high CO_2 concentrations in the feed stream in some of these applications (Staudt-Bickel & J Koros, 1999).

There have been limited studies on evaluating the performance of polymeric membrane and hollow fibers due to the effects of heavy hydrocarbon vapor impurities in natural gas feed streams. Most of the research works have shown that the presence of heavy hydrocarbon vapor impurities contributed to detrimental effect on the polymeric membranes performance (Vu, et al., 2003a). Cellulose acetate membranes tend to show relatively low intrinsic CO_2/CH_4 selectivity, with no loss in flux or CO_2/CH_4 selectivity for contaminants such as benzene, toluene and xylene in natural gas streams (Schell et al., 1989). Polyimides have been identified as materials with high selectivities for CO_2/CH_4 (Tanaka, et al., 1996). For glassy polymeric membranes, particularly polyimide, with intrinsically high selectivity, one study cites harsh performance decline in the range of 50% reduction in CO_2/CH_4 selectivity accompanied with plasticization due to saturated concentrations of toluene or hexane in mixed gas feeds of CO_2/CH_4

(White, et al., 1995). Similar research has been done with 100 ppm and 300 ppm of toluene and n-heptane in 10% CO_2/90% CH_4 gas feeds showed similar selectivity losses (about 30-50%) for asymmetric polyimide hollow fibers membrane module (Djoekita, 2000). In addition to selectivity losses, reductions in flux (30 – 60%) were also observed and were attributed to competition effects and possible compaction of the transition layer in the asymmetric hollow fiber structure (Djoekita, 2000). High selectivity polyimide membrane materials may be susceptible to heavy hydrocarbon exposure because of their greater reliance on diffusivity selectivity (White, et al., 1995). Therefore, disruption of polymer chain mobility possibly caused by condensable penetrants can play a more detrimental role in diffusivity-selectivity polymers. As a result, heavy and condensable hydrocarbons have been suspected of causing membrane performance declines in the fields. Mixed matrix membranes, a new class of hybrid membrane materials, have attractive CO_2/CH_4 separation properties comprising highly selective carbon molecular sieve (CMS) particles dispersed within glassy polymer matrices (Vu, Koros, & Miller, 2003b)

For glassy polymeric membranes, the effect of heavy hydrocarbons or impurities in pure carbon molecular sieve (CMS) membranes is an important concern. Toluene and n-heptane were separately used as representative aromatic and paraffinic impurities, respectively, in 10% CO_2/90% CH_4 gas feeds streams containing up to 300 ppm of these impurities at shell-side feed pressures of up to 900 psia and temperatures of 35 and 50 °C (Vu, et al., 2003a). In this work, Vu et al. show that the CMS membranes maintained CO_2/CH_4 selectivity with only 7-20% reduction in CO_2 permeance during exposure to gas feeds containing these impurities, in comparison to natural gas feeds without these impurities. The results demonstrated that the impurity penetrants are only effective in entering and blocking non-selective micropores and are not able to enter the smaller and selective ultra-micropores.

2.7 MEMBRANE POTENTIAL DETERIORATION FACTORS

The difference between the membrane permeability and selectivity under the influence of heavy hydrocarbon can be caused by the following possible non-ideal effects: (i) competition (ii) plasticization (iii) compaction (iv) conditioning and (v) concentration polarization. (Al-Juaied & Koros, 2006; Paul, et al., 2004).

(i) Competition Effect

The presence of a penetrant that inhibits the transport of the other components contributed to this effect. According to Chern et al, the competition effect should be most apparent for highly condensable feed components, like toluene as suggested by the dual mode sorption theory. If this effect is present and depresses the CO_2/CH_4 selectivity, the selectivity should return to the original value upon removal of the preferentially sorbing penetrant. During exposure to such "C" components, sorption and transport (permeation) pathways are precluded to A and B, thereby reducing their ternary gas permeation in comparison to binary feeds.

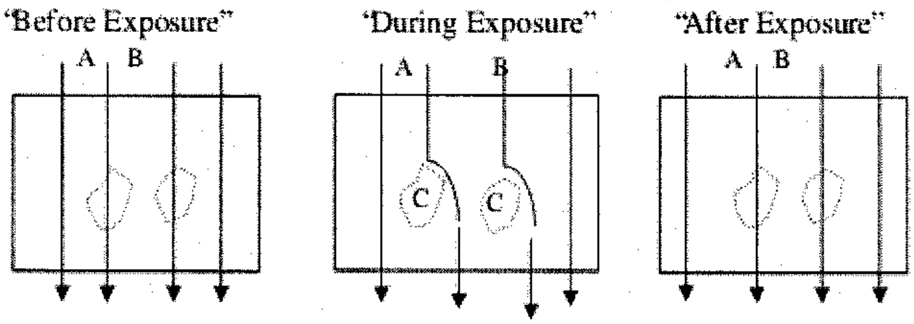


Figure 2.10: Depiction of competition effect caused by a third component, C, in a membrane system. Adapted from Al-Juaied & Koros (2006).

(ii) Plasticization

This effect happens when the presence of a given component in a polymer matrix causes the diffusion, and hence permeation of other components to increase compared to the case without that component present due to a swelling-induced facilitation of a local segmental motion. CO_2 or toluene, a strongly sorbing component, can cause plasticization even in the absence of other penetrants (Al-Juaied & Koros, 2006). The most important plasticizing component in natural gas is carbon dioxide. Membrane materials absorb 30-50 cm^3(STP) of CO_2/(cm^3 polymer) at the high pressure of natural gas operations, and this is equivalent to 5-10 wt% of CO_2 in the polymer and thus, the membrane materials become plasticized (Baker & Lokhandwala, 2008). Plasticization is apparent as non-constant, upwardly inflecting permeability or permeance as a function of CO_2 or toluene feed pressure (Jordan, Fleming, & Koros, 1990).

(iii) Compaction Effect

Plasticized glassy structures exposed to high trans membrane pressure can have reduced moduli and undergo significant rearrangements of the super-molecular morphology leading to a denser microstructure (Djoekita, 2000). The compaction can lead to subtle densification of the finely porous transition region between the more or less dense skin region and the highly porous support layer in an asymmetric hollow-fiber membrane. This results in added mass transfer resistance to the membrane. Such a change tends to reduce permeance and selectivity of all components. Hence, the effect of compaction will be a decrease in the flux and decrease in the selectivity (Paul, et al., 2004).

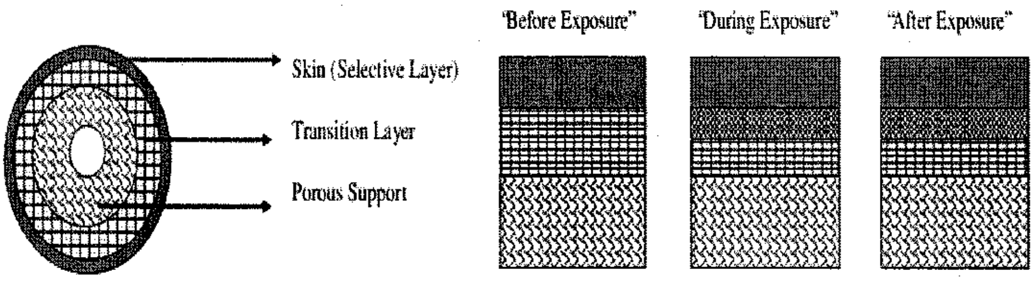


Figure 2.11: Depiction of Compaction Effect. Adapted from Al-Juaied & Koros (2006).

(iv) Swelling Induced Conditioning Effect

The exposure to a highly sorbing gas like CO_2 at high pressures will cause an increase in sorption and dilation levels as compared to levels in an as-received or unconditioned sample (Jordan, et al., 1990). This phenomena has been explained in part by attributing the increase in subsequent sorption and dilation levels to an increased number of subtle packing disruptions in the non-equilibrium polymer matrix, which makes it energetically easier for penetrant molecules to be sorbed and to diffuse (Al-Juaied & Koros, 2006). The swelling induced conditioning effect (SICE) is more pronounced if the secondary penetrant is introduced while the sample is still exposed to the conditioning agent. Upon exposing a glassy sample to a highly sorbing penetrant at a pre-determined pressure and then evacuating completely before exposure to the second penetrant, less dramatic effects are apparent. Toluene, an aromatic substance, is suspected to act as potent SICE agents due to its high condensability (Paul, et al., 2004).

v) Concentration Polarization

The feed mixture components permeate the membrane at different rate in membrane separation processes and cause a gradual build-up in the concentration of non-permeating or slowly permeating components in the feed. A layer is formed near the surface of the membrane, whereby the solution immediately adjacent to the membrane surface becomes depleted in the permeating solute on the feed side of the membrane, and its concentration is lower than that in the bulk fluid. The concentration of the non-permeating component increases at the membrane surface. Concentration polarization is the polarization component that is caused by the concentration changes in the environment adjacent to the membrane surface, it serves to reduce the permeating components' concentration difference across the membrane and thus reduce flux and selectivity. Concentration polarization can be minimized by increasing turbulent mixing at membrane surface to reduce the film thickness (Wind, Paul, & Koros, 2004).

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

In this project, **polyimide membrane** is used to study the effect of heavy hydrocarbon on the membrane performance in removing gas carbon dioxide from natural gas under different operating parameters. The performance of a membrane is characterized by the selectivity and permeance for asymmetric membrane. The permeance, P/t, is the pressure normalized flux and is the preferred productivity measure for asymmetric membranes where the actual thickness of the selective skin layer is not clearly measurable. Using these parameters, the performance of the membrane can be examined based on determination of CO_2/CH_4 selectivity and permeance. The experiments were completed by evaluating the performance of membrane in two different conditions: the first is the feed gas stream without any hydrocarbon, namely **Dry Condition** and the second is the feed gas stream with heavy hydrocarbon (pentane) as **Wet Condition.**

The investigated operating parameters for the performance of membranes system are as follow:

- Feed Pressure = 10, 20, 40 and 50 bar
- Operating Temperature = 30, 40 and 50 °C
- Concentration of CO_2 in feed gas = 25, 40, 55 and 70 % of CO_2

Prior to the experiments, the flat sheet polyimide membrane is cut into a round shape by using a sharp razor blade and put into a membrane test cell holder. For the permeation tests, the manipulated variables of the experiments are feed pressure, temperature and carbon dioxide concentration in natural gas feed stream. **Pentane** is used to simulate the presence of heavy hydrocarbon in natural gas stream. The total feed stream flow rate is 50 SLPM (Standard Liter per Minute). The first set of experiment was started with 25% CO_2/75% CH_4 feed stream without any hydrocarbon at 30 °C and 10 bar. The same experiments were repeated in dry condition vary according to the specified feed pressure, temperature and CO_2 concentration in feed stream. A total of 48 set of experiments with different combination of feed pressure, temperature and CO_2 concentration in feed stream were completed to evaluate the performance of polyimide membrane in dry condition. Similarly, for wet condition, the experiments were repeated with different combination of feed pressure, temperature and CO_2 concentration in feed stream in the presence of heavy hydrocarbon.

In order to study the effect of heavy hydrocarbon in the feed stream, the selectivity and permeance of the membrane from the same module are compared. Subsequently, the effect of pentane on CO_2 permeance, CH_4 permeance and CO_2/CH_4 selectivity were studied. Testing with the same module minimizes the processing variability that could occur between modules and to avoid any hysteresis effect on the membrane performance.

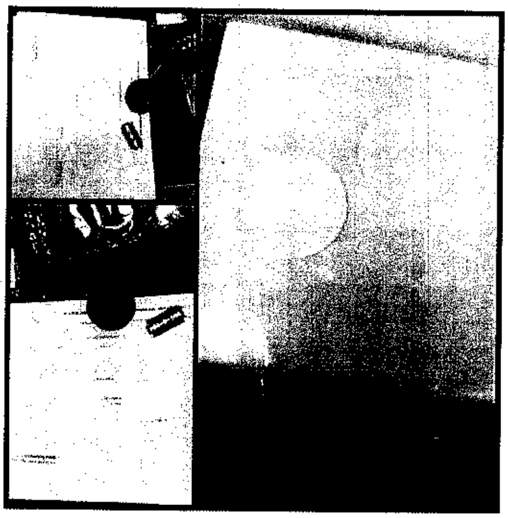


Figure 3.1: Polyimide membrane is cut using sharp razor blade

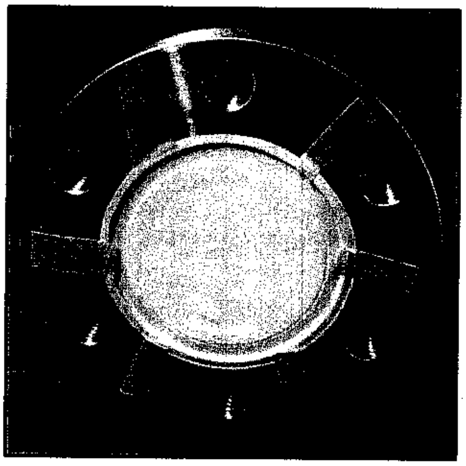


Figure 3.2: Membrane test cell with polyimide membrane

3.2 PROJECT ACTIVITIES

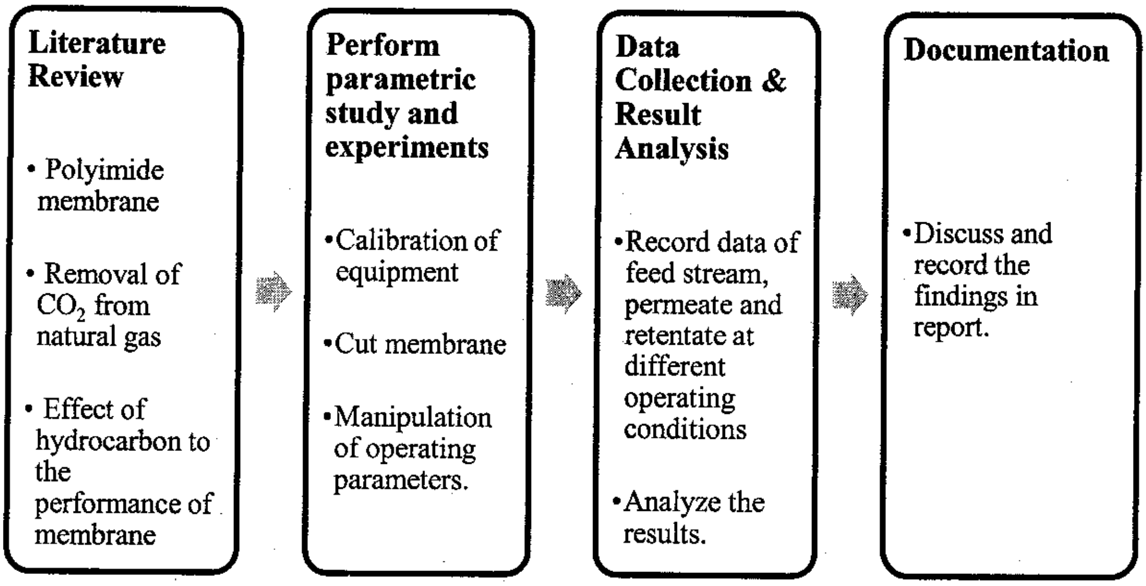


Figure 3.3: Research methodology flow chart

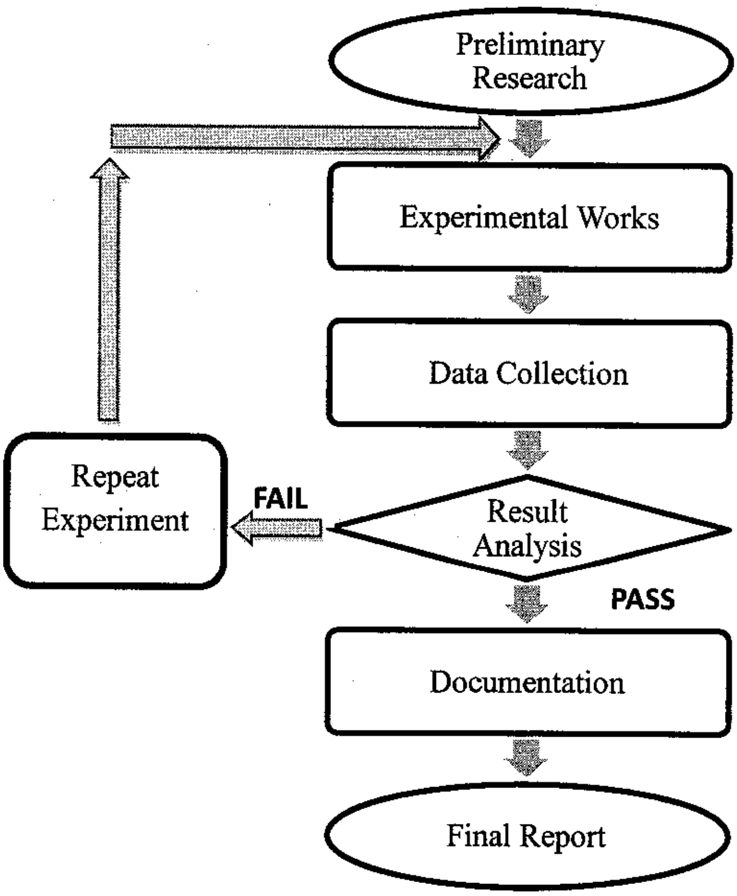


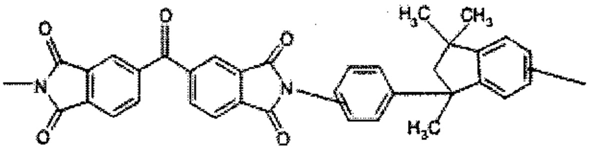
Figure 3.4: Flow Chart of final year project activities.

3.2.1 Material

The polyimide membrane used in this experimental works is Matrimid® 5218, a commercially available polyimide made from the monomers 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diaminophenylindane (Vu, et al., 2003a). The chemical structure and physical properties of the Matrimid® 5218 membrane was shown in **Table 3.1**. Matrimid® 5218 membrane possess high glass transition temperatures, T_g =302°C and density 1.24 g/cm^3. The Matrimid® 5218 membrane used in this study was purchased from Alpha Membrane Hi-Tech Pte. Ltd., Singapore.

Table 3.1: Chemical structure and physical properties of Matrimid® 5218.

Adapted from White et al., (1995).

Polymer	**Chemical Structure**	**Density (g/cm^3)**	**T_g (°C)**
Matrimid® 5218		1.24	302

The properties of the polyimide membrane used in the experiments are summarized in the table below:

Table 3.2: Polyimide Membrane Specification

Membrane Type	Polyimide Flat Sheet Membrane
Membrane Configuration	Asymmetric Membrane
Membrane Diameter	4.35 cm
Membrane Area	14.86 m^2
Membrane Thickness	200 micrometer
Condition	Dry State
Supplier	Alpha Membrane Hi-Tech Pte. Ltd., Singapore

3.2.2 Gas Permeation Experiments

Experimental laboratory works were conducted to evaluate the performance of the membrane in separating carbon dioxide from natural gas. The equipment set used for the experiment is **Carbon Dioxide Separation Membrane Unit (CO2SMU)**. Polyimide membrane in flat module is inserted into a membrane test cell where natural gas and gas carbon dioxide will pass through it for the permeation tests. Carbon Dioxide Separation Membrane Unit (CO2SMU) consists of different unit operations as follows:

i. Gas Feeding System (Automatic mass flow controller)
ii. Heating System (Oven)
iii. Compression System (Compressor)
iv. Back Pressure Regulator, Pressure Gauges and Transmitters System
v. Saturation System (Saturation Vessel)
vi. Separation System (Membrane Test Cell, Mixed Gas Flow Meter, Infrared (IR) Gas Analyzer)
vii. Post Treatment System (Toxicap Fume Hood)

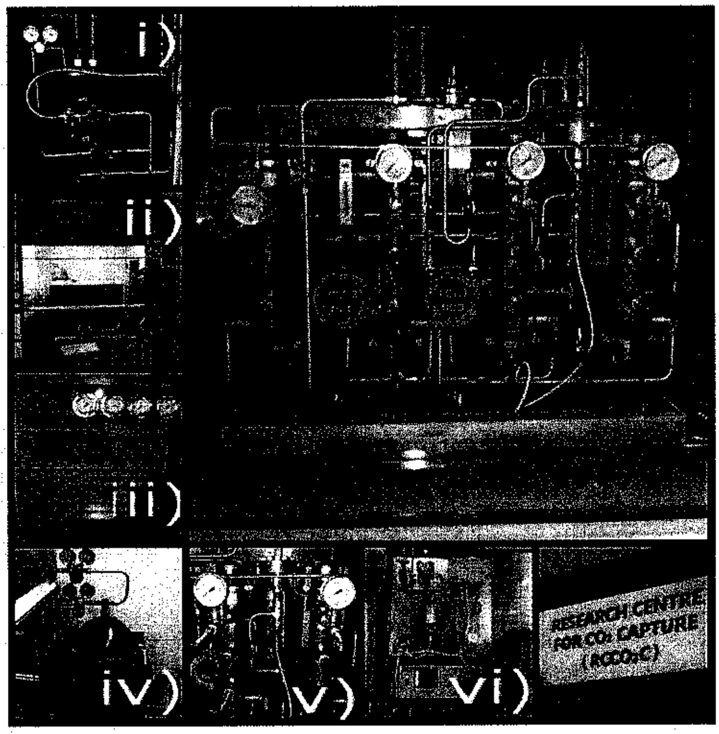


Figure 3.5: Carbon Dioxide Separation Membrane Unit (CO2SMU) at Block N, UTP

3.2.3 Experimental Setup of Carbon Dioxide Separation Membrane Unit

The experimental set-up for the full-scale module of Carbon Dioxide Separation Membrane Unit (CO2SMU) is illustrated in **Figure 3.6**.

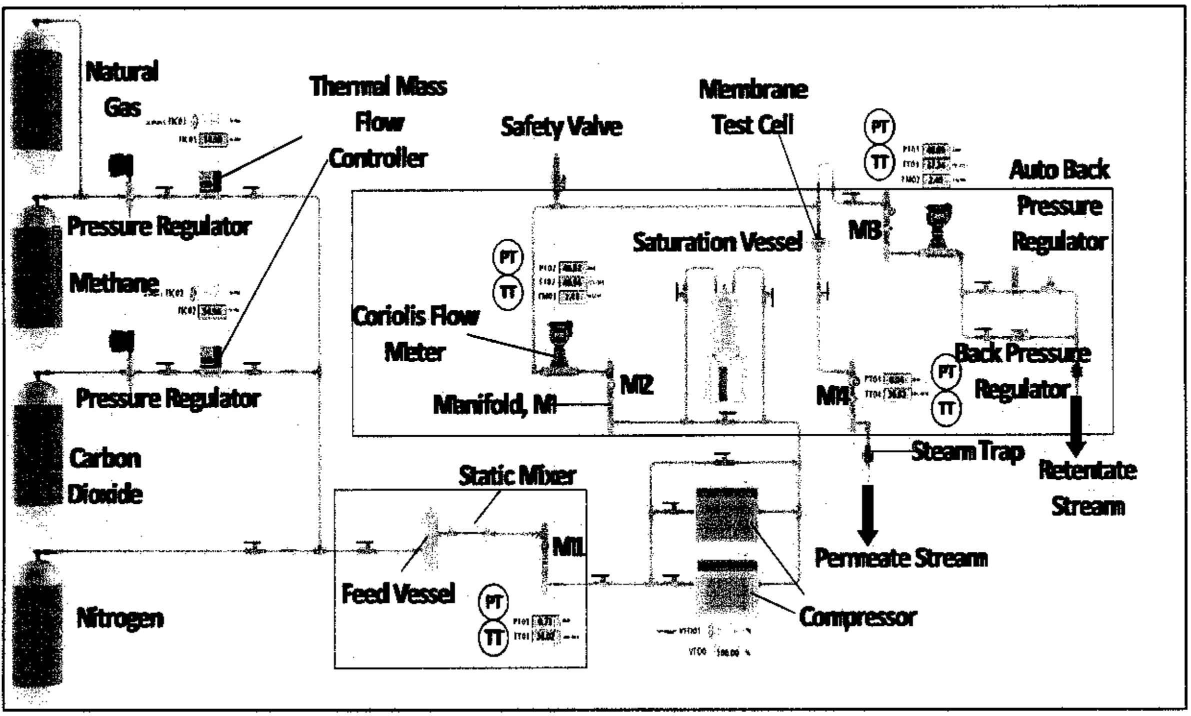


Figure 3.6: Flow Diagram of Experimental Setup for Carbon Dioxide Separation Membrane Unit (CO2SMU)

CO2SMU is equipped with a heating system or an **oven** (represented by the red boxes in **Figure 3.6**) where all the major equipment and process piping are stored in the oven. The gas feeding line and the membrane module were leak tested using nitrogen prior to the gas separation experiments. The gas feeding line consists of Natural Gas (NG), Methane (CH_4), Carbon Dioxide (CO_2), Nitrogen (N_2), and an additional point for other gases. Gas feeding system in CO2SMU consists of **automatic mass flow controller** serves as mass air flow sensor, controller and flow meter. The digital mass flow controller can be used to adjust and measure the flow rate of the gases before sending to feed vessel. The feed gases from gas tanks were admitted to **feed vessel** and **static mixer** to mix multiple gas streams homogeneously before entering gas compressor or saturation vessel. The feed pressure was automatically set with a pressure controller (use either **Equilibar** or **Bronkhorst**) in this experiment.

For experiments in dry condition (without heavy hydrocarbon), the feed gases bypass the **saturation vessel.** CO2SMU is a one-stage flow scheme where a feed gas is separated into a permeate stream rich in CO_2 and a retentate stream rich in methane. **Polyimide membrane** is placed in a **membrane test cell** which contains **milipore pressure filter holder** (XX45 047 00). It is equipped with a **pressure relief valve**. The feed and residue flow rates were measured with mixed gas flow meter (**Coriolis Digital Flow Controller**) and the permeate flow rate was measured with a **Rotameter**. The membrane module was flushed with pure nitrogen after each experiment to avoid the accumulation of any remaining hydrocarbon on membrane test cell.

For temperature control, the entire set-up of COSMU (except compressor, gas analyzer, gas feeding and gas storage system) are stored in the oven. The temperature inside the oven can be controlled from ambient temperature to 100 °C. The temperatures and pressures of all the gas streams (namely, feed, permeate and retentate) were monitored by thermocouples and pressure transducers, respectively. The measured gas flow rate, temperature and pressure were all logged onto a computer using data logger. All experimental data were continuously monitored. The gas composition was analyzed by an **Infra-red (IR) Gas Analyzer** that was equipped with a thermal conductivity detector. At least three samples were collected and analyzed to determine the gas composition and the concentrations were measured in terms of mol% or vol%. The CO2SMU is equipped with a **Toxicap Fume Hood** as a post treatment system to filter the impurities prior to vent the gases to atmosphere.

3.2.4 Experiment Procedures

The start-up procedures of the experiment are as the following:

1. The main breaker/isolator (MEM/EATON) in the main panel board is switched on.
2. The MCB breakers in control panel board are switched on.

   i) Control Panel 1: On switches for Compressor 1 and Compressor 2. All MCB breakers are switched on except MCB 3.

   ii) Control Panel 2: All MCB breakers are switched on except MCB 1.

3. Analyzer switch, Hot Box switch and computer are switched on.
4. The valves of the three gas tubes for Natural gas, carbon dioxide and nitrogen tanks are opened.
5. The heater regulator for carbon dioxide is switched on.
6. The value of the mass flow controller (SIERRA digital mass flow controller) is set based on the desired value in standard liter per minute (SLPM).
7. The valves for gas inlet of CO_2 and CH_4 and the outlet valve of mass flow controller are opened.
8. The heater regulator for CH_4 and CO_2 are set to 7 bars and 100psi, respectively.
9. The temperature of the oven is set from the control panel.
10. Polyimide membrane is prepared with diameter of 4.5 cm and put in the membrane test cell.
11. For experiments in dry conditions (without heavy hydrocarbon), the system will bypass the saturation vessel. Saturation vessel is only used for experiments in wet conditions (with heavy hydrocarbon) to saturate mixed gases with heavy hydrocarbon (pentane as a basis).
12. The valve of equilibar is opened, the valve of Bronkhorst and by-pass valve of Flow Meter 2, FM 02 are closed.
13. The valve of membrane test cell is opened to allow the mixed gases pass through the membrane. The total feed flow rate of mixed gases is set at 50 SLPM.

14. The mixture of methane and carbon dioxide gases pass through the membrane test cell. The feed and residue flow rates were measured with mixed gas flow meter (Coriolis Digital Flow Controller) and the permeate flow rate was measured with a Rotameter.
15. The temperatures and pressures of feed, permeate and retentate streams were monitored by thermocouples and pressure transducers, respectively and the raw data were all logged onto a computer using data logger.
16. The gas composition was analyzed by an Infra-red (IR) Gas Analyzer that was equipped with a thermal conductivity detector.
17. The same experiments are repeated for pressure of 10 bar, 20 bar, 40 bar and 50 bar while the temperature maintain at 30 °C with 25 % concentration of carbon dioxide in feed gas.
18. The same experiments are repeated for the following operating conditions:
    a. Feed Pressure = 10, 20, 40 and 50 bar
    b. Operating Temperature = 30, 40 and 50 °C
    c. Concentration of carbon dioxide in feed gas = 25, 40, 55 and 70 %
19. In dry condition, 48 set of experiments with different combination of feed pressure, temperature and CO_2 concentration in feed stream were completed to evaluate the performance of polyimide membrane.
20. Procedures 1 to 18 are repeated to evaluate the performance of polyimide membrane with the presence of hydrocarbon (in wet condition). Liquid Pentane will be filled into saturation vessel to allow the mixed gases in feed stream saturated with heavy hydrocarbon before sending to membrane test cell.

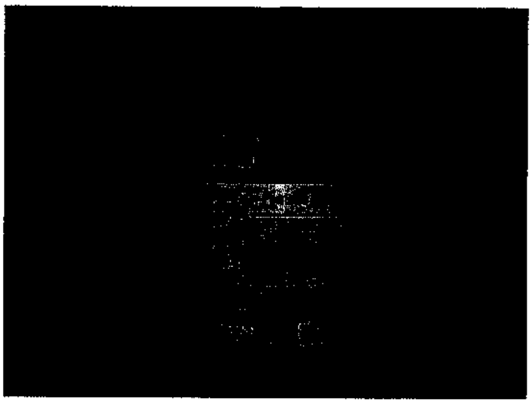


Figure 3.7: Liquid Pentane for experiments in Wet conditions

3.3 TOOLS AND EQUIPMENT

Table 3.3: Equipment or tools of Carbon Dioxide Separation Membrane Unit

No.	Equipment / tools	Descriptions	Unit
1	Feed Gas Unit	Gas Feeding line consists of Methane (CH_4), Carbon Dioxide (CO_2), Nitrogen (N_2), Natural Gas (NG), and an additional point for other gases. Gas CH_4 Tank = 1 x 50L Gas CO_2 Tanks = 3 x 25kg Gas N_2 Tank = 1 x 50L Gas NG Tanks = 3 x 50L	5
2	Pressure Regulating System	To regulate the outlet pressure from gas tank before reaching the mass flow controller. Inlet Pressure = Max. 200 barg. Outlet Pressure = 10 – 80 barg.	1
3	Automatic Mass Flow Controller (SIERRA)	To measure the mass of gas volume in the range of 10 to 100 SLPM under standard conditions of pressure and temperature.	3
4	Feed Vessel	To mix multiple gas streams before feed into the static mixer. Maximum operating pressure = 80 bar.	1
5	Static Mixer	To mix multiple gas streams homogeneously before entering gas compressor or saturation vessel or membrane test cell. Maximum operating pressure = 80 bar.	1
6	Gas Compressor	To increase the pressure of mixed gas stream and to ensure smooth and continuous flow of outlet gas. Range of flow rate = 10 – 100 SLPM Maximum operating pressure = 80 bar. Maximum CO_2 concentration = 70 %.	2
7	Mixed Gas Flow Meter	Coriolis type flow meter is used to measure and indicate the flow rate of the mixed gas before entering and after pass through the membrane test cell. Range of flow rate = 10 – 100 SLPM	2

No.	Equipment / tools	Descriptions	Unit
8	Saturation Vessel	To saturate mixed gases with heavy hydrocarbon (pentane as a basis) or water. It is equipped with heated which is able to heat the process fluid up to 100 °C. Maximum operating pressure = 80 bar.	1
9	Membrane Test Cell	To place the membrane in the milipore pressure filter holder (XX45 047 00). It is equipped with pressure relief valve. Maximum operating pressure = 80 bar. Maximum operating temperature = 70 °C.	1
10	Back Pressure Regulator (BPR)	To maintain the pressure within the system at a particular set point. Two BPR: Automatic BPR and Manual BPR. Maximum operating pressure = 80 bar. Maximum operating temperature = 70 °C.	2
11	Steam Trap	To collect any gases/liquid carries over from the membrane test cell.	2
12	Infrared (IR) Gas Analyzer	To measure concentration of CO_2 and CH_4. Detection range: CO_2: 0-100 %, CH_4:0-100 % and CO_2 - CH_4 mixture at any combination between 0-100 %.	1
13	Oven	To control the temperature in the system which accommodates all the process piping and major equipment except compressor, IR gas analyzer, gas feeding line and gas storage system.	1
14	Toxicap Fume Hood	Consists of two levels of molecular filters to separate the impurities before release the gas to the atmosphere. It equipped with fan failure alarm system in case of ventilation failure.	1
15	Control Panel	To display and control the measurement of instruments: pressure, temperature, flow rate or concentration.	1

3.4 GANTT CHARTS AND KEY MILESTONE

Table 3.4: Project Activities and Planning for FYP I January 2012 semester

NO	Week Details	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	▨■	▨■						Mid –Semester Break							
2	Preliminary Research Work		▨■	▨■	▨■	▨■										
3	Submission of Extended Proposal Defense						●■	■								
4	Proposal Defense									●						
5	Project Work Continues	▨	▨	▨	▨	▨	▨	▨		▨■	▨■	▨■	▨■	▨■	▨■	▨■
6	Prepare Interim Draft Report									▨■	▨■	▨■	▨■	▨■	▨■	
7	Submission of Interim Report															●■

Table 3.5: Project Activities and Planning for FYP II May 2012 semester

NO	Week Details	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continues	▨■	▨■	▨■	▨■	▨■	▨■	▨■	Mid –Semester Break							
2	Submission of Progress Report									●■						
3	Project Work Continues									▨■	▨■	▨■	▨■	▨■		
4	Pre-EDX												●■			
5	Submission of Draft Report													●■		
6	Submission of Dissertation (Soft bound)														●■	
7	Submission of Technical Paper														●■	
8	Oral Presentation															●■
9	Submission of Project Dissertation															●■

▨ Planned Activities of FYP ■ Completed Activities of FYP ● Key Milestone

CHAPTER 4

RESULTS AND DISCUSSION

4.1 DATA GATHERING

In this report, polyimide flat sheet membrane was used in the experiments to study the effect of pentane on the membrane performance. For the gas permeation tests, the manipulated variables of the experiments are feed pressure, temperature and carbon dioxide concentration in natural gas feed stream. Since heavy hydrocarbons and aromatics compound can bring significant effect to the performance of polyimide membrane, pentane is used to simulate the presence of heavy hydrocarbon in the working environment in laboratory. A flat sheet polyimide membrane with an area of 14.86 cm^2 was tested with both mixed gas measurements in both Dry (without pentane) and Wet (with pentane) conditions, and the CO_2/CH_4 permeance and selectivity of the membrane are calculated to evaluate the performance of the membrane. The permeance is expressed as a thickness normalized permeability and is given in gas permeation units, GPU (1 GPU = 10^{-6} cm^3 (STP) cm^{-2} s^{-1} cm Hg^{-1}). The selectivity of the mixed gas was calculated as the ratio of the respective gas permeance obtained in the experiments.

In order to calculate the permeance of CO_2 and CH_4, the membrane system is treated as a complete-mixing model for gas separation. According to Weller and Steiner, the permeate flow rate is a small fraction of the entering feed rate when a membrane system is operated at a low recovery, and thus, there is a minimal change in composition. With the use of complete-mixing model, the permeance of CO_2 and CH_4 and selectivity can be calculated.

Complete-Mixing Model for gas separation by polyimide membranes

A detailed process flow diagram is shown for complete mixing for gas separation by polyimide membrane in **Figure 4.1** (Geankoplis, 2003). The section below will explain the steps of calculations and theories involved in the project in order to channel the results obtained to graphical form.

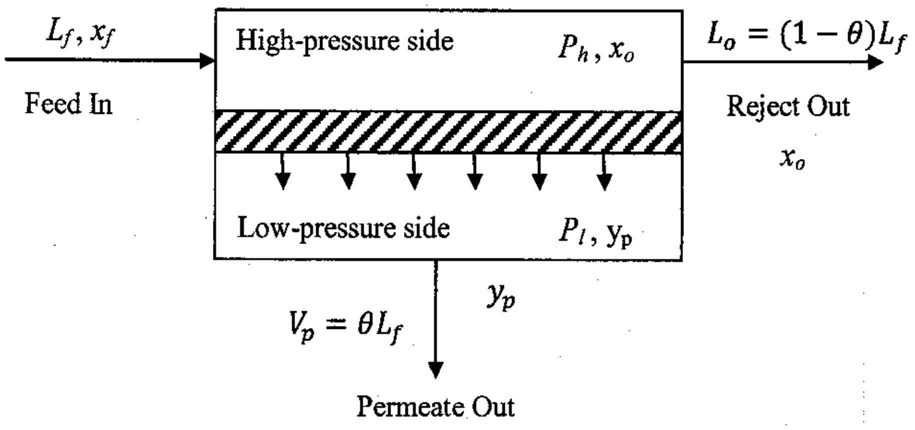


Figure 4.1: Process flow for complete mixing case. Adapted from Geankoplis (2003).

Using the feed and non-permeate flow rate as L and composition x (in mole fraction) and the permeate flow rate as V and composition y (in mole fraction), the overall material balance is as follows:

$$L_f = L_o + V_p$$

where L_f is total feed flow rate, cm^3 (STP)/s; L_o is outlet reject flow rate, cm^3 (STP)/s; V_p is outlet permeate flow rate, cm^3 (STP)/s

The stage cut or fraction of feed permeated,

$$\theta = \frac{V_p}{L_f}$$

The rate of diffusion or permeation of species A (in a binary of A and B) is given below:

$$\frac{V_A}{A_m} = \frac{V_p y_p}{A_m} = \left(\frac{P'_A}{t}\right)(p_h x_o - p_l y_p)$$

Where P'_A is permeability of A in the membrane, cm^3 (STP) · cm/(s · cm^2 · cm Hg); V_A is flow rate of A in permeate, cm^3 (STP)/s; A_m is membrane area, cm^2; t is membrane thickness, cm; $p_h$is total pressure in the high-pressure (feed) side, cm Hg; p_l is the total pressure in the low pressure or permeate side, cm Hg; x_o is mole fraction of A in reject side; x_f is mole fraction of A in feed; and y_p is mole fraction of A in permeate.

A similar equation can be written for component B.

$$\frac{V_B}{A_m} = \frac{V_p(1-y_p)}{A_m} = \left(\frac{P'_B}{t}\right)\left[p_h(1-x_o) - p_l(1-y_p)\right]$$

where P'_B is permeability of B in the membrane, cm^3 (STP) · cm/(s · cm^2 · cm Hg).

(Note: $p_h x_o$ is the partial pressure of A in the reject gas phase and $p_l y_p$ is the partial pressure in the permeate side. Component A = CO_2 and Component B = CH_4)

The ideal selectivity, α^*

$$\alpha^* = \frac{P'_A}{P'_B}$$

where P'_A is permeability of A in the membrane, cm^3 (STP) · cm/(s · cm^2 · cm Hg) and P'_B is permeability of B in the membrane, cm^3 (STP) · cm/(s · cm^2 · cm Hg).

The gas-mixed (real) selectivity (separation factor), $\alpha_{A/B}$

$$\alpha_{A/B} = \left(\frac{y_A}{y_B}\right) \cdot \left(\frac{x_B}{x_A}\right)$$

where x_A is mole fraction of A in feed, y_A is mole fraction of A in permeate,

x_B is mole fraction of B in feed, y_B is mole fraction of B in permeate.

All the results of experiments are summarized in table form (for both dry and wet conditions) as shown in appendices.

4.2 DATA ANALYSIS

4.2.1 Effect of Operating Pressure

Feed pressure contributes to significant effects of the membrane performance. It serves as one of the main driving forces with feed concentration and temperature for membrane separation (Hwang et al., 2011). By using a compressor at the feed side, the pressure difference across the polyimide membrane was controlled in the experiments. The dry condition is a situation where there is no existence of pentane in the feed gas stream whereas the wet condition is the feed gas stream with pentane to simulate heavy hydrocarbon as aforementioned. To study the effects of pentane on operating pressure on the performance of membrane, CO_2 permeance and CO2/CH4 selectivity are plotted versus the feed pressure in both dry and wet condition as shown in **Figure 4.2**.

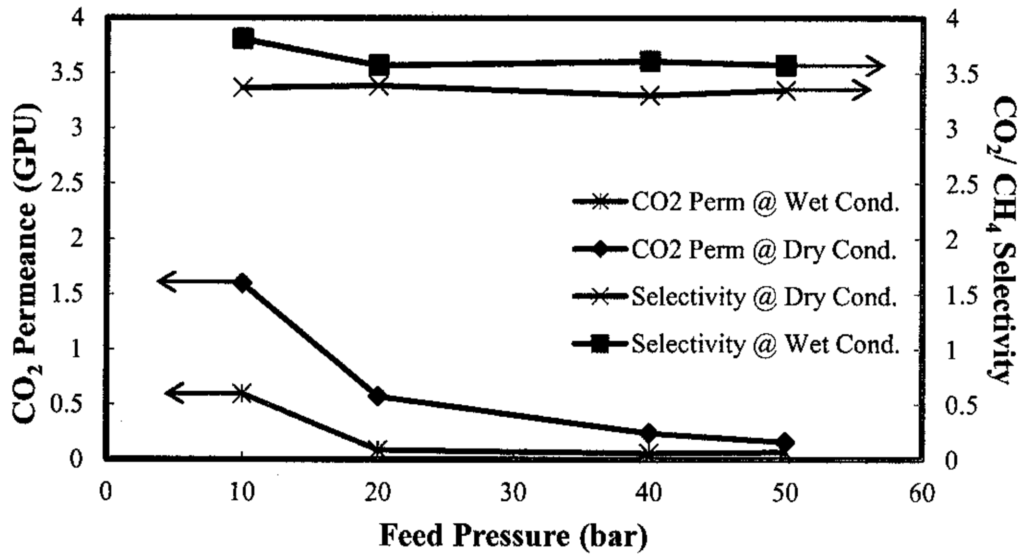


Figure 4.2: CO_2 permeance and CO_2/CH_4 selectivity as a function of operating feed pressure. Temperature: 50 °C and Feed Composition: 40% of CO_2 concentration.

The effects of the operating pressures with 40% of CO_2 concentration in mixed gas feed stream at 50 °C is showed in **Figure 4.2**. The feed pressure was varied in 10 bar steps from 10 to 50 bar_a with 40% of CO_2 concentration in mixed gas feed stream at 50 °C. It was speculated that the presence of pentane in the feed might influence the membrane performance. Experimental results were shown in **Figure 4.2** with the plot of CO_2 permeance and CO_2/CH_4 selectivity as a function of operating feed pressure. Higher operating pressures at the feed side demonstrated decreased permeance of CO_2 in both dry and wet conditions. It is obvious that the CO_2 permeance decreases with the increased of feed pressure whereas the CO_2/CH_4 selectivity increased with higher operating pressures in both dry and wet conditions. An increased operating pressure resulted in low permeation flux but high CO_2/CH_4 selectivity.

Similarly, the CH_4 permeance displayed an inverse relationship with the increased of operating pressures as shown in **Figure 4.3**. The higher the operating feed pressure, the lower the CH_4 permeance on the membrane performance. The CO_2/CH_4 selectivity in Wet Condition is higher than CO_2/CH_4 selectivity in Dry Condition.

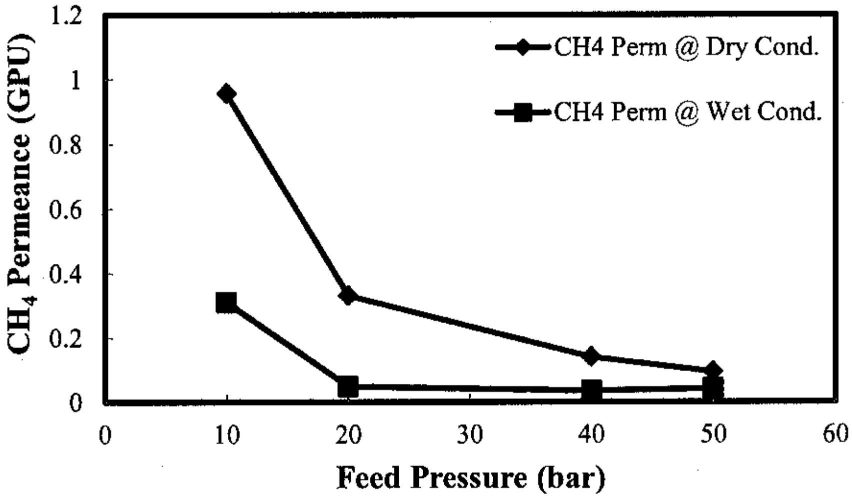


Figure 4.3: CH_4 permeance as a function of operating feed pressure. Temperature: 50 °C and Feed Composition: 40% of CO_2 concentration.

Initially, the experimental results were suspected as experimental inaccuracies. Therefore, several set of experiments were conducted to verify the consistency and reproducibility of the experimental results. The experimental results are further corroborated in **Figure 4.4** and **4.5** where the permeance of CO_2, CH_4 and CO_2/CH_4 selectivity are plotted as a function of operating pressure.

In **Figure 4.4** and **4.5**, the operating temperature of the experiment is 30 °C with 55% of CO_2 concentration in mixed gas feed stream. The results showed that both CO_2 and CH_4 permeance varied instantaneously with the change in feed pressure.

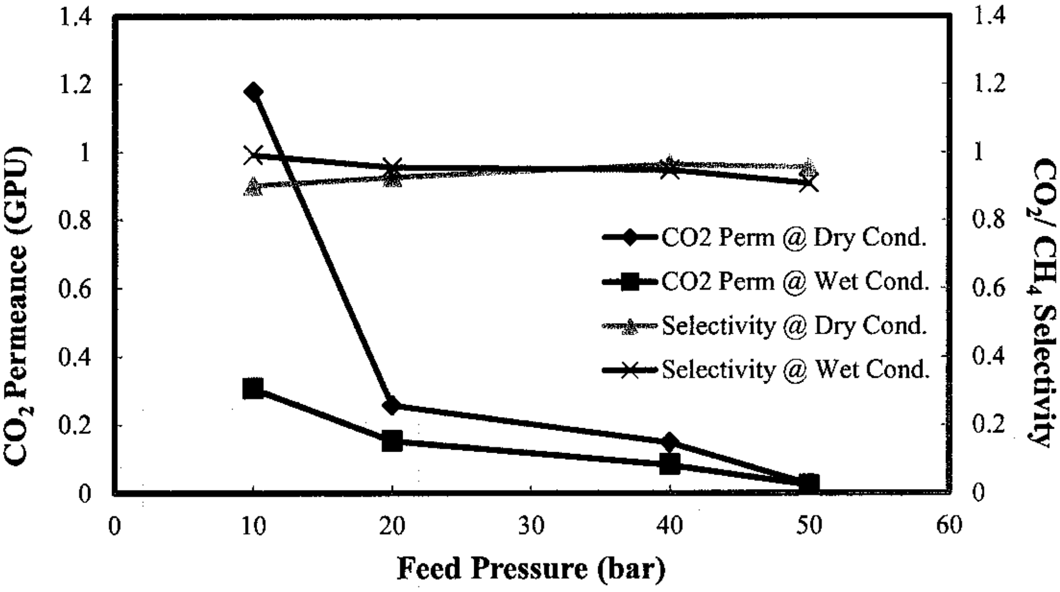


Figure 4.4: CO_2 Permeance and CO_2/CH_4 Selectivity as a function of operating feed pressure. Temperature: 30 °C, Feed Composition: 55% of CO_2 concentration.

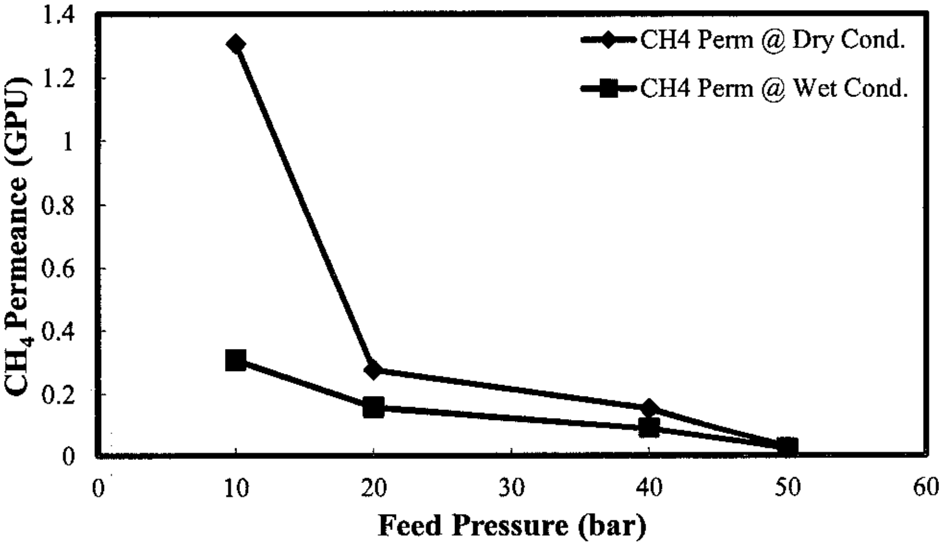


Figure 4.5: CH_4 Permeance as a function of operating feed pressure. Temperature: 30 °C, Feed Composition: 55% of CO_2 concentration.

Since the trend of graphs is similar in the previous case, it is confirmed that the results on the effects of operating pressures are valid.

A major problem that always encountered for gas separation in glassy polymer, especially for separation of CO_2/CH_4 is plasticization (Liu, Wang, & Chung, 2001). Plasticization pressure of polyimides is normally above 10 bar (Bos, Pünt, Wessling, & Strathmann, 1999). From the gas permeance versus pressure plot, the minimum pressure noticed is called the plasticization pressure. At **Figure 4.2** and **4.4,** the minimum permeance of CO_2 was observed at the pressure of 50 bar for the CO_2 permeance versus pressure plot. This indicates that the polyimide membrane was undergoing the plasticization phenomenon at that particular pressure. For glassy polymer, the CO_2 permeance decreases with increasing feed pressure can be explained by the dual sorption model. An increase of operating pressure will diminish the rate of the permeation flux (Shi, Kong, Yu, Wang, & Yang, 2006). Plasticization is highly undesired since it will cause a drastic decrease in selectivity when mixed gas experiments are performed. To overcome this problem, cross-linking modification can be applied when it can enhance the transport properties of polymeric membrane and reduce the plasticization effect.

The ratio of the permeate flux to the feed flux is known as Stage cut. As shown in **Figure 4.6**, the increasing feed pressure decreased the stage cut. There is a slight increase of stage cut with the presence of pentane, indicating a plasticization effect, where more permeate flow through the membrane at Wet condition compare to Dry condition.

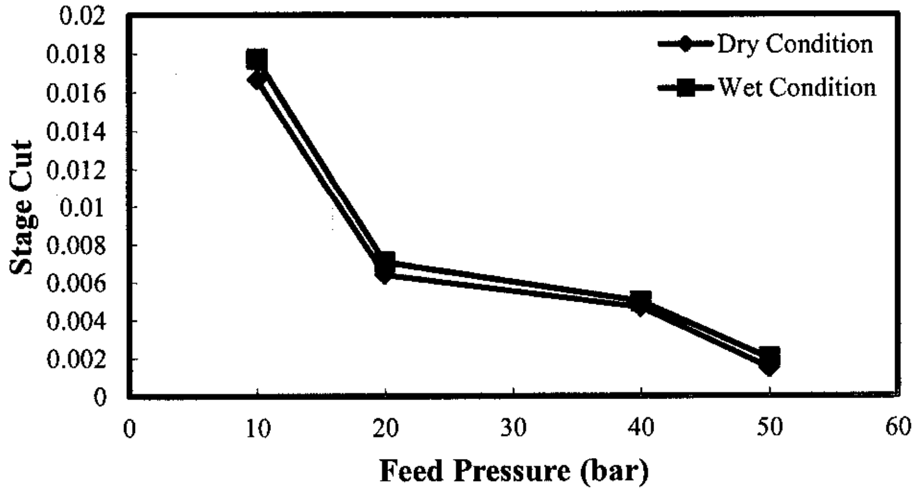


Figure 4.6: Stage Cut as a function of feed pressure. Temperature: 30 °C, Feed Composition: 55% of CO_2 concentration.

An increase in feed pressure resulted in CO_2 permeance decreases but CO_2/CH_4 selectivity increases in polyimide membrane. A greater driving force across the membrane can be created with the increase in operating pressure and thus, the membrane selectivity increases and less membrane area requirement for the system.

Generally, the designers of the membrane system will attempt to utilize the maximum operating pressure possible to obtain a cheaper, smaller and effective system as the membrane area requirement is highly affected by the feed pressure (Dortmundt & Doshi, 1999). Also, the designers have to take into consideration of the cost and weight of equipment at a higher pressure rating and the maximum pressure limit for the membrane elements to withstand in equipment detailed design.

4.2.2 Effect of Operating Temperature

Operating temperature plays an important role on the performance of polyimide membrane. The permeability of membrane increases with an increase in feed temperature but membrane selectivity decreases. An increase in feed temperature also results in decrease of membrane area requirement and causes the increases of hydrocarbon losses (Dortmundt & Doshi, 1999).

The effects of pentane on operating temperature can be observed from the plot of CO_2 permeance and CO_2/CH_4 selectivity versus temperature as shown in **Figure 4.7**. According to Hogsett & Mazur (1983), the permeability of most polymers increases with the increased of operating temperature but contributes to a slight decreases in selectivity. The operating temperature is chosen to be above the dew point of the residue gas in the range of 30 to 50 °C. Based on **Figure 4.7**, it is shown that higher temperature produced higher CO_2 permeance whereas CO_2/CH_4 selectivity decreased with the increase of operating temperature in both dry and wet condition. **Figure 4.7** also depicted the CO_2 permeance in dry condition is higher than wet condition at 30 °C but CO_2 permeance in dry condition is lower than CO_2 permeance in wet condition at 40 and 50 °C.

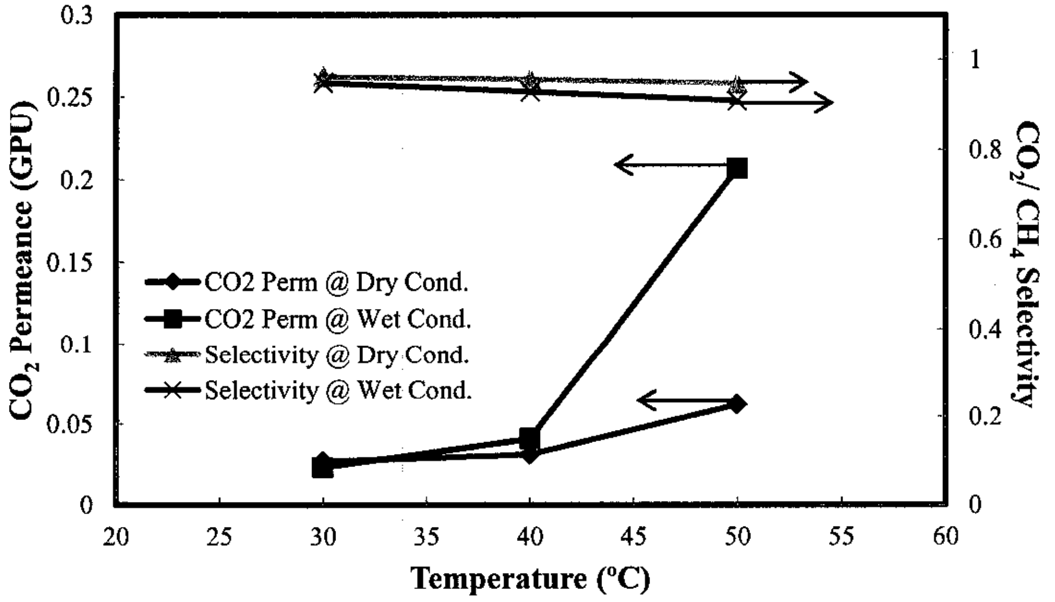


Figure 4.7: The effects of operating temperature on the CO_2 permeance and CO_2/CH_4 selectivity. Pressure: 50 bar and Feed composition: 55% CO_2 concentration.

The CO_2/CH_4 selectivity is about 0.961 and 0.948 for polyimide membrane at 50 °C and 50 bar in dry and wet condition, respectively as shown in **Figure 4.7**. The CO_2/CH_4 selectivity for both dry and wet conditions is quite similar and close to unity, this indicates there is less separation of CO_2 from the mixed gas experiments. At high CO_2 partial pressures, there is considerable CO_2 absorbed in the membrane. The plasticization effect of CO_2 increases the effective diffusion coefficients for all gases and makes the selectivity less than that based on pure-gas data (Hogsett & Mazur, 1983).

Similarly, CH_4 permeance is higher at Wet condition compare to Dry condition versus operating temperature plot as shown in **Figure 4.8**.

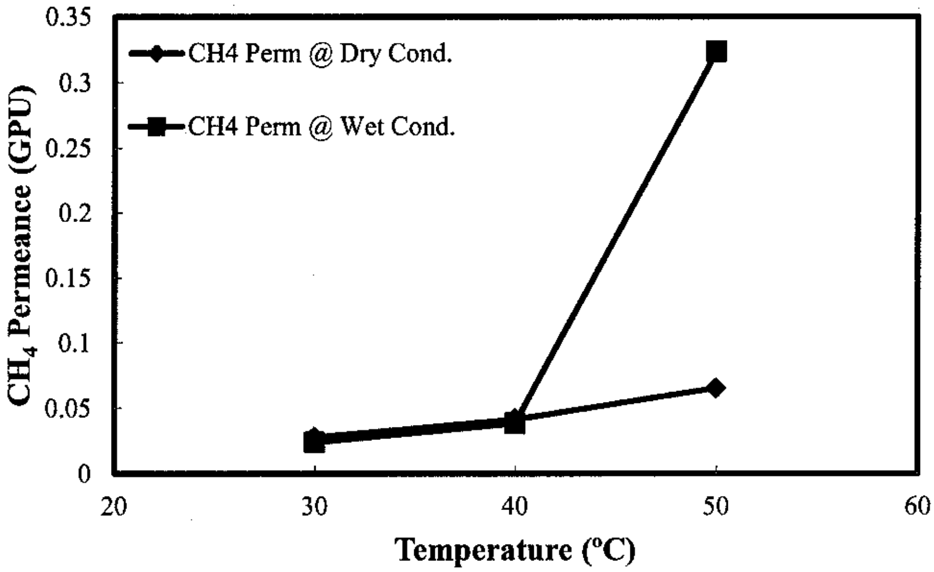


Figure 4.8: The effects of operating temperature on the CH_4 permeance. Pressure: 50 bar and Feed composition: 55% CO_2 concentration.

The decreasing selectivity of CO_2/CH_4 can be explained in terms of a difference in permeation activation energy between gases. Equation of activation energy, $Q = A \exp [-E/RT]$, contributes to the change in permeability where the activation energies, E that range from 1 to 5 kcal/mol (Hwang, et al., 2011). The CO_2 and CH_4 permeance through the membrane layer increased with an increase in the operating temperature due to the increase in activation energy of permeate gases but the selectivity of gas pairs decreased.

In industrial applications, natural gas stream is often heated to prevent condensation of heavy hydrocarbons in feed stream. Generally, the gas permeability of membranes can be improved by high temperature. However, high operating temperature can often degrade the membrane performance at the same time.

The stage cut is determined as the ratio of the permeate flow rate (kg/h) to the feed flow rate (kg/h). The increasing operating temperature increased the stage cut as shown in **Figure 4.9**.

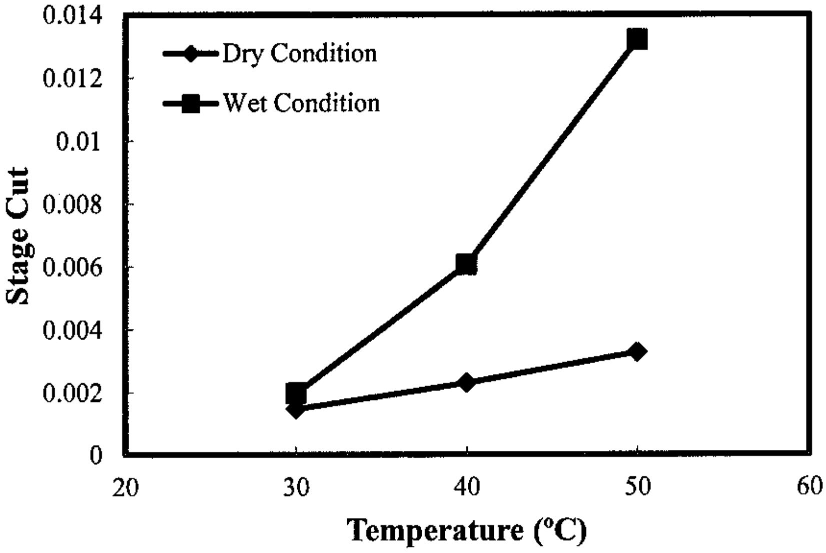


Figure 4.9: Stage Cut as a function of operating temperature. Pressure: 50 bar, Feed Composition: 55% of CO_2 concentration.

Based on **Figure 4.9**, it is indicated that more permeate flow through the membrane system as the temperature increases. At 30 °C, we noticed that the stage cut for both Dry and Wet Conditions are similar, this shows that the separation performance has no vast different at room temperature (about 30 °C) compare to high temperature (40 to 50 °C). The graphs also showed that the stage cut is higher in Wet Condition with the influence of pentane than the stage cut in Dry Condition as a function of operating temperature. The effect of pentane caused more permeates flow through the membrane and thus contributed to higher stage cut value.

High gas productivity can be achieved at higher operating temperatures; however, the gas purity will be affected due to the decrease of selectivity at high temperature. From **Figure 4.10**, the selectivity at dry condition is higher than selectivity at wet condition with an increase in operating temperature. Without the presence of pentane, higher gas productivity was obtained in the mixed gas experiment. Generally, a minimum selectivity of 4 is needed for a good membrane separation. Low CO_2/CH_4 selectivity obtained in this project can be related to the defect of polyimide membrane or the presence of pentane. Further studies have to be conducted to investigate on these matters.

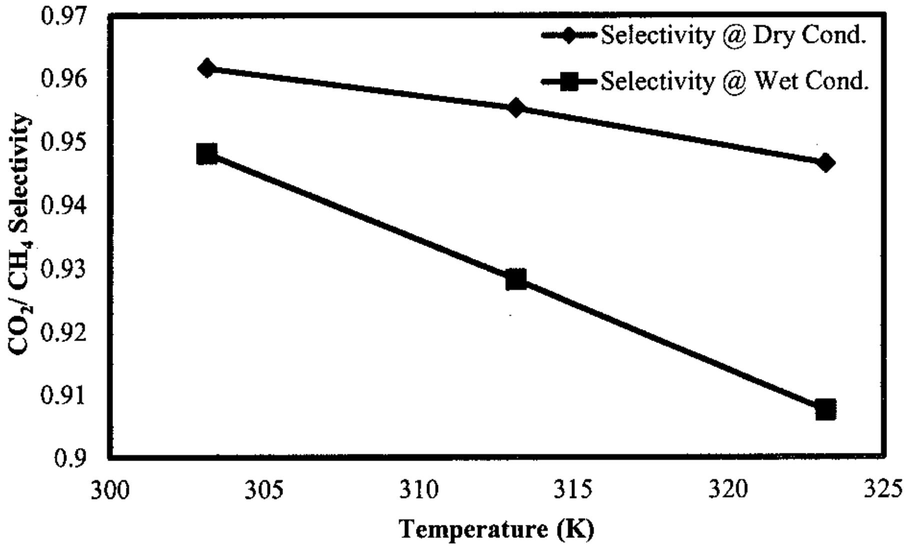


Figure 4.10: CO_2/CH_4 selectivity as a function of Temperature (T). Pressure: 50 bar and Feed composition: 55% CO_2 concentration.

For most polymeric membrane, the permeability of membrane increases with temperature due to the increase of diffusivity more than offsets any decrease in solubility. Since the membrane selectivity is inversely proportional to the operating temperature, an increase in temperature often decreases the selectivity of membrane. Therefore, the operating temperature is usually determined based on the trade-off between high temperature and high selectivity. Also, the existence of pentane decreased the membrane selectivity but increased permeability at high operating temperature in the mixed gas experiments.

4.2.3 Effect of Feed Composition

The effects of pentane on feed composition can be observed from the plot of CO_2 permeance and CH_4 permeance versus CO_2 concentration in feed stream as shown in **Figure 4.11** and **4.12**.

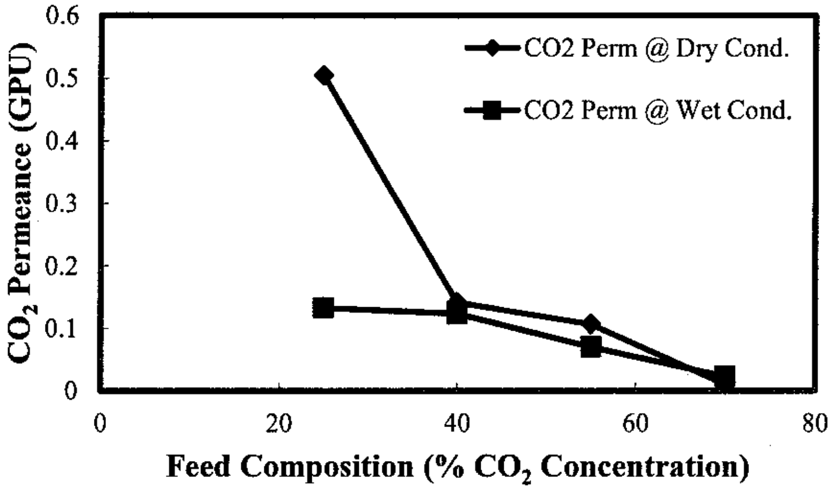


Figure 4.11: CO_2 Permeance as a function of feed composition. Pressure: 50 bar and Temperature: 30 °C.

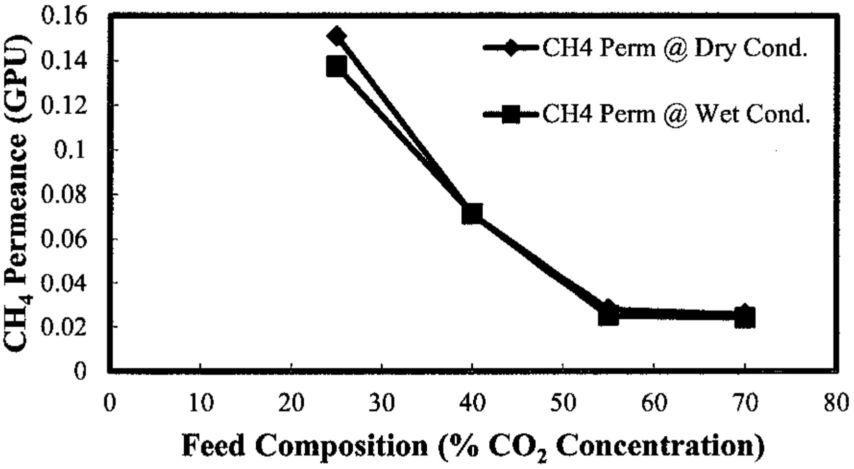


Figure 4.12: CH_4 Permeance as a function of feed composition. Pressure: 50 bar and Temperature: 30 °C.

The CO_2 mole fraction has a significant impact on the bulk contribution of CO_2 and CH_4. The CO_2 and CH_4 permeance decreases with an increase in CO_2 concentration in feed composition due to the plasticization and compaction effect. Generally, an increase in CO_2 concentration in feed stream increases the losses of hydrocarbon and membrane area. This is because the more CO_2 permeate; the more hydrocarbons permeate through the membrane (Dortmundt & Doshi, 1999). Based on **Figure 4.11**, it is shown that the CO_2 permeance decrease with an increase in CO_2 concentration in the feed stream. Similarly, the CH_4 permeance decreased with an increase in CO_2 concentration in feed composition as shown in **Figure 4.12**.

This phenomenon can be explained by a coupling effect which is often due to the presence of other gas, such as pentane or methane in the mixed gas stream. The coupling effect on permeation is strongly related to deviations in the solubility coefficient, while the diffusivity coefficient is not affected by the presence of other gas (Hwang, et al., 2011). As CO_2 concentration in the feed increases, the solubility coefficient increases while the diffusivity coefficient is remained constant and thus, resulting in an increase in CO_2 permeance and concentration in permeate.

Asymmetric polyimide membranes with high CO_2/CH_4 selectivity are highly sensitive to the presence of heavy hydrocarbons in the feed. As shown in **Figure 4.13**, The CO_2/CH_4 selectivity decreases with the increase in CO_2 concentration in the feed stream.

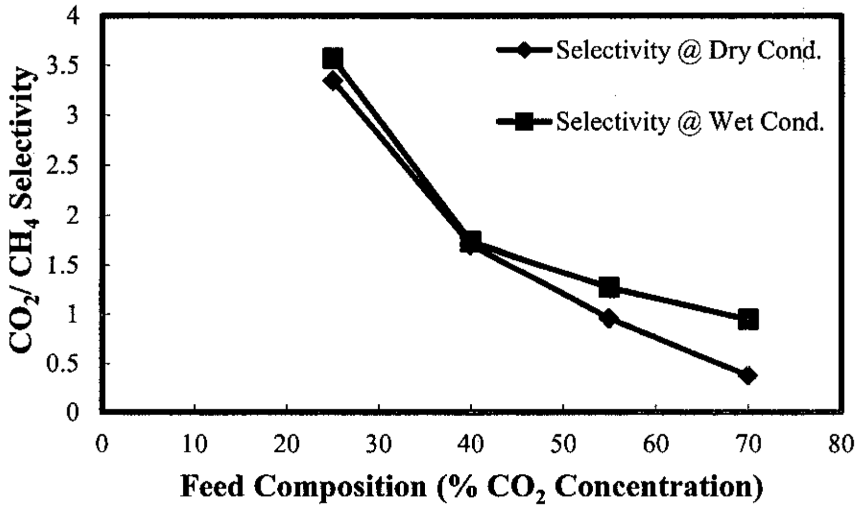


Figure 4.13: CO_2/CH_4 selectivity as a function of feed composition. Pressure: 50 bar and Temperature: 30 °C.

Based on **Figure 4.13**, it can be observed that the CO_2/CH_4 selectivity at Dry condition is lower than CO_2/CH_4 selectivity at Wet condition due to coupling effect on permeation. Upon exposure of the mixed gas to the liquid pentane in saturation vessel, the results from experiments showed that both have an immediate negative impact on membrane selectivity. It was postulated that pentane sorbed caused plasticization of the active skin layer on the polyimide membrane and thus contributing to the loss of membrane selectivity. The presence of pentane is a significant contaminant in most raw natural gas streams. The ability of pentane to permeate through this polyimide membrane indicates plasticization of the polymer membrane (White, et al., 1995). Heavy hydrocarbons and aromatics compound can bring significant effect to the performance of polyimide membrane as the presence of these components causes swelling or plasticization of glassy membranes. Thus, the selectivity of membrane will be reduced (Chenar, Savoji, Soltanieh, Matsuura, & Tabe, 2010). Also, the loss of loss of flux and membrane performance in the experiment can be related to the effect of pentane as the heavy hydrocarbon contamination even at low mass fractions (Al-Juaied & Koros, 2006).

The results presented in **Figure 4.14** shows the changes of stage cut as a function of CO_2 concentration in feed stream.

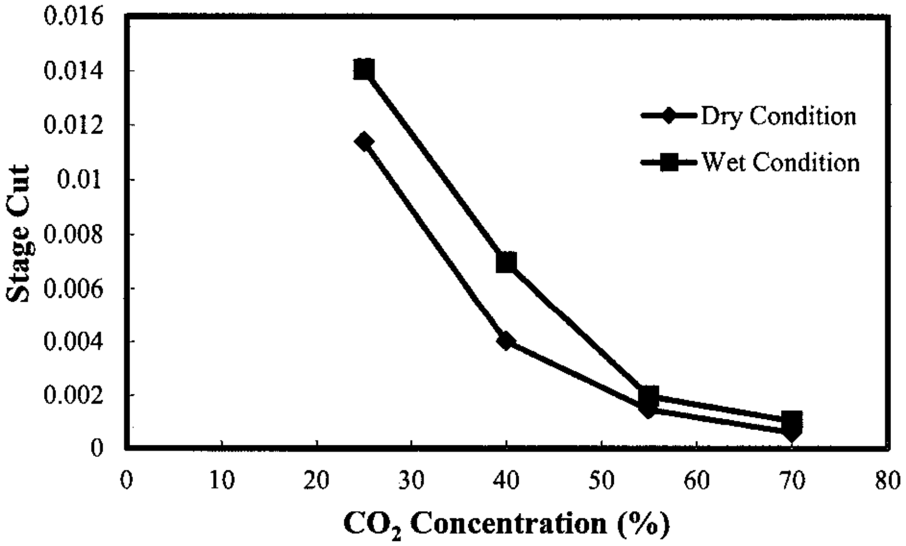


Figure 4.14: Stage Cut as a function of CO_2 concentration in feed. Pressure: 50 bar and Temperature: 30 °C.

The increase of CO_2 concentration in feed stream decreases the stage cut of the membrane. The results indicated the stage cut is higher at Wet Condition with the influence of pentane than the stage cut at Dry Condition as a function of CO_2 concentration. The effect of pentane caused plasticization of the membrane; resulting more permeates flow through the membrane and thus contributed to higher stage cut value compare to Dry condition.

The results from the feed composition effect on the membrane performance indicate that impurities and heavy hydrocarbon can bring significant effect on separation efficiency. In order to have good membrane performance, CO_2 enrichment in feed gas is necessary to decrease the CO_2 permeance and later increase the CO_2/CH_4 selectivity. Also, the condensation of hydrocarbons in feed stream must also be avoided. Any form of liquid presence in the membrane system can increase the membrane resistance and also damage the membrane by swelling or softening.

Both permeability and selectivity are important considerations when selecting a commercial membrane. Higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby reducing the capital cost of membrane units. Higher selectivity results in higher purity product gas (Freeman, 1999). However, high CO_2 permeability does not correspond to high selectivity, instead the membrane scientists have to settle for a high selective or permeable membrane or somewhere in-between on both parameters (Dortmundt & Doshi, 1999).

Generally, polymeric membranes undergo a trade-off limitation between permeability and selectivity. As selectivity increases, the gas permeability will decrease and vice versa (Freeman, 1999). According to Dortmundt and Doshi (1999), the usual choice of membrane in industrial applications is to use a highly selective material and then make it as thin as possible to increase the permeability. However, this reduced thickness makes the membrane extremely fragile and therefore unusable.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In summary, the objective to study the effect on heavy hydrocarbon on polyimide membrane performance in natural gas sweetening process is successfully achieved. Parametric analyses through experimental works have been conducted to evaluate the polyimide membrane performance at different operating parameters, i.e. feed pressure, temperature and CO_2 concentration in feed. Higher operating pressures at the feed side demonstrated decreased permeance of CO_2 and CH_4 in both dry and wet conditions. An increased operating pressure resulted in low permeation flux but high CO_2/CH_4 selectivity. The permeability of membrane increases with an increase in feed temperature but membrane selectivity decreases. The existence of pentane decreased the membrane selectivity due to plasticization effect but increased permeability at high operating temperature in the mixed gas experiments. Plasticization phenomenon happened at the pressure of 50 bars in the experiments. The CO_2 permeance decreases with an increase in CO_2 concentration in the feed stream due to coupling effect. An increase in CO_2 concentration in feed composition increases the losses of hydrocarbon and membrane area, and thus reduces the CO_2/CH_4 selectivity. The presence of pentane as heavy hydrocarbon in natural gas stream contributed to the loss of membrane selectivity due to swelling, compaction or plasticization effect of glassy membrane. It can be concluded that the presence of heavy hydrocarbon reduced the separation performance of polyimide membrane.

5.2 RECOMMENDATIONS

Experimental works in the laboratory have to be conducted based on standard procedures and must adhere to the rules and regulations to ensure personal safety. Personal Protective Equipment (PPE) has to be worn in the laboratory at all times, particularly when handling with liquid Pentane and Toluene for mixed gas experiments in Wet Conditions.

Process Optimization should be included in CO2SMU system to prevent losses of methane and other costly gases to the atmosphere. The system should be integrated with high efficiency equipment to maximize the utilities consumptions and to minimize hydrocarbon loss. Also, a vacuum pump should be installed in the CO2SMU system to ensure the membrane test cell is free from any impurities before conducting the experiment. Instead of an Infra-red (IR) Gas analyzer, a Gas Chromatography (GC) analyzer should be equipped in the membrane system since GC analyzer is more accurate and precise compare to IR Gas analyzer.

In addition, complete understanding of the observed phenomena is important for further developments and improvements of polyimide membrane. In order to fully evaluate the performance and robustness of polyimide membrane, further study of asymmetric polyimide membrane under mixed gas feeds in the presence of condensable vapor impurities is mandatory to improve the separation efficiency. The future research work should focus on the investigation of different types of impurities besides carbon dioxide and pentane, such as toluene, ethane and steady state performance of membrane. In addition, the performance of membrane should be examined under the presence of water vapor in feed streams due to the detrimental effects of condensate water vapor to polymeric membrane materials. Once the potential effects of the impurities can be identified, a more comprehensive and thorough preventive measures, particularly on the pre-treatment of process streams, pre-treatment of membrane materials, or post-treatment steps of membrane can be developed and thus contributing to the betterment of the membrane technology development in the future.

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APPENDICES

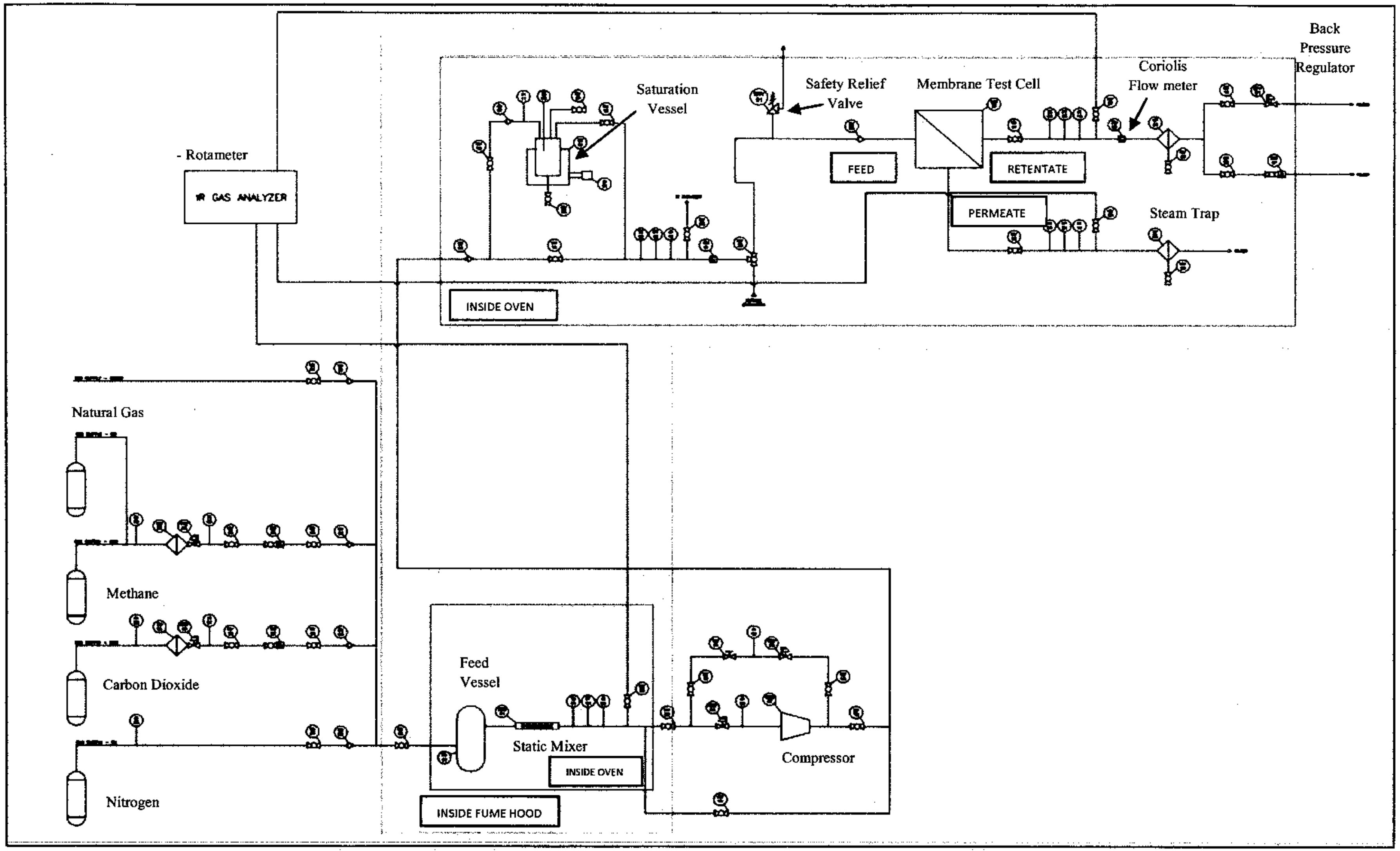

Figure A1: Process Flow Diagram of Carbon Dioxide Separation Membrane Unit (CO2SMU)

A2-Experiments data of Polyimide membrane at Dry Conditions (Without Pentane)

Table 1 of 2

				Feed CONCENTRATION				permeate CONCENTRATION				retentate CONCENTRATION				Area	Feed PRESSURE		retentate PRESSURE		permeate PRESSURE	
No.	condition			CO2	CH4	CO2	CH4	CO2	CH4	CO2	CH4	CO2	CH4	CO2	CH4							
	Conc	T ©	P (bar)	feed conc		feed frction		perm conc		perm frction		ret conc		ret frction		cm2	bar	cm Hg	bar	cm Hg	bar	cm Hg
1	25	30	10	23.3	77.4	0.23138	0.76862	23.33	76.9	0.232765	0.767235	23.1	77.6	0.229394	0.770606	14.86	11.634	872.6245	9.551	716.3861	1.049	78.68171
2	25	30	20	23.1	77.6	0.229394	0.770606	23.65	76.48	0.236193	0.763807	23	77.7	0.228401	0.771599	14.86	23.649	1773.826	23.527	1764.676	1.049	78.68171
3	25	30	40	23.4	76.9	0.2333	0.7667	23.4	76.3	0.234704	0.765296	23.3	76.8	0.232767	0.767233	14.86	41.178	3088.614	40.392	3029.659	1.048	78.60671
4	25	30	50	23.1	77.4	0.229851	0.770149	23.5	76.61	0.234742	0.765258	23.1	77.2	0.230309	0.769691	14.86	52.413	3931.31	51.585	3869.205	1.05	78.75672
5	25	40	10	23.3	77.5	0.231151	0.768849	23	75.8	0.232794	0.767206	23.2	77.4	0.230616	0.769384	14.86	12.39	929.3293	10.235	767.6905	1.051	78.83173
6	25	40	20	23.3	77.4	0.23138	0.76862	23.5	75	0.238579	0.761421	23.1	77.3	0.23008	0.76992	14.86	23.851	1788.978	22.654	1699.195	1.048	78.60671
7	25	40	40	23.3	77.4	0.23138	0.76862	24.1	75.4	0.242211	0.757789	23.2	77.4	0.230616	0.769384	14.86	43.189	3239.451	42.374	3178.321	1.045	78.38169
8	25	40	50	23.3	77.6	0.230922	0.769078	23.85	77.175	0.23608	0.76392	23.2	77.4	0.230616	0.769384	14.86	52.987	3974.364	52.321	3924.41	1.048	78.60671
9	25	50	10	23.1	77.7	0.229167	0.770833	23.088	76.105	0.232758	0.767242	23.4	74.4	0.239264	0.760736	14.86	12.47	935.3298	9.938	745.4136	1.015	76.1315
10	25	50	20	23.2	78	0.229249	0.770751	23.5	70.8	0.249205	0.750795	23.4	77.4	0.232143	0.767857	14.86	22.045	1653.516	20.88	1566.134	1.056	79.20676
11	25	50	40	23.4	77.7	0.231454	0.768546	23.5	76.7	0.234531	0.765469	23.3	77.5	0.231151	0.768849	14.86	41.431	3107.59	40.482	3036.409	1.051	78.83173
12	25	50	50	23.698	77.457	0.234274	0.765726	24.294	76.037	0.242139	0.757861	23.618	77.602	0.233333	0.766667	14.86	51	3825.326	50.125	3759.696	1.052	78.90673
13	40	30	10	38.1	63.5	0.375	0.625	38.51	62.59	0.38091	0.61909	38	63.4	0.374753	0.625247	14.86	13.543	1015.812	10.921	819.1449	1.061	79.58179
14	40	30	20	38.1	63.3	0.37574	0.62426	38.37	62.5	0.380391	0.619609	37.6	64.1	0.369715	0.630285	14.86	24.053	1804.129	22.626	1697.095	1.058	79.35677
15	40	30	40	37.7	63.7	0.371795	0.628205	38.98	62.26	0.385026	0.614974	37.5	63.8	0.370188	0.629812	14.86	41.326	3099.714	40.385	3029.133	1.055	79.13175
16	40	30	50	37.5	63.5	0.371287	0.628713	41.3	58.3	0.414659	0.585341	37.5	63.9	0.369822	0.630178	14.86	49.876	3741.019	48.885	3666.688	1.027	77.03157
17	40	40	10	37.4	63.5	0.370664	0.629336	37.3	62.8	0.372627	0.627373	38.2	62.8	0.378218	0.621782	14.86	13.002	975.2332	10.557	791.8426	1.054	79.05675
18	40	40	20	37.3	63.7	0.369307	0.630693	37.3	63	0.371884	0.628116	37.9	63.1	0.375248	0.624752	14.86	21.556	1616.838	20.119	1509.054	1.055	79.13175
19	40	40	40	37.5	64	0.369458	0.630542	38	62.5	0.378109	0.621891	37.5	63.6	0.37092	0.62908	14.86	40.323	3024.483	39.419	2956.677	1.055	79.13175
20	40	40	50	37.3	63.8	0.368942	0.631058	39.3	60.3	0.394578	0.605422	37.7	63.2	0.373637	0.626363	14.86	49.998	3750.17	49.125	3684.689	1.044	78.30668
21	40	50	10	37.3	63.5	0.37004	0.62996	39.3	62.9	0.38454	0.61546	37.8	62.9	0.375372	0.624628	14.86	13.099	982.5088	10.564	792.3676	1.054	79.05675
22	40	50	20	37.4	63.6	0.370297	0.629703	37.3	62.9	0.372255	0.627745	36.9	63.8	0.366435	0.633565	14.86	24.211	1815.98	22.781	1708.721	1.054	79.05675
23	40	50	40	37.1	63.6	0.368421	0.631579	37.6	62.4	0.376	0.624	36.8	63.6	0.366534	0.633466	14.86	42.308	3173.371	41.406	3105.715	1.053	78.98174
24	40	50	50	37.1	63.5	0.368787	0.631213	37.5	62.7	0.374251	0.625749	37	63.5	0.368159	0.631841	14.86	49.217	3691.59	48.486	3636.76	1.053	78.98174
25	55	30	10	56.5	43	0.567839	0.432161	51.8	47.4	0.522177	0.477823	52.4	47.3	0.525577	0.474423	14.86	11.54	865.5739	10.327	774.5911	1.052	78.90673
26	55	30	20	51.1	48.6	0.512538	0.487462	51.2	48.1	0.515609	0.484391	51.8	48	0.519038	0.480962	14.86	24.789	1859.334	23.442	1758.3	1.057	79.28176
27	55	30	40	51	48.3	0.513595	0.486405	51.8	47.5	0.521652	0.478348	50.7	48.8	0.509548	0.490452	14.86	43.089	3231.951	42.234	3167.82	1.054	79.05675
28	55	30	50	51.1	48.4	0.513568	0.486432	51.4	48.2	0.516064	0.483936	50.9	48.6	0.511558	0.488442	14.86	52.528	3939.936	51.719	3879.256	1.056	79.20676
29	55	40	10	53	48.5	0.522167	0.477833	52.8	48	0.52381	0.47619	53.2	48.1	0.525173	0.474827	14.86	14.519	1089.018	11.036	827.7706	1.073	80.48187
30	55	40	20	52.9	48.7	0.520669	0.479331	52.8	48.2	0.522772	0.477228	53	48.8	0.520629	0.479371	14.86	24.023	1801.879	22.863	1714.871	1.052	78.90673
31	55	40	40	50.8	49.2	0.508	0.492	50.8	48.8	0.51004	0.48996	50.6	49.5	0.505495	0.494505	14.86	41.343	3100.99	40.552	3041.66	1.051	78.83173
32	55	40	50	50.7	49.7	0.50498	0.49502	51.8	47.7	0.520603	0.479397	50.9	48.9	0.51002	0.48998	14.86	52.875	3965.963	52.123	3909.559	1.052	78.90673
33	55	50	10	51.7	48.9	0.513917	0.486083	52	48.2	0.518962	0.481038	51.5	49.4	0.510406	0.489594	14.86	13.099	982.5088	10.355	776.6913	1.058	79.35677
34	55	50	20	52.1	48.3	0.518924	0.481076	52.2	47.8	0.522	0.478	51.3	49.2	0.510448	0.489552	14.86	22.477	1685.919	20.967	1572.659	1.055	79.13175
35	55	50	40	51.7	48.5	0.515968	0.484032	51.6	48.3	0.516517	0.483483	51.9	48.3	0.517964	0.482036	14.86	40.437	3033.034	39.455	2959.378	1.057	79.28176
36	55	50	50	51.7	48.7	0.51494	0.48506	54	45.2	0.544355	0.455645	51.8	48.9	0.514399	0.485601	14.86	50.749	3806.5	50.052	3754.22	1.035	77.63162
37	70	30	10	71	27.5	0.720812	0.279188	73.7	17.2	0.810781	0.189219	70.9	27.6	0.719797	0.280203	14.86	11.883	891.3011	9.489	711.7357	1.018	76.35652
38	70	30	20	70.8	27.6	0.719512	0.280488	80.3	14.1	0.850636	0.149364	70.8	27.6	0.719512	0.280488	14.86	22.187	1664.167	20.548	1541.232	1.024	76.80655
39	70	30	40	70.9	27.6	0.719797	0.280203	72.4	25.9	0.736521	0.263479	70.7	27.4	0.720693	0.279307	14.86	42.349	3176.446	41.533	3115.241	1.064	79.80681
40	70	30	50	71.4	27.1	0.724873	0.275127	75.1	22.8	0.767109	0.232891	71.8	26.7	0.728934	0.271066	14.86	41.869	3140.443	41.645	3123.642	1.052	78.90673
41	70	40	10	70.8	28.5	0.712991	0.287009	70.8	27.9	0.717325	0.282675	71.6	27.6	0.721774	0.278226	14.86	14.394	1079.642	11.424	856.8731	1.078	80.8569
42	70	40	20	71.3	27.8	0.719475	0.280525	71.8	27.8	0.720884	0.279116	71.6	27.6	0.721774	0.278226	14.86	22.696	1702.345	20.97	1572.884	1.072	80.40686
43	70	40	40	71	28	0.717172	0.282828	72.7	25.8	0.738071	0.261929	71.4	27.9	0.719033	0.280967	14.86	41.219	3091.689	40.327	3024.783	1.059	79.43178
44	70	40	50	71.2	27.6	0.720648	0.279352	83.1	13.9	0.856701	0.143299	71.5	27.6	0.721493	0.278507	14.86	52.946	3971.289	51.963	3897.558	1.041	78.08166
45	70	50	10	66.1	34	0.66034	0.33966	67	32.4	0.674044	0.325956	66.7	33.3	0.667	0.333	14.86	14.112	1058.49	10.668	800.1683	1.077	80.78189
46	70	50	20	67.1	32.9	0.671	0.329	70.7	22.1	0.761853	0.238147	66.2	34	0.660679	0.339321	14.86	23.4	1755.15	21.461	1609.712	1.019	76.43152
47	70	50	40	66.4	33.6	0.664	0.336	76.6	20.6	0.788066	0.211934	66.8	33	0.669339	0.330661	14.86	41.241	3093.339	40.143	3010.982	1.024	76.80655
48	70	50	50	66.8	33	0.669339	0.330661	79.3	18.2	0.813333	0.186667	66.9	32.7	0.671687	0.328313	14.86	54.004	4050.646	53.152	3986.74	1.029	77.18159

A2-Experiments data of Polyimide membrane at Dry Conditions (Without Pentane)

Table 2 of 2

				STAGE CUT				PERMEANCE								SELECTIVITY		
No.	condition			MEB		ROTAMETER		MEB		ROTAMETER		MEB		ROTAMETER		Ideal		Real
	Conc	T ©	P (bar)	kg/hr	cm3 STP/s	kg/hr	cm3/s	CO2	CO2	CO2	CO2	CH4	CH4	CH4	CH4	MEB	ROTA	MEB
									GPU		*GPU*		*GPU*		*GPU*	*CO2/CH4*	*CO2/CH4*	*CO2/CH4*
1	25	30	10	0.006986	4.8E-06	18.63946	0.014417	1.48E-06	1.480413	0.004446	4445.759	4.4E-07	0.439858	0.001321	1320.916	3.365664	3.365664	1.007798
2	25	30	20	0.00144	9.56E-07	13.53851	0.010104	1.39E-07	0.138705	0.001466	1465.862	4.1E-08	0.040974	0.000433	433.0202	3.385205	3.385205	1.038803
3	25	30	40	0.008608	5.75E-06	13.43823	0.0101	4.61E-07	0.460553	0.000809	808.6112	1.4E-07	0.139685	0.000245	245.2514	3.297071	3.297071	1.007864
4	25	30	50	0.01139	7.97E-06	14.63813	0.011535	5.04E-07	0.504202	0.000729	729.3395	1.51E-07	0.150792	0.000218	218.1235	3.3437	3.3437	1.027807
5	25	40	10	0.002332	1.6E-06	14.13049	0.011209	4.57E-07	0.457062	0.003208	3207.627	1.37E-07	0.136845	0.00096	960.3661	3.340005	3.340005	1.009263
6	25	40	20	0.003738	2.54E-06	8.898359	0.00701	3.63E-07	0.363232	0.001001	1000.727	1.08E-07	0.108308	0.000298	298.3938	3.353712	3.353712	1.040858
7	25	40	40	0.018349	1.27E-05	0.769613	0.000617	9.78E-07	0.978385	4.75E-05	47.50741	2.93E-07	0.292788	1.42E-05	14.21688	3.341619	3.341619	1.061771
8	25	40	50	0.087305	5.9E-05	8.96599	0.007013	3.69E-06	3.686043	0.000438	437.9693	1.1E-06	1.104174	0.000131	131.1961	3.338281	3.338281	1.029242
9	25	50	10	0.082921	6.65E-05	14.62514	0.013795	1.81E-05	18.09356	0.003754	3754.131	5.71E-06	5.708752	0.001184	1184.477	3.169442	3.169442	1.020428
10	25	50	20	0.004329	2.8E-06	12.42278	0.009561	4.32E-07	0.431901	0.001473	1472.566	1.3E-07	0.129946	0.000443	443.0529	3.32368	3.32368	1.115941
11	25	50	40	0.002686	1.91E-06	11.35315	0.009583	1.53E-07	0.153253	0.000768	767.9226	4.61E-08	0.046052	0.000231	230.7579	3.327827	3.327827	1.017367
12	25	50	50	0.00574	4.1E-06	11.32259	0.009587	2.63E-07	0.26331	0.000616	615.5036	8.01E-08	0.080055	0.000187	187.133	3.289123	3.289123	1.044295
13	40	30	10	0.015396	1.15E-05	21.44948	0.01766	1.84E-06	1.839905	0.002827	2826.663	1.1E-06	1.100321	0.00169	1690.434	1.672153	1.672153	1.025457
14	40	30	20	0.002232	1.61E-06	14.65925	0.011714	1.42E-07	0.141724	0.001032	1031.545	8.3E-08	0.082958	0.000604	603.8127	1.708386	1.708386	1.019977
15	40	30	40	0.002235	1.61E-06	7.290704	0.005831	8.06E-08	0.080638	0.000293	292.7574	4.73E-08	0.047318	0.000172	171.7885	1.704173	1.704173	1.057866
16	40	30	50	0.004023	2.93E-06	0.78463	0.000639	1.22E-07	0.121747	2.65E-05	26.5221	7.12E-08	0.071159	1.55E-05	15.50175	1.71091	1.71091	1.199565
17	40	40	10	0.00987	6.79E-06	21.16562	0.016835	1.12E-06	1.121363	0.002782	2781.717	6.84E-07	0.683534	0.001696	1695.615	1.640536	1.640536	1.008443
18	40	40	20	0.000789	5.43E-07	17.67572	0.014049	5.27E-08	0.052732	0.001365	1364.713	3.17E-08	0.031696	0.00082	820.2982	1.663679	1.663679	1.011111
19	40	40	40	0.000395	2.7E-07	17.85887	0.014067	1.38E-08	0.013848	0.000722	722.4341	8.16E-09	0.008159	0.000426	425.611	1.697405	1.697405	1.037653
20	40	40	50	0.004129	2.95E-06	0.753792	0.00062	1.21E-07	0.120577	2.54E-05	25.36198	7.18E-08	0.071789	1.51E-05	15.10005	1.679595	1.679595	1.114775
21	40	50	10	0.014326	9.65E-06	23.75297	0.019067	1.6E-06	1.599332	0.00316	3159.766	9.58E-07	0.957841	0.001892	1892.385	1.669727	1.669727	1.06367
22	40	50	20	0.009501	6.52E-06	20.00285	0.016347	5.75E-07	0.57468	0.001441	1441.338	3.32E-07	0.331998	0.000833	832.6755	1.730972	1.730972	1.008425
23	40	50	40	0.007154	4.87E-06	16.75675	0.01361	2.41E-07	0.241126	0.000673	673.3979	1.39E-07	0.139374	0.000389	389.2337	1.73006	1.73006	1.032967
24	40	50	50	0.005675	3.8E-06	20.45805	0.016328	1.6E-07	0.160178	0.000689	688.7035	9.33E-08	0.093279	0.000401	401.0621	1.717199	1.717199	1.023678
25	55	30	10	0.016659	8.69E-06	19.39955	0.011462	1.18E-06	1.177886	0.001554	1553.633	1.31E-06	1.306674	0.001724	1723.504	0.901438	0.901438	0.831709
26	55	30	20	0.006401	4.23E-06	28.6294	0.021467	2.57E-07	0.256847	0.001303	1302.619	2.77E-07	0.277351	0.001407	1406.604	0.926074	0.926074	1.012372
27	55	30	40	0.006598	4.22E-06	23.64393	0.017163	1.47E-07	0.147445	0.000599	599.4749	1.53E-07	0.153	0.000622	622.0592	0.963694	0.963694	1.032793
28	55	30	50	0.001464	9.41E-07	23.52484	0.017163	2.67E-08	0.026728	0.000487	487.4397	2.8E-08	0.027983	0.00051	510.319	0.955167	0.955167	1.010045
29	55	40	10	0.013506	1.08E-05	25.02529	0.022802	1.14E-06	1.143917	0.002414	2413.695	1.27E-06	1.265757	0.002671	2670.782	0.903741	0.903741	1.006604
30	55	40	20	0.011816	7.04E-06	20.90181	0.014218	4.4E-07	0.440323	0.000889	889.0436	4.78E-07	0.478032	0.000965	965.1799	0.921117	0.921117	1.008463
31	55	40	40	0.000789	4.75E-07	19.87826	0.013945	1.75E-08	0.017457	0.000512	512.0343	1.78E-08	0.017836	0.000523	523.1646	0.978725	0.978725	1.008197
32	55	40	50	0.002292	1.41E-06	23.23576	0.016692	3.99E-08	0.039936	0.000472	472.3707	4.15E-08	0.041533	0.000491	491.268	0.961534	0.961534	1.064535
33	55	50	10	0.019566	1.29E-05	20.89334	0.016367	1.57E-06	1.569432	0.001994	1994.037	1.63E-06	1.631234	0.002073	2072.56	0.962113	0.962113	1.02041
34	55	50	20	0.003654	2.34E-06	21.41995	0.016353	1.6E-07	0.160331	0.001119	1119.362	1.67E-07	0.166795	0.001164	1164.486	0.96125	0.96125	1.0124
35	55	50	40	0.00357	2.35E-06	20.82529	0.016337	8.61E-08	0.086118	0.000599	598.7885	9.26E-08	0.092551	0.000644	643.5188	0.930491	0.930491	1.002199
36	55	50	50	0.003261	2.11E-06	21.20301	0.016329	6.16E-08	0.061642	0.000478	477.9941	6.51E-08	0.065135	0.000505	505.0788	0.946375	0.946375	1.125366
37	70	30	10	0.002803	1.73E-06	0.908259	0.000633	1.67E-07	0.167275	6.12E-05	61.19275	4.12E-07	0.412076	0.000151	150.7465	0.405932	0.405932	1.659638
38	70	30	20	0.007162	4.46E-06	0.9021	0.000633	2.21E-07	0.220708	3.14E-05	31.35794	5.49E-07	0.548758	7.8E-05	77.96702	0.402195	0.402195	2.220099
39	70	30	40	0.001859	1.17E-06	22.44779	0.015848	2.93E-08	0.029299	0.000398	398.4506	7.54E-08	0.075448	0.001026	1026.039	0.388339	0.388339	1.088182
40	70	30	50	0.000592	3.84E-07	7.897366	0.005768	9.66E-09	0.00966	0.000145	145.1414	2.58E-08	0.025849	0.000388	388.3689	0.373721	0.373721	1.25019
41	70	40	10	0.010592	7.59E-06	23.87681	0.019713	5.9E-07	0.58994	0.001533	1532.701	1.53E-06	1.533172	0.003983	3983.277	0.384784	0.384784	1.021505
42	70	40	20	0.009138	6.24E-06	28.66591	0.022551	2.99E-07	0.299054	0.00108	1080.205	7.76E-07	0.775977	0.002803	2802.888	0.38539	0.38539	1.007013
43	70	40	40	0.005202	3.12E-06	16.2921	0.011261	8.08E-08	0.080801	0.000292	291.771	2.06E-07	0.206267	0.000745	744.8306	0.391728	0.391728	1.111257
44	70	40	50	0.05875	3.42E-05	0.921817	0.000619	6.85E-07	0.685063	1.24E-05	12.40208	1.75E-06	1.750992	3.17E-05	31.69919	0.391243	0.391243	2.317476
45	70	50	10	0.015566	1.17E-05	6.133496	0.005467	1.01E-06	1.005814	0.000471	470.5535	2.01E-06	2.009378	0.00094	940.0547	0.50056	0.50056	1.063671
46	70	50	20	0.004386	3.18E-06	0.698285	0.000602	1.62E-07	0.162085	3.06E-05	30.63042	3.09E-07	0.30919	5.84E-05	58.43018	0.524223	0.524223	1.568558
47	70	50	40	0.00406	2.72E-06	0.76401	0.000604	7.58E-08	0.075844	1.69E-05	16.86165	1.51E-07	0.15145	3.37E-05	33.6701	0.50079	0.50079	1.881624
48	70	50	50	0.001507	9.49E-07	0.806594	0.000602	2E-08	0.020012	1.27E-05	12.70141	4.04E-08	0.040436	2.57E-05	25.66393	0.494913	0.494913	2.152481

A3-Experiments data of Polyimide membrane at Wet Conditions (Pentane)

Table 1 of 2

				Feed CONCENTRATION				permeate CONCENTRATION				retentate CONCENTRATION				Area	Feed PRESSURE		retentate PRESSURE		permeate PRESSURE	
No.	condition			CO2	CH4	CO2	CH4	CO2	CH4	CO2	CH4	CO2	CH4	CO2	CH4							
	Conc	T ©	P (bar)	feed conc		feed frction		perm conc		perm frction		ret conc		ret frction		cm2	bar	cm Hg	bar	cm Hg	bar	cm Hg
1	25	30	10	23.1	86.7	0.210383	0.789617	23.89	86.43	0.216552	0.783448	22.9	86.8	0.208751	0.791249	14.86	12.521	939.1551	10.564	792.3676	1.051	78.83173
2	25	30	20	23.5	84	0.218605	0.781395	23.97	83.19	0.223684	0.776316	23.6	84.1	0.219127	0.780873	14.86	21.43	1607.387	20.562	1542.282	1.039	77.93165
3	25	30	40	23.2	83.2	0.218045	0.781955	24.2	81.64	0.228647	0.771353	23.2	83.5	0.217432	0.782568	14.86	40.835	3062.886	40.259	3019.683	1.015	76.1315
4	25	30	50	23.5	82.6	0.221489	0.778511	24.8	80.3	0.235966	0.764034	23.3	83	0.219191	0.780809	14.86	50.892	3817.226	50.362	3777.472	1.032	77.4066
5	25	40	10	18.6	89.9	0.171429	0.828571	19.2	86	0.18251	0.81749	18.8	92.2	0.169369	0.830631	14.86	10.864	814.8695	10.379	778.4914	1.022	76.65654
6	25	40	20	21.9	85	0.204864	0.795136	19.9	78.9	0.201417	0.798583	22.3	85.6	0.206673	0.793327	14.86	20.591	1544.457	20.257	1519.405	1.021	76.58153
7	25	40	40	20.3	84.8	0.193149	0.806851	25.1	70.1	0.263655	0.736345	19.9	84.1	0.191346	0.808654	14.86	40.668	3050.36	40.315	3023.883	1.02	76.50653
8	25	40	50	34.7	68.5	0.33624	0.66376	49.7	46.9	0.514493	0.485507	34.7	68.3	0.336893	0.663107	14.86	50.806	3810.775	50.308	3773.422	1.022	76.65654
9	25	50	10	26	80.2	0.244821	0.755179	25.4	76.3	0.249754	0.750246	25.5	81.2	0.238988	0.761012	14.86	11.059	829.4958	10.455	784.1919	1.024	76.80655
10	25	50	20	22.6	81.4	0.217308	0.782692	21.4	76.5	0.21859	0.78141	22.6	81.2	0.217726	0.782274	14.86	23.829	1787.328	21.721	1629.214	1.079	80.93191
11	25	50	40	23.1	81.9	0.22	0.78	22.5	77.1	0.225904	0.774096	23.3	82.3	0.220644	0.779356	14.86	42.414	3181.321	41.137	3085.538	1.085	81.38194
12	25	50	50	21.2	77.4	0.21501	0.78499	22.3	76.8	0.225025	0.774975	21.2	77.5	0.214792	0.785208	14.86	52.134	3910.384	51.044	3828.627	1.095	82.13201
13	40	30	10	37.3	69.8	0.348273	0.651727	37.4	69.2	0.350844	0.649156	37.6	69.5	0.351074	0.648926	14.86	13.61	1020.837	11.558	866.924	1.055	79.13175
14	40	30	20	37.9	67.8	0.358562	0.641438	38.2	66.7	0.364156	0.635844	37.9	67.7	0.358902	0.641098	14.86	21.679	1626.064	20.684	1551.432	1.046	78.45669
15	40	30	40	37.6	65.7	0.363988	0.636012	44.6	57.9	0.435122	0.564878	37.6	65.6	0.364341	0.635659	14.86	41.031	3077.588	40.401	3030.334	1.032	77.4066
16	40	30	50	37.8	65.2	0.36699	0.63301	47.8	53.6	0.4714	0.5286	37.8	65.1	0.367347	0.632653	14.86	50.986	3824.276	50.437	3783.098	1.028	77.10658
17	40	40	10	36.3	70.5	0.339888	0.660112	34.8	66.7	0.342857	0.657143	36.6	71.3	0.339203	0.660797	14.86	11.066	830.0208	10.54	790.5675	1.025	76.88156
18	40	40	20	37.3	69.7	0.348598	0.651402	36.1	63.4	0.362814	0.637186	37	69.1	0.348728	0.651272	14.86	20.709	1553.308	20.331	1524.955	1.023	76.73155
19	40	40	40	36.6	67.4	0.351923	0.648077	40.2	58	0.409369	0.590631	37.2	68.3	0.352607	0.647393	14.86	40.703	3052.985	40.315	3023.883	1.021	76.58153
20	40	40	50	45	58.4	0.435203	0.564797	58.2	37.9	0.605619	0.394381	45.1	58	0.437439	0.562561	14.86	50.849	3814	50.265	3770.197	1.016	76.2065
21	40	50	10	37.4	69.2	0.350844	0.649156	40.5	51.6	0.439739	0.560261	37	68.5	0.350711	0.649289	14.86	11.48	861.0735	10.57	792.8176	1.025	76.88156
22	40	50	20	37.8	67.8	0.357955	0.642045	36.3	58.8	0.381703	0.618297	37.4	66.7	0.35927	0.64073	14.86	20.88	1566.134	20.442	1533.281	1.023	76.73155
23	40	50	40	38.9	63.3	0.380626	0.619374	29.62	54.33	0.352829	0.647171	38.8	63.2	0.380392	0.619608	14.86	40.23	3017.507	40.11	3008.507	1.021	76.58153
24	40	50	50	38.8	63.1	0.380765	0.619235	26.4	47.5	0.35724	0.64276	38.7	62.7	0.381657	0.618343	14.86	50.69	3802.074	50.327	3774.847	1.022	76.65654
25	55	30	10	51.9	51.7	0.500965	0.499035	37.4	61	0.380081	0.619919	52	51.6	0.501931	0.498069	14.86	14.342	1075.742	12.209	915.7531	1.018	76.35652
26	55	30	20	52.9	51.3	0.507678	0.492322	52.5	46	0.532995	0.467005	52	51.3	0.503388	0.496612	14.86	22.003	1650.366	20.759	1557.058	1.019	76.43152
27	55	30	40	63.3	47.9	0.569245	0.430755	67.4	31.9	0.678751	0.321249	53.4	47.7	0.52819	0.47181	14.86	41.096	3082.463	40.425	3032.134	1.024	76.80655
28	55	30	50	52.7	48.8	0.519212	0.480788	74.5	23.4	0.760981	0.239019	52.3	48.6	0.518335	0.481665	14.86	51.026	3827.277	50.425	3782.198	1.032	77.4066
29	55	40	10	49.2	57.4	0.461538	0.538462	45.7	54.6	0.455633	0.544367	48.3	58.8	0.45098	0.54902	14.86	11.198	839.9217	10.574	793.1177	1.026	76.95657
30	55	40	20	53.7	48.6	0.524927	0.475073	55.2	46.4	0.543307	0.456693	53.7	48.6	0.524927	0.475073	14.86	21.012	1576.034	20.675	1550.757	1.012	75.90648
31	55	40	40	41	62.4	0.396518	0.603482	42.1	56	0.429154	0.570846	39.8	65	0.379771	0.620229	14.86	40.735	3055.386	40.32	3024.258	1.016	76.2065
32	55	40	50	49.6	52.3	0.486752	0.513248	60.7	35.5	0.630977	0.369023	50.5	52.6	0.489816	0.510184	14.86	50.824	3812.125	50.245	3768.697	1.023	76.73155
33	55	50	10	46	51.7	0.470829	0.529171	47.5	50	0.487179	0.512821	47.7	50	0.488229	0.511771	14.86	12.904	967.8826	10.384	778.8665	1.088	81.60696
34	55	50	20	47.5	49.7	0.488683	0.511317	47.5	49.5	0.489691	0.510309	47.5	50	0.487179	0.512821	14.86	24.122	1809.304	21.938	1645.49	1.098	82.35703
35	55	50	40	48.3	46.5	0.509494	0.490506	48.7	46	0.514256	0.485744	48.4	46.7	0.508938	0.491062	14.86	42.262	3169.92	41.054	3079.313	1.084	81.30694
36	55	50	50	48.8	46.1	0.514226	0.485774	50.1	44.3	0.53072	0.46928	48.9	46.3	0.513655	0.486345	14.86	52.119	3909.259	51.031	3827.652	1.095	82.13201
37	70	30	10	65	40	0.619048	0.380952	65	39.6	0.621415	0.378585	64.6	40.5	0.614653	0.385347	14.86	16.01	1200.852	14.087	1056.615	1.06	79.50678
38	70	30	20	66.1	37.9	0.635577	0.364423	66.5	37.53	0.639239	0.360761	66.1	38.6	0.631328	0.368672	14.86	22.24	1668.142	20.886	1566.584	1.06	79.50678
39	70	30	40	66.2	37.1	0.640852	0.359148	67.4	35.3	0.65628	0.34372	66.1	37.5	0.638031	0.361969	14.86	41.211	3091.089	40.481	3036.334	1.049	78.68171
40	70	30	50	66	37.3	0.638916	0.361084	74.6	26.7	0.736426	0.263574	66.1	37.3	0.639265	0.360735	14.86	51.108	3833.427	50.467	3785.348	1.045	78.38169
41	70	40	10	64.5	37.6	0.631734	0.368266	60.5	37.2	0.619243	0.380757	64.5	38.9	0.623791	0.376209	14.86	11.258	844.4221	10.597	794.8428	1.028	77.10658
42	70	40	20	67	35.9	0.651118	0.348882	67.5	35.2	0.657254	0.342746	67.3	35.8	0.652764	0.347236	14.86	22.246	1668.592	20.991	1574.459	1.056	79.20676
43	70	40	40	67.3	35	0.657869	0.342131	69.3	32.2	0.682759	0.317241	67.3	35	0.657869	0.342131	14.86	41.356	3101.965	40.909	3068.437	1.049	78.68171
44	70	40	50	67.2	35.6	0.653696	0.346304	69.9	31.7	0.687992	0.312008	67.1	35.5	0.653996	0.346004	14.86	51.143	3836.052	50.514	3788.873	1.033	77.48161
45	70	50	10	62.6	31.4	0.665957	0.334043	62.7	31.2	0.667732	0.332268	62.8	31.5	0.66596	0.33404	14.86	15.678	1175.95	13.548	1016.187	1.089	81.68197
46	70	50	20	62.6	31.6	0.664544	0.335456	63	31	0.670213	0.329787	62.6	31.5	0.66525	0.33475	14.86	27.096	2032.373	25.242	1893.312	1.09	81.75698
47	70	50	40	62.6	31.7	0.663839	0.336161	63.1	31	0.670563	0.329437	62.8	31.7	0.66455	0.33545	14.86	42.846	3213.724	41.256	3094.464	1.097	82.28202
48	70	50	50	65.5	28.5	0.696809	0.303191	67.4	26.4	0.71855	0.28145	65.9	28.2	0.700319	0.299681	14.86	52.438	3933.186	51.198	3840.178	1.098	82.35703

A3-Experiments data of Polyimide membrane at Wet Conditions (Pentane)

Table 2 of 2

				STAGE CUT				PERMEANCE								SELECTIVITY		
No.	condition			MEB		ROTAMETER		MEB		ROTAMETER		MEB		ROTAMETER		Ideal		Real
	Conc	T ©	P (bar)	kg/hr	cm3 STP/s	kg/hr	cm3/s	CO2	CO2	CO2	CO2	CH4	CH4	CH4	CH4	MEB	ROTA	MEB
									GPU		GPU		GPU		GPU	CO2/CH4	CO2/CH4	CO2/CH4
1	25	30	10	0.003456	2.61E-06	20.76755	0.017471	8.17E-07	0.81717	0.005474	5474.019	2.1466E-07	0.214658	0.001438	1437.938	3.806852	3.806852	1.03743
2	25	30	20	0.008533	5.23E-06	16.90247	0.011596	8.76E-07	0.875902	0.001942	1942.402	2.4546E-07	0.245461	0.000544	544.334	3.5684	3.5684	1.029931
3	25	30	40	0.003876	1.99E-06	14.76912	0.008603	1.72E-07	0.17249	0.000744	743.8837	4.7845E-08	0.047845	0.000206	206.3367	3.605193	3.605193	1.063035
4	25	30	50	0.004051	1.94E-06	10.49135	0.005717	1.33E-07	0.133221	0.000392	391.7223	3.7322E-08	0.037322	0.00011	109.7424	3.56947	3.56947	1.085546
5	25	40	10	0.004624	1.4E-06	3.972201	0.001398	6.34E-07	0.633659	0.000632	631.9846	1.2795E-07	0.127955	0.000128	127.6167	4.952208	4.952208	1.07907
6	25	40	20	0.010444	2.74E-06	4.593238	0.001398	5.05E-07	0.50529	0.000258	258.025	1.3186E-07	0.131855	6.73E-05	67.33158	3.832154	3.832154	0.978928
7	25	40	40	0.008734	1.9E-06	2.431989	0.000615	1.89E-07	0.189293	6.12E-05	61.2021	4.4254E-08	0.044254	1.43E-05	14.30812	4.277438	4.277438	1.495738
8	25	40	50	0.016908	3.41E-06	9.014033	0.002103	1.54E-07	0.153605	9.48E-05	94.78031	7.6773E-08	0.076773	4.74E-05	47.37182	2.000774	2.000774	2.091918
9	25	50	10	0.004004	1.28E-06	3.70569	0.001389	4.02E-07	0.402273	0.000435	435.0003	1.2557E-07	0.125568	0.000136	135.7832	3.203638	3.203638	1.026858
10	25	50	20	0.008237	8.55E-06	2.312653	0.002792	1.29E-06	1.291042	0.000421	421.4493	3.5924E-07	0.359243	0.000117	117.2717	3.593785	3.593785	1.007554
11	25	50	40	0.009483	9.05E-06	4.860562	0.005487	7.43E-07	0.742526	0.00045	450.1932	2.1005E-07	0.210048	0.000127	127.3521	3.535027	3.535027	1.034666
12	25	50	50	0.009485	8.67E-06	7.003643	0.007558	5.92E-07	0.591784	0.000516	516.0043	1.6167E-07	0.161671	0.000141	140.9684	3.660424	3.660424	1.060105
13	40	30	10	0.000771	5.55E-07	21.12628	0.017212	9.42E-08	0.094168	0.002919	2919.386	5.095E-08	0.05095	0.00158	1579.542	1.848248	1.848248	1.011375
14	40	30	20	0.000941	5.52E-07	12.92946	0.008593	5.58E-08	0.055775	0.000868	868.2194	3.1188E-08	0.031188	0.000485	485.4864	1.788349	1.788349	1.024538
15	40	30	40	0.00429	2.08E-06	1.144697	0.00063	1.07E-07	0.107278	3.25E-05	32.46548	6.1005E-08	0.061005	1.85E-05	18.46195	1.758507	1.758507	1.345965
16	40	30	50	0.006961	3.02E-06	1.276081	0.000629	1.24E-07	0.12393	2.58E-05	25.7839	7.1299E-08	0.071299	1.48E-05	14.83383	1.738182	1.738182	1.538222
17	40	40	10	0.004591	1.44E-06	1.712448	0.000619	3.17E-07	0.316679	0.000136	136.1388	1.6229E-07	0.162289	6.98E-05	69.76708	1.951333	1.951333	1.013295
18	40	40	20	0.004753	1.41E-06	1.812977	0.00062	1.54E-07	0.15422	6.77E-05	67.70762	8.2312E-08	0.082312	3.61E-05	36.13772	1.8736	1.8736	1.064001
19	40	40	40	0.003311	8.09E-07	2.17057	0.000615	4.34E-08	0.043423	3.3E-05	33.02357	2.35E-08	0.0235	1.79E-05	17.87167	1.847817	1.847817	1.276371
20	40	40	50	0.002959	6.78E-07	9.51219	0.002523	2.34E-08	0.023435	8.72E-05	87.22639	1.797E-08	0.01797	6.69E-05	66.8867	1.304092	1.304092	1.992894
21	40	50	10	0.008871	2.87E-06	3.587392	0.001372	6E-07	0.599561	0.000287	286.843	3.116E-07	0.311602	0.000149	149.0771	1.924125	1.924125	1.452245
22	40	50	20	0.002901	8.31E-07	1.98306	0.000679	8.74E-08	0.087381	7.14E-05	71.38057	4.875E-08	0.04875	3.98E-05	39.8239	1.792405	1.792405	1.107305
23	40	50	40	0.003902	1.14E-06	2.088673	0.000705	5.73E-08	0.057284	3.53E-05	35.28069	3.5275E-08	0.035275	2.17E-05	21.7257	1.623915	1.623915	0.887155
24	40	50	50	0.006818	1.71E-06	2.340469	0.00069	6.73E-08	0.067259	2.72E-05	27.16464	4.1602E-08	0.041602	1.68E-05	16.80242	1.61671	1.61671	0.903874
25	55	30	10	0.001774	1.39E-06	0.707525	0.00063	1.53E-07	0.15304	6.92E-05	69.15809	1.6008E-07	0.160079	7.23E-05	72.339	0.956028	0.956028	0.610752
26	55	30	20	0.00707	4.32E-06	0.91231	0.000631	3.07E-07	0.306769	4.48E-05	44.7929	3.0917E-07	0.309171	4.51E-05	45.14373	0.992228	0.992228	1.106785
27	55	30	40	0.004975	2.32E-06	1.196904	0.000632	8.26E-08	0.082635	2.25E-05	22.4748	9.1093E-08	0.091093	2.48E-05	24.77516	0.907151	0.907151	1.598825
28	55	30	50	0.001969	7.86E-07	1.399939	0.000632	2.29E-08	0.022908	1.84E-05	18.40466	2.4162E-08	0.024162	1.94E-05	19.41258	0.948079	0.948079	2.94815
29	55	40	10	0.014763	4.87E-06	0.738754	0.000281	7.95E-07	0.794747	4.59E-05	45.89059	6.5159E-07	0.651591	3.76E-05	37.62445	1.219701	1.219701	0.976496
30	55	40	20	0.010076	5.75E-06	5.515428	0.003573	4.1E-07	0.410115	0.000255	254.9096	4.5147E-07	0.451465	0.000281	280.611	0.908409	0.908409	1.076671
31	55	40	40	0.02821	7.71E-06	1.951154	0.000617	3.83E-07	0.383252	3.07E-05	30.68053	2.3341E-07	0.233412	1.87E-05	18.68538	1.641954	1.641954	1.144181
32	55	40	50	0.006054	1.32E-06	13.98143	0.003514	4.06E-08	0.040644	0.000108	108.3551	3.8572E-08	0.038572	0.000103	102.8289	1.053742	1.053742	1.802936
33	55	50	10	0.009529	8.68E-06	3.124068	0.003398	1.12E-06	1.124648	0.00044	440.2698	1.0733E-06	1.073329	0.00042	420.1799	1.047813	1.047813	1.067717
34	55	50	20	0.005287	4.64E-06	3.223982	0.003387	3.09E-07	0.309216	0.000226	225.843	2.9361E-07	0.293614	0.000214	214.448	1.053136	1.053136	1.00404
35	55	50	40	0.007763	6.2E-06	7.181334	0.006821	2.21E-07	0.221209	0.000243	243.4188	2.2913E-07	0.229133	0.000252	252.1386	0.965417	0.965417	1.019241
36	55	50	50	0.013194	1.07E-05	9.307912	0.008943	3.07E-07	0.306793	0.000255	255.2911	3.2355E-07	0.323547	0.000269	269.2322	0.948219	0.948219	1.068354
37	70	30	10	0.025092	1.75E-05	25.57404	0.020145	1.43E-06	1.427103	0.00164	1640.39	2.2717E-06	2.271715	0.002611	2611.233	0.628205	0.628205	1.010101
38	70	30	20	0.007548	4.84E-06	24.05034	0.017336	2.71E-07	0.270997	0.00097	969.9267	4.6328E-07	0.463275	0.001658	1658.114	0.584958	0.584958	1.01597
39	70	30	40	0.004101	2.31E-06	15.87874	0.010076	6.74E-08	0.067402	0.000294	294.2044	1.1856E-07	0.118563	0.000518	517.5154	0.568494	0.568494	1.070043
40	70	30	50	0.010359	5.14E-06	2.572968	0.00144	1.21E-07	0.120508	3.37E-05	33.74064	2.1169E-07	0.211686	5.93E-05	59.26947	0.569275	0.569275	1.579038
41	70	40	10	0.006392	1.99E-06	3.922179	0.001407	2.33E-07	0.232641	0.000165	164.6865	3.8649E-07	0.386493	0.000274	273.5988	0.601927	0.601927	0.94807
42	70	40	20	0.000704	4.17E-07	28.90407	0.019717	2.25E-08	0.022526	0.001066	1066.096	4.2304E-08	0.042304	0.002002	2002.164	0.532472	0.532472	1.027497
43	70	40	40	0.003125	1.64E-06	9.331655	0.005644	4.64E-08	0.046383	0.000159	159.2969	8.8933E-08	0.088933	0.000305	305.4253	0.521558	0.521558	1.119258
44	70	40	50	0.018899	9.56E-06	13.21254	0.007722	2.18E-07	0.218252	0.000176	176.3624	4.1125E-07	0.411252	0.000332	332.3194	0.530701	0.530701	1.16815
45	70	50	10	0.001215	1E-06	4.238897	0.004124	7.71E-08	0.077076	0.000317	317.4252	1.5357E-07	0.153572	0.000632	632.4589	0.501891	0.501891	1.008018
46	70	50	20	0.005562	4.59E-06	4.380013	0.004266	1.99E-07	0.198554	0.000184	184.3986	3.9422E-07	0.394217	0.000366	366.1135	0.503665	0.503665	1.025868
47	70	50	40	0.012661	1.09E-05	8.350662	0.008509	2.94E-07	0.294078	0.000229	229.3523	5.8218E-07	0.582176	0.000454	454.0417	0.505135	0.505135	1.030748
48	70	50	50	0.009473	7.44E-06	10.21465	0.009548	1.55E-07	0.154844	0.000199	198.6547	3.6118E-07	0.36118	0.000463	463.3707	0.428717	0.428717	1.110861