Separation of Carbon Dioxide from Natural Gas using Inorganic Membrane

by

Mohd Jefri b Yusof

Dissertation submitted in partial fulfilment of

the requirements for the

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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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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 or done by unspecified sources or persons.

MOHD JEFRI B YUSOF

ABSTRACT

Nowadays, natural gas has become one of the most efficient energy in the globalization uses. The principal constituent of natural gas is methane. Carbon dioxide is impurity in natural gas. Separation of carbon dioxide from natural gas before continues to separate each hydrocarbon is one of the important processes in natural gas processing. Membrane is one low cost technology that gives promising performance in gas separation. The objectives of project are to study on carbon dioxide and methane permeability and selectivity, to study on carbon dioxide separation using inorganic membrane and to study on membrane performance at certain operating conditions. The experimental works were conducted using inorganic tubular membrane module in membrane pilot gas to investigate permeability and selectivity for carbon dioxide and methane gas individually at different feed flowrate of 1000 ml/min, 2000 ml/min and 3000ml/min and feed pressure of 1, 3, and 5 bars with room temperature. Blending gas experimental also been conducted to study on membrane separation performance and methane recovery. As the result, it is found that higher flowrate and higher pressure gave higher permeability until reach the constant value. Results show that for ideal selectivity for CO_2:CH_4 was found to be range of 0.7 to 3.5. Selectivity reduced as feed pressure increase, thus reduce methane recovery in retentate stream. At 15% carbon dioxide and 85% methane in feed concentration at 3 bar feed pressure, we got 94% methane recovery in retentate stream, which was the highest recovery for all of experiments. We found that increase carbon dioxide concentration from 15% to 30%, based on analysis, has lower methane recovery in retentate stream. For the conclusion, the study shows that the natural gas separation using inorganic tubular membrane module has a very promising potential to be used for carbon dioxide and methane separation.

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First of all, I would like to thank to the Almighty for his blessing that I can finally complete my project. Next not to forget, I would like to thank you my project supervisor, Associate Professor Dr. Hilmi Mukhtar with his help and guidance along the way as the project started until the completion of the project. His knowledge and understanding had been very helpful in the progress of the project. Then, not to forget Mr. Yusof, a Senior Technician of University Teknologi PETRONAS for his assistance and help to make sure the lab equipment in good condition and help I finish the project as according to the schedule. Those two people had been very helpful with their deep understanding in the Membrane separation.

Also, I want to show my deepest gratitude to the laboratory technician for their help with the equipments, and experience. And finally, I would like to share my happiness with family and friends who have shown their support and encouragements along the way I am doing my project.

CHAPTER 1 : INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas is combination of light hydrocarbons components together with inorganic compounds. Mostly methane is major component hydrocarbon, together with small amount of other light hydrocarbon such as ethane, propane, butane and little small of heavy hydrocarbon. As for inorganic compound, it includes mostly carbon dioxide gas, nitrogen gas, hydrogen sulfide, water vapor and small amount of inert gas. Different location of reservoir has different value of concentration for natural gas.

First developed membrane was in 1961. However membrane area only become establishes and famous in research and commercial since 1980s, because of economic downturn in 1981, while industry is looking for new alternative that has low cost and good performance. Before 1980s, membrane initial acceptance was slow and limited due to unknown process design parameter for most process, but it also has economic risk with investment in membrane research at the time. Membrane has been proven that has good performance in gas separation as the time come by.

1.2 PROBLEM STATEMENT

Natural gas contains light gas, mostly methane. Ethane, propane and butane are also natural gas composition. Besides, there are inert gases like carbon dioxide and nitrogen. Carbon dioxide is the impurity in the natural gas, mostly to methane and ethane product purity. Act as impurity in the natural gas, carbon dioxide reduce the quality of natural gas. Besides, carbon dioxide also has no heating value to the natural gas treatment process. The condition cause natural gas has low heating value in the treatment process. Heating value is the amount of heat released during the combustion of specified amount of natural gas. Moreover, excess carbon dioxide act as inert gas can take capacity in pipeline instead of methane or ethane. This problem will reduce the product quality. Carbon dioxide also can freeze in the pipeline and heat exchanger surface if been send to low temperature unit, that usually range of -45^{o}C to -60^{o}C.

Current technology used in separate carbon dioxide from natural gas is amine system. Liquid alkanoamine has performance in absorbing carbon dioxide molecule from natural gas. However, there are issues with amine system. It cause the foaming problem in absorber, where require the uses of anti-foam chemical. Another issue is high market price which become a great deal to gas processing plant.

Membrane has shows positive results in separating carbon dioxide from natural gas. It has become best alternative due to its low production cost and gives promising result in treating natural gas. Polymide membrane and cellulose acetate is the example of organic membrane that successfully can handle medium scale of gas stream. However, it has low selectivity and flux when be treated with large-scale gas stream and become unstable when treat in high temperature.

1.3 OBEJCTIVE OF THE PROJECT

a) To study on carbon dioxide separation from natural gas using inorganic membrane
b) To study on characteristics of the inorganic membrane when treated with natural gas on certain operating conditions.
c) To study on permeability and ideal selectivity of carbon dioxide on inorganic membrane

1.4 SCOPE OF STUDY

As outlined in the objectives, the purpose of this project is to investigate the performance of inorganic membrane in separate carbon dioxide from natural gas. Equipment use is membrane test unit, which specifically for the gas treating is been used for the study. The simulation use is National Instrument (NI), Labview. Parameters used in observing the membrane module performance are feed pressure, feed flow rate and feed concentration. Transport equation, flux and selectivity of inorganic membrane also been studied with treated with those parameters. Percentages of feed gas before and after membrane separation also been calculated.

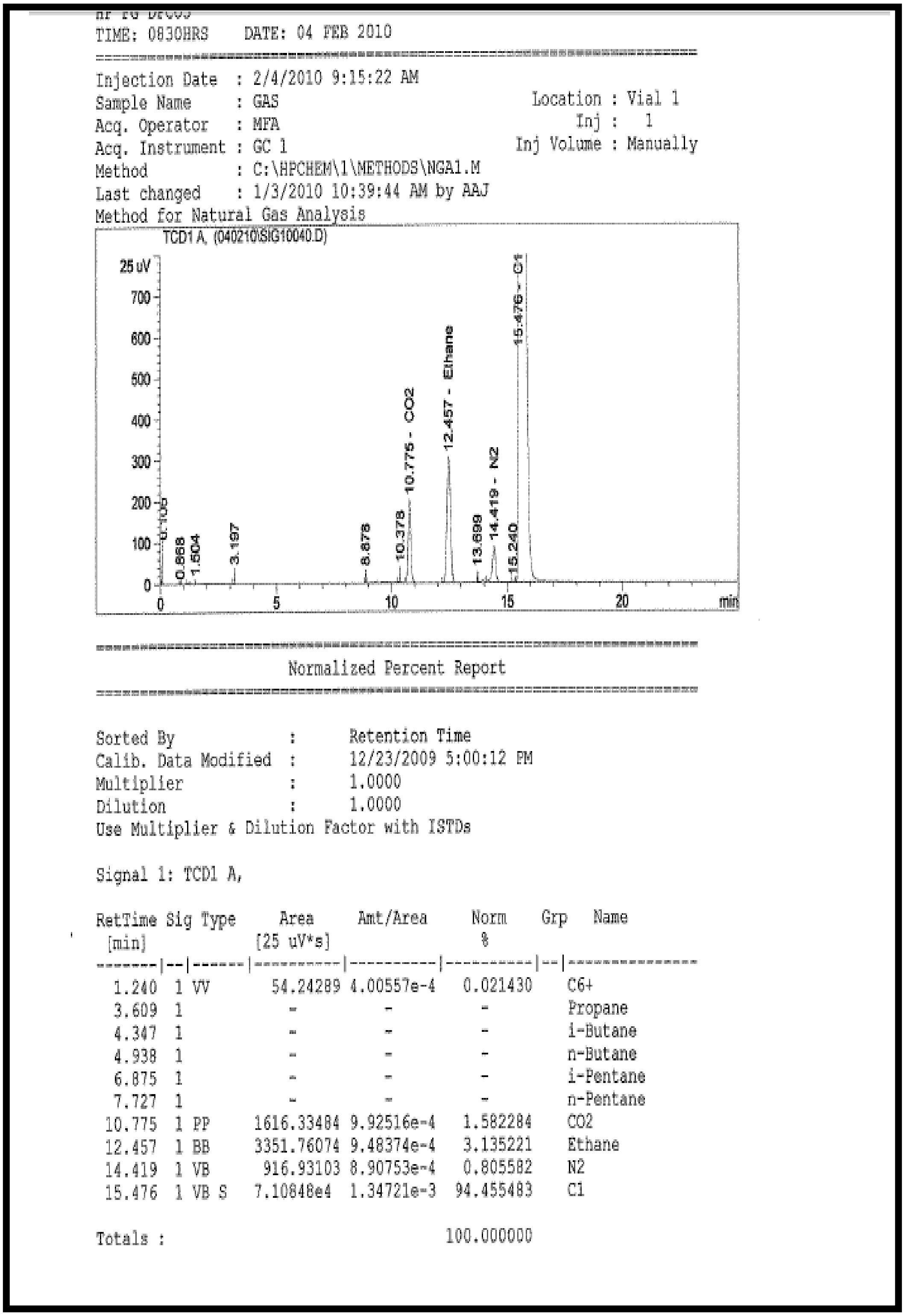
CHAPTER 2 : LITERATURE REVIEW

2.1 NATURAL GAS

Natural gas is a subcategory of petroleum, which contain complex mixture of hydrocarbon, minor inorganic compounds. Major component in the natural gas is methane (CH_4), while other hydrocarbon have minor amount. The inorganic compounds like nitrogen, carbon dioxide (CO_2) and H_2S are impurities and undesirable due to no heating value and can cause problem in gas processing plant aside of their hazard to environment. The composition of the natural gas is different at different area of reservoir.

The hydrocarbon like ethane, propane and butane, those hydrocarbons will be use as feed in the petrochemical industry. Currently the demand of the petrochemical industry is increasing, as the many products in the market are made from petrochemical product.

Below is shown the figure of natural gas composition result from gas chromatography analysis, taken from Chromatography Lab, Gas Processing Plant B (GPPB), Petronas Gas Berhad, Kerteh, Terengganu on 4th February 2010.



```
TIME: 0830HRS    DATE: 04 FEB 2010
=========================================================================
Injection Date  : 2/4/2010 9:15:22 AM
Sample Name     : GAS                          Location : Vial 1
Acq. Operator   : MFA                               Inj :   1
Acq. Instrument : GC 1                       Inj Volume : Manually
Method          : C:\HPCHEM\1\METHODS\NGA1.M
Last changed    : 1/3/2010 10:39:44 AM by AAJ
Method for Natural Gas Analysis
```

```
=========================================================================
                       Normalized Percent Report
=========================================================================

Sorted By             :      Retention Time
Calib. Data Modified  :      12/23/2009 5:00:12 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: TCD1 A,

RetTime Sig Type     Area      Amt/Area      Norm     Grp   Name
 [min]             [25 uV*s]                  %
-------|--|------|----------|----------|----------|--|--------------
  1.240  1 VV       54.24289 4.00557e-4   0.021430     C6+
  3.609  1             -          -          -         Propane
  4.347  1             -          -          -         i-Butane
  4.938  1             -          -          -         n-Butane
  6.875  1             -          -          -         i-Pentane
  7.727  1             -          -          -         n-Pentane
 10.775  1 PP     1616.33484 9.92516e-4   1.582284     CO2
 12.457  1 BB     3351.76074 9.48374e-4   3.135221     Ethane
 14.419  1 VB      916.93103 8.90753e-4   0.805582     N2
 15.476  1 VB S   7.10848e4  1.34721e-3  94.455483     C1

Totals :                                100.000000
```

Figure 2. 1: Natural gas composition analysis from GPPB lab

Source from Chromatography Lab, Gas Processing Plant B (GPPB), Petronas Gas Berhad, Kerteh , Terengganu on 4th February 2010

2.2 CARBON DIOXIDE IN NATURAL GAS

Carbon dioxide is inert gas in the natural gas, together with nitrogen. Both of the gases, nitrogen and carbon dioxide are impurities that lower the quality of natural gas. Besides, they are inorganic compounds, which undesirable due to heating value and can cause problem in gas processing plant aside of their hazard to environment. Both of gases is having no heat value to the processing, which will increase the consumption of the energy needed to separate the natural gas.

Different with nitrogen, carbon dioxide is the hazardous gas, which can cause problems in the gas processing plant if no separation of CO_2 has be done. CO_2 can freeze in heat exchanger and make corrosion. In the gas processing plant, there is one unit called low temperature separation unit, where the demethanizer column, function is to separate methane from ethane and heavier hydrocarbon, placed. The temperature for the heat exchanger in this unit can reach up to -60 degC using propane refrigerant. At this low temperature, water vapor and CO_2 will freeze in the heat exchanger. The formation of solid in the heat exchanger will close the surface area of braze-plate aluminum in the heat exchanger. The effect of this phenomena, damage braze-plate aluminum, and low production because of low feed gas enter the plant. For this problem, it can be detected by checking the pressure difference across the heat exchanger. The possible action to be taken in order to remove the solid CO_2 in heat exchanger is by doing the thawing. Beside, at the pipeline of the gas, freezing solid CO_2 also can happen along the pipeline, due to low temperature of the unit. Heat exchanger at gas processing plant, or usually known as cold box, has cold temperature down to -45^oC until -60^oC.

Next, CO_2 is among methane and ethane composition. If the CO_2 is not properly removed from the natural gas, it will end up in methane and ethane product. This will reduce the quality of the product and excess carbon dioxide in pipeline for the transfer, act as inert gas can take capacity in pipeline instead of methane or ethane.

2.3. INORGANIC MEMBRANE

Membrane has two types of classes which are dense membrane and porous membrane. Dense membrane is solid layer of metal with non-porous structure. While porous membrane has porous wall, which has variety of pore shapes. Another type of membrane is asymmetric membrane, which actually is combination of dense and porous structure. Usually, dense membrane as the main layer, and porous membrane at the top as support. Basically this type or support porous membrane is metal-oxide.

Types of microporous membrane are non-crystalline (X-ray amorphous), zeolite types and crystalline (non-zeolites type). For the non-crystalline, it formed by silica or carbon membrane and it has very low of porosity. For the zeolites type, it is in MFI type, from silicalite type. Its permeance value is lower than amorphous membrane. While for crystalline, it has wide pore and good stability. Its packing formed with very small particle diameter (1 – 2nm). Membrane with wide pore and good stability is very difficult to be made from zeolite.

Permeation means the penetration of permeate (gas, liquid, or solid) through solid layer. The grade of transmissibility is called permeability, which depends on many things, such as time, type of permeate, operating condition (temperature, pressure, pH, velocity, flowrate), membrane thickness and area size. Permeate or the substance get through the membrane, will migrate from high concentration of solvent, to lower concentration area. There are three types of permeation process, little bit discuss below.

1. Sorption
   -it happen on the surface of membrane, where gases. Vapor, dissolved chemical adsorbed at the surface of membrane
2. Diffusion
   -it happen when the permeate penetrates throughout the membrane pores
3. Desorption
   -the adsorbate leaves the membrane a gas.

2.4. MEMBRANE MODULE FOR GAS SEPARATION

2.4.1. Spiral Wound module

Spiral module consists of four sheets wrapped around a central core of a perforated collecting tube. Its concept is a house inside a metal shell. Sour natural gas enter left end of shell, then enter the fed channel, will flow through this channel in axial direction of spiral until reach the right end. Here, it called as sweet natural gas or retentate. The process of permeation happened on the surface of the membrane inside the feed channel. Acid gas as permeate, flow through permeate channel to perforated collecting tube. Below shown the spiral-wound elements and its assembly figure and gas flow path for spiral-wound module.

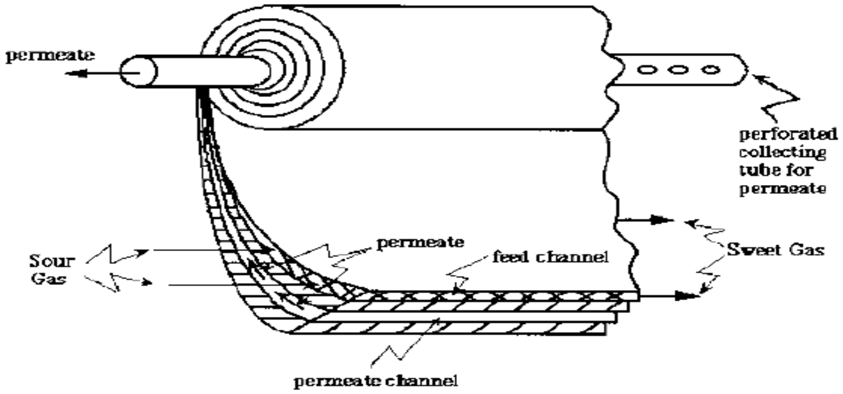


Figure 2. 2: Spiral-wound elements and assembly

2.4.2. Hollow fiber module

Hollow fiber module consist of bundle of very small-diameter hollow fibers. The design of module reassembles shell and tube heat exchanger. Thousand of fine tubes are bound together at each end into a tube sheet, which surround by metal shell. Sour natural gas enter the equipment from the bottom, flowing inside the equipment while acid gas diffuses through very thin membrane, and exit at bottom while the sweet natural gas exit at the top of equipment. Hollow fiber is known to be having large surface area of membrane, which in this case, it can up to 3000 ft^2/ft^3. Besides, other advantages of this module are low pumping power, very high packing density, and ability to achieve high concentrations in the retentate.

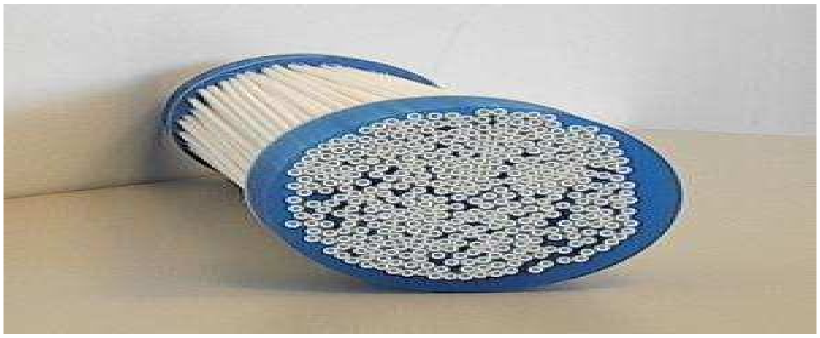


Figure 2. 3: Example of hollow fiber module

2.4.3. Tubular membrane module

Tubular membranes operate in tangential, or cross-flow, design where process fluid is pumped along the membrane surface in a sweeping type action. Several tubular membranes arranged as in a shell and tube type heat exchanger. The membrane is cast on the inside surface of a porous tube. These cross-flow velocities minimize the formation of a concentration polarization layer on the membrane surface, promoting high and stable flux and easy cleaning. The advantages of this module are low fouling, easy cleaning and high transmembrane pressures.

Figure 2. 4: Example of tubular membrane module

2.5. CURRENT TECHNOLOGY AND PROBLEMS

2.5.1. Amine System

Amine system is mostly used in large-gas stream plant because of its capability to absorb acid gas (CO_2) from natural gas greatly at high pressure (35-80 bars). Separation of CO_2 from gas stream by alkanoamines is exothermic reaction. Amine itself has groups, which are primary amine, secondary amine and tertiary amine. Different amine has different reaction rates with respect to several of acid gases and has different sensitivities with respect to solvent stability and corrosion factors.

a. Primary amine (monoethanol amine, MEA, and digylcolamine, DGA)
   MEA is the cheapest amine, and has lowest molecular weight. This group can absorb CO2 in low pressure condition due to its high reaction of energy.
b. Secondary amine (diethanolamine, DEA and di-siopropylamine, DIPA)
   Heat of reaction is lower than primary amine
c. Tertiary amine (triethanolamine, TEA and methyl-diethanolamine, MDEA)
   Lowest heat of reaction, low tendency to degrade the product and more easy to regenerate

Absorption using amine system, liquid amine and natural gas (gas stream) will have contact by countercurrent flow in the absorber. Natural gas will enter absorber from bottom, flow up and leaves at the top column while liquid amine will enter the absorbers at the top, flow down, and rich amine will leaves the bottom column with CO_2 and H_2S into the regeneration system afterward. In the regeneration system, CO_2 and H_2S will be separate and send into incinerator to be burn.

The problems or issues with amine system are its market price is very high, foaming problem in absorber and amine loss in the system. From operational side of view, amine system can lead to extensive of foaming in the acid gas removal unit, which require to have antifoam injection into the system. This issue can increase the operational cost in purchasing antifoam in order to control foaming. Foaming can decrease the absorption process in the absorber, due to less contact of surface area of countercurrent flow. Amine losses to system are common problem in gas processing plant, which it affects in reducing concentration or strength of the amine. Certain level of amine strength and concentration is needed to extract the CO_2 and H_2S into certain specifications. Every time capacity is reduce, additional amount of amine need to be top up into the system. This can increase the cost of purchase the new amine in some period of time. Based on current market, the price of amine is very expensive, depends on the group and type of amine use for the plant. The upper level of amine group, the strong the amine in absorption and the higher price is. Different type of natural gas field that has different carbon dioxide concentration may use different type of amine group.

2.5.2. Physical Solution Absorption

The process is according to Henry's Law, which depends on pressure and temperature and CO_2 in higher partial pressure. Typical solvent is selexol (dimethylether of polyethylene glycol). Selexol has been used since 1969 to sweeten natural gas, both for bulk CO_2 removal and H_2S removal. Absorption takes place at low temperature (0 - 5 ^{o}C). Desorption of the rich Selexol solvent can be accomplished either by letting down the pressure (CO_2 removal) or by stripping with air, inert gas or steam. Additionally, the low absorption temperature used requires that the lean solvent be returned to the absorber via a refrigeration unit. Absorption of heavy hydrocarbon in refinery plant is drawback of this process.

2.5.3. Solid Physical Adsorption

This process consists of two major steps, which are adsorption and desorption. The adsorption controls the technical feasibility step, and desorption control the economic feasibility step. The main advantage of this process than absorption process is the process is simple and energy efficient operation and regeneration. This can be achieving with pressure or temperature swing cycle. The primary material is using zeolites or molecular sieve. However, this system cannot handle large concentration of CO_2 in gas stream.

2.5.4. Membrane

Separation membranes are thin barriers that allow selective permeation of certain gases. They are predominately based on polymeric materials. Membranes for gas separation are usually formed as hollow fibers arranged in the tube-and-shell configuration, or as flat sheets, which are typically packaged as spiral-wound modules. The membrane process also has been widely used on the commercial scale for hydrogen recovery from purge gases in ammonia synthesis, refinery and natural gas dehydration, sour gas removal from natural gas, and nitrogen production from air.

Membrane can be use to separate high concentration of acid gas from hydrocarbon gases. The process is involving the permeation of acid gas through the membrane. It use large pressure drop as the driving force, to separate permeate (acid gas) from retentate (natural gas). The process is simple but it require large amount of horsepower and compressor if acid gas must be recompressed for disposal (after separation)

The commercial membranes for CO_2 separation are mainly prepared from cellulose acetate, polysulfone, and polyimide which are organic membranes. However, this organic membrane cannot handle large concentration of CO_2 in gas stream and unstable when treating in high temperature.

2.5.5. Summary Advantages and Disadvantages of Amine System and Membrane System

Technology	Advantages	Disadvantages
Amine System	Can operate at high and extreme operating condition	Foaming Problem
	Good performance in treating high concentration of natural gas	Loss of concentration in system and has environmental impact
	Can absorb carbon dioxide in high perofrmance	High price and amine regeneration cost
Membrane System	Cost benefit : low cost	Commercial membrane cannot operate at high or extreme operating condition
	Lack of mechanical complex	Low flux in treating high concentration of natural gas
	No phase change involve and low environmental impact	Fragile and unstable with chemical attack and heavy hydrocarbon

2.6. LATEST RESEARCHS ON NATURAL GAS TREATING USING MEMBRANES

2.6.1. POLYETHER BASED BLOCK COPOLYMER MEMBRANES

In this research, it presented a polyether based segmented block copolymer system as soft segment combine with short monodisperse di-amide as a hard segment. Polyether and especially poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) based segmented block copolymers are very well known for their high CO_2 permeability combined with a high CO_2/light gas selectivity, but most (commercially) available block copolymers have incomplete phase separation between the soft and hard blocks in the polymer leading to reduced performance.

Block copolymer has been used in investigations for carbon dioxide removal from light gas. It consists of an alternating series of exible soft segment, dominant phase for gas permeation and crystallizable hard segment for its mechanical stability. The type of soft and hard segment can be chosen independently, this makes them a versatile instrument to tune the properties of gas separation membranes.

This research study on the effect of the length of the PEO soft segment, the type of soft segment (PPO vs. PEO) and the use of a mixture of these two different types of soft segment. For the first experiment, The CO_2 permeability increases with increasing PEO soft segment length and the polymers show an increase in gas permeability with increasing temperature.

For second experiment which study on type of soft segment (PPO vs PEO), the permeability of the PPO based block copolymers is a factor 4{5 higher than the permeability of the PEO based block copolymers. This can be attributed to the extra methyl side group in PPO compared to PEO, which prevents close chain packing (leading to soft phase crystallization), thus increasing the free volume and gas permeability.

2.6.2. Thermal Rearranged Membrane

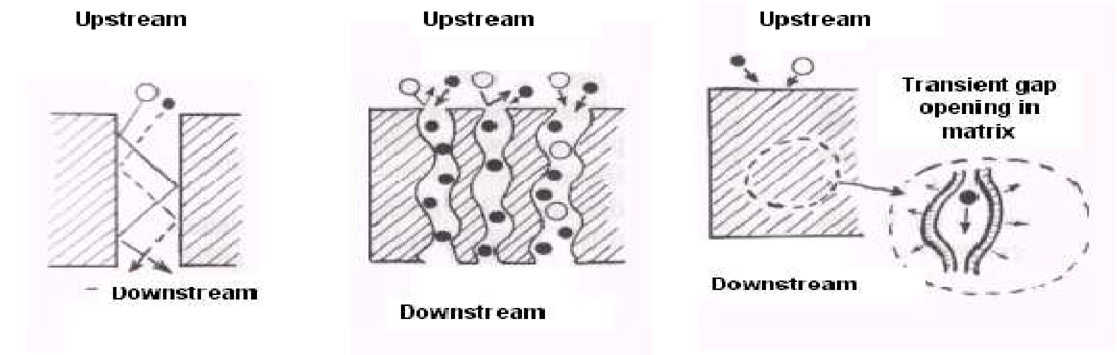
The new plastic membrane permits carbon dioxide and others small molecules to go through hour-glass shaped pores within it while impeding natural gas (methane) movement through. This thermal rearranged plastic works four times better than membranes at separating the carbon dioxide. It is also found that by Dr. Hom Bum Park that this TR act quicker in separating the carbon dioxide. Beside than that, this new membrane also can tolerate 600 degree Fahrenheit, which be able to transformed the material into the better performing membrane.

2.7. FUNDAMENTAL OF TRANSPORT MECHANISM IN MEMBRANE SEPARATION PROCESS

There are three types of transport mechanisms, which are Knudsen diffusion, molecular sieving and solution-diffusion. Based on Knudsen diffusion, separation is achieved if the free path of molecules is large relative to the membrane pore radius. It is based on the inverse square root ratio of two molecular weights, assume that gas mixture only consist of two type of molecules. The process is limited to systems with large values for the molecular weight ratio (Jennifer Chih-Yi Chen, 2002)

For the molecular sieving, the separation happened when based on molecular size and membrane pore size. Smaller molecules have higher diffusion rates. This can happen when sufficient driving force applied. The main limitation is that condensable gases cause fouling, and alter the structure of the membrane (Jennifer Chih-Yi Chen, 2002)

Solution-diffusion separation is based on both solubility and mobility factors. It is the most commonly used model in describing gas transport in non-porous membranes and it is applied in our studies. (Jennifer Chih-Yi Chen, 2002)



1. Knudsen diffusion 2. Molecular sieving 3. Solution Diffusion

Figure 2. 5: General transport mechanisms for gas separations using membranes

The upstream gas, which has a pressure of $p1$, comes in contact with the membrane interface. With a driving force (e.g.,chemical potential, concentration gradient, etc.), the permeate gas forms a concentration profile across the membrane with respect to membrane thickness, l. The normalized flux is gas flow rate divided by the membrane surface area and it is denoted as NA. Separation of the gas mixture is achieved when one of the components interacts more strongly with the membrane material or, in other words, diffuses faster through the membrane.

Among the three solution-diffusion stages, the diffusion step is the slowest; hence, it is the rate determining step in permeation. (Jennifer Chih-Yi Chen, 2002)

The relationship between the linear flux, J and the driving force is:

$$J = -A(dX/dx) \qquad \textbf{(Equation 2. 1)}$$

Where A = some phenomenological coefficient,

X = potential, and

x denotes the space coordinate measured normal to the section.

To describe gas diffusion in the membrane, or known as Fick's first law:

$$J = -D(dC/dx) \qquad \textbf{(Equation 2. 2)}$$

where D = diffusion coefficient,

X in Equation 1 now defines concentration and is denoted as C

When the solubility of a penetrant gas in a polymer is sufficiently low, the concentration of the penetrant is proportional to the vapor pressure of penetrant in polymer.

$$C = S * p \qquad \textbf{(Equation 2. 3)}$$

Where S = solubility coefficient

p = vapor pressure of penetrant

At steady state, the permeation of gas A through membrane defined as:

$$P_A = N_A / [(p1-p2)/l] \qquad \textbf{(Equation 2. 4)}$$

Where P_A = permeation rate of gas A
N_A = membrane surface area
l = membrane thickness

If Henry's law applies, then *S* is constant at a given temperature and so is *D*. The permeability coefficient, *P*, can also be defined as

$$P = D * S \qquad \textbf{(Equation 2. 5)}$$

The diffusion coefficient, *D*, is a kinetic term governed by the amount of energy necessary for a particular penetrant to execute a diffusive jump through the polymer and the intrinsic degree of segmental packing in the matrix. The solubility coefficient, *S*, is a thermodynamic term that depends on factors such as condensibility of the penetrant, interactions between the polymer and penetrant, and the amount of penetrant-scale non-equilibrium excess volume in glassy polymers. (Jennifer Chih-Yi Chen, 2002)

For a binary gas mixture permeating through a polymer membrane, the selectivity of a polymer membrane towards two different penetrant gases, A and B, is commonly expressed in terms of the ideal selectivity or ideal permselectivity, a_{AB}. (Jennifer Chih-Yi Chen, 2002)

When the downstream pressure is negligible relative to the upstream pressure, a_{AB} can be written as the ratio of permeabilities:

$$a_{AB} = P_A/P_B \qquad \textbf{(Equation 2. 6)}$$

Substitute the above equation with diffusivity and solubility terms,

$$a_{AB} =(D_A/D_B)(S_A/S_B) \qquad \textbf{(Equation 2. 7)}$$

Where D_A/D_B is the ratio of the concentration-averaged diffusion coefficients of penetrants A

and B, and is referred to as the membrane's"diffusivity selectivity". S_A/S_B is the ratio of solubility coefficients of penetrants A and B, and is called the"solubility selectivity" (Jennifer Chih-Yi Chen, 2002).

CHAPTER 3 : METHODOLOGY

3.1 MATERIALS

3.1.1. Methane

Methane is the lightest hydrocarbon, but most of the natural gas composition is methane. At room temperature and standard pressure, methane is a colorless, odorless gas; the smell characteristic of natural gas as used in homes is an artificial safety measure caused by the addition of an odorant, often methanethiol or ethanethiol. Methane is non toxic substance, however it is highly flammable. Methane is also an asphyxiant and may displace oxygen in an enclosed space

3.1.2. Carbon Dioxide

CO_2 is an acidic oxide: an aqueous solution turns litmus from blue to pink. It is the anhydride of carbonic acid, an acid which is unstable in aqueous solution, from which it cannot be concentrated. O_2 is toxic in higher concentrations: 1% (10,000 ppm) will make some people feel drowsy. Concentrations of 7% to 10% cause dizziness, headache, visual and hearing dysfunction and unconsciousness within a few minutes to an hour

3.2 EQUIPMENT

3.2.1. Membrane Pilot Gas or Membrane Separation Test Unit

Name of equipment use is Membrane Test Unit. This unit is from Singapore product. Consists of four types of membrane modules, identified as tubular, hollow fiber, spiral wound and flat sheet membrane module. There is one more module which use for research and development membrane called R & D module. All of the feed flowrate, composition, temperature and pressure are controlled and determined using software name National Instrument (NI) Labview, which is installed in the computer, next to the equipment. Tubular membrane module is used, as it is ceramic and porous membrane.

3.3 EXPERIMENT

3.3.1. Permeability test for methane and carbon dioxide

The reasons for these two tests are:

3.3.1.1. To study permeability and selectivity of carbon dioxide and methane in tubular membrane module.

3.3.1.2. To make hypothesis on membrane module performance when treating one type of gas.

3.3.2. Conduct experiment on parameter

3.3.2.1. Carbon dioxide concentration in feed
3.3.2.2. Feed flowrate
3.3.2.3. Operating pressure

These types of parameters have effect on gas separation. Different parameter value will affect the gas separation in module. This is where we do the study on carbon dioxide separation from methane, with different changing parameters to evaluate the performance of the membrane module

Table 3. 1: CO_2 permeability test on flowrate of 1000 ml/min

CO_2 Permeability Test		
Feed type	Feed Pressure, bar	Total Flowrate ml/min
1	1	1000
2	3	1000
3	5	1000

Repeat experiment with listed pressure, but using different total flowrate, which here is CO_2 flowrate at 2000 ml/min and 3000 ml/min

Table 3. 2: CH_4 permeability test on flowrate of 1000 ml/min

CH_4 Permeability Test		
Feed type	Feed Pressure, bar	Total Flowrate ml/min
1	1	1000
2	3	1000
3	5	1000

Table 3. 3: Gas blending with 15% CO_2 and 85% CH_4 with 2000 ml/min flowrate at different pressure

Feed type	Feed Pressure, bar	Total Flowrate ml/min	CO2/CH4 ratio
1	3	2000	15% CO2 : 85 % CH4
2	5	2000	15% CO2 : 85 % CH4

Table 3. 4 : Gas blending with 30% CO_2 and 70% CH_4 with 2000 ml/min flowrate at different pressure

Feed type	Feed Pressure, bar	Total Flowrate ml/min	CO2/CH4 ratio
1	3	2000	30% CO2 : 70% CH4
2	5	2000	30% CO2 : 70% CH4

3.4 PROCEDURES

3.4.1. Equipment Start-up

1. Turn on the computer that is linked to the system
2. Open software ‘National Instrument (NI), Labview” in the start-up menu
3. Do line tracing including checking the valve positioning mode on the overall equipment condition before proceed to next stage.
4. Click on which module that need to use. In this procedure, the tubular membrane module has been choosing.

3.4.2. Running the Experiment

1. Set membrane 1, tubular membrane module on operation in the Labview software
2. Perform line tracing and necessary valve positioning exercise to ensure the flow of feed gas into the membrane is not obstructed
3. Make sure valve positioning for tubular membrane as per table below. Be in mind that we are conducting Tubular Membrane module, so other modules valve positioning should be close.

Table 3. 5: Valve Positioning for Tubular Membrane Module

Line	Open	Close
Feed	V_{feed}, V_{1feed}, $V_{1(heater)in}$, $V_{1(heater)out}$	$V_{r\&d(feed)}$
Retentate	$V_{tubular\text{-}ret}$, $SV_{1A(retentate)}$, $V_{1(retentate)vent}$	$V_{r\&d\text{-}ret}$, $SV_{1B(retentate)}$,
Permeate	$V_{tubular\text{-}per}$, $V_{1(permeate)vent}$	$V_{r\&d\text{-}per}$, $SV_{1A(permeate)}$, $S_{V1B(permeate)}$,

4. Set the flow of each gases (carbon dioxide and methane) in accordance to the mass flow controller setting (MFC)
5. Note the gas inlet temperature. Only turn on the heater if conducted the experiment under elevated temperature.
6. Turn on vacuum pump to ensure all gas are cleared from gas analyzer and cooling chamber into vent
7. To run data, go to top left corner of application and click “Run Continuously” button. Be note that all data is record in an Excel file the minute “Run” mode is selected. Experiment data must be retrieved and save after each experiment set.
8. Gas pressure can be set up and detect manually from each gas vessel.
9. Repeat the procedure from 1 until 9 for other membrane module by changing membrane module operation and valve numbering.

3.4.3. Equipment Shut Down

1. Turn off heater if used
2. Set flow of all gases to zero value in NI (Labview)
3. Close gas vessel valves
4. Monitor temperature of the outlet temperature of gas leaving the equipment. If temperature is lower than 30oC, stop cold water circulation by close V_{water} manually and turn off vacuum pump.
5. Save and print all experiment data in pen drive. Make sure there is no data record in saved in the computer hard disk.
6. Shut down the computer

3.4.4. Purging the System

1. Purging the system can be done before experiment start or after experiment done
2. Make sure the valve positioning is same as running the experiment procedure
3. Turn on the vacuum pump
4. Introduce compressed air into the equipment for several minutes.
5. Stop nitrogen gas supply
6. Stop vacuum pump after nitrogen supply stop a while
7. Close all valves

3.4.5. Process Schematic of Experimental Apparatus

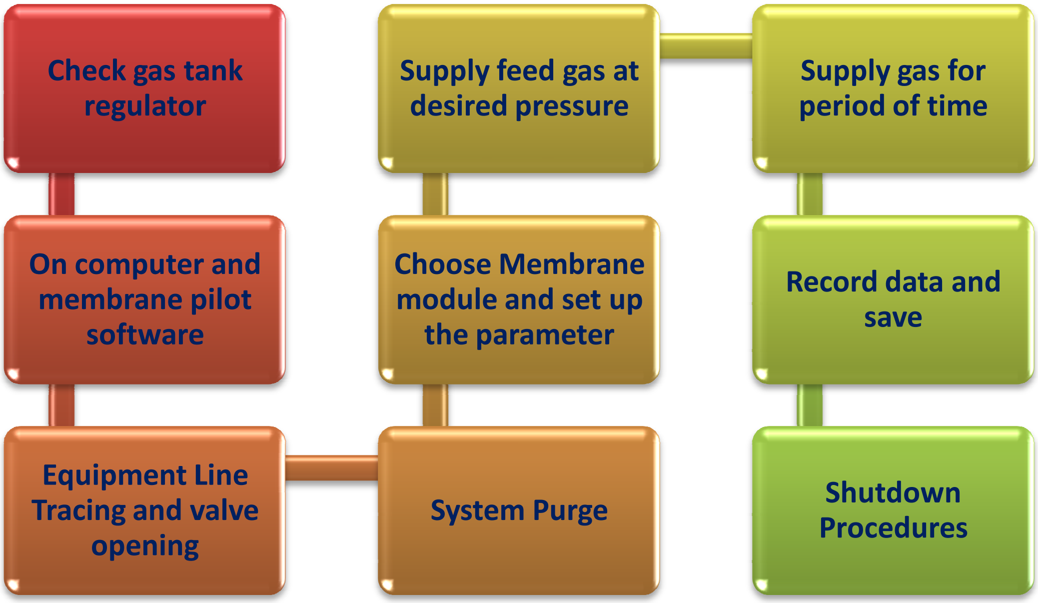


Figure 3.1: Process Schematic of Experimental Apparatus in handling experiment

CHAPTER 4 : RESULT AND DISCUSSION

All of important parameter needed to test in experiment has been tested, like permeability test, feed composition test, feed flowrate test and feed pressure test. For the permeability test, gas methane (CH_4) and carbon dioxide (CO_2) has been used in tubular membrane module.

Permeability test and blending test experiments have been done in order to find permeability and selectivity of carbon dioxide and membrane. For all of experiments, the temperature is fixed to room temperature, or at 25^oC.

4.1 PERMEABILITY TEST

Permeability test for both gases has been done two to three times at same condition to find the stable data.

4.1.1 CO_2 Permeability Test

CO_2 permeability test with different feed flow rate at same feed pressure

1. 1 bar feed pressure
2. 3 bar feed pressure
3. 5 bar feed pressure

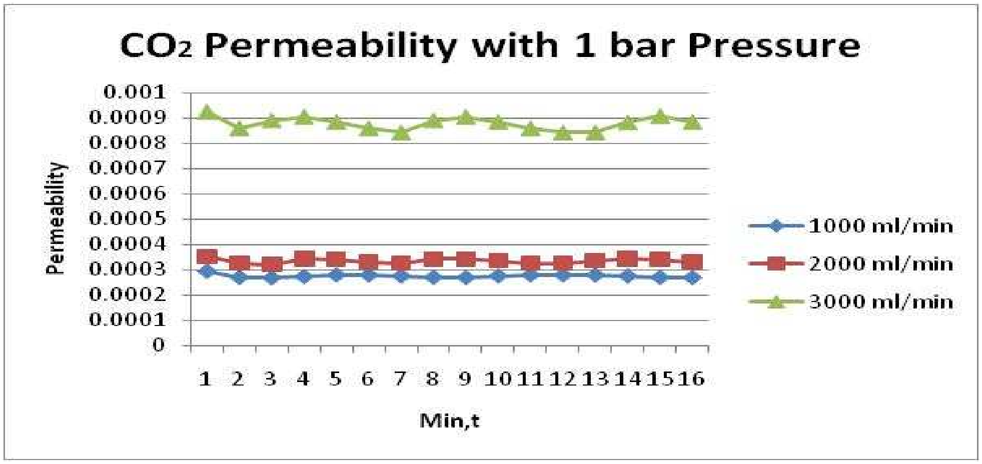


Figure 4-1 : CO_2 Permeability with different flow rate and 1 bar feed pressure

Figure 4.1 shows higher permeability value of 3000 ml/min of feed flowrate than 2000 ml/min and 1000 ml/min at same pressure (1 bar). By this we found that higher feed flowrate give higher permeability. This support by Knudsen Diffusion theory, where the free path of molecule is large relative to the membrane pore radius. Increasing number of carbon dioxide in the feed allow much more molecule to pass through membrane as long as membrane pore radius still allow molecule to pass through it.

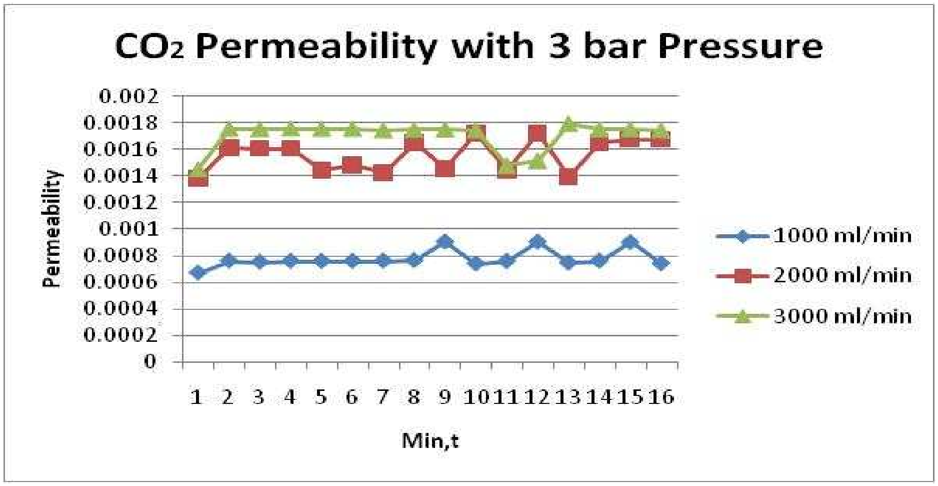


Figure 4-2 : CO_2 Permeability with different flowrate and 3 bar feed pressure

Figure 4.2 shows higher permeability obtain when feed pressure is increase to 3 bars for 3 types of feed flowrates. From the graph, both 2000 ml/min and 3000 ml/min do not has very obvious different in permeability, whereas for 1000 ml/min is low permeability than others. But still, in this graph, increasing feed flowrate and feed flowrate has higher permeability. However, as it reaching certain pressure and time, the permeability will remain constant and stable because it is not a linear line.

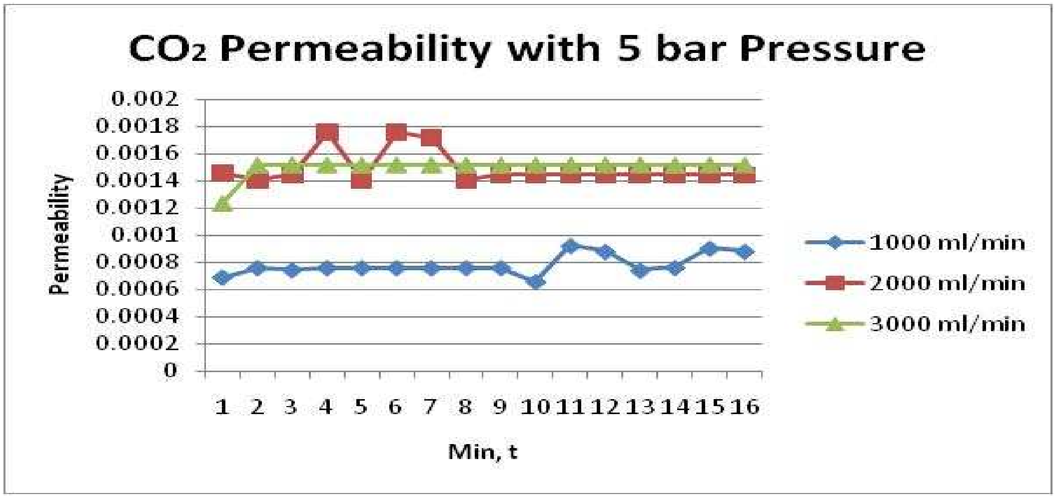


Figure 4-3 : CO_2 Permeability with different flowrate and 5 bar feed pressure

Figure 4.3 shows the same trend as figure 4.2, but it clearly shows here that, at feed pressure of 5 bars for both 2000 ml/min and 3000 ml/min experiment, the trends has same value. This because of as pressure increase until reach the membrane limit, the permeability will not increase anymore. It remains at constant value, as the permeation still happen, but the molecule is permeating through membrane in slow speed. We can say that the porous or path way of membrane pore is ingested with molecules, due to higher flowrate and higher pressure as driving force for permeation.

CO_2 permeability comparison between feed pressure and feed flowrate.

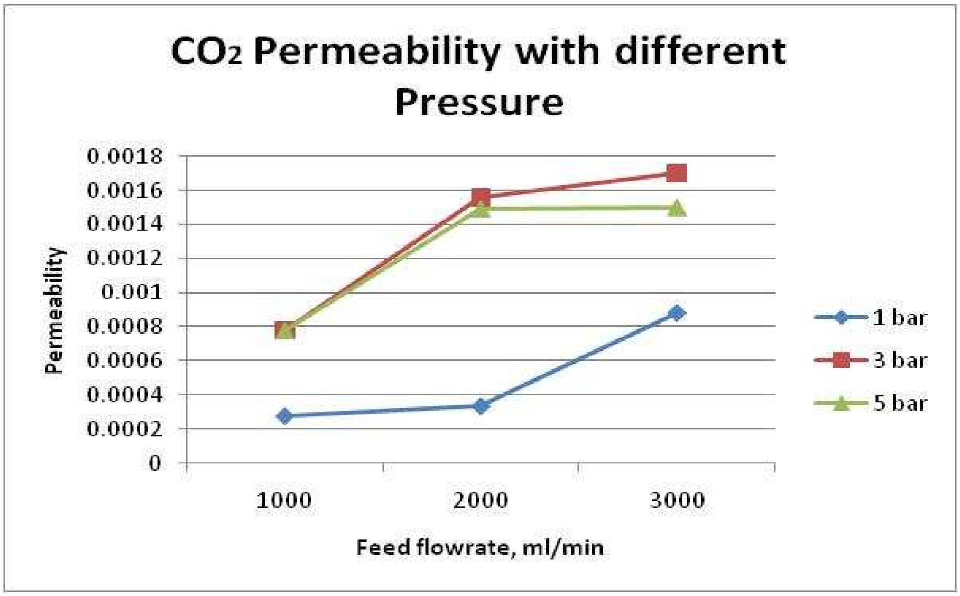


Figure 4-4 : CO_2 Permeability at different pressure at increasing feed flowrate

Figure 4.4 shows 3 different pressures graph with increasing feed flowrate. As from above trending, as feed flowrate increasing, the permeability is increasing. Same goes to increasing feed pressure. However, 5 bar feed pressure has lower permeability than 3 bar pressure with increasing flowrate from 2000 ml/min until 300 ml/min. it shows that with 2000 ml/min and 3000 ml/min at 5 bar pressure, the membrane pore is ingested and full with molecules. It cannot increase permeation rate but constantly allow molecule to permeate through it. Whereas, for 3 bar pressure favor more permeation rate than 5 bar. Theoretically increasing pressure will both permeability and selectivity although it give higher driving force to allow higher permeation. But with increasing feed flowrate, lower pressure (3 bars) gave higher permeability than high pressure (5 bars)

4.1.2 CH_4 Permeability Test

CH_4 permeability test with different feed pressure at same feed flowrate. Graphs below show the comparison between same flowrate but at different pressure

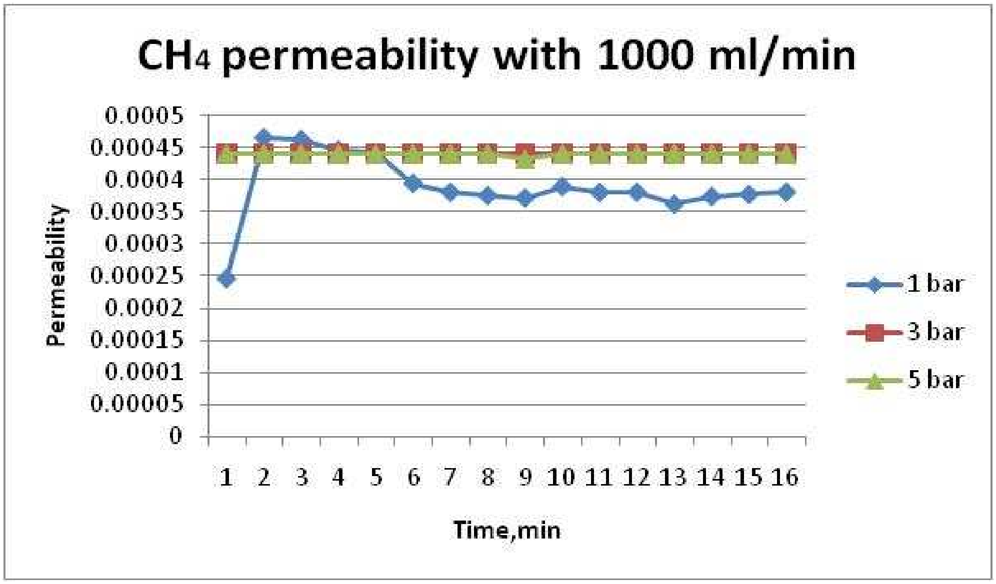


Figure 4-5 : CH_4 Permeability with different pressure at 1000 ml/min flowrate

Figure 4.5 shows that at 1000 ml/min feed flowrate, 3 bars and 5 bars feed pressure has same permeability, while for 1 bar pressure, has lower permeability. All of them have stable permeability across the membrane. It seems that as increasing feed pressure, it increase the permeability, but until reach its limit, and the permeability will become constant. With the ingested molecule in membrane pores due to high feed flowrate, it deny higher permeation rate, but allow slow and constant permeation of molecule through membrane. The higher driving force here is different pressure across membrane cannot increase permeability of methane.

4.1.3 CO_2 and CH_4 permeability comparison

Below show the graphs that compare the carbon dioxide permeability and methane permeability. Since 2000 ml/min and 3000 ml/min of methane permeability give almost the same pattern, only one pattern has been trend here.

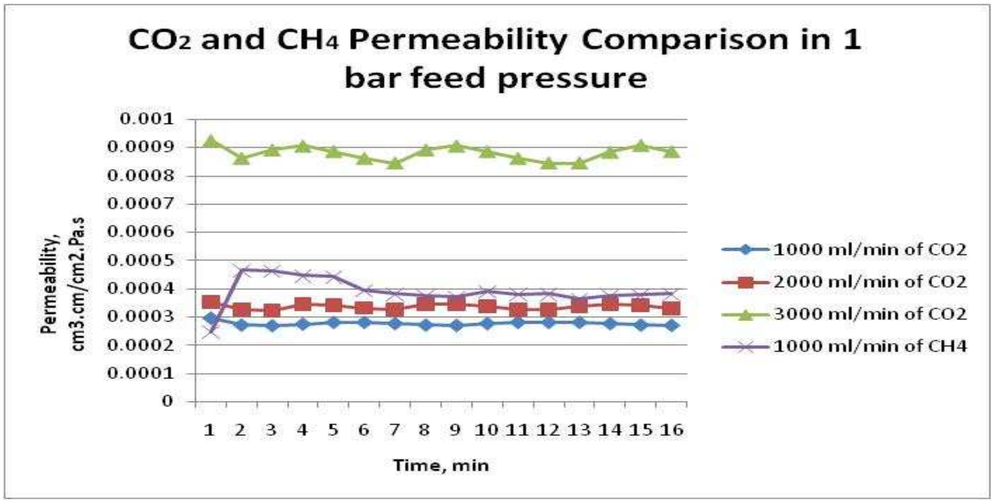


Figure 4-6 : CO_2 and CH_4 permeability comparison at 1 bar feed pressure

Figure 4.6 indicate that higher flowrate (3000 ml/min) has higher permeability than other flowrates. From the graph, methane permeability at 1000 ml/min has higher permeability than 1000 ml/min and 2000 ml/min of carbon dioxide permeability. At 1 bar feed pressure, low different pressure across membrane may lower the carbon dioxide permeability at 1000 ml/min and 2000 ml/min than methane permeability. Insufficient driving force may have denied molecular sieving theory where smaller molecules have higher diffusion rates.

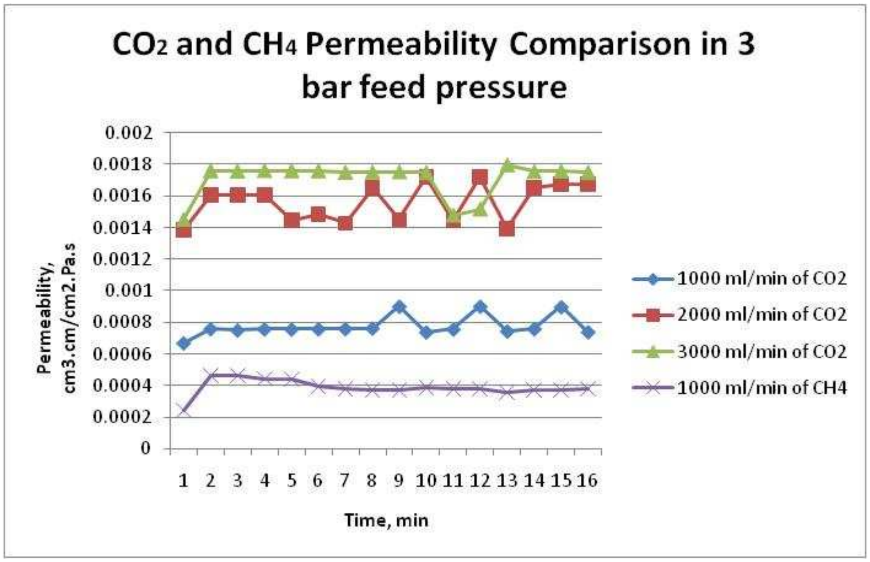


Figure 4-7 : CO_2 and CH_4 permeability comparison at 3 bar feed pressure

Figure 4.7 show that methane has lower permeability than carbon dioxide at 3 bar feed pressure. It also show that higher flowrate has higher permeability for carbon dioxide permeability than methane, although for 2000 ml/min and 3000 ml/min do not show much different in permeability value. From this graph, we can say that carbon dioxide has higher permeability value than methane. For fundamental transport theory using molecular sieving transport, it says that smaller molecules have higher diffusion rates and this can happen when sufficient driving force applied. This is at 3 bars feed pressure, carbon dioxide has higher permeability than methane, which is carbon dioxide molecule is smaller than methane.

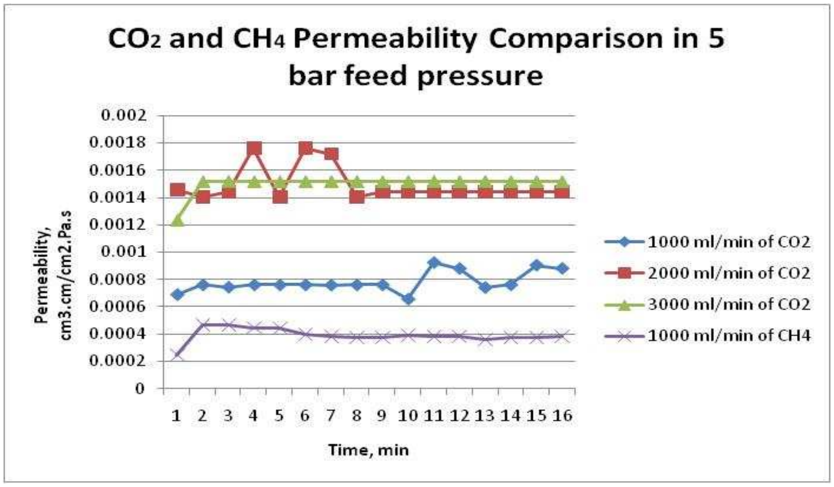


Figure 4-8 : CO_2 and CH_4 permeability comparison at 3 bar feed pressure

Figure 4.8 show the same trend and almost have same value as Figure 4.7. Carbon dioxide permeability is higher than methane permeability. It supports the molecular sieving theory that smaller molecules have higher diffusion rates.

4.1.4 Ideal Selectivity of methane and dioxide

The formula of calculation ideal selectivity of tubular membrane for both gases is same as Equation 2.6 and shown below:

$a_{AB} = P_A/P_B$

Where P_A is permeability of CO_2, while P_B is permeability of CH_4, with respect to operating condition.

Table 4-1 : Ideal selectivity of different pressure at different flowrate

	1000ml	**2000ml**	**3000ml**
1 bar	0.727	0.883	2.314
3 bar	1.763	3.542	3.870
5 bar	1.773	3.390	3.405

Table 4.1 as per above is the average value of selectivity at different feed pressure and feed flowrate.

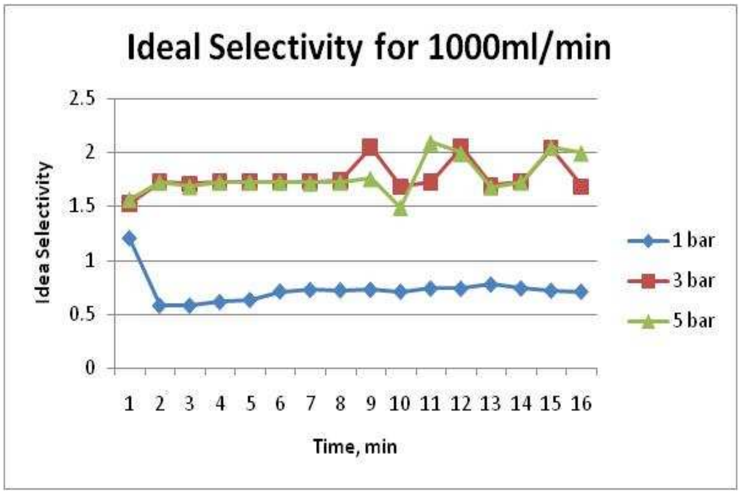


Figure 4-9 : CO_2/CH_4 selectivity with different pressure at 1000 ml/min

Figure 4.9 give us three type selectivity of different feed pressure. 1 bar feed pressure has lowest permeability while 3 bars and 5 bars feed pressure seem look alike, although from table 4.1; average selectivity for 5 bars has slightly highest value than 3 bars. From these results, the carbon dioxide permeates 0.7 to 1.77 faster than methane.

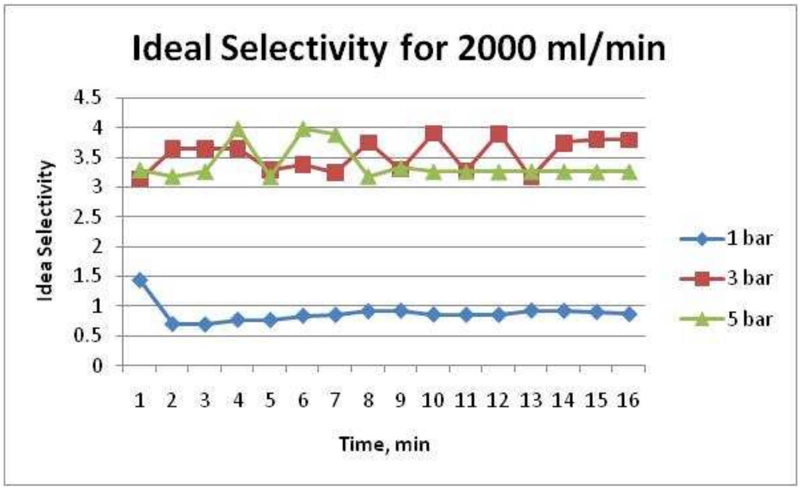


Figure 4-10 : CO_2/CH_4 selectivity with different pressure at 2000 ml/min

Figure 4.10 give us the same trend of selectivity but in different value from Figure 4.9. Higher feed flowrate give higher selectivity value. For comparison, from Table 4.1, 3 bars feed pressure has higher average selectivity than 5 bar pressure. From this graph, carbon dioxide permeates 0.883 to 3.542 faster than methane.

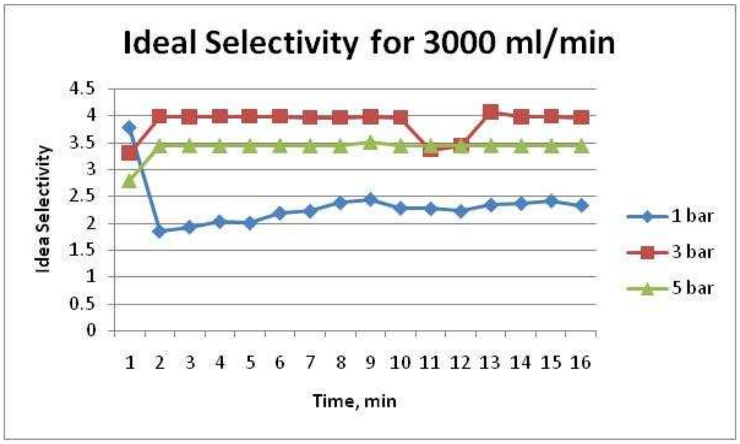
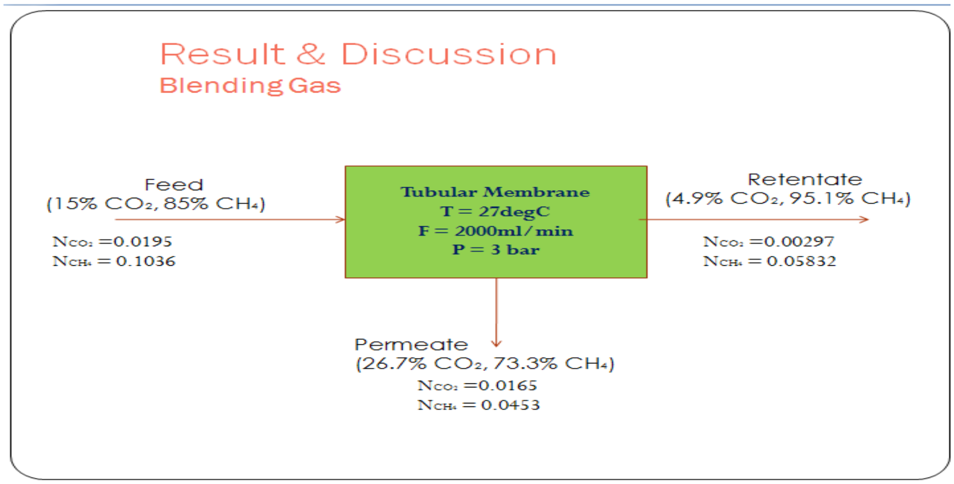


Figure 4-11 : CO_2/CH_4 selectivity with different pressure at 3000 ml/min

Figure 4.11 show the stable selectivity for 3 bars and 5 bars feed pressure. All of selectivity has slightly higher value than Figure 4.10, but still 3 bars feed pressure has the higher selectivity over 5 bars feed pressure. It may due to membrane reach it limitation for both permeability and selectivity, based on these 3 feed pressures. Membrane has the higher permeability and selectivity at 3 bars feed pressure, where higher driving force or higher feed pressures do not improve selectivity. Higher pressure is used, the selectivity will become lower or reduces, where it give other molecules to past thru the membrane.

4.2 BLENDING GAS OF METHANE AND CARBON DIOXIDE IN FEED COMPOSITION

In order to calculate the composition of retentate and permeate, I calculated the number of mole for feed stream and permeate stream. From the number of mol for each stream, we can find the amount percentages of methane and carbon dioxide gas inside each stream. Figure 4.12 below shows how much methane recovery we got in retentate stream and the composition of permeate stream after gas separation.



Result & Discussion

Blending Gas

Feed
($15\%\ CO_2$, $85\%\ CH_4$)
$N_{CO_2} = 0.0195$
$N_{CH_4} = 0.1036$

Tubular Membrane
T = 27degC
F = 2000ml/min
P = 3 bar

Retentate
($4.9\%\ CO_2$, $95.1\%\ CH_4$)
$N_{CO_2} = 0.00297$
$N_{CH_4} = 0.05832$

Permeate
($26.7\%\ CO_2$, $73.3\%\ CH_4$)
$N_{CO_2} = 0.0165$
$N_{CH_4} = 0.0453$

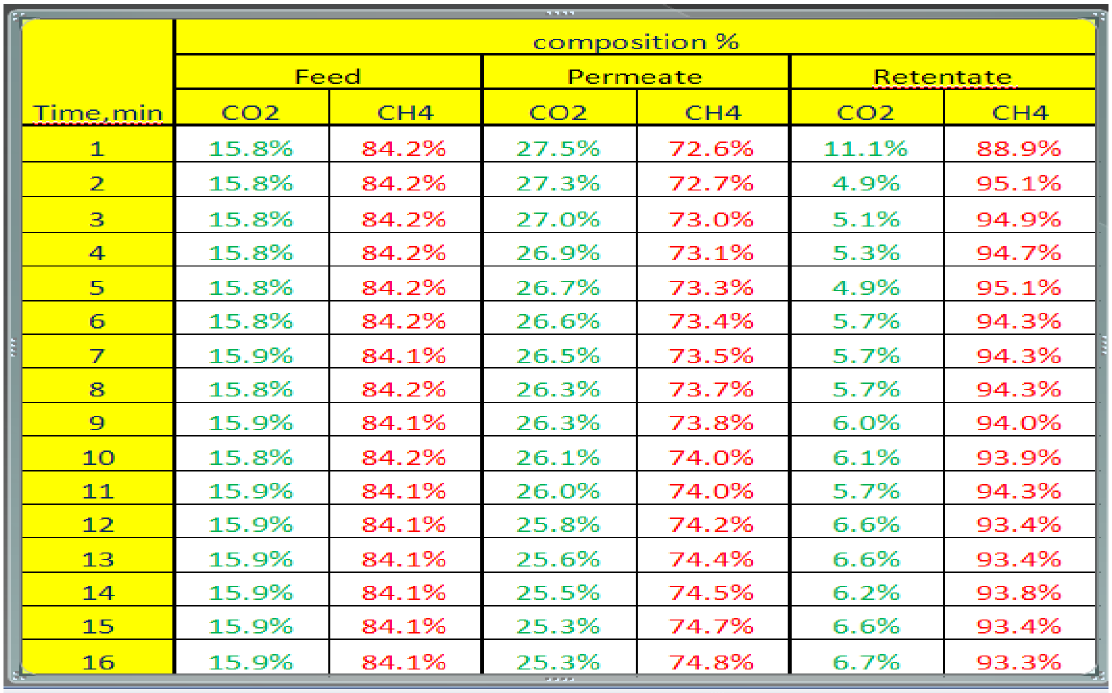
Figure 4-12 : Block diagram of blending gas separation

Figure 4.12 show the example of experiment at operating pressure of 3 bar, with feed flowrate of 2000 ml/min on 15% CO_2 and 85% CH_4 concentration in feed. By the figure, we has achieve high methane recovery on retentate stream, up to 95% purity of methane, with 5 % of impurity of carbon dioxide.

4.2.1 Feed Composition of 15% Carbon Dioxide gas with different Feed Pressure

Below shows the tables of composition percentage at 2000 ml/min at 15 % CO_2 concentration in feed at 3 bar feed pressure and 5 bar feed pressure.

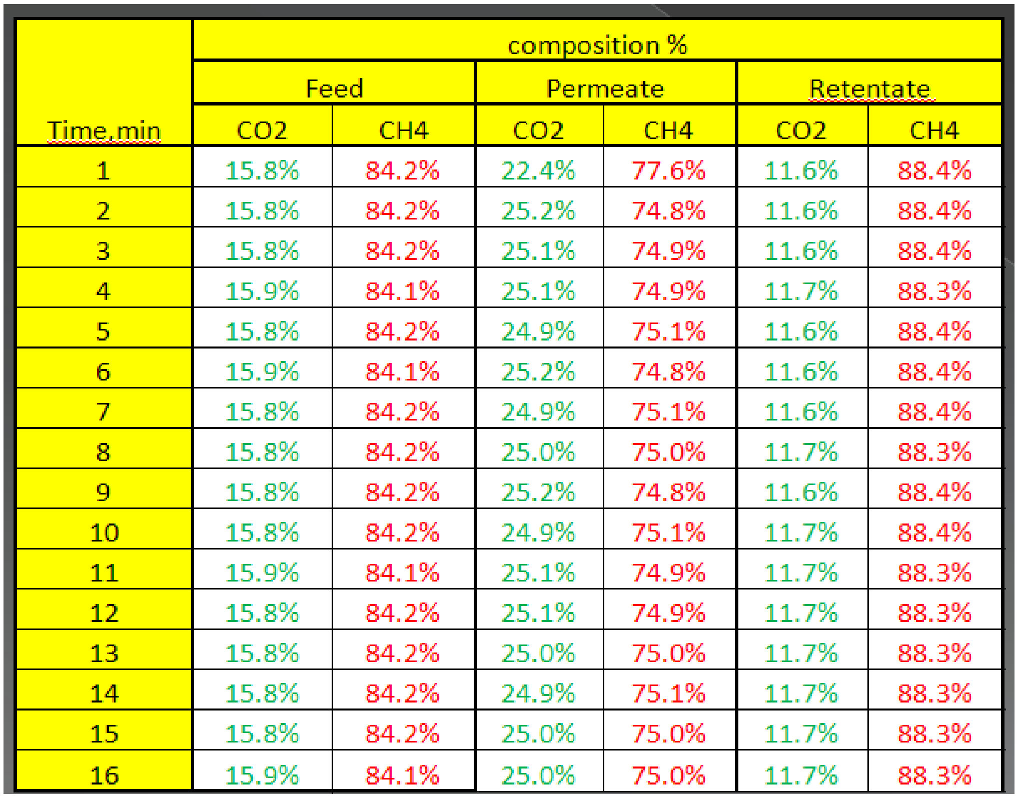
Table 4-2 : Composition in each stream for 15% CO_2 and 85% CH_4 as feed concentration at 3 bar feed pressure



	composition %					
	Feed		Permeate		Retentate	
Time,min	CO2	CH4	CO2	CH4	CO2	CH4
1	15.8%	84.2%	27.5%	72.6%	11.1%	88.9%
2	15.8%	84.2%	27.3%	72.7%	4.9%	95.1%
3	15.8%	84.2%	27.0%	73.0%	5.1%	94.9%
4	15.8%	84.2%	26.9%	73.1%	5.3%	94.7%
5	15.8%	84.2%	26.7%	73.3%	4.9%	95.1%
6	15.8%	84.2%	26.6%	73.4%	5.7%	94.3%
7	15.9%	84.1%	26.5%	73.5%	5.7%	94.3%
8	15.8%	84.2%	26.3%	73.7%	5.7%	94.3%
9	15.9%	84.1%	26.3%	73.8%	6.0%	94.0%
10	15.8%	84.2%	26.1%	74.0%	6.1%	93.9%
11	15.9%	84.1%	26.0%	74.0%	5.7%	94.3%
12	15.9%	84.1%	25.8%	74.2%	6.6%	93.4%
13	15.9%	84.1%	25.6%	74.4%	6.6%	93.4%
14	15.9%	84.1%	25.5%	74.5%	6.2%	93.8%
15	15.9%	84.1%	25.3%	74.7%	6.6%	93.4%
16	15.9%	84.1%	25.3%	74.8%	6.7%	93.3%

Table 4.2 shows high carbon dioxide permeability to permeate stream, where at the retentate stream, only 5 % to 7 % of carbon dioxide left. This has give higher methane recovery in retentate stream, which almost 94% of recover methane. This can be support by Figure 4.2 and Table 4.1 where at 3 bars feed pressure; it has high permeability and high selectivity for carbon dioxide. So it permeates carbon dioxide with easy and repels methane out.

Table 4-3 : Composition in each stream for 15% CO_2 and 85% CH_4 as feed concentration at 5 bar feed pressure



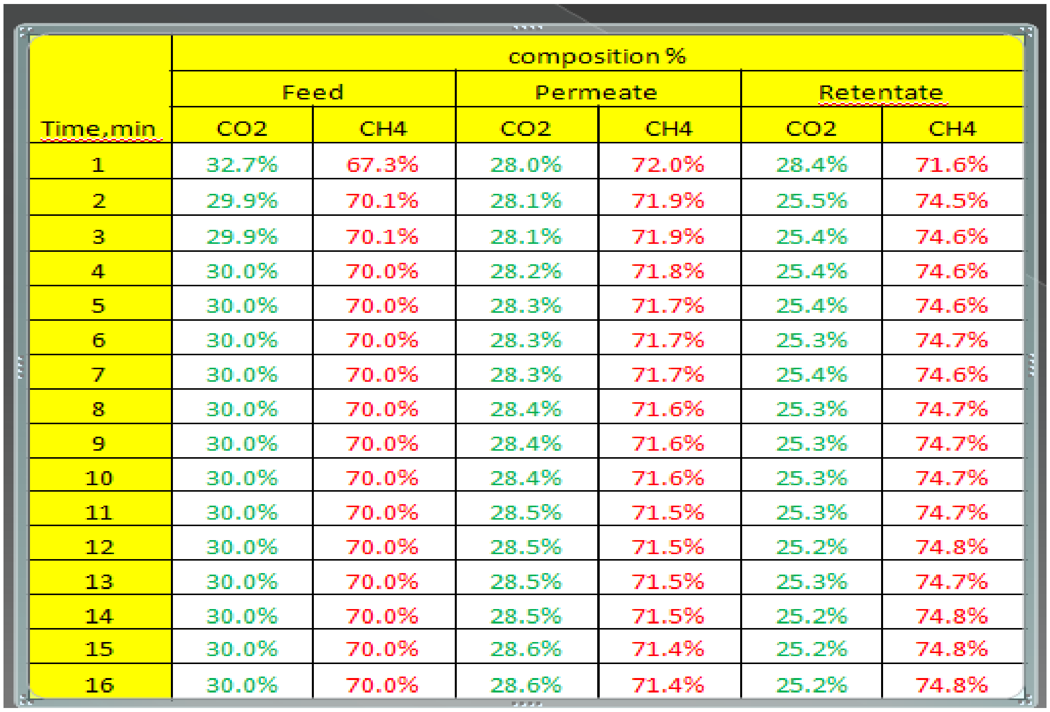
	composition %					
	Feed		Permeate		Retentate	
Time,min	CO2	CH4	CO2	CH4	CO2	CH4
1	15.8%	84.2%	22.4%	77.6%	11.6%	88.4%
2	15.8%	84.2%	25.2%	74.8%	11.6%	88.4%
3	15.8%	84.2%	25.1%	74.9%	11.6%	88.4%
4	15.9%	84.1%	25.1%	74.9%	11.7%	88.3%
5	15.8%	84.2%	24.9%	75.1%	11.6%	88.4%
6	15.9%	84.1%	25.2%	74.8%	11.6%	88.4%
7	15.8%	84.2%	24.9%	75.1%	11.6%	88.4%
8	15.8%	84.2%	25.0%	75.0%	11.7%	88.3%
9	15.8%	84.2%	25.2%	74.8%	11.6%	88.4%
10	15.8%	84.2%	24.9%	75.1%	11.7%	88.4%
11	15.9%	84.1%	25.1%	74.9%	11.7%	88.3%
12	15.8%	84.2%	25.1%	74.9%	11.7%	88.3%
13	15.8%	84.2%	25.0%	75.0%	11.7%	88.3%
14	15.8%	84.2%	24.9%	75.1%	11.7%	88.3%
15	15.8%	84.2%	25.0%	75.0%	11.7%	88.3%
16	15.9%	84.1%	25.0%	75.0%	11.7%	88.3%

Table 4.3 shows the composition for all streams with 15% carbon dioxide and 85% methane as feed composition at 5 bars. Looking at the data calculated methane recovery in retentate stream only improve 3% and have carbon dioxide impurity of 11.6%. if compare with table 4.2, this experiment has lower methane recovery at higher pressure. By using data of table 4.1, higher feed pressure at 2000 ml/min will has low selectivity than 3bar pressure. Low selectivity effect in more permeation of methane, which reduce the methane recovery in retentate stream.

4.2.2 Feed Composition of 30% Carbon Dioxide gas with different Feed Pressure

Below shows the tables of composition percentage at 2000 ml/min at 30 % CO_2 concentration in feed at 3 bar feed pressure and 5 bar feed pressure.

Table 4-4 : Composition in each stream for 30% CO_2 and 70% CH_4 as feed concentration at 3 bar feed pressure



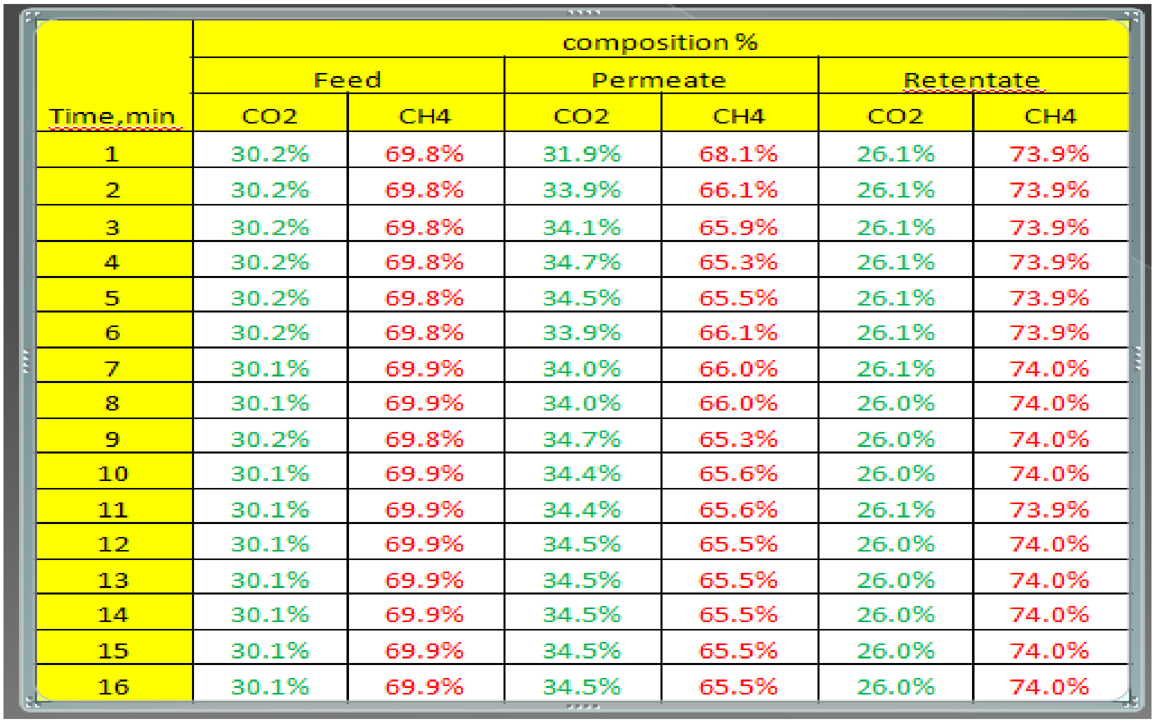
	composition %					
	Feed		Permeate		Retentate	
Time,min	CO2	CH4	CO2	CH4	CO2	CH4
1	32.7%	67.3%	28.0%	72.0%	28.4%	71.6%
2	29.9%	70.1%	28.1%	71.9%	25.5%	74.5%
3	29.9%	70.1%	28.1%	71.9%	25.4%	74.6%
4	30.0%	70.0%	28.2%	71.8%	25.4%	74.6%
5	30.0%	70.0%	28.3%	71.7%	25.4%	74.6%
6	30.0%	70.0%	28.3%	71.7%	25.3%	74.7%
7	30.0%	70.0%	28.3%	71.7%	25.4%	74.6%
8	30.0%	70.0%	28.4%	71.6%	25.3%	74.7%
9	30.0%	70.0%	28.4%	71.6%	25.3%	74.7%
10	30.0%	70.0%	28.4%	71.6%	25.3%	74.7%
11	30.0%	70.0%	28.5%	71.5%	25.3%	74.7%
12	30.0%	70.0%	28.5%	71.5%	25.2%	74.8%
13	30.0%	70.0%	28.5%	71.5%	25.3%	74.7%
14	30.0%	70.0%	28.5%	71.5%	25.2%	74.8%
15	30.0%	70.0%	28.6%	71.4%	25.2%	74.8%
16	30.0%	70.0%	28.6%	71.4%	25.2%	74.8%

Table 4.4 shows improvement in methane recovery, where it increase methane purity from 70% to 74% with impurity of 26%. With high concentration of carbon dioxide in feed concentration, the membrane seems to only can separate carbon dioxide molecule up to 5%. Increasing amount of molecule in feed may have reduced the free path of carbon dioxide free path to permeate through membrane. As lot of molecules inside the membrane pore, the pore becomes ingested and full with molecules. This may reduce or lower the permeation rate of molecules through membrane. The permeation still happen,

but in slow speed due to low free path of molecule and small space of molecules pore, as it transport theory is based on Knudsen Diffusion.

Beside, the methane composition in permeate also increase than feed composition, as the selectivity is reducing as impurity concentration increase.

Table 4-5 : Composition in each stream for 30% CO_2 and 70% CH_4 as feed concentration at 5 bar feed pressure



Time,min	composition %					
	Feed		Permeate		Retentate	
	CO2	CH4	CO2	CH4	CO2	CH4
1	30.2%	69.8%	31.9%	68.1%	26.1%	73.9%
2	30.2%	69.8%	33.9%	66.1%	26.1%	73.9%
3	30.2%	69.8%	34.1%	65.9%	26.1%	73.9%
4	30.2%	69.8%	34.7%	65.3%	26.1%	73.9%
5	30.2%	69.8%	34.5%	65.5%	26.1%	73.9%
6	30.2%	69.8%	33.9%	66.1%	26.1%	73.9%
7	30.1%	69.9%	34.0%	66.0%	26.1%	74.0%
8	30.1%	69.9%	34.0%	66.0%	26.0%	74.0%
9	30.2%	69.8%	34.7%	65.3%	26.0%	74.0%
10	30.1%	69.9%	34.4%	65.6%	26.0%	74.0%
11	30.1%	69.9%	34.4%	65.6%	26.1%	73.9%
12	30.1%	69.9%	34.5%	65.5%	26.0%	74.0%
13	30.1%	69.9%	34.5%	65.5%	26.0%	74.0%
14	30.1%	69.9%	34.5%	65.5%	26.0%	74.0%
15	30.1%	69.9%	34.5%	65.5%	26.0%	74.0%
16	30.1%	69.9%	34.5%	65.5%	26.0%	74.0%

Table 4.5 shows methane recovery in retentate stream is 74%, increase 4% than feed composition, while it has higher carbon dioxide composition in permeate stream. It is known that, when feed pressure is increased, the methane recovery in residue stream should be increased. This mean carbon dioxide recovery in permeate stream is increased. This is due to higher pressure give greater driving force across membrane.

This give high permeability to carbon dioxide and methane to separated thru membrane. As known, usually, when permeability is high, the selectivity will be low or reduce.

If we compare table 4.4 and table 4.5, both give us same methane recovery in retentate stream, around 74%, which only increase 4% from methane composition in feed. However, the permeation of carbon dioxide into permeate stream for table 4.5 is higher than table 4.4, and also has low methane recovery. We can conclude for this comparison that, at high carbon dioxide concentration, high feed pressure give high permeation rate for carbon dioxide to past through membrane. High pressure will be increase the different pressure between feed pressures and permeate pressure, and become sufficient driving force to separate carbon dioxide.

CHAPTER 5 : CONCLUSION

The separation of carbon dioxide from methane is very challenging in term of process and technology. Experiments result show that membrane process has a promising technology to be used for carbon dioxide and methane separation. From the result and discussion, we found that higher feed flowrate and higher feed pressure gave higher permeability, but it gave almost same permeability value for feed pressure at 3 and 5 bars. This is because of membrane permeability is not linear with increasing pressure and it will be a constant value once it reach its limitation. This is due to constant permeation transport, using Knudsen Diffusion, as many molecules in stream have reduced the free path of molecule relative to membrane pore size in permeating through membrane. Carbon dioxide has higher selectivity than methane, average value of 3.5 which mean that carbon dioxide permeate through membrane 3.5 faster than methane. Found that selectivity both gases reduced as feed pressure increased. As we know, as pressure increase, both permeability and selectivity decrease, with give us higher driving force which increase permeation rate of both gases.

Blending gas experiment using different feed concentration and feed pressure as the operating parameter gave us some interesting results. At 15% carbon dioxide and 85% methane in feed concentration at 3 bar feed pressure, we got 94% methane recovery in retentate stream, which was the highest recovery for all of experiments. We found that increase carbon dioxide concentration from 15% to 30%, based on analysis, has lower methane recovery in retentate stream. Based on Knudsen Diffusion, as many of molecule in the stream, the free path of molecule is reduced, relatively with membrane pore. Pores become ingested with lots of permeating molecules, effect in slow speed of permeation rate.

From here, the first objective is to study permeability and selectivity of carbon dioxide and methane is achieved. Second objective is to study on carbon dioxide separation using inorganic membrane is achieved during blending test, where there is carbon dioxide been separated when blend with methane, although only slightly amount of carbon dioxide be separated at certain operating parameters. Last objective is to study on membrane performance in separation at certain operating condition also has been achieved. It is found that at 15% carbon dioxide and 85% methane at 3 bars feed pressure of 2000 ml/min, the methane recovery is the highest, with up to 94% purity. The purity can be increase by doing multi-staged of membrane system, or the residue (retentate) stream is supply to amine system.

Recommendations for project improvement and future work are

1. Use temperature as one the manipulating parameter in experiment and membrane research for this project
2. Exposed and supply membrane module with desired gas for long period of time such as one hour per experiment in order make separation more stable and get a good data
3. Use known membrane materials, or develop personal inorganic membrane where student can fully understand the characteristics of the membrane material

REFERENCES

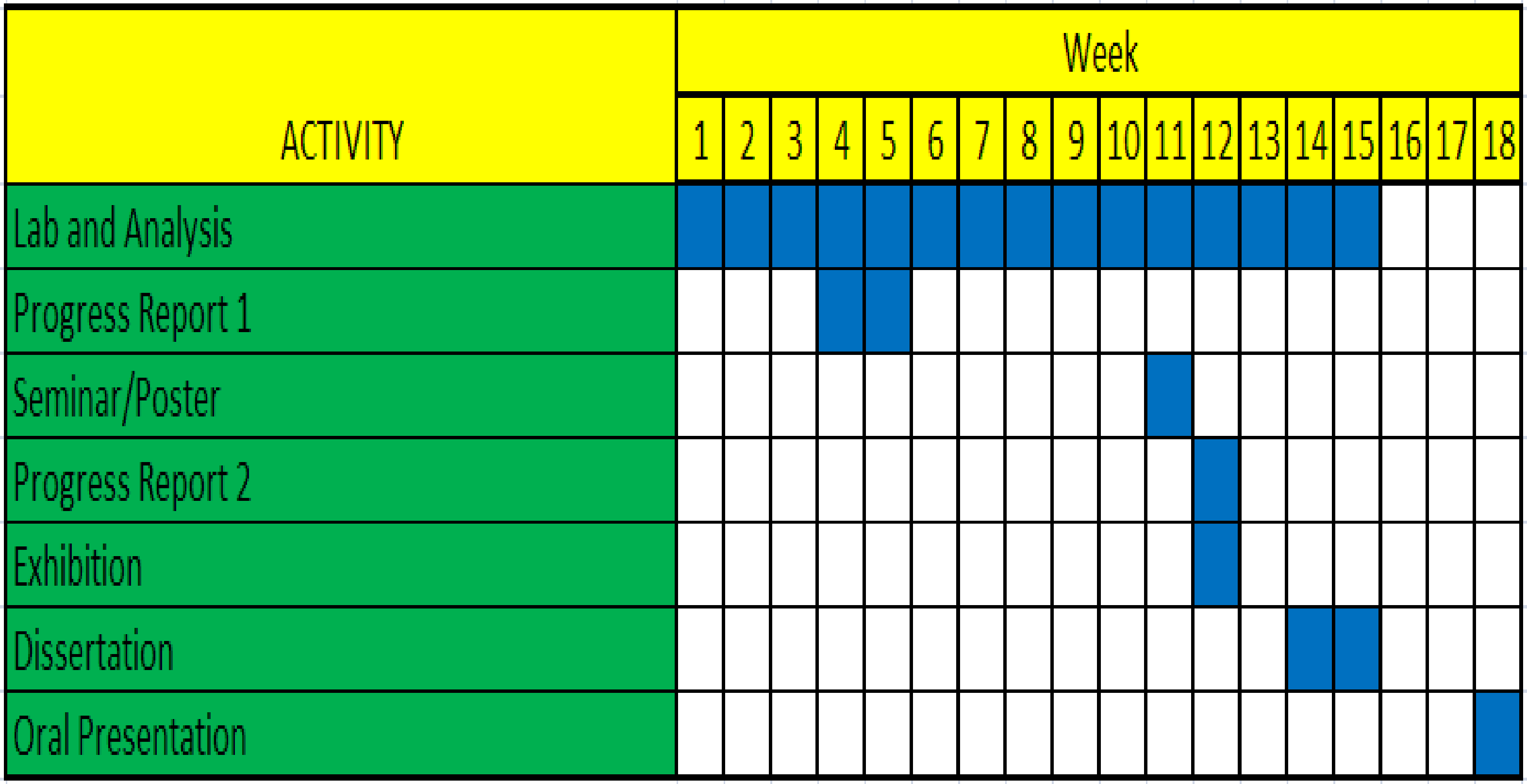
1. Chun Cao, Tai-Shung Chung, Ye Liu, Rong Wang,. Pramoda K. P. (2003). Chemical cross-linking modification of 6FDA-2,6-DAT hollow. Journal of Membrane Science, Volume 216, Issues 1-2, 1, Pages 257-268
2. Colin A.S., Sandra E.K., and Geoff W.S. (2007). Carbon Dioxide Separation through Polymeric Membrane System for Flue Gas Application. Recent Patent on Chemical Engineering, Volume 1, Pages 52-66
3. Freemantle M. (2005). Membrane for Gas Separation Advanced Organic and Inorganic Materials being developed for separation offer cost benefits for environment and energy-related processes. Chemical and Engineering News, Volume 83, Number 40, Pages 49-57
4. Hongqun Yang**,** Zhenghe Xu**,** Maohong Fan**,** Rajender Gupta**,** Rachid B Slimane**,** Alan E.B.**,** and Ian W. (2008)**.** Progress in Carbon Dioxide Separation and Capture. Journal of Environmental Sciences, Volume 20, Issue 1, Pages 14-27.
5. Jha P., Mason L.W., Way J.D. (2006). Characterization of substituted polyphosphazene membranes—pure and mixed gas results, Industrial & Engineering Chemistry Research 45 (19) 6570–6577
6. Jennifer Chih-Yi Chen (2008). Evaluation of Polymeric Membranes for Gas Separation Processes: Poly(ether-*b*-amide) (PEBAXR2533) Block Copolymer. University of Waterloo, Waterloo, Ontario, Canada.
7. Jerry Y.S.L. (2010). Novel Inorganic Membrane for High Temperature Carbon Dioxide Separation,. University of Cincinnati
8. John D.W., Donald R.P., and William J.K. (2004). Natural Gas Permeation in Polymide Membrane. Journal of Membrane Science, Volume 228, Issue 2, Pages 227-236.
9. Mohammadhosein Safari, Amin Ghanizadeh, Mohammad Mehdi Montazer-Rahmati (2008). Optimization of membrane-based CO2-removal from natural

gas using simple models considering both pressure and temperature effects. International Journal of Green House Gas Control, Volume 3, Page 3-10.

10. Narendra Verma, Anil Verma (2009). Amine System Problems arising from Heat Stable Salts and Solutions to improve System Performance. Fuel Processing Technology, Volume 90, Issue 4, Pages 483-489
11. Baker R. W., Wijmans J. G., and Kaschemekat J. H. (1998). The Design of Membrane Vapor-Gas Separation Systems. Journal of Membrane Science, Volume 151, Issue 1, Pages 55-62.
12. Sam Wong and Rob Bioletti (2002). Carbon Dioxide Separation Technologies, Carbon & Energy Management. Alberta Research Council Edmonton, Alberta, T6N 1E4, Canada
13. Sander R.R. (2010). Tuning of mass transport properties in multi-block copolymers for CO_2 capture applications. Polyether Baed Block Copolymer Membranes for CO_2 Separation, University of Twente, Enschede,The Netherlands, page 14-42.
14. Supakorn Atchariyawut, Ratana Jiraratananon, Rong Wang (2007). Separation of CO_2 from CH_4 by using gas-liquid membrane contacting process. Journal of Membrane Science, Volume 304, Issues 1-2, 1 Pages 163-172.

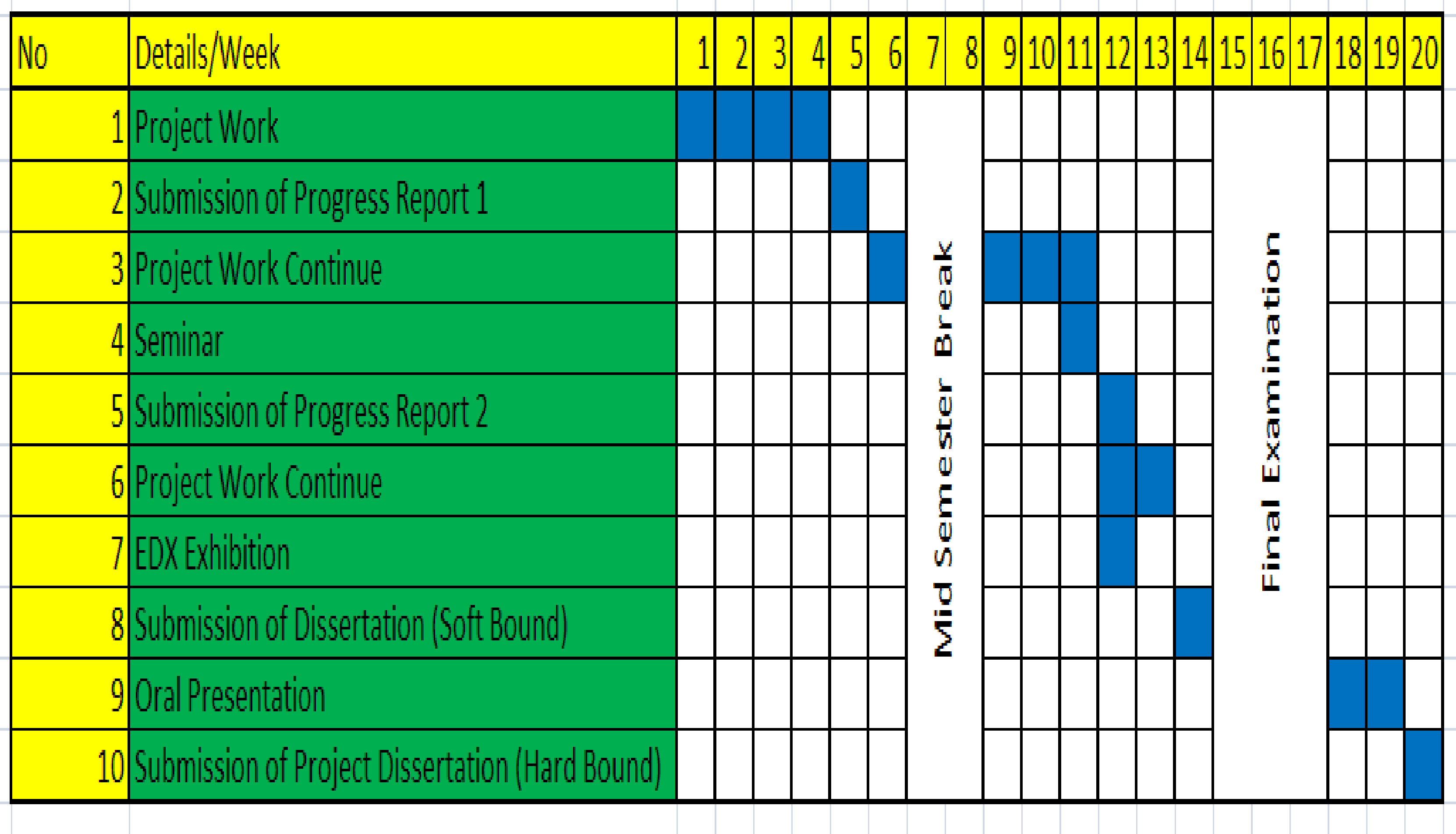
APPENDIX

GANTS CHART FOR THE FYP II



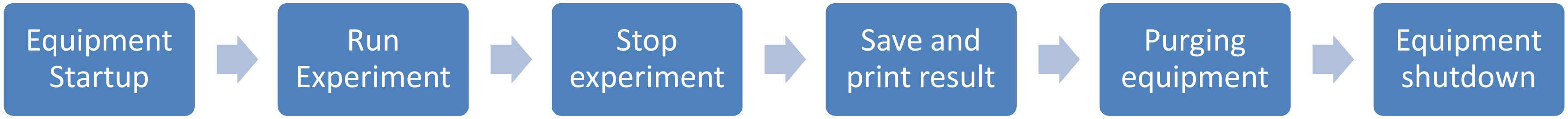
ACTIVITY	Week																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Lab and Analysis	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦			
Progress Report 1				🟦	🟦													
Seminar/Poster											🟦							
Progress Report 2												🟦						
Exhibition												🟦						
Dissertation														🟦	🟦			
Oral Presentation																		🟦

MILESTONES FOR FYP II



No	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	Project Work	■	■	■	■			Mid Semester Break								Final Examination					
2	Submission of Progress Report 1					■															
3	Project Work Continue						■			■	■	■									
4	Seminar											■									
5	Submission of Progress Report 2												■								
6	Project Work Continue												■	■							
7	EDX Exhibition												■								
8	Submission of Dissertation (Soft Bound)														■						
9	Oral Presentation																		■	■	
10	Submission of Project Dissertation (Hard Bound)																				■

FLOW OF THE PROCEDURES IN DOING THE EXPERIMENT



PICTURES OF THE LAB EQUIPMENT

Membrane Separation Pilot

Tubular Membrane Module

TABLE OF THE PERMEABILITY TEST RESULT

Table of permeability test carbon dioxide in tubular membrane module

FEED			RETENTATE			PERMEATE		
CH_4 (%)	CO_2(%)	Flowrate (ml/min)	Flowrate (ml/min)	CH_4 (%)	CO_2(%)	Flowrate (mil/min)	CH_4 (%)	CO_2(%)
3.33	98.30	1074.27	0.00	92.29	9.38	961.18	95.07	6.60
3.27	97.21	1074.25	0.00	58.06	43.61	954.00	79.16	22.50
3.24	96.31	1074.15	0.00	-0.10	101.77	942.45	45.13	56.53
3.20	94.92	1074.73	0.00	-0.10	101.77	945.13	25.06	76.61
3.15	93.59	1074.53	0.00	-0.10	101.77	954.32	14.48	87.18

Table of permeability test methane in tubular membrane module

Time Stamp	CH4 Flowrate	Feed CH4	Feed CO2	Feed O2	Feed Pressure	Feed (2) Pressure	Feed (2) Temperature	Feed (2) Flowrate	DP (2)	Retentate (2) Flowrate	Retentate (2) Pressure	Retentate (2) CH4	Retentate (2) CO2	Retentate (2) O2	Permeate (2) Flowrate	Permeate (2) Pressure	Permeate (2) CH4	Permeate (2) CO2	Permeate (2) O2
5:39:09 PM	-296.25	96.35	0	0	0.48	0.4	26.9	1252	36.64	0	0.57	72.55	15.25	0.05	914	0.41	45.34	7.95	0.06
5:39:10 PM	-296.25	96.28	0	0	0.48	0.4	27	1252	36.67	0	0.57	72.22	15.18	0.05	1246	0.41	45.16	7.88	0.06
5:39:30 PM	-296.25	96.31	0	0	0.48	0.4	27	1252	36.93	0	0.57	70.38	14.64	0.05	1245	0.41	43.44	7.61	0.06
5:39:31 PM	-296.25	96.26	0	0	0.48	0.4	27	1253	36.93	0	0.57	70.34	14.61	0.05	1245	0.41	43.36	7.65	0.06
5:39:32 PM	-296.25	96.26	0	0	0.48	0.4	27	1253	36.93	0	0.57	70.23	14.62	0.05	1246	0.41	43.29	7.6	0.05
5:40:00 PM	-296.25	96.23	0	0	0.48	0.4	27.1	1252	37.31	0	0.57	68.9	14.06	0.05	1245	0.41	42.34	7.31	0.05
5:40:01 PM	-296.25	96.23	0	0	0.48	0.4	26.9	1252	37.31	0	0.57	68.87	14.05	0.05	1245	0.41	42.28	7.3	0.05
5:40:02 PM	-296.25	96.27	0	0	0.48	0.4	27	1254	37.34	0	0.57	68.87	13.99	0.05	1245	0.41	42.32	7.25	0.05

5:40:30 PM	-296.25	96.18	0	0	0.48	0.4	27.1	1253	37.72	0	0.57	68.84	13.37	0.05	1246	0.41	43.01	6.98	0.05
5:40:31 PM	-296.25	96.18	0	0	0.48	0.4	27.2	1253	37.72	0	0.57	68.89	13.37	0.05	1246	0.41	43.11	6.92	0.05
5:40:32 PM	-296.25	96.21	0	0	0.48	0.4	27.1	1253	37.72	0	0.57	68.9	13.4	0.05	1246	0.41	43.13	6.96	0.05
5:41:00 PM	-296.25	96.1	0	0	0.48	0.4	27.2	1254	38.13	0	0.57	70.22	12.69	0.05	1247	0.41	45.47	6.53	0.06
5:41:01 PM	-296.25	96.15	0	0	0.48	0.4	27.4	1253	38.13	0	0.57	70.26	12.66	0.05	1247	0.41	45.57	6.49	0.06
5:41:02 PM	-296.25	96.14	0	0	0.48	0.4	27.3	1253	38.13	0	0.57	70.34	12.61	0.05	1246	0.41	45.71	6.51	0.06
5:41:30 PM	-296.25	96.14	0	0	0.48	0.4	27.3	1253	38.51	0	0.57	72.25	11.92	0.05	1247	0.41	48.77	6.09	0.06
5:41:31 PM	-296.25	96.15	0	0	0.48	0.4	27.2	1254	38.51	0	0.57	72.36	11.86	0.05	1246	0.41	48.93	6.07	0.06
5:41:32 PM	-296.25	96.1	0	0	0.48	0.4	27.3	1254	38.55	0	0.57	72.46	11.87	0.05	1247	0.41	49.01	6.09	0.06
5:42:00 PM	-296.25	96.07	0	0	0.48	0.4	27.4	1254	38.9	0	0.57	74.58	11.01	0.05	1247	0.41	52.39	5.6	0.06
5:42:01 PM	-296.57	96.01	0	0	0.48	0.4	27.4	1254	38.93	0	0.57	74.65	11.01	0.05	1247	0.41	52.45	5.61	0.06
5:42:02 PM	-296.25	96.07	0	0	0.48	0.4	27.4	1255	38.93	0	0.57	74.73	10.96	0.05	1247	0.41	52.61	5.56	0.06
5:42:30 PM	-296.25	96.01	0	0	0.48	0.4	27.6	1254	39.34	0	0.57	77.02	10.13	0.05	1249	0.41	56.12	5.11	0.06
5:42:31 PM	-296.25	95.99	0	0	0.48	0.4	27.5	1255	39.34	0	0.57	77.11	10.12	0.05	1247	0.41	56.12	5.12	0.06
5:42:32 PM	-296.25	96.04	0	0	0.48	0.4	27.5	1255	39.37	0	0.57	77.17	10.1	0.05	1248	0.41	56.24	5.12	0.06
5:43:00 PM	-296.25	95.92	0	0	0.48	0.4	27.4	1254	39.72	0	0.57	79.15	9.42	0.05	1247	0.41	59.58	4.7	0.06
5:43:01 PM	-296.25	95.99	0	0	0.48	0.4	27.6	1254	39.75	0	0.57	79.25	9.41	0.05	1247	0.41	59.67	4.68	0.06
5:43:02 PM	-296.25	95.94	0	0	0.48	0.4	27.5	1254	39.75	0	0.57	79.37	9.33	0.05	1247	0.41	59.8	4.66	0.06
5:43:30 PM	-296.25	95.89	0	0	0.48	0.4	27.6	1255	40.1	0	0.57	81.15	8.71	0.05	1248	0.41	62.57	4.34	0.06
5:43:31 PM	-296.57	95.92	0	0	0.48	0.4	27.7	1254	40.13	0	0.57	81.26	8.68	0.05	1248	0.41	62.71	4.27	0.06
5:43:32 PM	-296.25	95.87	0	0	0.48	0.4	27.5	1254	40.13	0	0.57	81.32	8.7	0.05	1247	0.41	62.76	4.32	0.06

Table of Feed Concentration Selectivity

Separation Factor for Feed Concentration							
1;10		1;5		1;3.5		1;2	
CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2
2.7156	0.3682	2.6440	0.3782	0.6050	1.6529	0.4896	2.0425
2.6599	0.3760	2.1165	0.4725	0.5802	1.7237	0.5028	1.9887
2.5891	0.3862	1.7526	0.5706	0.5668	1.7642	0.5364	1.8641
2.4721	0.4045	1.5057	0.6641	0.5589	1.7893	0.6204	1.6119
2.3640	0.4230	1.3461	0.7429	0.5602	1.7851	0.7336	1.3631

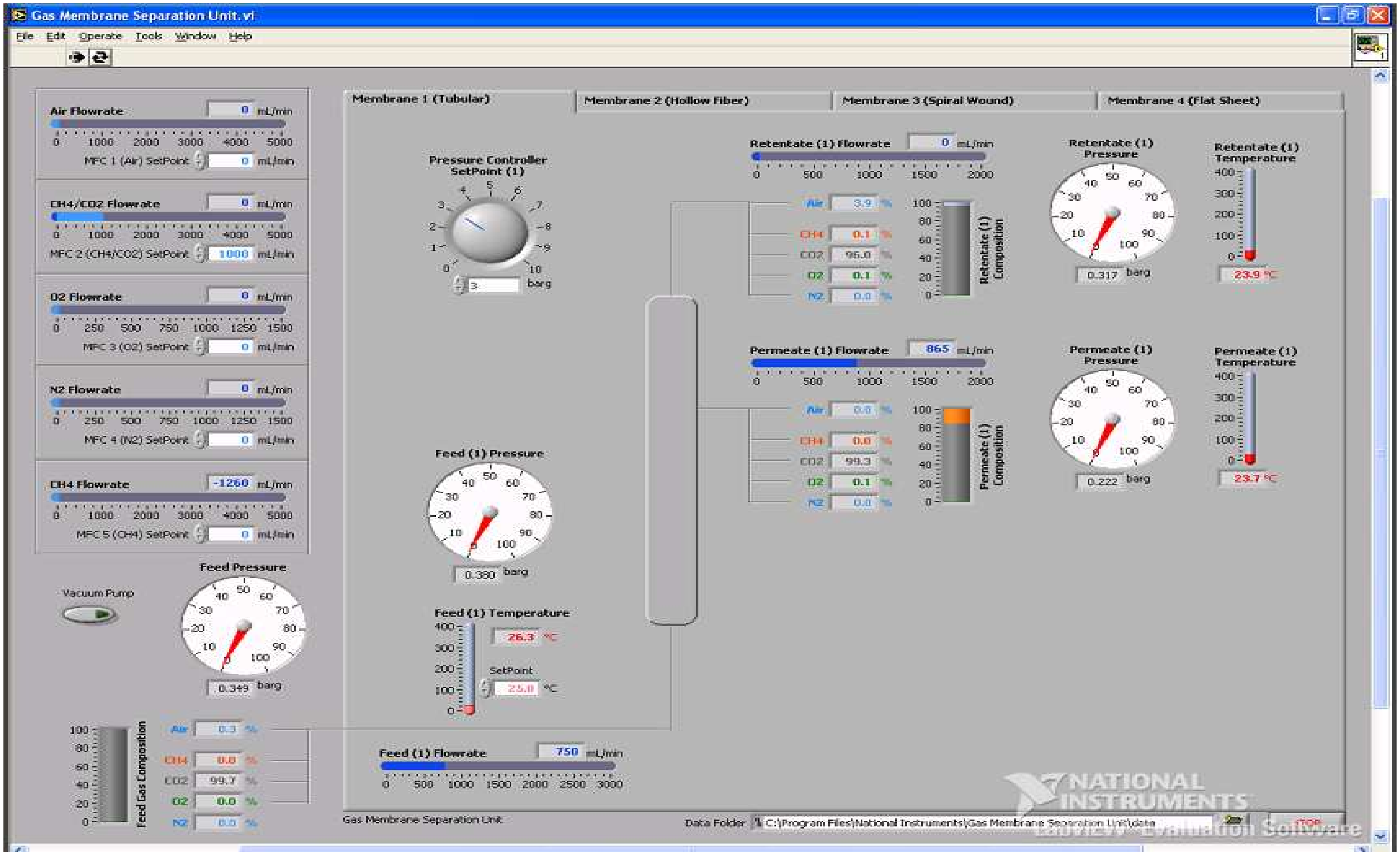
Table of Feed Flowrate Selectivity

Separation Factor for Feed Flowrate							
500ml/min		1000ml/min		2000ml/min		3000ml/min	
CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2
2.026024	0.493578	2.904425	0.344302	1.577966	0.633727	0.310135	3.224404
2.074048	0.482149	2.791927	0.358176	1.703746	0.586942	0.579164	1.726626
2.135745	0.468221	2.645279	0.378032	1.801049	0.555232	0.741081	1.349381
2.190512	0.456514	2.306402	0.433576	1.858428	0.538089	0.856587	1.167423
2.241699	0.44609	1.888485	0.529525	1.886787	0.530002	1.014359	0.985844

Table of Feed Pressure Selectivity

Separation Factor for Feed Pressure							
3 bar		5 bar		6 bar		9 bar	
CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2	CO_2/CH_4	CH_4/CO_2
0.556583	1.796677	0.960836	1.040761	0.996471	1.003541	1.034109	0.967016
0.732622	1.36496	0.97354	1.027179	1.003904	0.996112	1.030468	0.970433
0.83917	1.191654	0.988121	1.012022	1.00718	0.992871	1.020906	0.979522
0.895785	1.116339	0.992359	1.0077	1.008331	0.991738	1.014712	0.985502
0.926174	1.079711	0.991448	1.008626	1.008295	0.991774	1.014611	0.9856

Gas Membrane Separation Unit Control from computer



Air Flowrate 0 mL/min
MFC 1 (Air) SetPoint 0 mL/min

CH4/CO2 Flowrate 0 mL/min
MFC 2 (CH4/CO2) SetPoint 1000 mL/min

O2 Flowrate 0 mL/min
MFC 3 (O2) SetPoint 0 mL/min

N2 Flowrate 0 mL/min
MFC 4 (N2) SetPoint 0 mL/min

CH4 Flowrate -1260 mL/min
MFC 5 (CH4) SetPoint 0 mL/min

Feed Pressure 0.349 barg

Feed Gas Composition
Air 0.3 %
CH4 0.0 %
CO2 99.7 %
O2 0.0 %
N2 0.0 %

Pressure Controller SetPoint (1) 3 barg

Feed (1) Pressure 0.380 barg

Feed (1) Temperature 26.3 °C
SetPoint 25.0 °C

Feed (1) Flowrate 750 mL/min

Retentate (1) Flowrate 0 mL/min
Air 3.9 %
CH4 0.1 %
CO2 96.0 %
O2 0.1 %
N2 0.0 %

Retentate (1) Pressure 0.317 barg

Retentate (1) Temperature 23.9 °C

Permeate (1) Flowrate 865 mL/min
Air 0.0 %
CH4 0.0 %
CO2 99.3 %
O2 0.1 %
N2 0.0 %

Permeate (1) Pressure 0.222 barg

Permeate (1) Temperature 23.7 °C

Data Folder C:\Program Files\National Instruments\Gas Membrane Separation Unit\data