CERTIFICATION OF APPROVAL

Modeling Of Carbon Dioxide and Nitrogen Removal From Natural Gas Using Membrane Processes

By

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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.

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ABSTRACT

Removal of carbon dioxide and nitrogen from natural gas is very critical processes. The carbon dioxide contributes to the corrosive problem to the pipeline and equipments when react with water while nitrogen needs to be reduced less than 4 % in order to meet the pipeline specifications. The objectives of this project are to develop a mathematical model for carbon dioxide and nitrogen removal from natural gas and to study the effects of PEBAX membrane pore size, mole fraction of gas species and operating pressure on permeability of gas species. Three factors including membrane pore size, mole fraction and operating pressure have been analyzed. The permeability models are developed by incorporating three main mechanisms that are viscous diffusion, Knudsen diffusion and surface diffusion. The modeling result shows the permeability of carbon dioxide was found to be highest followed by nitrogen and methane. At small pore size of 0.2 nm, the permeability of gases is dominated by surface diffusion while Knudsen diffusion overlook at large pore size of larger than 2 nm. Meanwhile the viscous flow is slightly increases with increasing pore size. The composition of mole fraction in the feed influenced the permeability of binary mixture. The permeability of CO_2/CH_4 mixture lay in between of pure carbon dioxide and pure methane permeability. Similarly the binary mixture of CO_2/N_2 and CH_4/N_2 lay in between the pure gases. For the tertiary mixture, the permeability of carbon dioxide and methane at fixed nitrogen concentration increases a bit compared to the binary mixture. At the mean time, increasing the operating pressure slightly increases the methane permeability whilst the permeability of carbon dioxide and nitrogen were found out almost independent. As the conclusion, the developed models were able to predict the permeability of pure carbon dioxide, methane, nitrogen and the mixtures of these gases.

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d_i	diameter of gas molecule specie *i*	[m]
d_p	membrane pore diameter	[m]
D_b	bulk diffusivity	$[cm^2.s^{-1}]$
$D_{e,i}$	effective diffusivity of gas *i*	$[cm^2.s^{-1}]$
D_i	ordinary gas diffusivity for *i*	$[cm^2.s^{-1}]$
$D_{k,i}$	Knudsen diffusivity for I	$[cm^2.s^{-1}]$
D_s	surface diffusivity	$[cm^2.s^{-1}]$
D_v	viscous diffusivity	$[cm^2.s^{-1}]$
f	equilibrium loading factor	$[m^3.kg^{-1}]$
M_i	molecular weight of gas *i*	[kg/kmol]
M_j	molecular weight of gas *j*	[kg/kmol]
P	average pressure across the membrane	[atm]
P_i'	permeability of gas *i*	$[mol.s.kg^{-1}]$
P_k	Knudsen permeability	$[mol.s^{-1}][m][m^{-2}][kg^{-1}.m.s]$
P_s	surface permeability	$[mol.s^{-1}][m][m^{-2}][kg^{-1}.m.s]$
P_v	viscous permeability	$[mol.s^{-1}][m][m^{-2}][kg^{-1}.m.s]$
R	universal gas constant	$[82.06\ cm^3.atm.mol^{-1}.K^{-1}]$
T	temperature	[K]
t_m	membrane thickness	[m]
v	structural volume increment	$[m^3]$
z	compressibility factor	[-]
ε	membrane porosity	[-]
μ_i	viscosity of gas *i*	$[kg.m^{-1}.s^{-1}]$
τ	membrane tortuosity	[-]
ρ_m	membrane density	$[kg.m^{-3}]$
ΔH	heat of vaporization	[J/mol]

CHAPTER 1

INTRODUCTION

1.1 Background of study

Natural gas is defined as a mixture of hydrocarbon compounds, primarily methane together with ethane and propane and others small quantities of various non-hydrocarbon such as carbon dioxide, hydrogen sulfide and nitrogen. It was found typically exists in gases phases as well as in solution with the crude oil in natural underground reservoir. Currently, natural gas is being used along with the crude oil as a fuel.

The composition of carbon dioxide and nitrogen in natural gas are different in certain places. In Malaysia, about 8 % of the current natural gas reserves are carbon dioxide. In some of these reserves, the concentration of the carbon dioxide is estimated as high as 60 % (Ng et. al, 2004). At North German Plain, Germany and Krecsegopan, Poland, Hilmi and Lim (2004) reported that the composition of carbon dioxide was found as high as 60% and 80%, respectively. For the some natural gas wells, the carbon dioxide composition is shown in Table 1.1.

Table 1.1: Compositions of Carbon Dioxide in some natural gas wells (Hilmi and Lim, 2004)

No	Location	Composition (%)
1	Uch, Pakistan	46.2
2	Kapuni, New Zealand	43.8
3	Krecsegopan, Poland	83.0
5	North German Plain, Germany	60.0
6	Duri, Indonesia	23.0

The composition of natural gases (volume %) in several places around the world are tabulated in Table 1.2 (Moulijn et al, 2001).

Table 1.2: Composition of selected non-associated natural gas (volume %) (Moulijn et al, 2001).

Composition	Hasi-R'Mel, Algeria	Lacq, France	Gron, Holland	Kapuni, N. Zealand	West Sole, North Sea	Rio Arriba, N. Mexico	Cliffside, Texas	Olds, Canada
CH_4	83.5	69.3	81.3	46.2	94.4	96.9	65.8	52.4
C_2H_6	7.0	3.1	2.9	5.2	3.1	1.3	3.8	0.4
C_3H_8	2.0	1.1	0.4	2.0	0.5	0.2	1.7	0.1
C_4H_{10}	0.8	0.6	0.1	0.6	0.2	0.1	0.8	0.2
C_5+	0.4	0.7	0.1	0.1	0.2	-	0.5	0.4
N_2	6.1	0.4	14.3	1.0	1.1	0.7	26.4	2.5
CO_2	0.2	9.6	0.9	44.9	0.5	0.8	-	8.2
H_2S	-	15.2	Trace	-	-	-	-	35.8

Referring to Table 1.2, the composition of nitrogen in natural gas has found to as low as 0.4 vol % and as high as 26.4 vol % in Lacq, France and Cliffside, Texas, correspondingly. These data indicate that removal of carbon dioxide and nitrogen from natural gas is very critical at several places.

The natural gas needs to be purified from undesired gases like carbon dioxide and nitrogen in order to achieve high calorific value (Hilmi and Lim, 2004) before entering the pipeline. Besides, the carbon dioxide will cause the corrosive problem to the pipeline and equipments when react with the water (Dortmundt and Doshi, 1999). According to Chan and Miskon (2004), carbon dioxide has to be removed in liquefied natural gas (LNG) system to avoid hydrate formation. In order to meet the natural gas pipeline specification for inert gas, the nitrogen content needs to be reduced less than 4 percent (Leppin and Meyer, 1991). Further, this nitrogen-contaminated natural gas has a low heating value and wasted pipeline capacity (Lokhandwala et al, 1998).

To purify the natural gas from carbon dioxide and nitrogen, there are several processes are available. The processes are including amine absorption process (Li and Teo, 1997), cryogenics process, pressure swing adsorption process and thermal swing adsorption (Dostmondt and Doshi, 1999). In addition, membrane processes are also applicable to purify natural gas from sub-quality gases of carbon dioxide and hydrogen sulfide like used at Grissik gas plant in Sumatera (Anderson and Siahaan, 2005). Besides, Alvarado et al (1998) revealed that the most reliable and widely used to separate nitrogen from natural gas is via fractionation by liquefying the feed stream containing nitrogen using temperature of 300 °F.

The usage of natural gas is going up exponentially around the world. It is expected to be the fuel of choice in many countries since it burns cleaner than oil or coal and not as controversial as nuclear power (Harrje, 2000). The increasing in demand is caused by the reasonable price, environmental advantages, high efficiency technologies and abundant global reserves. The worldwide natural gas reserves are shown in Table 1.3.

Table 1.3: Natural gas reserves in worldwide (Harrje, 2000)

Proved Natural Gas Reserves by Region at End of 1998 (Trillion Cubic Feet)	
North America	294.6
Central & South America	219.0
Europe	183.9
Middle East	1749.6
Former Soviet Union	2002.3
Africa	361.1
Asia Pacific	359.5
Source: BP Amoco Statistical Review of World Energy 1999	

Harrje (2000) reported that the demand of the natural gas is expected to increase in various sectors including the residential and commercial sectors for gas heating and cooling while in industrial applications, it is used to produce the chemicals, foods, pulp and paper. In the transportation sector, natural gas is used by fleet buses and fleet light trucks. Besides, natural gas also has been used in power distribution and central generation fuel. The projected natural gas consumptions in each sector are figured in appendices section from Figure C.1 to Figure C.5.

1.2 Problem Statement

In the natural gas stream, one of the acid gases that commonly found at level as high as 80 % is carbon dioxide (Dortmundt and Doshi, 1999). The carbon dioxide need to be removed because it is highly corrosive with the present of water hence destroying the pipeline and equipments. With higher freezing point than liquefied natural gas (LNG), it has to be removed to prevent the formation of hydrates in the pipeline at the low-temperature LNG apart (Chan and Miskun, 2004).

The research done by Lokhanwala et al (1998) shows that about 17 % or equivalent to 10 billion standard cubic feet per day of the United State natural gas reserves can not be used due to high nitrogen content. The nitrogen need to be removed in order to fulfill the natural gas pipeline specification for inert gas which is less than 4 percent (Alvarado et al, 1998). Further, this contaminated natural gas has a low heating value and need to be increased by reducing the nitrogen fraction in the natural gas.

1.3 Objectives and Scope of Study

1.3.1 Objectives

The objectives of this final year research project are (i) to develop a mathematical model for carbon dioxide and nitrogen removal from natural gas using membrane processes and (ii) to analyze the effects of PEBAX 1657 pore size, mole fraction of gas specie and operating pressure on permeability of carbon dioxide, methane and nitrogen as pure gases and in the binary as well as tertiary mixtures.

1.3.2 Scope of study

In this project, PEBAX 1657 membrane has been selected to be used in purifying natural gas from carbon dioxide and nitrogen using membrane processes. The study focuses on gathering the information of membrane materials and manipulating operating parameters such as membrane pore size and operating pressure that influence the membrane performance. The concentration of gas specie in the binary and tertiary mixture also has been considered in this study since it affects the membrane performance as well.

1.3.3 The relevancy of the project

The project provides summary information of removing carbon dioxide and nitrogen from natural gas using the membrane processes. The simulation steps to calculate the permeability of carbon dioxide, methane and nitrogen as pure gases and in the binary plus tertiary mixtures are provided.

1.3.4 Feasibility of the project within the scope and time frame

Due to the time constraint for about one semester or 13 weeks, the project focuses only for removal of carbon dioxide and nitrogen from the natural gas mixtures. The permeability of all three gases is analyzed as functions of membrane pore size, mole fraction and operating pressure. Only one type of membrane is used this study. This project shall be completed within the targeted time frame.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Literature Review

2.1.1 Membrane Processes

According to Moulijn et al (2001), membrane is defined as a selective barrier allowing separation of compounds on the basis of molecular properties such as molecular size, strength of adsorption or solubility in the membrane material. The separation occurs by the membrane controlling the movement rate of various molecules between two liquid, two gas phases, or a liquid and a gas phase (Geankoplis, 2003).

The basis of membrane processes is illustrated in Figure 2.1 below. The feed stream containing the mixture of desired and undesired gases enters on side of the membrane at high operating pressure. The selective gases permeate through the membrane to the permeate side while the unselective gases remains and exit to the retentate side. N order to prevent some undesired gases pass through the membrane, the purge gas is used. The pressure at permeate side is maintained to be lower than the feed stream since the separation is realized by applying an external pressure difference (Corti et al., 2004).

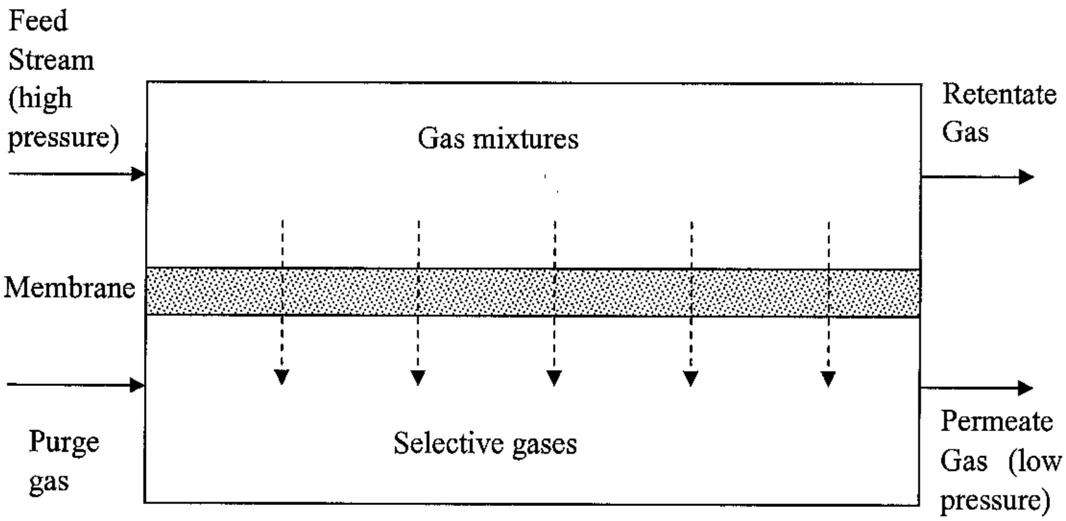

Figure 2.1: Basis concepts of transport across membrane. (Redrawn from Corti et al, 2004)

As compared to other purification methods like absorption and adsorption, membrane processes offers several advantages. Moulijn et al, (2001) discovered that the energy consumption in membrane processes is low as no phase transfer occurs. The separation in the membrane processes take place continuously. With no moving part except recycle compressor is used, it is easier to be operated. However, membranes processes do have some drawbacks. The selectivity to separate specific gases is often low. Besides, membrane processes expose to the fouling problems hence shortening its lifetime. The advantages and disadvantages of membranes are summarized in Table 2.1.

Table 2.1: The advantages and disadvantages of membranes (Moulijn et al, 2001)

Advantages	Disadvantages
Low energy consumption (no phase transfer)	Fouling
Mild condition	Short life time
Low pressure drop	Often low selectivity
No additional phase required	No economy of scale (scale-up factor ~ 1)
Continuous separation	
Easy operation	
No moving parts (except recycle compressor is used)	

2.1.2 The membrane modules

The membrane could be manufactured from various materials. Typically natural fibers, synthetic polymers, ceramics or metals are used to fabricate the membranes either in flat sheets, tubular, hollow fibers or spiral wound sheets (Seader and Henley, 1998). To characterize the permeability of membrane in an experiment, flat membrane modules are mainly used (Geankoplis, 2003). The hollow fibers modules resemble a shell and tube heat exchanger is suitable for gas permeation application. Meanwhile, tubular and spiral wounded are widely used in reverse osmosis and ultra-filtration applications. The characteristics of some membrane modules are listed in Table 2.1.

Table 2.2: Typical characteristics of membrane modules (Seader and Henley, 1998)

Membrane modules	Plate and Frame	Spiral Wounded	Tubular	Hollow Fiber
Packing density, m^2/m^3	30 to 50	200 to 800	30 to 200	500 to 9000
Resistance to fouling	Good	Moderate	Very good	Poor
Ease of cleaning	Good	Fair	Excellent	Poor
Relative cost	High	Low	High	Low

2.1.3 Types of flow in gas permeation through membrane

Generally, an isothermal conditions and negligible pressure drop in the feed and permeate streams are assumed in deriving theoretical models for gas separation. The permeability of each gas components and the effects of total pressure of the gas are estimated negligible. According to Geankoplis (2003), there are four types of ideal flow patterns called complete mixing, cross-flow, counter-current flow and co-current flow. In complete mixing flow, the permeate composition of the residue and products are presumed equal to their respective uniform composition while in cross-flow, the feed composition and local permeate concentration are varies along the flow and membrane paths, respectively.

As for counter-current and co-current flows, the feed and permeate streams composition are varies along its flow path. All the flow types for gas permeation through membrane are figured in Figure 2.2.

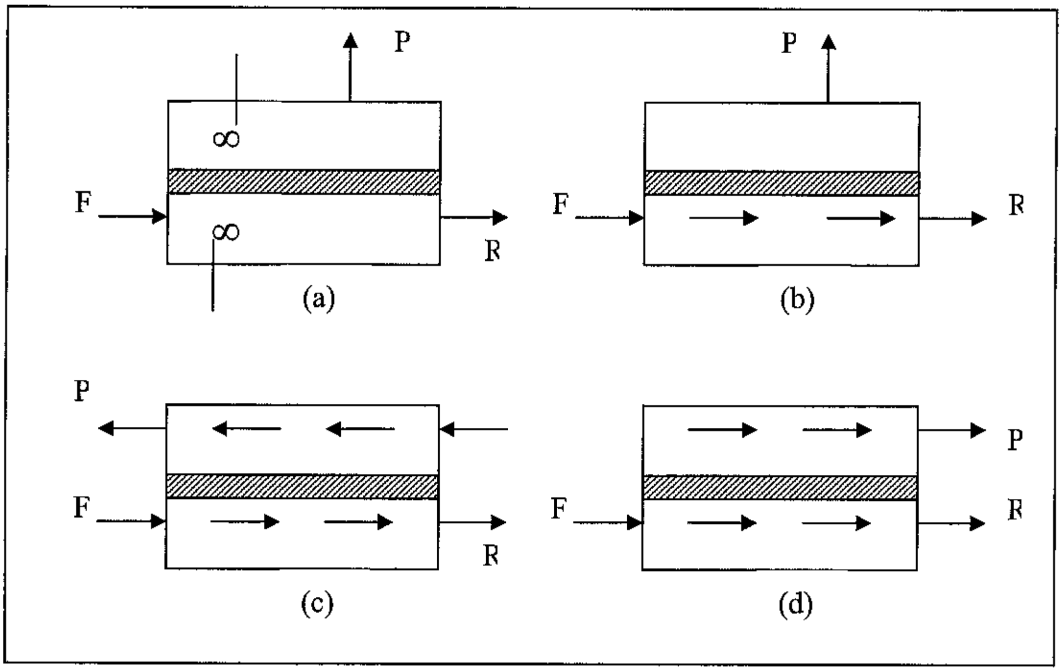

Figure 2.2: Ideal flow patterns in membrane separator for gases: (a) complete mixing (b) cross-flow (c) counter-current flow (d) co-current flow. [F-feed, R-retentate, P-permeate] (Adapted from Geankoplis, 2003)

2.2 Theory of molecular transport across membrane

2.2.1 Introduction

To be effective in separating a mixture of chemical components, a membrane must possesses high permeance and a high permeance ratio for the two species being separated (Seader and Henley, 1998). The permeance for a given species diffusing through a membrane of given thickness is analogous to a mass transfer coefficient like the flow rate of that species per unit cross-sectional area of membrane per unit driving force. The molar trans-membrane flux of species *i* is given by

$$N_i = \frac{P'_i}{t_m} f_d \qquad (2.1)$$

where P'_i is the permeability of gas specie *i*, f_d is driving force and t_m is membrane thickness.

When the mixture on either side of a micro-porous membrane is gas, the rate of species diffusion can be expressed in terms of Fick's law. If pressure and temperature on either side of the membrane are equal and ideal gas law is holds, the trans-membrane flux can be written in terms of a partial pressure driving force as

$$\mathrm{N_i = \frac{D_{e,i}c_m}{Pt_m}\left(p_{i,O} - p_{i,L}\right)} \qquad (2.2)$$

which c_m is the total concentration of the gas mixture given as P/RT by the ideal gas law. Thus, Equation 2.2 can be written otherwise as

$$\mathrm{N_i = \frac{D_{e,i}}{RTt_m}\left(p_{i,O} - p_{i,L}\right)} \qquad (2.3)$$

2.2.2 *Permeability, P'$_i$ of pure gas i*

As stated by Hilmi and Lim (2004), there are three main mechanisms influence the permeability, *P'$_i$* of a gas *i* across a membrane. The mechanisms are viscous diffusion, Knudsen diffusion and surface diffusion. The total permeability of gas specie *i*, *P'$_i$* could be obtained by summation of all the tree mechanisms permeability, expressed as

$$P'_i = \frac{\varepsilon r_p^2 P}{8\tau\mu_i zRT} + \frac{\varepsilon}{z\tau RT}\left[\left(\frac{1}{1/D_i + 1/D_{k,i}}\right) + 2\frac{t_m\varepsilon}{r_p\tau}(1-\varepsilon)(D_s\rho_m f)\right] \qquad (2.4)$$

P'$_i$ represent the total permeability of gas i, ε is membrane porosity, rp is pore size, τ is tortuosity, μ_i is the viscosity of gas i, z is compressibility factor of gas i depending on pressure, tm is membrane thickness, ρm is membrane density and f is equilibrium loading factor. Meanwhile, R in Equation 2.4 above stand for the universal gas constant which is equal to 82.06 cm^3.atm/mol.K, P is the operating pressure and T is the operating temperature. D_i and $D_{k,i}$ signify the ordinary and Knudsen diffusion of gas i while D_s is surface diffusion. From the equation above, the membrane properties like porosity (ε), density (ρm), tortuosity (τ) and membrane thickness (tm) influence the permeability of gas specie i together with operating pressure, P and temperature, T.

The first part of Equation 2.4 above characterizes the permeability of gas specie due to viscous diffusion. Bird et al (2002) derived the viscosity of a pure monatomic gas of molecular weight M_i using the Lennard-Jones parameters as

$$\mu_i = 2.6693 \times 10^{-5} \frac{\sqrt{M_i T}}{\sigma_i^2 \Omega_{i,\mu}} \qquad (2.5)$$

where σ and Ω are Lennard-Jones parameters (attached in appendices A). The gas viscosity, μ is carrying the unit of g/cm.s provided the unit of T in Kelvin and σ in m (10^{-10} m). The dimensionless quantity Ω_μ is a slowly varying function of the dimensionless temperature κT/ε of the order of magnitude of unity. It accounts for the details of the paths that the molecules take during a binary collision. Because of that, it is called as collision integral for viscosity.

The Ω_μ is exactly unity if the gas were made up of rigid diameter spheres, σ instead of real molecules with attractive and repulsive forces. Therefore, the function of Ω_μ maybe interpreted as describing the deviation from rigid-sphere behaviors. Even though the Equation 2.5 is a result of the kinetic theory of monatomic gases, it has been found to be remarkably good for polyatomic gases as well (Bird et al, 2002).

The second part of right hand side of Equation 2.4 estimates the permeability of gas specie *i* due to ordinary and Knudsen diffusion. According to Seader and Henley (1998), the ordinary and Knudsen diffusions, D_i and $D_{k,i}$ of gas specie *i* can be estimated using Equation 2.6 and Equation 2.7, respectively written as

$$D_i = \frac{0.86}{P} \qquad (2.6)$$

and

$$D_{K,i} = \frac{d_p \overline{\upsilon_i}}{3} \qquad (2.7)$$

which P is operating pressure in atm, d_p is pore diameter in meter and υ_i is the average molecule velocity given by

$$\overline{\upsilon_i} = \left(\frac{8RT}{\pi M_i}\right)^{\frac{1}{2}} \qquad (2.8)$$

By combining Equation 2.7 and Equation 2.8, the Knudsen diffusion of gas specie *i* can be stated as

$$D_{K,i} = \frac{d_p - d_i}{3}\left(\frac{8RT}{\pi M_i}\right)^{\frac{1}{2}} \qquad (2.9)$$

At low total pressure and small pore diameter, the ordinary diffusion may occur in series with Knudsen diffusion in Knudsen flow region where the collision between gas molecules and pore size occur mainly compared to the collision between gas molecules. It is important to take note that the Knudsen diffusion only applicable for pore diameter larger than the diameter of gas molecule i, d_i. With the present of the membrane porosity and tortuosity, the ordinary and Knudsen diffusions can be jointed together to form the effective diffusion of gas specie i, $D_{e,i}$ that is written as

$$D_{e,i} = \frac{\varepsilon}{\tau}\left[\frac{1}{\left(\frac{1}{D_i}\right)+\left(\frac{1}{D_{k,i}}\right)}\right] \qquad (2.10)$$

By integrating the Equation 2.1, 2.3 and 2.10, the final equation to calculate the permeability of gas specie *i* through the membrane due to Knudsen and ordinary diffusions can be expressed as

$$P'_{k,i} = \frac{\varepsilon}{RT\tau}\left[\frac{1}{(1/D_i)+(1/D_{k,i})}\right] \qquad (2.11)$$

The permeability of gas specie *i* due to the surface diffusion is represented by third part of Equation 2.4. The surface diffusion, $D_{s,i}$ for gas specie *i,* could be obtained by using Equation 2.12 as proposed by Seader and Henley (1998).

$$D_{s,i} = 1.6\times10^{-2}e^{[-0.45(-\Delta H)/mRT]} \qquad (2.12)$$

where ΔH is the specific enthalpy of gas specie *i.* For conducting adsorbent such as carbon, m is equal to 2 and for insulating adsorbents, m equal to 1 is used. Typically, the values of surface diffusivity of light gases for physical adsorption are in the range of 5 x 10^{-3} to 10-6 cm^2/s. In case of a low differential heat of adsorption, larger values of D_s are applied.

2.2.3 Permeability, P'_i of gas specie i in the mixtures

To determine the permeability of gas specie *i* in the mixture, a similar equation as proposed by Hilmi and Lim (2004) is used. The equation (Roslee, 2001) can be expressed as

$$P'_{i,mix} = \frac{\varepsilon r_p^2 P}{8\tau\mu_{i,mix} zRT} + \frac{\varepsilon}{z\tau RT}\left[\left(\frac{1}{1/D_{i,mix} + 1/D_{k,i}}\right) + 2\frac{t_m\varepsilon}{r_p\tau}(1-\varepsilon)(D_s\rho_m f)\right] \quad (2.13)$$

From the Equation 2.13, the permeability of gas specie *i* in the mixture due to Knudsen and surface diffusions are remained the same. The only terms that vary are the viscous and ordinary diffusions. The compute the viscosity of gas specie *i* in the mixture, semi-empirical formula (Bird et al, 2002) can be used given by

$$\mu_{i,mix} = \sum_{i=1}^{N} \frac{x_i \mu_j}{\sum_j x_j \Phi_{ij}} \quad (2.14)$$

in which the dimensionless quantities $\Phi_{\alpha\beta}$ are estimated as

$$\Phi_{ij} = \frac{1}{\sqrt{8}}\left(1 + \frac{M_i}{M_j}\right)^{\frac{-1}{2}}\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}}\left(\frac{M_j}{M_j}\right)^{\frac{1}{4}}\right]^2 \quad (2.15)$$

Here x_i is the mole fraction of species *i*, μ_i is the viscosity of pure species *i* at the system temperature and pressure, and M_i is the molecular weight of species *i*.

For a binary gas mixture, the ordinary gas diffusion of specie *i* is given by Seader and Henley (1998) as

$$D_{ij} = D_{ji} = \frac{0.00143T^{1.75}}{PM_{ij}^{0.5}\left[\left(\sum v\right)_i^{1/3} + \left(\sum v\right)_j^{1/3}\right]^2} \quad (2.16)$$

where D_{ij} is in cm^2/s, P is in atm and T is in K. Σv is the summation of atomic and structural volumes given in appendices B which includes diffusion volumes of some simple molecules. The average molecular weight, M_{ij} in Equation 2.16 can be determined from Equation 2.17 below.

$$M_{ij} = \frac{2}{\left(\frac{1}{M_i} + \frac{1}{M_j}\right)} \tag{2.17}$$

In case of unavailable data for atomic and structural volumes, Bird et al (2002) estimate the gas diffusivity, D_{ij} in binary mixture as

$$\frac{PD_{ij}}{\left(p_{ci}p_{cj}\right)^{1/3}\left(T_{ci}T_{cj}\right)^{5/12}\left(\frac{1}{M_i} + \frac{1}{M_j}\right)^{0.5}} = a\left(\frac{T}{\sqrt{T_{ci}T_{cj}}}\right)^{b} \tag{2.18}$$

For non-polar gas pairs excluding helium and hydrogen, the dimensionless constants a and b are equal to 2.745 x 10^{-4} and 1.823, respectively. For pairs consisting of H_2O and a non-polar gas, the value of a is equal to 3.640 x 10^{-4} while b is equal to 2.334.

Meanwhile, the ordinary gas diffusion of specie *i* in the gas mixtures is given by

$$D_{i,mix} = \frac{1}{\frac{x_j}{D_{i,j}} + \frac{x_k}{D_{i,k}} + \dots + \frac{x_z}{D_{i,z}}} \tag{2.19}$$

where i, j, k and z are the individual species of gas and x is the mole fraction of the gas in that mixtures.

2.3 Selectivity

In order to find out the efficiency of the membrane in separating the desired gas, an ideal separation factor, α (also known as selectivity) is calculated. Illing et al (2004) expressed the selectivity as the quotient of the permeability of two different gases given by

$$\alpha_{ij} = \frac{P_i^{'}}{P_j^{'}} \qquad (2.20)$$

The term of α_{ij} is representing the selectivity of gas specie *i* to gas specie *j* while P'$_i$ and P'$_j$ are the permeability of gas specie *i* and *j*, accordingly. The higher the value of α_{ij} means the better separation through that particular membrane has occurred.

2.4 Assumption

1. The equilibrium loading factor, f is assumed to be independent of operating pressure. It is calculated through Equation 2.21 written as

   $$f = \frac{1}{\rho m} \qquad (2.21)$$

   where ρm is membrane density.

2. The membrane is assumed to operate isothermally with constant pressure. The effects of pressure drop in the feed and retentate side.

3. The capillary condensation is neglected even though it is possible to occur in the membrane at high pressure and low temperature.

4. No reaction in the membrane barrier.

5. The heats of adsorption, ΔH of gases in the mixture are assumed equal to the heat of adsorption, ΔH of pure gases.

   $$\Delta H_{i,mix} = \Delta H_i \qquad (2.22)$$

6. The molecules of the gases are assumed in spherical shape.

CHAPTER 3

METHODOLOGY

3.1 Model development

The selected membrane in this study is Poly (amide-6-b-ethylene oxide) copolymer 1657, also known as PEBAX 1657 (trade name) and γ-alumina. The physical properties of the membranes are tabulated in Table 3.1.

Table 3.1: The physical properties of PEBAX 1657 (Kim et al, 2000)

Membrane	Density, ρ (kg/m^3)	Thickness, t (μm)	Tortuosity, τ	Porosity, ε
PEBAX 1657	1140	0.6	3.676	0.272
γ-alumina	3040	1	1.65	0.6

Generally, Equation 2.4 has been used to determine the total permeability of pure carbon dioxide, methane and nitrogen. Meanwhile, for the binary and tertiary mixtures of carbon dioxide-methane, carbon dioxide-nitrogen, methane-nitrogen and carbon dioxide-methane-nitrogen, Equation 2.13 together with Equation 2.14 and 2.19 have been used.

In order to solve the complex equations, mathematical software called MathCAD 12 has been utilized. MathCAD provides hundreds of operators and built in functions for solving technical problems. Its 2-D and 3-D graphing capabilities allow the author to work and modify the graphs easily.

In analyzing the effects of pore size, mole fraction and operating pressure on permeability of pure and mixtures of carbon dioxide, methane and nitrogen, the operating temperature and membrane thickness have been fixed to 300 K and 0.6 μm, respectively. While estimating the effects of membrane pore size and concentration, the operating pressure is kept at 60 atm. In the other hand, the pore size of 1 nm has been used in analyzing the effects of operating pressure as well as the effects of concentration.

3.2 Physical Data Input

The required physical data of carbon dioxide, methane and nitrogen in completing the models are tabulated in Table 3.2. The molecular weight and Lennard-Jones constant are used to estimate the viscosity of gases as expressed in Equation 2.5 whereas the kinetic diameter is required in measuring the permeability of gas due to Knudsen diffusion as given in Equation 2.9. Meanwhile, the critical temperature and critical pressure are used in calculating the gas diffusion in binary mixture (Equation 2.18).

Table 3.2: Physical properties of carbon dioxide, methane and nitrogen (Perry and Green, 1997 and Bird et al, 2002)

Properties	Carbon dioxide	Methane	Nitrogen
Molecular weight, Mw (g/mol)	44.01	16.043	28.01
Kinetic diameter, Φ (x 10^{-10} m)	3.3	3.88	3.667
Lennard-Jones constant, Ω	1.2988	1.1361	1.04
Critical temperature, T_c (K)	304.21	190.24	126.2
Critical pressure, P_c (atm)	72.934	45.3	33.457

The compressibility factors of the three gases which are needed in evaluating the gas permeability are shown in Table 3.3. The values are adapted from Perry and Green, 1997.

Table 3.3: The compressibility factors of carbon dioxide, methane and nitrogen at T=300 K (Perry and Green, 1997)

Pressure (atm)	Carbon dioxide	Methane	Nitrogen
42	0.9860	0.902	0.9960
44	0.9860	0.899	0.9967
46	0.850	0.896	0.9968
48	0.9850	0.893	0.9769
50	0.9840	0.890	0.997
52	0.9840	0.887	0.997
54	0.9830	0.884	0.9971
56	0.9830	0.881	0.9972
58	0.9820	0.878	0.9973
60	0.9820	0.875	0.9974
62	0.9810	0.872	0.997
64	0.9810	0.869	0.9976
66	0.9800	0.866	0.9977
68	0.9800	0.863	0.9978
70	0.9800	0.86	0.998

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The modeling results of carbon dioxide and nitrogen removal from natural gas using membrane processes are discussed in detail in this chapter. The effects of membrane pore size, mole fraction and operating pressure to the permeability of pure carbon dioxide, methane, nitrogen and mixtures of these gases are compared. The selectivity is measured to predict the efficiency of PEBAX 1657 membrane in the processes.

4.2 Effects of pore size

To model the effects of pore size, the operating temperature and pressure are set to be 300 K and 60 atm, respectively. Meanwhile, the membrane pore size range of 0.2 nm to 4 nm is selected. In the binary mixture, combination of 70/30 mol % of methane/carbon dioxide, methane/nitrogen and carbon dioxide/nitrogen were used. The effects of pore size on the permeability of these gases in pure and binary mixture are then compared.

Figure 4.1 shows the effects of membrane pore size on permeability of pure methane caused by three mechanisms of gas diffusion. The total permeability of pure methane decreases significantly as the pore size increases from 0.2 nm to 2 nm. At pore size larger than 2 nm, the total permeability of pure methane re-increases but not too significant. These two conditions are mainly distributed by the surface and Knudsen diffusion mechanisms. At small pore size, the permeability of pure methane is dominated by surface diffusion. This is due to high and strong interaction between the molecules and membrane pore wall. The viscous and Knudsen diffusion are not apparent because of the hindered pathways of travel. The effects are clearly visualized at pore size less than 1 nm. As the pore size further increases, the surface diffusion lost it effects whereas the Knudsen diffusion starts to overlook. At high pore size, the mean free path of gas molecules travel became larger hence increases the transport of gas molecules. The collision between the gas molecules and pore wall occur more frequently rather than the collision between gas molecules, themselves. The effects are noticeably at the pore size larger than 3 nm. At the same time, increasing the pore sizes will slightly increase the viscous diffusion as well. As for pure carbon dioxide and pure nitrogen, the same permeability trends are observed.

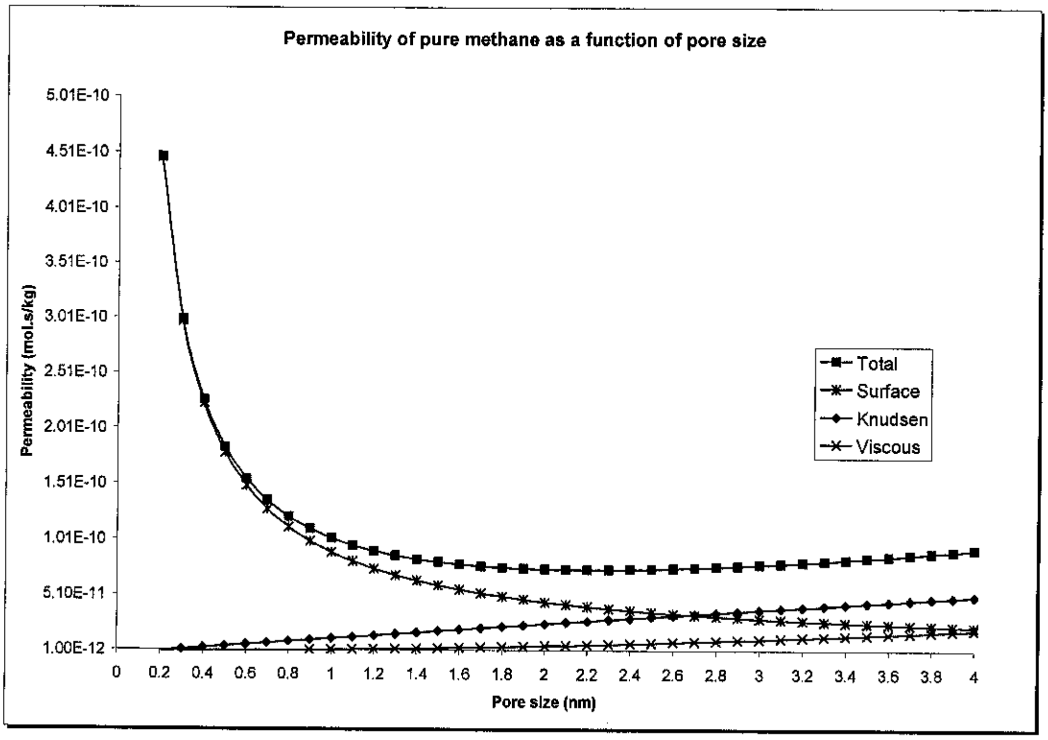

Figure 4.1: Effects of membrane pore size on pure methane permeability due to surface, Knudsen and viscous diffusion mechanisms. (T=300 K, P=60 atm, tm=0.6 μm)

The total permeability of pure carbon dioxide, methane and nitrogen are illustrated in Figure 4.2. From the figure, the permeability of pure carbon dioxide has found to be highest. The result is probably caused by the different of surface diffusion mechanism effects. The adsorption heat, ΔH of carbon dioxide (-17116 J/mol) is larger than the adsorption heat of methane (-21000 J/mol) and nitrogen (-19900 J/mol). Therefore, the ability of carbon dioxide molecules to diffuse through the membrane is higher than methane and nitrogen molecules hence impacting the total permeability of these

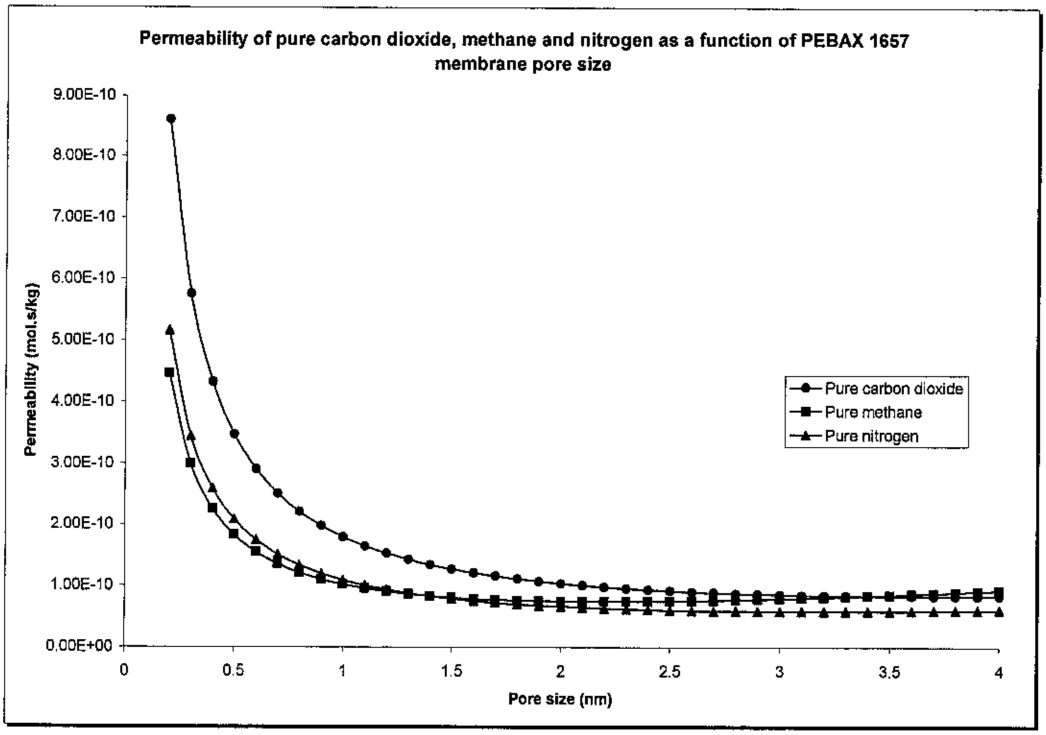

Figure 4.2: Effects of PEBAX 1657 membrane pore size on total permeability of pure carbon dioxide, methane and nitrogen. (T=300 K, P=60 atm, tm= 0.6 μm)

three gases. At small pore size less than 1.5 nm, the total permeability of nitrogen is higher than the total permeability of methane. However, at pore size larger than 1.5 nm, methane permeability has found to be greater than nitrogen permeability. This situation occurs as at larger pore size, the viscous and Knudsen diffusion mechanisms affects more to methane molecules rather than nitrogen molecules. Even though the molecular diameter, Φ and Lennard-Jones parameter, Ω of nitrogen are smaller than methane, probably Φ=3.67 Å m and Ω=1.04 for nitrogen while Φ=3.88 m and Ω=1.13 for methane, their effects are not as much as the effects of different in molecular weight, Mw between both gases. Since the molecular weight of methane (16 kg/kmol) is lower than nitrogen (28.02 kg/kmol), the permeability of methane due to viscous and Knudsen diffusion mechanisms are higher compared to nitrogen hence contributed to the higher total permeability of methane at larger pore size. The relationships between the molecular diameter, Lennard-Jones parameter, molecular weight, viscous and Knudsen diffusion mechanisms to the gas permeability are illustrated through Equation 2.5 and Equation 2.9, respectively. These effects are more obvious if γ-alumina membrane is used as shown in Figure 4.3.

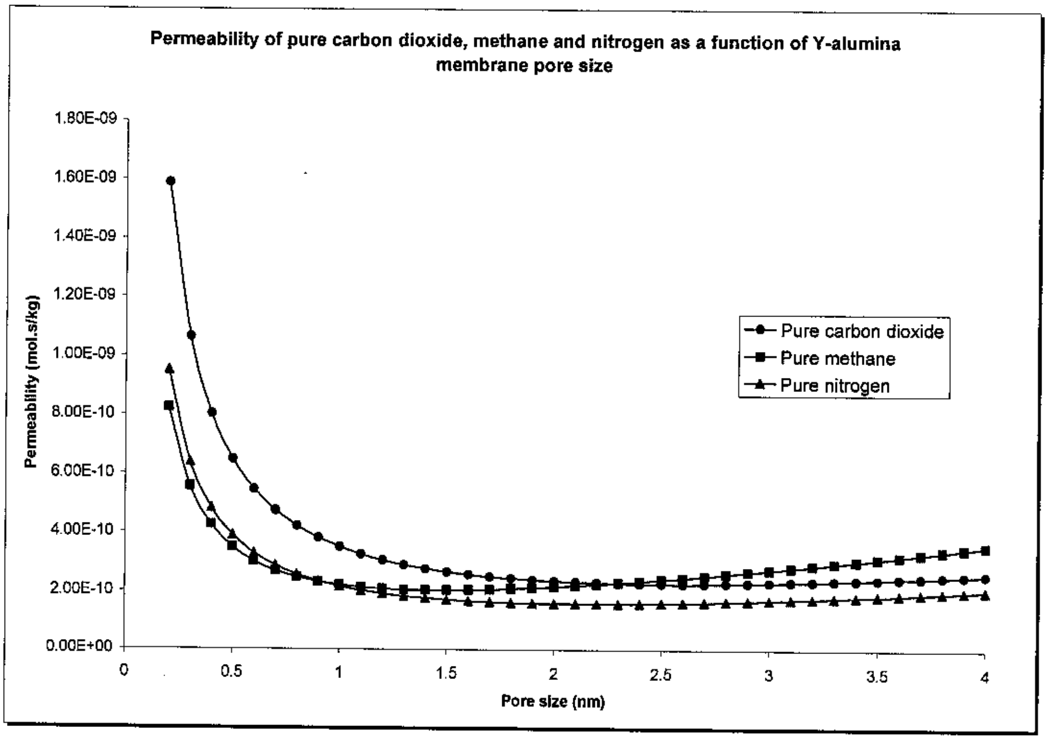

Figure 4.3: The effects of γ-alumina membrane pore size on total permeability of pure carbon dioxide, methane and nitrogen. (T=300 K, P=60 atm, tm=0.6 μm)

In order to discover the effects of membrane pore size on permeability of gases in binary mixture, a mixture of 70 mol % of methane and 30 mol % of carbon dioxide is selected. The result is figured out in Figure 4.4. The permeability of carbon dioxide and methane in that mixture lay in between the permeability of pure carbon dioxide and pure methane. In the binary mixture, it has found that the viscosity of carbon dioxide increases while methane decreases as compared to their pure viscosity. As a result, the total permeability of carbon dioxide decreases and methane increases since the viscous diffusion is inversely proportional to the permeability. Similarly, the same results were obtained for binary mixture of carbon dioxide/nitrogen and methane/nitrogen.

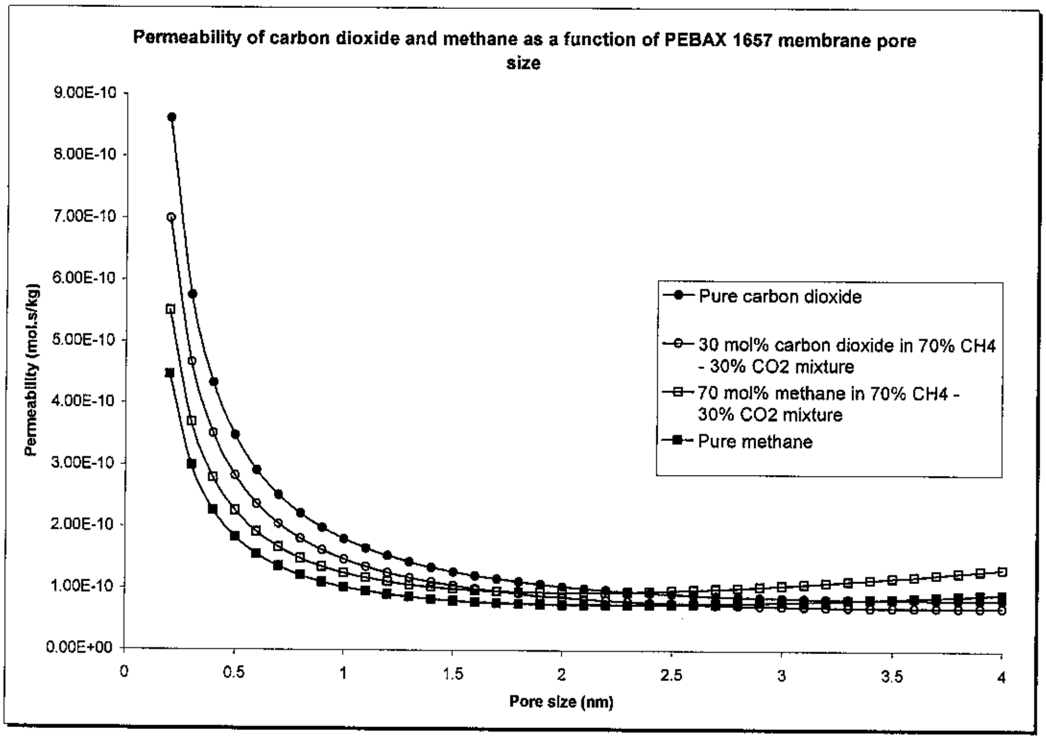

Figure 4.4: The comparison of PEBAX 1657 membrane pore size effects on permeability of pure carbon dioxide, methane and a mixture of these gases with 70 mol % CH_4 – 30 mol % CO_2. (T=300 K, P=60 atm, tm= 0.6 μm)

4.3 Effects of concentration (mole fraction)

To demonstrate the effects of mole fraction on carbon dioxide, methane and nitrogen permeability, the mole fraction of the gases in the binary mixture is varied accordingly from 10 mol % to 90 mol %. For the tertiary mixture, the mole fraction of nitrogen is fixed to 10 mol % while the methane concentration varies from 10 mol % to 90 mol %. The operating temperature and pressure are remained constant at 300 K and 60 atm, respectively. Meanwhile, the PEBAX 1657 membrane pore size of 1 nm is selected for both conditions.

The permeability of carbon dioxide in carbon dioxide/methane mixture has found decreases while the permeability of methane increases with the increasing of methane mole fraction. The effects are pointed out in Figure 4.5. At 10 mol % of methane (90 mol % of carbon dioxide), its permeability is about 4×10^{-11} mol.s/kg. As its mole fraction increases to 90 mol % (10 mol % of carbon dioxide), its permeability also

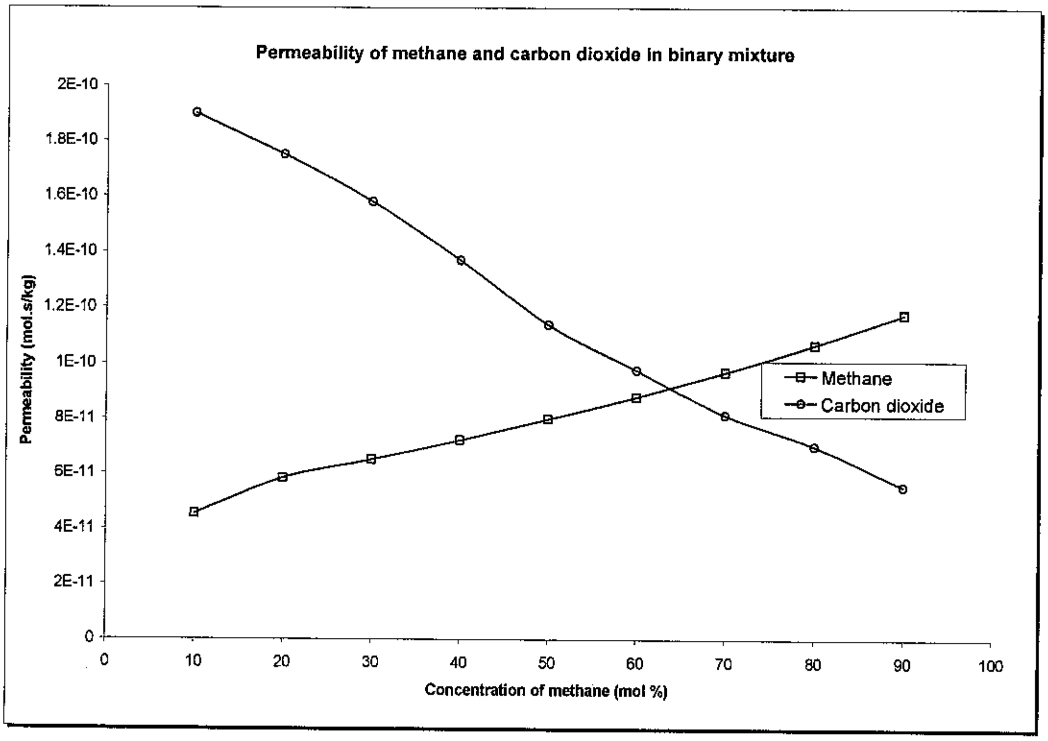

Figure 4.5: The effects of mole fraction on carbon dioxide and methane permeability in carbon dioxide/methane mixture. (T=300 K, P=60 atm, tm=0.6 μm, rp=1 nm)

increase approaching to 1.2×10^{-10} mol.s/kg. In contrast, the permeability of carbon dioxide decreases from approximately 1.9×10^{-10} mol.s/kg to 5×10^{-11} mol.s/kg. The increment and decrement of both gases in the mixture is mostly as a result of viscous and normal diffusion mechanisms as shown in Equation 2.5. Generally, increasing the mole fraction of methane reduces its viscosity causes an increment of its permeability. In the other hand, increasing the mole fraction of methane also reduces the mole fraction of carbon dioxide hence causing a decrement of carbon dioxide permeability. For the binary mixture of methane/nitrogen and carbon dioxide/nitrogen, alike trends are observed.

Meanwhile, the effects of concentration on carbon dioxide, methane and nitrogen in tertiary mixture are illustrated in Figure 4.6. The effects have found to be more or less the effects in binary system. As the mole fraction of methane increases, the methane permeability increases, carbon dioxide decreases as its mole fraction decreasing with increasing of methane mole fraction and nitrogen remains constant as its mole fraction is fixed.

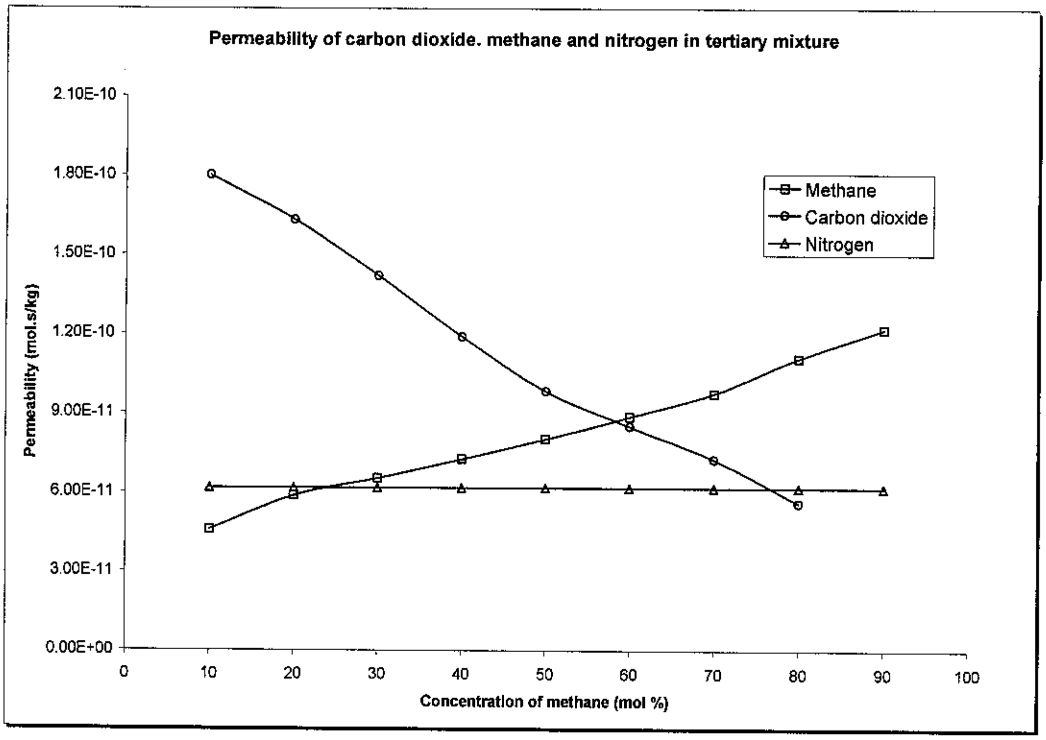

Figure 4.6: The effects of mole fraction on carbon dioxide, methane and nitrogen permeability in carbon dioxide/methane/nitrogen mixture. (T=300 K, P=60 atm, tm=0.6 μm, rp=1 nm)

4.4 Effects of operating pressure

To reveal the effects of operating pressure on permeability of pure carbon dioxide, methane, nitrogen and mixtures of these gases, the operating pressure is varied from 40 atm to 70 atm while the operating temperature is maintained at 300 K. Besides, the effects are evaluated using PEBAX 1657 membrane with the pore size of 1 nm.

Figure 4.7 shows the plot of methane permeability as a function of operating pressure. At pore size of 1 nm, the methane permeability experiences a little increment as the operating pressure increases from 40 atm to 70 atm. This circumstance occurs as a result of strong surface diffusion mechanism. Increasing operating pressure would increase the collision aw well as the interaction between the gas molecules and membrane surface which make surface diffusion more favorable. The viscous and Knudsen diffusion mechanisms are seem to be independent with operating pressure.

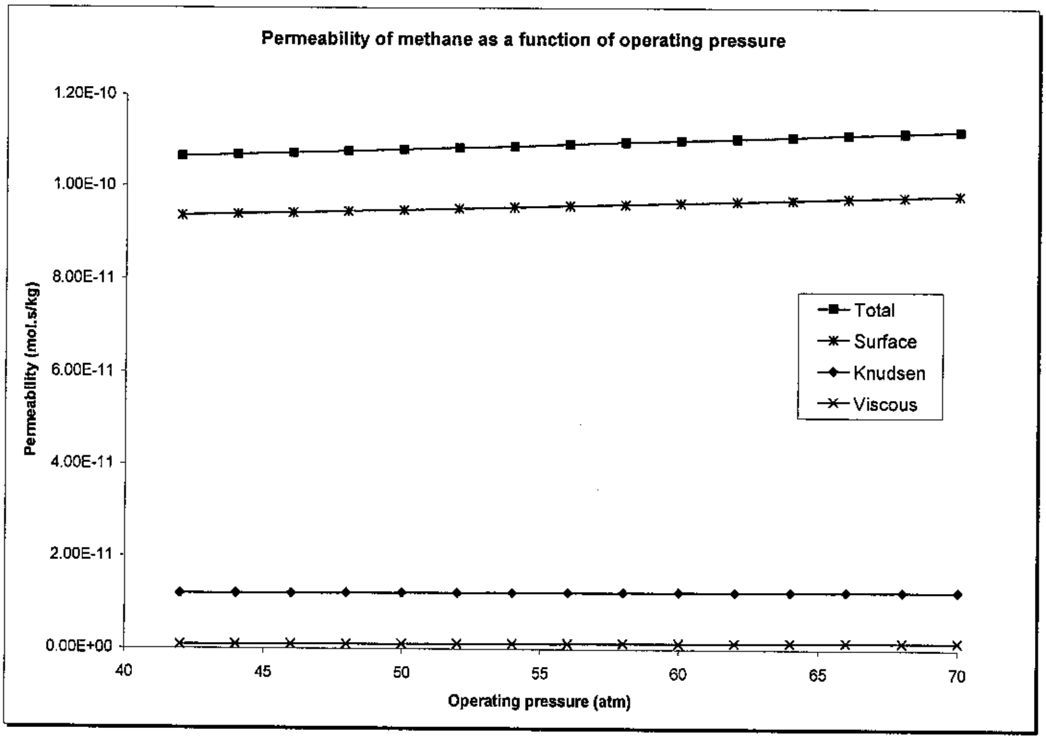

Figure 4.7: Effects of operating pressure on methane permeability due to viscous, Knudsen and surface diffusion mechanisms. (T=300 K, tm=0.6 μm, rp=1 nm)

The total permeability of methane is slightly increasing as the operating pressure increases like shown in Figure 4.8. The increments possibly caused by one of its physical properties that is called compressibility factor, z. The compressibility factors for methane decrease gradually with the increment of operating pressure hence cause the increment of methane permeability. Unlike methane, the decrement and increment of carbon dioxide and nitrogen compressibility factors are not as significant as methane. Therefore, their total permeability appears independently with the increasing of operating pressure.

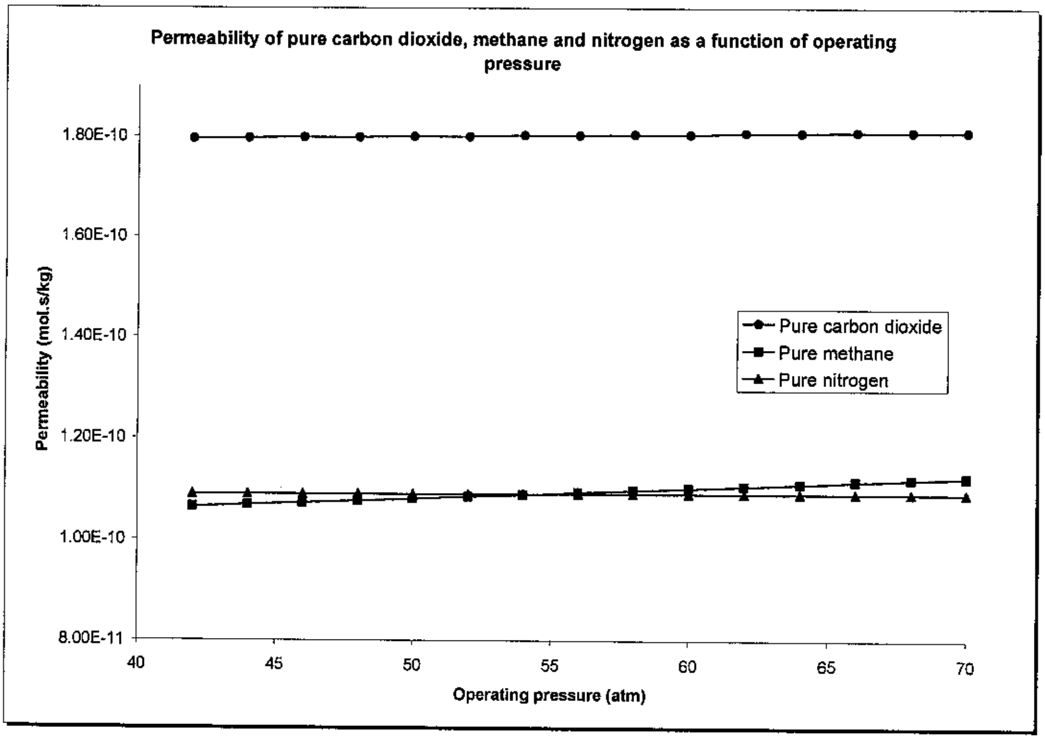

Figure 4.8: The effects of operating pressure on total permeability of pure carbon dioxide, methane and nitrogen. (T=300 K, tm=0.6 μm, rp=1 nm)

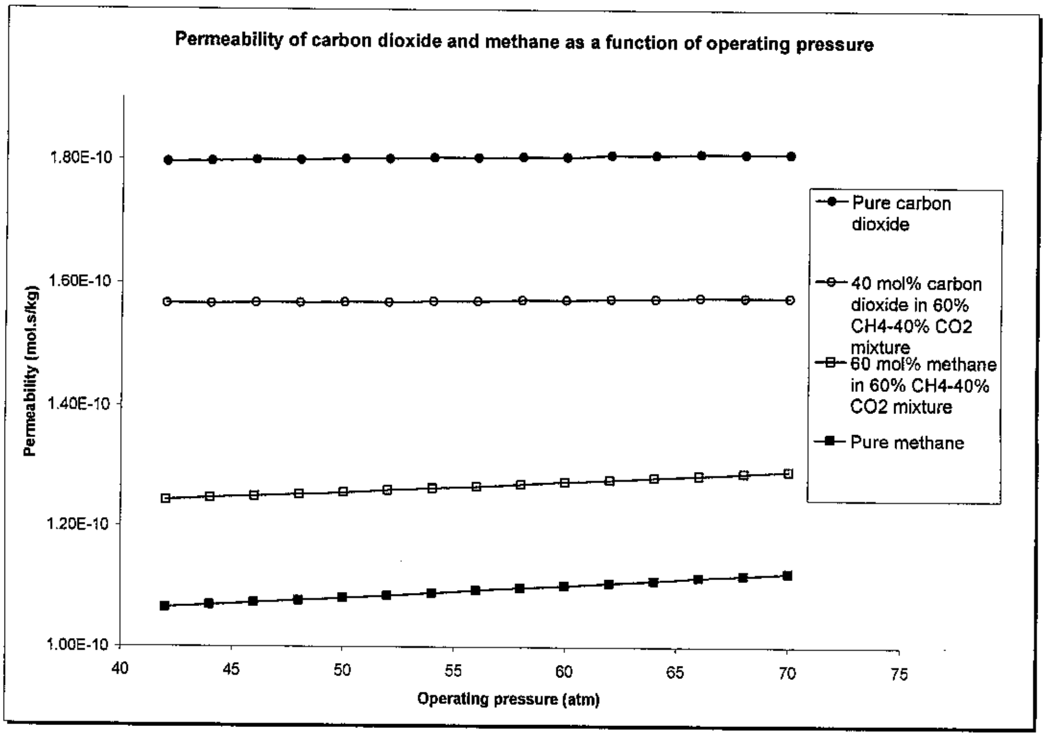

Figure 4.9: The effects of operating pressure on the permeability of pure carbon dioxide, methane and a mixture of 60 mol% methane-40 mol % carbon dioxide. (T=300 K, tm=0.6 μm, rp=1 nm)

Figure 4.9 illustrates the effects of operating pressure on the permeability of pure carbon dioxide and methane as well as in 60/40 mol % of methane/carbon dioxide mixture. As discussed in previous section, the permeability of carbon dioxide and methane in the binary mixture laid in between of the pure carbon dioxide and methane permeability. Alike pure gases, the permeability of methane and carbon dioxide in the binary mixture experience a little increment and quite independent with operating pressure, respectively.

The present of another gas molecule affected the permeability of gases in the binary mixture. This situation is pictured in Figure 4.10. Initially, the permeability of methane in binary system is higher than permeability of pure methane. Nevertheless, with the present of 10 mol % nitrogen replacing 10 mol % of carbon dioxide, the permeability of methane in the mixture decreases compared to binary mixture. The methane molecules now tend to collide and interact more frequent with carbon dioxide and nitrogen molecules rather than with the pore surface. Therefore, its permeability in tertiary mixture is lower than in the binary mixture. The same effects also observed for carbon dioxide as shown in Figure 4.11.

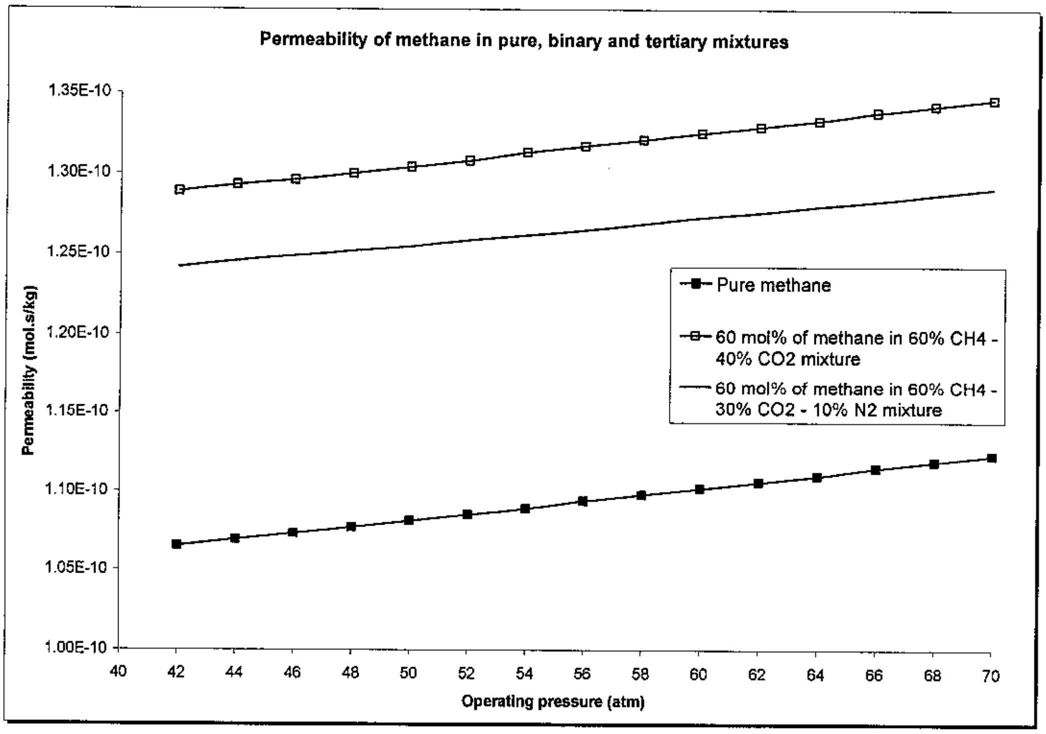

Figure 4.10: The comparison of total permeability of pure methane, methane in binary and tertiary mixtures. (T=300 K, tm=0.6 μm, rp=1 nm)

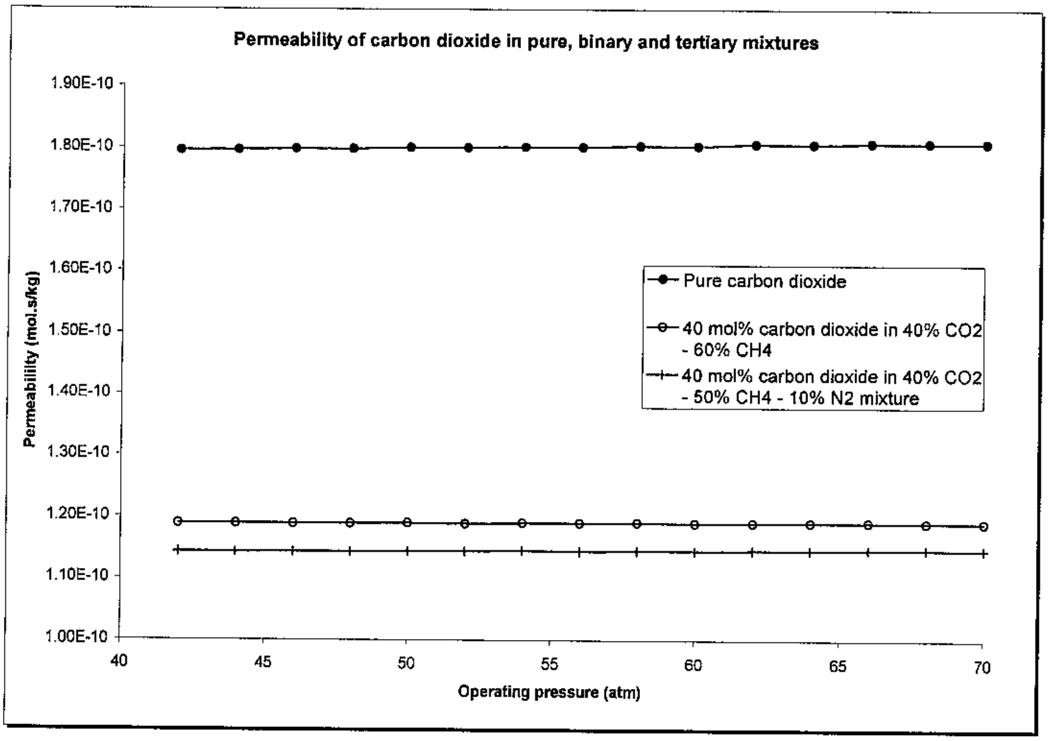

Figure 4.11: The comparison of total permeability of pure carbon dioxide, carbon dioxide in binary and tertiary mixtures. (T=300 K, tm=0.6 μm, rp=1 nm)

4.5 Selectivity

Figure 4.12 shows the selectivity of carbon dioxide to methane, carbon dioxide to nitrogen and nitrogen to methane as a function of membrane pore size. From the figure, it reveals that the selectivity decreases with increasing pore size and quite independent to pressure. The highest selectivity occurs at pore size of 0.2 nm. The highest selectivity of carbon dioxide to methane is 1.9, nitrogen to methane is 1.2 and carbon dioxide to nitrogen is 1.7. Those values indicate that the carbon dioxide permeate 1.9 time faster than methane and 1.7 time faster than nitrogen while nitrogen permeate 1.2 time faster than methane at pore size of 0.2 nm. The higher selectivity values while using PEBAX 1657 membrane signify that PEBAX 1657 offers a better separation than γ-alumina membrane.

Meanwhile, the effects of operating pressure on selectivity are shown in Figure 4.13. The selectivity of carbon dioxide to methane, nitrogen to methane and carbon dioxide to nitrogen are independent of operating pressure.

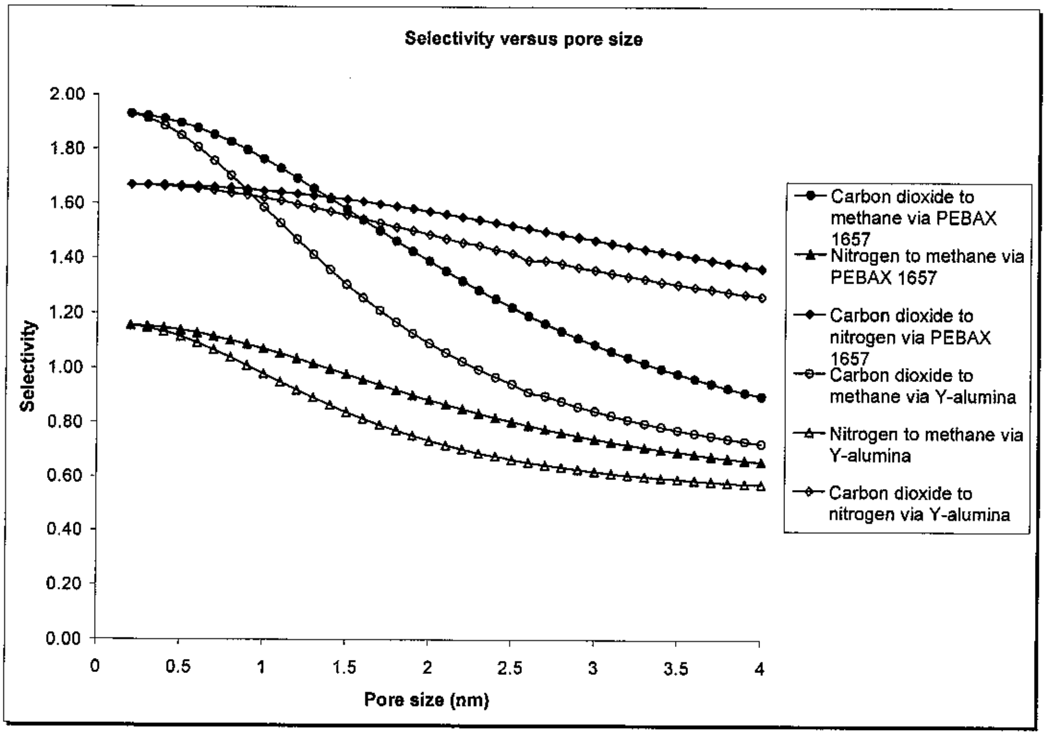

Figure 4.12: The effects of PEBAX 1657 and γ- alumina membranes pore size on carbon dioxide to methane, carbon dioxide to nitrogen and nitrogen to methane selectivity.(T=300K, P=60 atm, tm=0.6 μm)

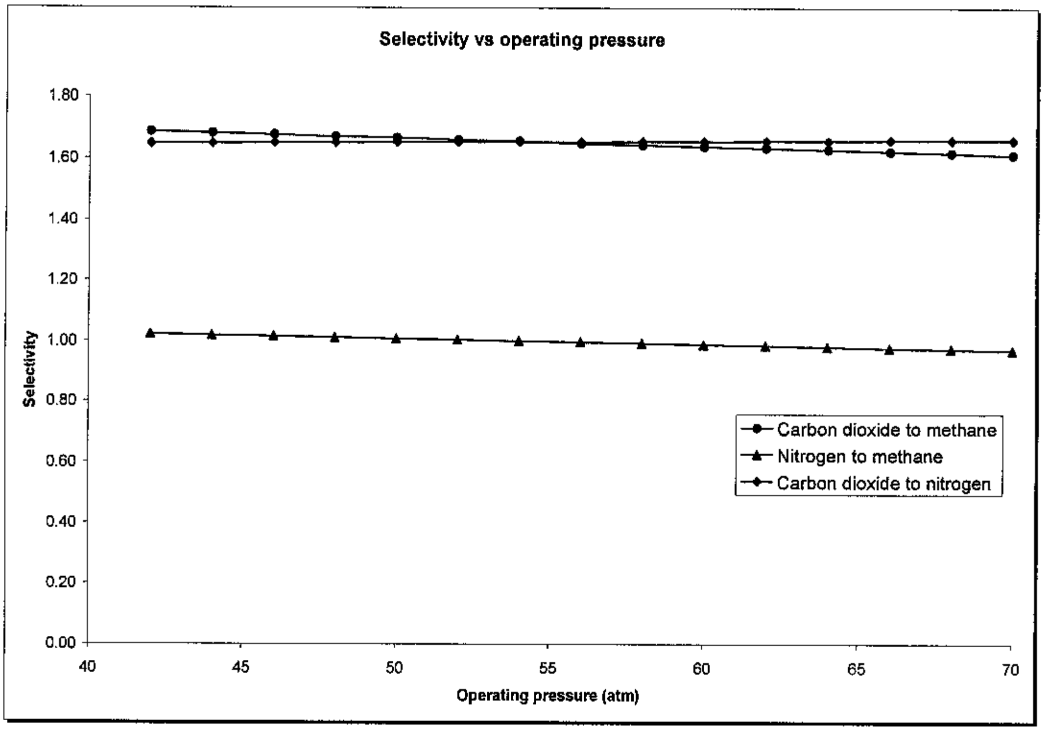

Figure 4.13: The effects of operating pressure on selectivity. (T=300 K, tm=0.6 μm, rp=1 nm)

From the selectivity analysis, it could be concluded that the removal of carbon dioxide and nitrogen using PEBAX 1657 and γ-alumina membranes is not economically viable. To be economically viable, the selectivity of nitrogen to methane should be at least 15 (Lokhandwala et al, 1998). However, the results would vary if the relationship of equilibrium loading factor, f with the operating pressure is found.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the results of developed models, increasing the pore sizes decreases the total permeability of pure carbon dioxide, methane, nitrogen and mixtures of these gases. The highest permeability has been achieved by carbon dioxide. The permeability of nitrogen was higher than methane at pore size smaller than 1.5 nm but at pore size larger than 1.5 nm, the methane permeability was higher than nitrogen. At smaller pore sizes, the permeability of gas species was dominated by surface diffusion while at larger pore size, the Knudsen diffusion has found to become more apparent.

As the concentration of methane in methane-carbon dioxide mixture increases, the permeability of methane also increased approaching the pure methane permeability. In the meantime, the permeability of carbon dioxide decreased. Similar results have found to the binary mixture of carbon dioxide-nitrogen and nitrogen-methane as well as to the tertiary mixture. However, the permeability of gas specie in the binary mixtures was higher than the permeability in the tertiary mixture.

With the existing assumption, the permeability of methane has found to slightly increase with the operating pressure whereas the permeability of carbon dioxide and nitrogen were found to be quite independent with operating pressure.

Meanwhile, the selectivity of carbon dioxide to methane, carbon dioxide to nitrogen and nitrogen to methane have found to decrease with increasing membrane pore size and quite independent with operating pressure. Higher selectivity also has found when PEBAX 1657 membrane was used instead of γ-alumina which indicated the PEBAX 1657 offered a better separation than γ-alumina. Nevertheless, the use of these two membranes has appeared not to be economically viable since the highest selectivity of nitrogen to methane was less than 2. In order to be economically viable, the selectivity of nitrogen to methane should be at least 15.

In general, the developed models were able to predict the permeability of pure carbon dioxide, methane, nitrogen and mixtures of these gases.

5.2 Recommendations

1. From the results of developed models, the processes are recommended to be operated at small pore size since the highest selectivity was obtained at smallest pore size.

2. With the current assumptions remain the same, the processes should be operated at fair operating pressure as required by the whole system to reduce the costs because the permeability of gases has insignificant effects on operating pressure.

3. Based on this study, the use of PEBAX 1657 and γ-alumina membranes in removal carbon dioxide and nitrogen from natural gas are not recommended as the separation between these gases failed to occur efficiently.

4. It is highly recommended to find the relationship between the equilibrium loading factor with operating pressure in the future work so that the estimation of carbon dioxide, methane and nitrogen permeability will be better. Further, it is believed that the equilibrium factor will affect the permeability of gas specie with the changes of operating pressure as studied by Hilmi and Lim, 2004.

5. Since this project is a pure modeling work, the results should be validated with the experimental values.

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APPENDICES

APPENDIX A

LENNARD-JONES PARAMETERS

Table A.1: Lennard-Jones parameters for some substances (Bird et al, 2002)

Substances	Molecular Weight (M)	Lennard-Jones Parameters		Critical Properties			
		σ (Å)	ε/κ (K)	T_c (K)	P_c (atm)	V_c (cm^3/g.moles)	μ_c (x 10^6 g/cm.s)
H_2	2.016	2.915	38	33.3	12.8	65.0	34.7
Air	28.964	3.167	97	5.26	37	86.7	193
N_2	28.013	3.667	99.8	132.4	33.5	90.1	180
O_2	31.999	3.433	113	126.2	49.7	74.4	250
CO_2	44.01	3.996	190	154.4	72.8	94.1	343
CH	16.04	3.78	154	191.1	45.8	98.7	159

Table A.2: Collision integral for use with Lennard-Jones parameters (Bird et al, 2002)

κT/ε	**Ω_μ**
0.30	2.840
0.35	2.676
0.40	2.531
0.45	2.401
0.50	2.284
0.55	2.178
0.60	2.084
0.65	1.999
0.70	1.922
0.75	1.853

APPENDIX B

DIFFUSION VOLUMES

Table B.1: Diffusion volumes for estimating binary gas diffusivity (Seader and Henley, 1998)

Atomic Diffusion Volumes			
C	15.9	F	14.7
H	2.31	Cl	21.0
O	6.11	Br	21.9
N	4.54	I	29.8
Aromatic ring	-18.3	S	22.9
Heterocyclic ring	-18.3		
Diffusion Volumes of Simple Molecules			
He	2.67	O_2	16.3
Ne	5.98	Air	19.7
Ar	16.2	CO	18.0
Kr	24.5	CO_2	26.7
Xe	32.7	N_2O	35.9
H_2	6.12	NH_3	20.7
D_2	6.84	H_2O	13.1
N_2	18.5	SF_6	71.3

APPENDIX C

NATURAL GAS CONSUMPTION

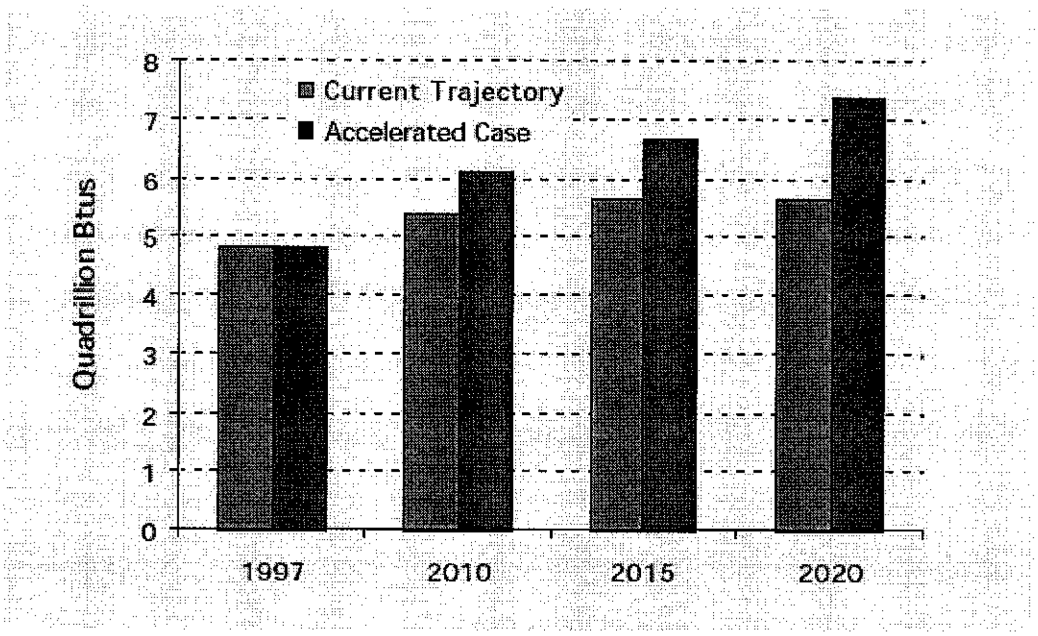


Figure C.1: Projected residential natural gas consumption (Harrje, 2000)

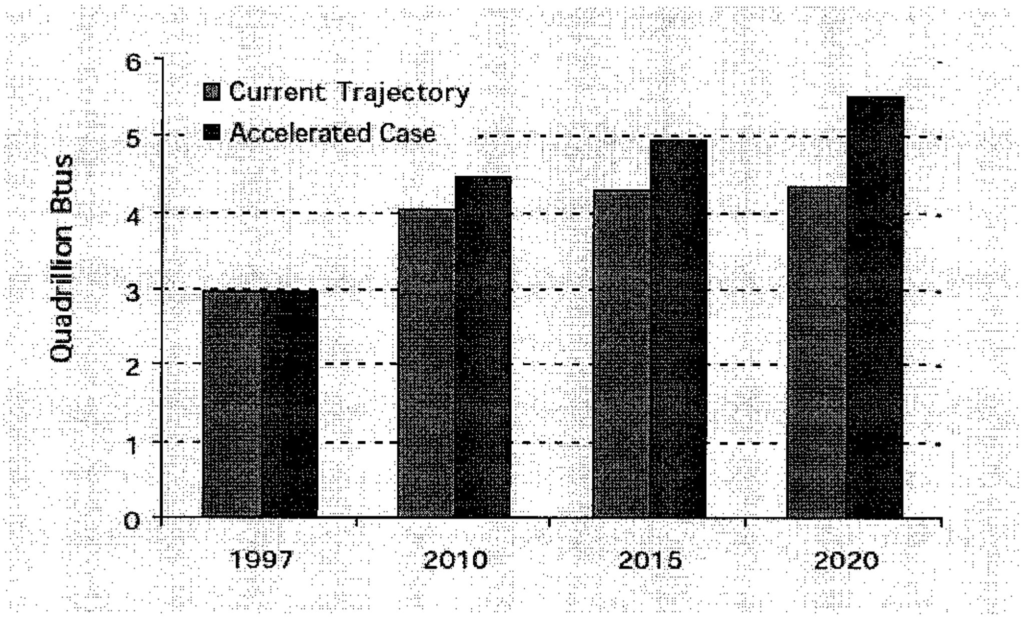


Figure C.2: Projected commercial natural gas consumption (Harrje, 2000)

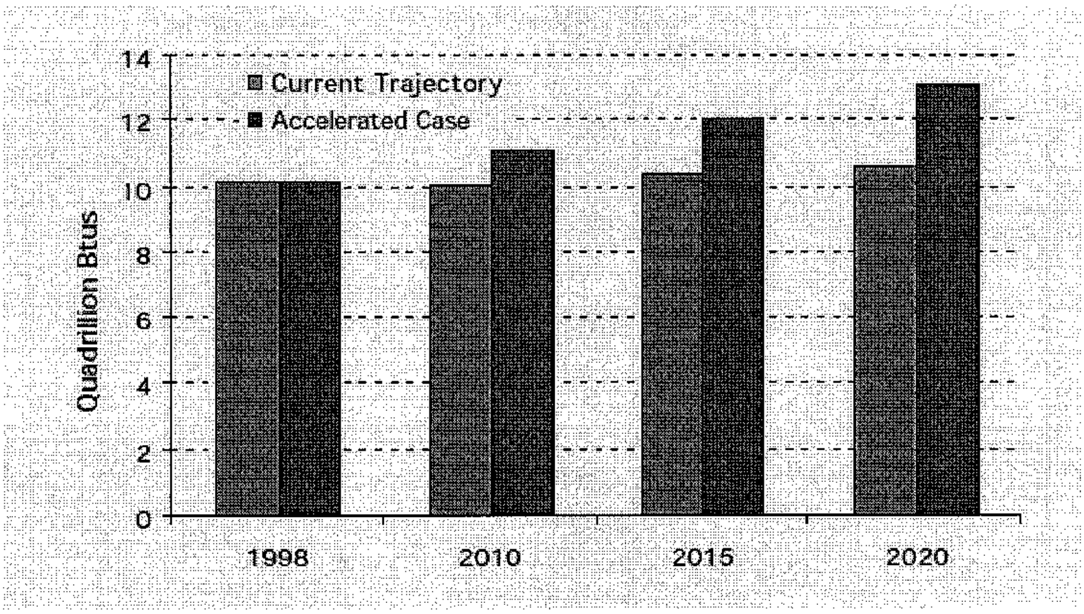


Figure C.3: Projected industrial natural gas consumption (Harrje, 2000)

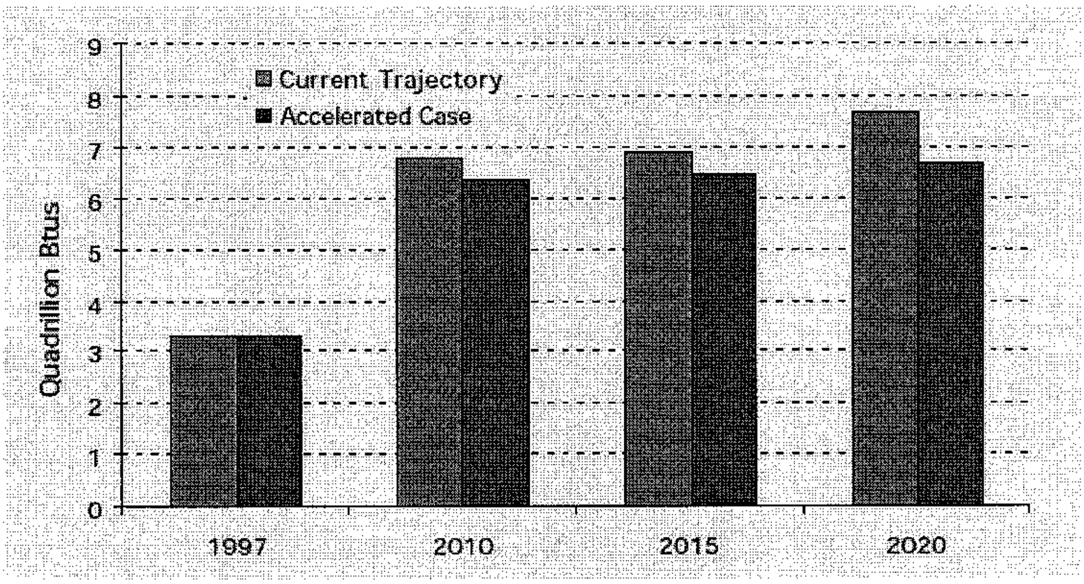


Figure C.4: Projected natural gas used for electrical generation (Harrje, 2000)

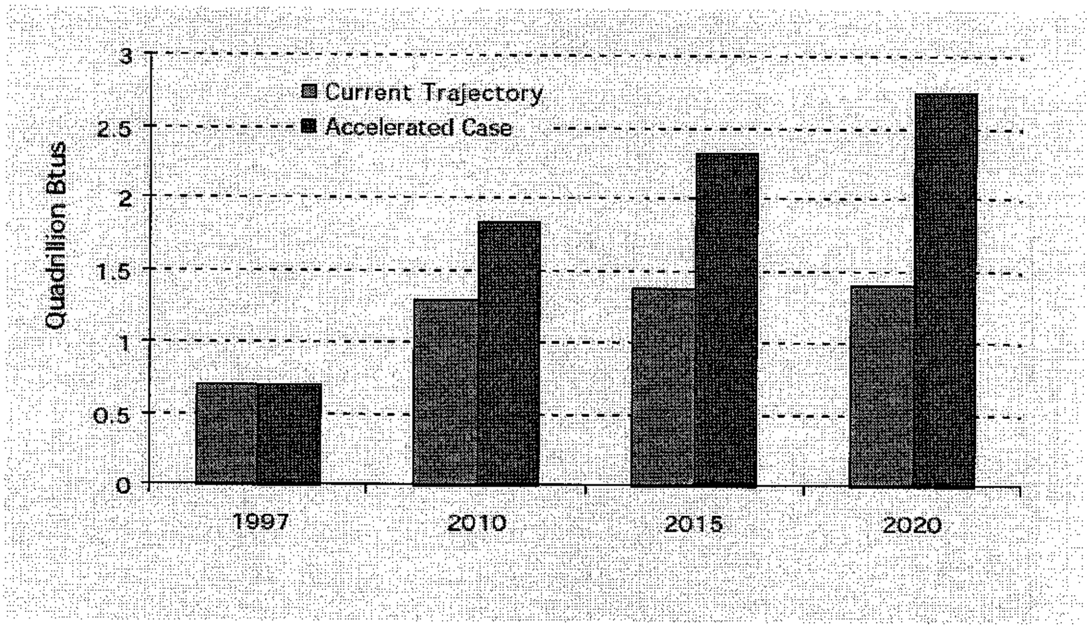
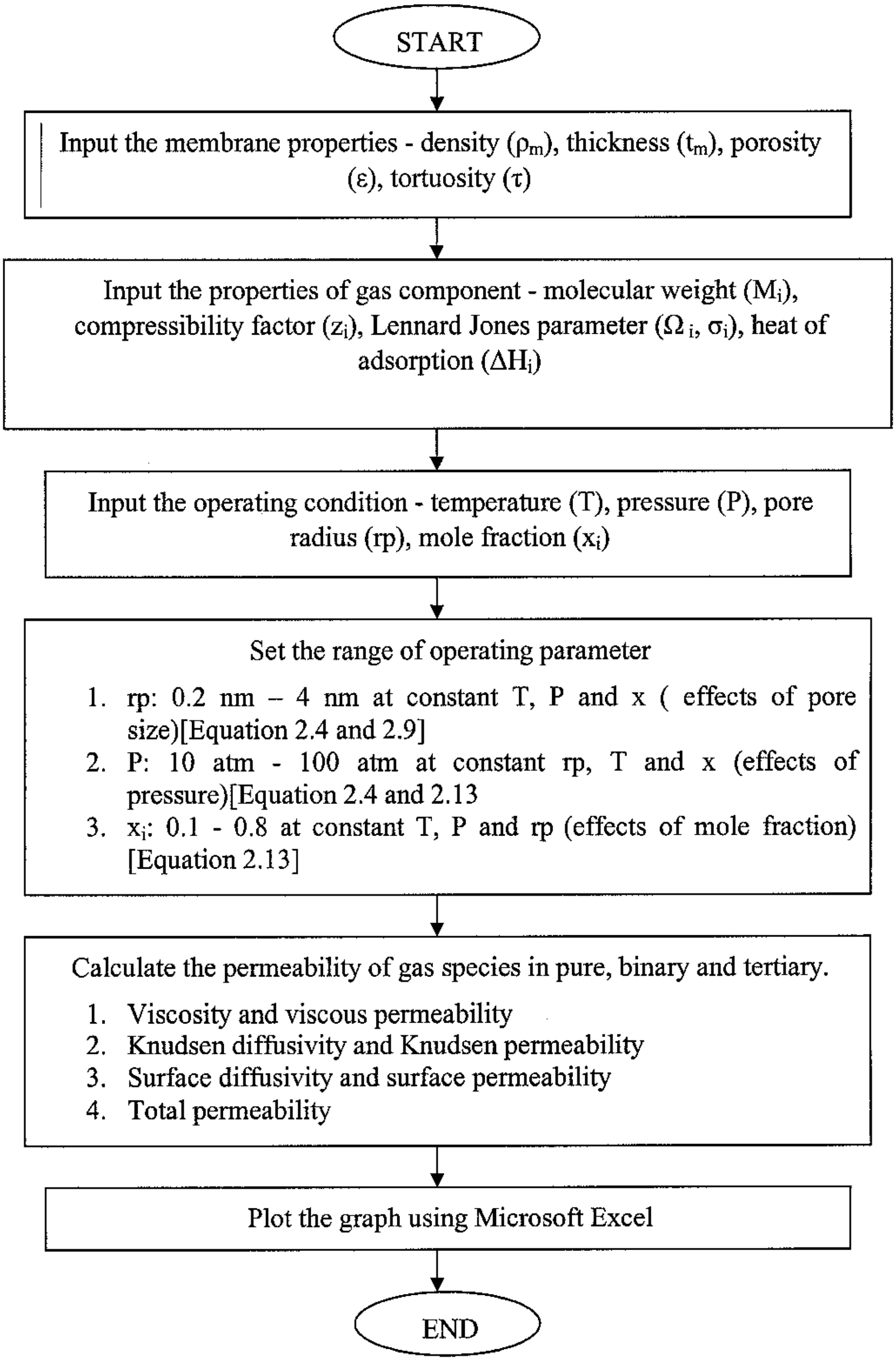


Figure C.5: Projected natural gas consumptions for transportation (Harrje, 2000)

APPENDIX D

THE FLOWS OF MODEL DEVELOPMENT



Input the membrane properties - density (ρ_m), thickness (t_m), porosity (ε), tortuosity (τ)

Input the properties of gas component - molecular weight (M_i), compressibility factor (z_i), Lennard Jones parameter (Ω_i, σ_i), heat of adsorption (ΔH_i)

Input the operating condition - temperature (T), pressure (P), pore radius (rp), mole fraction (x_i)

Set the range of operating parameter

1. rp: 0.2 nm – 4 nm at constant T, P and x (effects of pore size)[Equation 2.4 and 2.9]
2. P: 10 atm - 100 atm at constant rp, T and x (effects of pressure)[Equation 2.4 and 2.13
3. x_i: 0.1 - 0.8 at constant T, P and rp (effects of mole fraction) [Equation 2.13]

Calculate the permeability of gas species in pure, binary and tertiary.

1. Viscosity and viscous permeability
2. Knudsen diffusivity and Knudsen permeability
3. Surface diffusivity and surface permeability
4. Total permeability

Plot the graph using Microsoft Excel

APPENDIX E

TASK SCHEDULE

No	Task	Week																		
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	First meeting with supervisor	▨																		
2	FYP briefing	▨																		
3	Understanding/analyze the topic		▨																	
4	FYP 2nd briefing		▨																	
5	Preliminary research work		▨	▨																
6	Submission of preliminary report				▨															
7	Project work/ Further research				▨	▨	▨	▨												
8	Meeting with FYP Coordinator					▨														
9	Submission of progress report							▨												
10	Project work continue/Analyze research findings									▨	▨	▨								
11	Decision making/specification on solution or design										▨	▨								
12	Document design process											▨	▨	▨	▨					
13	Submission of dissertation draft											▨								
14	Submission of dissertation final draft														▨					
15	Preparation for oral presentation															▨	▨			
16	Oral presentation																	▨		
17	Submission of hardbound copy of project dissertation																		▨	▨

APPENDIX F

SAMPLE OF CALCULATION

Calculation of permeability of pure gas components as a function of pore size

1. Insert the desired pore size range, rp (m)

$i := 2, 3 .. 40$

$rp_i := 0.1 \cdot 10^{-9} \cdot i$

2. Input the desired operation temperature (K) and pressure (atm)

$T := 300$

$P := 60$

3. Input the membrane properties:
ε - porosity, τ - tortuosity, tm - thickness, ρm - density

$\varepsilon := 0.272$

$\tau := 3.676$

$tm := 0.6 \cdot 10^{-6}$

$\rho m := 1140$

4. Input the properties of the gas components:
1 - Carbon dioxide, 2 - Methane, 3 - Nitrogen
M - Molecular weight (g/mol), Φ - diameter (m), Ω - Lennard-Jones Constant,
ΔH - Heat of adsorption (J/mol), f - equilibrium loading factor (m3/kg), z - compressibility factor
Ru - universal gas constant (cm3.atm/mol.K)

$M1 := 44.01$

$M2 := 16.043$

$M3 := 28.01$

$\Phi 1 := 3.3$

$\Phi 2 := 3.88$

$\Phi 3 := 3.667$

$\Omega 1 := 1.2988$

$\Omega 2 := 1.1361$

$\Omega 3 := 1.04$

$$\Delta H1 := -1711$$

$$\Delta H2 := -2100$$

$$\Delta H3 := -6793.$$

$$f := \frac{1}{\rho m}$$

$$f = 8.772 \times 10^{-4}$$

$$z1 := 0.982$$

$$z2 := 0.904$$

$$z3 := 0.997$$

$$Ru := 82.0$$

5. Input the viscosity, μ of gas components

$$\mu 1 := 2.6693\,10^{-5} \cdot \frac{\sqrt{M1 \cdot T}}{\Phi 1^{2} \cdot \Omega 1} \cdot \frac{100}{1000}$$

$$\mu 1 = 2.169 \times 10^{-5}$$

$$\mu 2 := 2.6693\,10^{-5} \cdot \frac{\sqrt{M2 \cdot T}}{\Phi 2^{2} \cdot \Omega 2} \cdot \frac{100}{1000}$$

$$\mu 2 = 1.083 \times 10^{-5}$$

$$\mu 3 := 2.6693\,10^{-5} \cdot \frac{\sqrt{M3 \cdot T}}{\Phi 3^{2} \cdot \Omega 3} \cdot \frac{100}{1000}$$

$$\mu 3 = 1.75 \times 10^{-5}$$

6. Calculate the permeability (mol.s/kg) of gas components due to viscous diffusion.

$$Pv1_i := \frac{\varepsilon\cdot\left(rp_i\right)^2\cdot\left(\frac{P+1.2}{2}\right)}{8\cdot\tau\cdot\mu1\cdot z1\cdot Ru\cdot T\cdot\left(\frac{1}{10^6}\right)}$$

$$Pv2_i := \frac{\varepsilon\cdot\left(rp_i\right)^2\cdot\left(\frac{P+1.2}{2}\right)}{8\cdot\tau\cdot\mu2\cdot z2\cdot Ru\cdot T\cdot\left(\frac{1}{10^6}\right)}$$

$$Pv3_i := \frac{\varepsilon\cdot\left(rp_i\right)^2\cdot\left(\frac{P+1.2}{2}\right)}{8\cdot\tau\cdot\mu3\cdot z3\cdot Ru\cdot T\cdot\left(\frac{1}{10^6}\right)}$$

$Pv1 =$

	0
0	0
1	0
2	$2.159\cdot10^{-14}$
3	$4.858\cdot10^{-14}$
4	$8.636\cdot10^{-14}$
5	$1.349\cdot10^{-13}$
6	$1.943\cdot10^{-13}$
7	$2.645\cdot10^{-13}$
8	$3.455\cdot10^{-13}$
9	$4.372\cdot10^{-13}$
10	$5.398\cdot10^{-13}$
11	$6.531\cdot10^{-13}$
12	$7.773\cdot10^{-13}$
13	$9.122\cdot10^{-13}$
14	$1.058\cdot10^{-12}$
15	$1.214\cdot10^{-12}$

$Pv2 =$

	0
0	0
1	0
2	$4.695\cdot10^{-14}$
3	$1.056\cdot10^{-13}$
4	$1.878\cdot10^{-13}$
5	$2.934\cdot10^{-13}$
6	$4.225\cdot10^{-13}$
7	$5.751\cdot10^{-13}$
8	$7.511\cdot10^{-13}$
9	$9.507\cdot10^{-13}$
10	$1.174\cdot10^{-12}$
11	$1.42\cdot10^{-12}$
12	$1.69\cdot10^{-12}$
13	$1.984\cdot10^{-12}$
14	$2.3\cdot10^{-12}$
15	$2.641\cdot10^{-12}$

$Pv3 =$

	0
0	0
1	0
2	$2.635\cdot10^{-14}$
3	$5.93\cdot10^{-14}$
4	$1.054\cdot10^{-13}$
5	$1.647\cdot10^{-13}$
6	$2.372\cdot10^{-13}$
7	$3.228\cdot10^{-13}$
8	$4.217\cdot10^{-13}$
9	$5.337\cdot10^{-13}$
10	$6.589\cdot10^{-13}$
11	$7.972\cdot10^{-13}$
12	$9.487\cdot10^{-13}$
13	$1.113\cdot10^{-12}$
14	$1.291\cdot10^{-12}$
15	$1.482\cdot10^{-12}$

7. Calculate the Knudsen diffusivity (m2/s)

$$Dk1_i := \frac{2}{3}\cdot\left(rp_i - \frac{0.33\cdot 10^{-9}}{2}\right)\cdot\sqrt{\frac{8\cdot 8.314\cdot 1000\, T}{3.142\, M1}}$$

$$Dk2_i := \frac{2}{3}\cdot\left(rp_i - \frac{0.38\cdot 10^{-9}}{2}\right)\cdot\sqrt{\frac{8\cdot 8.314\cdot 1000\, T}{3.142\, M2}}$$

$$Dk3_i := \frac{2}{3}\cdot\left(rp_i - \frac{0.364\cdot 10^{-9}}{2}\right)\cdot\sqrt{\frac{8\cdot 8.314\cdot 1000\, T}{3.142\, M3}}$$

Dk1 =

	0
0	0
1	0
2	$8.864\cdot 10^{-9}$
3	$3.419\cdot 10^{-8}$
4	$5.951\cdot 10^{-8}$
5	$8.484\cdot 10^{-8}$
6	$1.102\cdot 10^{-7}$
7	$1.355\cdot 10^{-7}$
8	$1.608\cdot 10^{-7}$
9	$1.861\cdot 10^{-7}$
10	$2.115\cdot 10^{-7}$
11	$2.368\cdot 10^{-7}$
12	$2.621\cdot 10^{-7}$
13	$2.874\cdot 10^{-7}$
14	$3.128\cdot 10^{-7}$
15	$3.381\cdot 10^{-7}$

Dk2 =

	0
0	0
1	0
2	$4.194\cdot 10^{-9}$
3	$4.614\cdot 10^{-8}$
4	$8.808\cdot 10^{-8}$
5	$1.3\cdot 10^{-7}$
6	$1.72\cdot 10^{-7}$
7	$2.139\cdot 10^{-7}$
8	$2.559\cdot 10^{-7}$
9	$2.978\cdot 10^{-7}$
10	$3.397\cdot 10^{-7}$
11	$3.817\cdot 10^{-7}$
12	$4.236\cdot 10^{-7}$
13	$4.656\cdot 10^{-7}$
14	$5.075\cdot 10^{-7}$
15	$5.495\cdot 10^{-7}$

Dk3 =

	0
0	0
1	0
2	$5.714\cdot 10^{-9}$
3	$3.746\cdot 10^{-8}$
4	$6.92\cdot 10^{-8}$
5	$1.009\cdot 10^{-7}$
6	$1.327\cdot 10^{-7}$
7	$1.644\cdot 10^{-7}$
8	$1.962\cdot 10^{-7}$
9	$2.279\cdot 10^{-7}$
10	$2.597\cdot 10^{-7}$
11	$2.914\cdot 10^{-7}$
12	$3.232\cdot 10^{-7}$
13	$3.549\cdot 10^{-7}$
14	$3.866\cdot 10^{-7}$
15	$4.184\cdot 10^{-7}$

8. Calculate the permeability of gas components (mol.s/kg) due to Knudsen diffusion

$$Pk1_i := \frac{\varepsilon \cdot \left(\dfrac{1}{\dfrac{1}{1.723 \cdot 10^{-5}} + \dfrac{1}{Dk1_i}} \right)}{z1 \cdot \tau \cdot Ru \cdot T \cdot \left(\dfrac{101325}{1 \cdot 10^{6}} \right)}$$

$$Pk2_i := \frac{\varepsilon \cdot \left(\dfrac{1}{\dfrac{1}{1.723 \cdot 10^{-5}} + \dfrac{1}{Dk2_i}} \right)}{z2 \cdot \tau \cdot Ru \cdot T \cdot \left(\dfrac{101325}{1 \cdot 10^{6}} \right)}$$

$$Pk3_i := \frac{\varepsilon \cdot \left(\dfrac{1}{\dfrac{1}{1.723 \cdot 10^{-5}} + \dfrac{1}{Dk3_i}} \right)}{z3 \cdot \tau \cdot Ru \cdot T \cdot \left(\dfrac{101325}{1 \cdot 10^{6}} \right)}$$

Pk1 =

	0
0	0
1	0
2	$2.676 \cdot 10^{-13}$
3	$1.03 \cdot 10^{-12}$
4	$1.791 \cdot 10^{-12}$
5	$2.55 \cdot 10^{-12}$
6	$3.306 \cdot 10^{-12}$
7	$4.06 \cdot 10^{-12}$
8	$4.812 \cdot 10^{-12}$
9	$5.561 \cdot 10^{-12}$
10	$6.309 \cdot 10^{-12}$
11	$7.054 \cdot 10^{-12}$
12	$7.797 \cdot 10^{-12}$
13	$8.538 \cdot 10^{-12}$
14	$9.277 \cdot 10^{-12}$
15	$1.001 \cdot 10^{-11}$

Pk2 =

	0
0	0
1	0
2	$1.375 \cdot 10^{-13}$
3	$1.509 \cdot 10^{-12}$
4	$2.873 \cdot 10^{-12}$
5	$4.231 \cdot 10^{-12}$
6	$5.583 \cdot 10^{-12}$
7	$6.928 \cdot 10^{-12}$
8	$8.266 \cdot 10^{-12}$
9	$9.599 \cdot 10^{-12}$
10	$1.092 \cdot 10^{-11}$
11	$1.224 \cdot 10^{-11}$
12	$1.356 \cdot 10^{-11}$
13	$1.486 \cdot 10^{-11}$
14	$1.616 \cdot 10^{-11}$
15	$1.746 \cdot 10^{-11}$

Pk3 =

	0
0	0
1	0
2	$1.699 \cdot 10^{-13}$
3	$1.112 \cdot 10^{-12}$
4	$2.05 \cdot 10^{-12}$
5	$2.985 \cdot 10^{-12}$
6	$3.917 \cdot 10^{-12}$
7	$4.845 \cdot 10^{-12}$
8	$5.769 \cdot 10^{-12}$
9	$6.691 \cdot 10^{-12}$
10	$7.609 \cdot 10^{-12}$
11	$8.523 \cdot 10^{-12}$
12	$9.435 \cdot 10^{-12}$
13	$1.034 \cdot 10^{-11}$
14	$1.125 \cdot 10^{-11}$
15	$1.215 \cdot 10^{-11}$

9. Calculate the surface diffusivity (m2/s)

$$Ds1 := \frac{1.62 \cdot 10^{-2}}{1 \cdot 10^{4}} \cdot 2.712^{\frac{(-0.45)\cdot(-\Delta H1)}{8.314 \cdot T}}$$

$$Ds2 := \frac{1.62 \cdot 10^{-2}}{1 \cdot 10^{4}} \cdot 2.712^{\frac{(-0.45)\cdot(-\Delta H2)}{8.314 \cdot T}}$$

$$Ds3 := \frac{1.62 \cdot 10^{-2}}{1 \cdot 10^{4}} \cdot 2.712^{\frac{(-0.45)\cdot(-\Delta H3)}{8.314 \cdot T}}$$

$$Ds1 = 7.439 \times 10^{-8}$$

$$Ds2 = 3.697 \times 10^{-8}$$

$$Ds3 = 4.769 \times 10^{-7}$$

10. Calculate the permeability of gas components (mol.s/kg) due to surface diffusivity.

$$Ps1_i := \frac{2 \cdot \varepsilon^2 \cdot tm \cdot (1-\varepsilon) \cdot Ds1 \cdot \rho m \cdot f}{z1 \cdot \tau^2 \cdot Ru \cdot T \cdot rp_i \cdot \left(\frac{101325}{1 \cdot 10^6}\right)}$$

$$Ps2_i := \frac{2 \cdot \varepsilon^2 \cdot tm \cdot (1-\varepsilon) \cdot Ds2 \cdot \rho m \cdot f}{z2 \cdot \tau^2 \cdot Ru \cdot T \cdot rp_i \cdot \left(\frac{101325}{1 \cdot 10^6}\right)}$$

$$Ps3_i := \frac{2 \cdot \varepsilon^2 \cdot tm \cdot (1-\varepsilon) \cdot Ds3 \cdot \rho m \cdot f}{z3 \cdot \tau^2 \cdot Ru \cdot T \cdot rp_i \cdot \left(\frac{101325}{1 \cdot 10^6}\right)}$$

Ps1 =

	0
0	0
1	0
2	$7.261\cdot10^{-10}$
3	$4.841\cdot10^{-10}$
4	$3.631\cdot10^{-10}$
5	$2.904\cdot10^{-10}$
6	$2.42\cdot10^{-10}$
7	$2.075\cdot10^{-10}$
8	$1.815\cdot10^{-10}$
9	$1.614\cdot10^{-10}$
10	$1.452\cdot10^{-10}$
11	$1.32\cdot10^{-10}$
12	$1.21\cdot10^{-10}$
13	$1.117\cdot10^{-10}$
14	$1.037\cdot10^{-10}$
15	$9.681\cdot10^{-11}$

Ps2 =

	0
0	0
1	0
2	$3.918\cdot10^{-10}$
3	$2.612\cdot10^{-10}$
4	$1.959\cdot10^{-10}$
5	$1.567\cdot10^{-10}$
6	$1.306\cdot10^{-10}$
7	$1.119\cdot10^{-10}$
8	$9.795\cdot10^{-11}$
9	$8.707\cdot10^{-11}$
10	$7.836\cdot10^{-11}$
11	$7.124\cdot10^{-11}$
12	$6.53\cdot10^{-11}$
13	$6.028\cdot10^{-11}$
14	$5.597\cdot10^{-11}$
15	$5.224\cdot10^{-11}$

Ps3 =

	0
0	0
1	0
2	$4.585\cdot10^{-9}$
3	$3.056\cdot10^{-9}$
4	$2.292\cdot10^{-9}$
5	$1.834\cdot10^{-9}$
6	$1.528\cdot10^{-9}$
7	$1.31\cdot10^{-9}$
8	$1.146\cdot10^{-9}$
9	$1.019\cdot10^{-9}$
10	$9.169\cdot10^{-10}$
11	$8.336\cdot10^{-10}$
12	$7.641\cdot10^{-10}$
13	$7.053\cdot10^{-10}$
14	$6.55\cdot10^{-10}$
15	$6.113\cdot10^{-10}$

11. Calculate the total permeability of gas components (mol.s/kg).

$$Pt1_i := Pv1_i + Pk1_i + Ps1_i$$

$$Pt2_i := Pv2_i + Pk2_i + Ps2_i$$

$$Pt3_i := Pv3_i + Pk3_i + Ps3_i$$

Pt1 =

	0
0	0
1	0
2	$7.264\cdot10^{-10}$
3	$4.851\cdot10^{-10}$
4	$3.649\cdot10^{-10}$
5	$2.931\cdot10^{-10}$
6	$2.455\cdot10^{-10}$
7	$2.118\cdot10^{-10}$
8	$1.867\cdot10^{-10}$
9	$1.674\cdot10^{-10}$
10	$1.521\cdot10^{-10}$
11	$1.397\cdot10^{-10}$
12	$1.296\cdot10^{-10}$
13	$1.212\cdot10^{-10}$
14	$1.141\cdot10^{-10}$
15	$1.08\cdot10^{-10}$

Pt2 =

	0
0	0
1	0
2	$3.92\cdot10^{-10}$
3	$2.628\cdot10^{-10}$
4	$1.99\cdot10^{-10}$
5	$1.612\cdot10^{-10}$
6	$1.366\cdot10^{-10}$
7	$1.194\cdot10^{-10}$
8	$1.07\cdot10^{-10}$
9	$9.762\cdot10^{-11}$
10	$9.046\cdot10^{-11}$
11	$8.49\cdot10^{-11}$
12	$8.055\cdot10^{-11}$
13	$7.712\cdot10^{-11}$
14	$7.444\cdot10^{-11}$
15	$7.234\cdot10^{-11}$

Pt3 =

	0
0	0
1	0
2	$4.585\cdot10^{-9}$
3	$3.058\cdot10^{-9}$
4	$2.294\cdot10^{-9}$
5	$1.837\cdot10^{-9}$
6	$1.532\cdot10^{-9}$
7	$1.315\cdot10^{-9}$
8	$1.152\cdot10^{-9}$
9	$1.026\cdot10^{-9}$
10	$9.252\cdot10^{-10}$
11	$8.429\cdot10^{-10}$
12	$7.745\cdot10^{-10}$
13	$7.168\cdot10^{-10}$
14	$6.675\cdot10^{-10}$
15	$6.249\cdot10^{-10}$

12. Plot the graphs of permeability due to each diffusivity and total permeability against the pore size for every gas components.