CERTIFICATION OF APPROVAL

Mass Transfer Modelling for Compact Hybrid Membrane-Absorption Processes in Removal of CO_2 from Natural Gas

by

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A Project Dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirements for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

MAY, 2004

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May, 2004

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 original work contained herein have not been undertaken or done by unspecified sources of person.

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ABSTRACT

The removal CO_2 from natural gas has been the target for many gas processing industries. This is due to its importance for increasing the calorific value of natural gas (NG) and increasing the pipeline lifetime since CO_2 is having corrosive properties.

The main objective of this work is to model and predict the mass transfer for the compact hybrid membrane-absorption processes. A simulation model was developed using MathCad which able to predict the CO_2 transport across membrane, followed by absorption to amine solution.

The overall mass transfer coefficient at the membrane and liquid side was analyzed by varying the operating parameters such as the pressure and the temperature of the process. The membrane characteristics such as the pore size, membrane thickness, porosity and tortuosity are also considered in studying the mass transfer of CO_2. The significant value of overall mass transfer coefficient in the study signifies and shows that separation is very favourable for compact hybrid system.

Generally, the overall mass transfer coefficient for the compact hybrid membrane-absorption processes was found to decrease as the operating temperature increased. The overall mass transfer coefficient increases when the operating pressure increased. However, the increase in membrane thickness would reduce the overall mass transfer coefficient. In addition, when the porosity of the membrane increases, the overall mass transfer coefficient gradually increased. Lastly, the best operating condition for the compact hybrid membrane-absorption processes is in the region of low temperature between 300K and 400K and in the region of high pressure between 10 bar to 30 bar. In this range, the magnitude of the overall mass transfer coefficient is in the magnitude of 10^{-6} which is comparable with other researchers work such as the study and model developed by Li and Teo (1996).

ACKNOWLEDGEMENT

Upon the completion of this dissertation, I had received numerous assistance, help and guidance from various parties directly or indirectly in fulfilling the requirement for the Final Year Research Project. Thus appreciation and acknowledgement are conveyed to the person as mentioned below.

Sincere appreciation to my supervising lecturer, Dr. Hilmi Mukhtar for his guidance, advices and expertise that had been contributed during the period of the project. Besides that, his reminder and help had kept the project on the right track and ensuring that the project will finish in the specified period of time. Next, a lot of thanks to the coordinator of the Final Year Research Project especially to Puan Anis Suhaila Shuib and Ms. Nor Yuliana Yuhana for giving their full commitment and support throughout the project. With their responsibility, the author I managed to keep updates on the project and finished every report on the designated date.

Special thanks to Ms. Nun Zuraini Zailani who has provided me with valuable information regarding the membrane technology which had been studied by them before. Without their references, the project would not be completed. Not forgetting the author's colleague, Ms. Alia Najiah Alias who had given encouragement and guide throughout the project by giving and sharing information regarding the membrane technology.

Lastly, I would also like to acknowledge and appreciate others which are not named here for their support, help and guide in finishing this dissertation and project.

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GLOSSARY AND TERMINOLOGY

Absorption
A process where a gas mixture is contacted with a liquid solvent to selectively dissolve one or more components by mass transfer from the gas into liquid.

Compact hybrid
The combination of membrane permeation and amine absorption processes.

Diffusion
The process of dispersion and spreading of molecules from bulk gas or liquid into a medium of separation for example, a membrane.

Mass transfer
The movement of mass or molecules from one point to another due to concentration difference or gradient.

Mass transfer coefficient
The number of moles component or molecules transported due to concentration gradient over a series of resistance.

Membrane resistance
The restriction in movement of molecules due to the porosity and tortuosity of the membrane.

Overall mass transfer coefficient

The total number of moles component or molecules transported due to concentration gradient over a series of resistance namely gas, membrane and liquid.

Permeability

The rate of flow of gas or liquid through a porous material for example, a membrane.

Pore

The opening which allows the transfer of molecules which is smaller than the pore diameter across the membrane.

Pore size

The pore radius of the membrane (noted as r_p and in nanometer)

Porosity

The ratio of number of pores per unit square area of a membrane (values between 0 and 1)

Selectivity

The property of a membrane which has a tendency to separate towards one type of gas or liquid compared to another.

Thickness

The distance between the high pressure side and the low pressure side of a membrane.

Tortuosity

The ratio between the pore length and the membrane thickness (values larger than 1)

Voidage

The ratio between the distances of pores per unit square of area (values between 0 and 1)

ABBREVIATIONS AND NOMENCLATURES

D_V	Viscous diffusion for species of gas i	$[m^2.s^{-1}]$
$\overline{P}$	Average pressure in membrane pore	$[kg.m^{-1}.s^{-2}]$
r_P	Pore radius	$[m]$
μ	Viscosity	$[kg.m^{-1}.s^{-1}]$
D_K	Knudsen diffusion for species gas i	$[m^2.s^{-1}]$
$r_{g,A}$	Gas A radius	$[m]$
R	Universal gas constant	$[cm^3.atm.mol^{-1}.K^{-1}]$
T	Temperature	$[K]$
M_A	Molecular weight	$[g.mol^{-1}]$
D_B	Bulk diffusion for species gas i	$[m^2.s^{-1}]$
υ	Volume diffusion of atom and structure	$[-]$
D_S	Surface diffusion for species gas i	$[m^2.s^{-1}]$
ΔH_{ads}	Specific enthalpy difference of adsorption	$[kJ.mol^{-1}]$
m	Number of moles	$[g.gmol^{-1}]$
t_m	Membrane thickness	$[m]$
P_i	Permeability for species gas i	$[mol.s^{-1}][m][m^{-2}][atm^{-1}]$
ε	Porosity of membrane	$[-]$
z	Compressibility factor	$[-]$
τ	Tortuosity	$[-]$
D_g	Gas diffusion	$[m^2.s^{-1}]$
D_B	Bulk diffusion for species gas i	$[m^2.s^{-1}]$
D_V	Viscous diffusion for species of gas i	$[m^2.s^{-1}]$
ρ_M	Membrane density	$[kg.m^{-3}]$
f	Equilibrium loading factor	$[m^3.kg^{-1}]$
H_A	Henry's law constant	$[atm.m^3.mol^{-1}]$
D_A	Diffusion coefficient of gas A	$[m^2.s^{-1}]$
C_A	Concentration of gas A absorbed in liquid	$[mol.m^{-3}]$
k	Rate constant	$[m^3.mol^{-1}.s^{-1}]$

p^*_A	Partial pressure of gas A at equilibrium	[kg.m^{-1}.s^{-2}]
C^*_A	Concentration of gas A at equilibrium	[mol.m^{-3}]
K_{AG}	Overall mass transfer coefficient	[mol.s^{-1}.m^{-2}.atm^{-1}]
k_{AG}	Mass transfer coefficient on gas side	[mol.s^{-1}.m^{-2}.atm^{-1}]
k_{AM}	Mass transfer coefficient on membrane side	[mol.s^{-1}.m^{-2}.atm^{-1}]
k_{AL}	Mass transfer coefficient on liquid side	[m.s^{-1}]
$\left(\frac{P}{\delta}\right)$	Specific gas permeability	[mol^{-1}.s.m.atm]
d_o	Outer diameter of hollow fibre	[m]
Z	Hollow fibre length	[m]
Δp	Pressure difference across the membrane	[kg.m^{-1}.s^{-2}]

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural gas and oil generates huge quantities of carbon dioxide (CO_2) when it is used for industrial and domestic heating. Emission of CO_2 from these sources is regarded as the most serious potential cause of environmental problem such as global warming and acid rain. Li and Teo (1997) explained that in order to utilize these fuel gases for chemical processing and energy generation, elimination and limitation of emissions of CO_2 and other greenhouse gases are the current main objectives for all environmental organizations.

The most common process for the removal of CO_2 from the natural gas stream is gas absorption using a conventional absorption column such as packed or plate columns. An aqueous solution such as sodium hydroxide, sodium carbonate or amine derived solution such as monoethanolamine (MEA) or diethanolamine (DEA) is often employed. They are used not only to absorb CO_2, but also to react with the acidic CO_2 in order to increase the absorption rate and capacity.

In addition to the conventional absorption process for CO_2 removal, the use of membrane technology is also an attractive alternative. Li and Teo (1997) discussed that although recently discovered, membrane separation has many advantages due to the properties of the membrane which can be used as separation unit. In the former case, CO_2 removal is achieved due to the intrinsic selectivity of the membrane between CO_2 and other gases. In the latter case, CO_2 removal is accomplished by the gas absorption where the membranes, usually microporous, hydrophobic and highly-selective are employed as fixed interface of mass transfer. Thus by removing the CO_2 content, the treated gas can comply with the pipelines specifications right at the well head to meet typical Gas PETRONAS pipeline specifications such as < 2 mol % CO_2. Below is the typical pipeline composition of natural gas:

Table 1.0: Pipeline Composition of Natural gas

(Reference: GPP, 22 November 2003)

Component	**Typical Analysis (mole %)**	**Range (mole %)**
Methane	94.9	87.0 – 96.0
Ethane	2.5	1.8 – 5.1
Propane	0.2	0.1 – 1.5
i-Butane	0.03	0.01 – 0.3
n-Butane	0.03	0.01 – 0.3
i-Pentane	0.01	Trace – 0.14
n-Pentane	0.01	Trace – 0.04
Nitrogen	1.6	1.3 – 5.6
Carbon Dioxide	0.7	0.1 – 1.0
Oxygen	0.02	0.01 – 0.1
Hydrogen	Trace	Trace – 0.02
Hydrogen Sulphide	5 vol %	0 – 5 vol %

By having the compact hybrid membrane-absorption processes in removal of CO_2, the effectiveness and reliability of the separation process is increased. Falk-Pedersen (2000) discussed that currently, both separation technology are implemented as hybrid where the amine absorption is integrated together with the membrane permeation. The advancement in this technology further help in increasing the productivity of gas processing industry.

There are many advantages when using compact hybrid membrane-absorption processes in the industry. First it helps to increase the productivity of plant production by reducing the time to remove CO_2 from the natural gas. Besides that, it saved capital expenditure by removing the cost to install two units at the same time by having only to install one unit of hybrid membrane-absorption processes. Next, the system is robust and reliable since it is using membrane which is considered the preferred medium of separation in the future. Lastly, the advancement in the hybrid membrane-absorption processes is tangible and flexible because it can be used in many applications. However, all these advantages are clouded by a few disadvantages that it poses in the industry. The impurities content in the natural gas may affect the performance of the membrane. This is due to the nature of membrane being porous which can induce the permeation of impurities into the system. Besides that, the system needs to have reliable control system in order to ensure the operation of the hybrid membrane-absorption processes goes well.

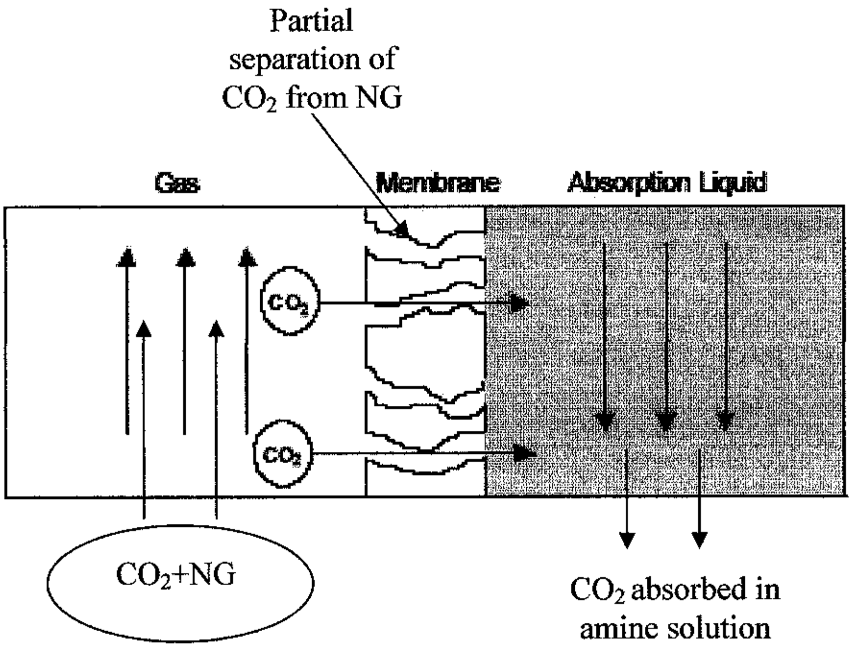


Figure 1.0: Membrane and amine separation system in CO_2 removal

(Reference: www.medal.liquide.com)

1.2 Problem Statement

The effective purification of high CO_2 concentration from natural gas poses challenge for technology providers. The absence of suitable single solvent for absorption high CO_2 concentration up to 60% attracts end user for an alternative membrane processes. Proposed hybrids processes consist of membrane modules followed by amine absorption bring an alternative for dealing with high CO_2 concentration. However, these processes impose some operational constraints such as large surface area and logistics area. Consequently, the compact hybrid membrane-absorption processes is chosen in this study.

The compact hybrid membrane-absorption processes for the removal of CO_2 from the natural gas focus on the study of mass transfer calculation, modelling and analyzing its operating parameters. The operating conditions that can be manipulated include the pressure and the temperature of the separation process will be analyzed. The aim for the study is to calculate and obtain the mass transfer coefficient for the compact hybrid membrane-amine absorption processes.

The separation of CO_2 from natural gas using compact hybrid membrane-absorption processes requires the detailed study of the mass transfer mechanism through the membrane as well as the CO_2 absorption process in amine solution. The problem statement above identifies the key tasks in which the topic is concerned which are to predict, model and calculate the mass transfer coefficient of the hybrid processes as well as to know the relationship between the mass transfer coefficients with the relevant operating parameters. By studying the above topic, the improvement in separation system is greatly achieved. The compact hybrid membrane-absorption processes will reduce the cost in implementing separate system thus reducing the capital investment as well as maintenance cost in long term. Besides that, it also signifies the advancement in chemical engineering technology which will help and assist the industrial world.

1.3 Objective and Scope of Study

The main objectives of the study are:

1.3.1 To model the mass transfer of CO_2 from natural gas in membrane by manipulating operating parameters such as the temperature and a pressure using MathCad for the membrane-absorption processes. Besides that, the membrane properties are also manipulated such as the pore size, porosity and the tortuosity.

1.3.2 To model the mass transfer of CO_2 from natural gas in amine absorption in combination with membrane separation (compact hybrid) by manipulating operating parameters such as the temperature and a pressure using MathCad.

The scopes of the study are:

1.3.3 Deriving and manipulating mathematical equations which are related to the mass transfer in membrane separation and amine absorption in order to model the processes without having to conduct experimental work.

1.3.4 Conducting mass transfer modelling using the developed mathematical equations to obtain the results for the compact hybrid membrane-absorption processes.

1.4 Relevancy of Project

Although a few established organization and institution had already done researches on the compact hybrid membrane-absorption process, their scope of study was basically experimental work on a laboratory scale. The experiments also suggest that only limited parameters can be studied at one time. Thus, experimental work is arduous and time consuming. There is an alternative which is the usage of mathematical modelling by using the established equations as mean to conduct the study. From this technique, an approximation can be obtained in order to justify the implementation and usage of compact hybrid membrane-amine absorption processes.

1.5 Feasibility of Project within the Scope and Time Frame

The project is considered feasible given the limited scope of study and time frame of which the project needs to be finished and finalized. In addition, with sufficient resources, information, consultations and help from many parties, the project is into its way in achieving all the objectives. Continuous effort shall be put forward in undertaking this project to ensure that the scope is fully completed in the given time.

CHAPTER 2

LITERATURE REVIEW

2.1 Principles and Fundamentals Aspect of Membrane Separation

A membrane is simply a synthetic barrier which prevents the transport of certain components based on various characteristics. Membranes are very diverse in nature with the one unifying theme to separate. Membrane can be liquid or solid, homogeneous or heterogeneous and can have range in thickness. They are manufactured to be electrically neutral, positive, negative or bipolar.

Membrane separation is currently one of the most innovative and rapidly growing fields across science and engineering. Membrane gas separation is a relatively straightforward process concept. Seader and Henley (1998) explained that it is concentration driven process which is directly related to pressure of the feed and permeate stream. A typical gas separation is shown in Figure 2.0. For example, natural gas is separated into methane and carbon dioxide components by passing the feed stream across a membrane surface.

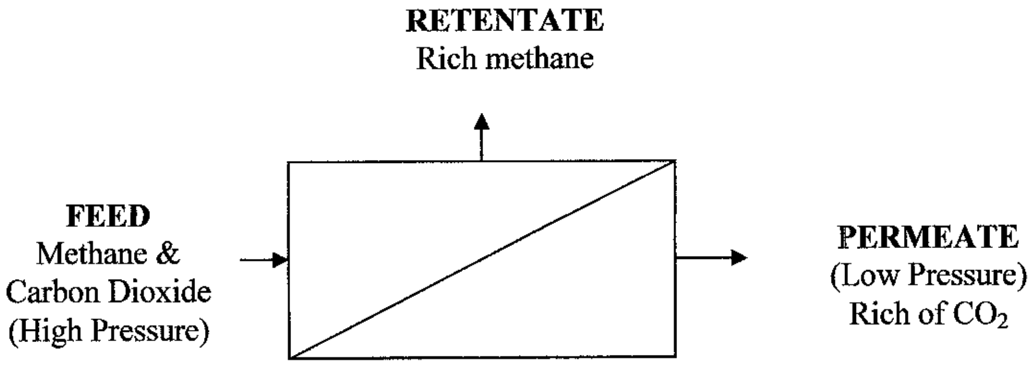


Figure 2.0: Basic principle of gas permeation.

Strathmann (2001) discussed that types of membrane used today include nonporous (dense) and porous polymers, ceramic and metal films with symmetric or asymmetric structures, liquid films with selective carrier components and electrically charged barriers. The performance of a membrane is determined by several key properties: high selectivity and permeability, mechanical stability under the process operating conditions and low maintenance with a good space efficiency. These factors are summarized for some important gas separation applications in Table 2.0:

Table 2.0: Module design used for various gas separation applications (References: Seader, Henley, 1998)

Application	**Typical membrane material**	**Selectivity, α**	**Pressure-normalized flux [$10^6 cm^3$(STP)/cm^2. s.cmHg]**	**Module design typically used**
H_2S/CH_4	Polyamide	6 – 7	1	Hollow-fibre
H_2/N_2	Polysulfone	100	1	Hollow-fibre
CO2/CH_4	Cellulose Acetate	15 – 20	2	Hollow-fibre or spiral
VOC/N_2	Silicone Rubber	10 – 30	100	Spiral
H_2O/Air	Hydrophilic Rubber	> 200	5	Capillary bore side feed

2.2 Principles and Fundamentals Aspect of Absorption Process

In absorption (also called gas absorption, gas scrubbing and gas washing), a gas mixture is contacted with a liquid (absorbent or solvent) to selectively dissolve one or more components by mass transfer from the gas to the liquid. The components transferred to liquid are referred as solutes or absorbate. Absorption is used to separate gas mixtures, remove impurities, contaminants, pollutants or catalyst poison from gas or recover valuable chemicals. Currently, absorption is widely implemented in gas processing plant as well as refinery complexes. The flexibility in absorption process by using various types of solvent makes the

Table 2.1: Different types of amine absorbent and its application (References: www.chemicalland21.com)

Amine Solution	**Usage and properties**
DEA	Neutralizing acid gases to make them non-irritating
MDEA	Scrubbing H2S and CO2 from petroleum gas stream as well as dispersing agent and corrosion inhibitor
MEA	Scrubbing H2S and CO2 from petroleum gas stream
DIPA	Absorbent for acid gas in refinery of natural gas and purification of ammonia
DGA	Mainly used in gas scrubbers
TEA	Soluble in water and in low alkalinity solution

2.3 Supporting Information from Other Studies.

Membrane-absorption processes have been gained an increasing attention since 1980s. However, with the founding of new technique such as the compact hybrid membrane-absorption in the 1990s, it had changed the perspective of separation method in gas processing industry. This separation technology is also known as gas-liquid separation. Work from Yang and Cussler (1986), Cooney and Jackson (1989), Ahmed and Semmens (1992) and the latest by Li, Tai and Teo (1994) had been very encouraging and further developed in years to come. Their work is basically experimental that involved different interpretations of gas-liquid system and mechanism that governs behind them.

Many significant works comes from National University of Singapore, Department of Chemical Engineering. In Li, Tai and Teo (1994) work, they emphasized on the usage of ultrathin skinned hollow fibre membrane module with concentrated alkaline solution system. The results were encouraging but with limitations. The experiment did not manipulate other factors that contribute to the results of the gas-liquid system such as the membrane thickness, number of membrane modules, different types of solvent and membrane system and others.

Only a few works such as the Use of Permeation and Absorption Methods for CO_2 Removal in Hollow Fibre Membrane Modules by Li and Teo (1997) have studied the effect of different modules physical characteristic such as number of fibre bundles, inner and outer diameter. Their work is based on the experimental and simulation comparison using MathCad. Their significant founding is important in modelling the gas-liquid separation system especially in hybrid membrane-absorption processes.

2.4 Transport Mechanism across Membrane

There are three main general transport mechanism used to describe gas transport across membrane: Knudsen diffusion, viscous diffusion and surface diffusion. Knudsen diffusion is achieved when the mean free path of the molecules are large relative to the membrane pore radius. The separation factor for Knudsen diffusion is based on the inverse square root ratio of two molecular weights, assuming the gas mixture consist of only two types of molecules. The process is limited to system with large values of molecular weight ratio. Due to their low selectivity, Knudsen diffusion membrane is not commercially attractive.

The viscous diffusion mechanism describes the ideal condition for the separation of vapour compounds of different molecular sizes through a porous membrane. Smaller molecules have the highest diffusion rates. This type of diffusion can happen only with sufficient driving force. In other words, the upstream partial pressure of the 'faster' gas should be higher than the downstream partial pressure.

Surface diffusion is the third contributor in gas permeation that can occur in small pore diameter membranes. Adsorption on the small pore becomes noticeable when the pore diameter drops below 10Å. At this diameter, the surface area of the pore walls is about 100 m^2/cm^3 of the specific material.

2.5 Compact Hybrid Membrane-Absorption Model

The compact hybrid membrane-absorption model that will be used thoroughly in this study is the hollow fibre module with dense ultrathin skinner layer. This dense outer layer prevents from amine solution leeching into the microporous membrane structure to ensure that no absorption process happen prior to membrane separation. Besides that, it provides a wetted wall condition to enhance and promote absorption process at the amine solution side. The typical compact hybrid amine-absorption module has the feed gas entering into the module on the tube side while the amine solution flows counter currently at the shell side of the module. The component which is going to be separated will permeates into the membrane and later absorbed by the amine solution. The rich amine solution is then send to downstream equipment for the recovery of solute absorbed. Meanwhile, the treated gas will then used for other purposes. The schematic of the process is shown below:

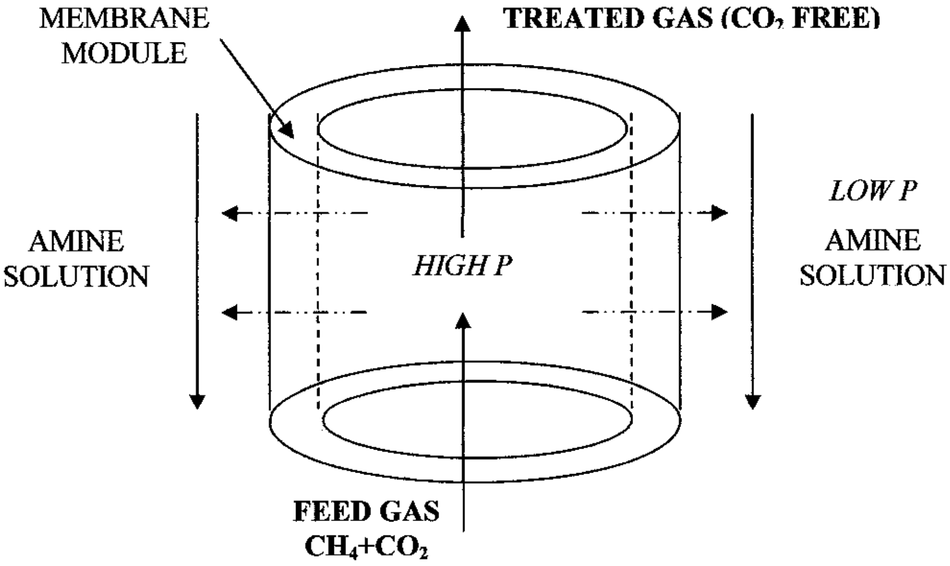


Figure 2.2: Typical membrane amine separation process system

It is required to remove CO_2 from the natural gas stream by using the compact hybrid membrane-absorption processes. The separation process can be viewed in two perspectives: the membrane only system and the compact hybrid membrane-absorption processes.

In membrane system, the separation is based on the permeation mechanism as the main mass transfer factor in separation and removing CO_2 from the natural gas. CO_2 which travels faster that natural gas will permeates into the membrane thus removed from the bulk natural gas volume. In this system, the driving force of separation is the difference in pressure on both sides of the membrane. The feed side pressure needs to be higher in order for the separation to occur. The membrane used in this study is 2-polyether-polyamide copolymers (trade name PEBAX). The physical properties of the membrane are shown below:

Table 2.2: Physical properties of PEBAX membrane.

Membrane	**Pore size, rp**	**Thickness, tm**	**Tortuosity, τ**	**Porosity ξ**	**Compressibility factor, z**
PEBAX	4nm	5μm	3.676	0.272	0.9685

However, there is a difference when we take into account the effect of compact hybrid membrane-absorption processes. The system is using absorption mechanism through the reaction between the amine solution and CO_2. The overall effect is referred to as mass transfer coefficient. There are three terms which can be considered as important: the mass transfer coefficient of CO_2 in gas, the mass transfer coefficient of CO_2 in membrane and the mass transfer coefficient due to the absorption in liquid phase. These three terms is also called the overall mass transfer coefficient, K_{AG}. In other words, each of this term makes the individual resistance of CO_2 in gas phase, membrane and liquid phase respectively.

Both of the system have similar operation but different in operating parameters. Thus, each of the system has its own special governing modelling equations which can be manipulated and utilized. It is easy to conduct such study if sufficient information is gathered. Algorithms are developed to establish a structural and step by step method to study the mass transfer of membrane-absorption process. After that, modelling can be done by coding the respective algorithm into MathCad software. In the end, the result of different manipulation in the system can be obtained graphically which is tangible and observable.

The amine absorption process is a part of the main function in the compact hybrid membrane-absorption processes. The absorption process is using monoethanolamine (MEA) solvent as the absorbent. Basically the mass transfer of CO_2 gas will occur in the liquid film of MEA after being permeated through the membrane. In addition, CO_2 solubility and solution speciation were simulated by six equilibrium reactions. Hongyi Dang (2001) experimented in the vapour-liquid equilibrium (VLE) model, one phase equilibrium and five chemical equilibria in the liquid phase were considered for CO_2/MEA/H2O system. The reactions are:

$$CO_2(aq) \xleftrightarrow{H_{CO_2}} CO_2(g) \tag{2.0}$$

$$2H_2O \xleftrightarrow{K_{H_2O}} H_3O^+ + OH^- \tag{2.1}$$

$$2H_2O + CO_2 \xleftrightarrow{K_{a,CO_2}} H_3O^+ + HCO_3^- \tag{2.2}$$

$$H_2O + HCO_3^- \xleftrightarrow{K_{a,HCO_3^-}} H_3O^+ + CO_3^{2-} \tag{2.3}$$

$$H_2O + MEAH^+ \xleftrightarrow{K_{a,MEA}} H_3O^+ + MEA \tag{2.4}$$

$$H_2O + MEA + CO_2 \xleftrightarrow{K_{MEACOO^-}} H_3O^+ + MEACOO^- \tag{2.5}$$

In the above reversible series of chemical reactions, only two main chemical equilibria are considered to be important which are 2.3, 2.4 and 2.5. In these series, water reacted with bicarbonate ions to produce reversibly hydronium ions and carbonate ions. Next, the effect of MEA reacted with CO_2 is observed where 2.4 shows the reaction between H_2O and MEA to produce hydronium ion. Later, the reversible reaction 2.5 between hydronium and $MEACOO^{-1}$ is the essential reaction which constitutes the liquid film reaction between CO_2 and MEA aqueous solution. So, the rate constant for the respective reaction, k_{MEA} (Hongyi Dang, 2001) is:

$$Log_{10}\left(0.001 x k_{MEA}\left(m^3.mole^{-1}.s^{-1}\right)\right) = 10.99 - \frac{2152}{T(K)} \tag{2.6a}$$

For MDEA, the rate constant for the respective reaction is:

$$Log_{10}\left(0.0023 x k_{MDEA}\left(m^3.mole^{-1}.s^{-1}\right)\right) = 15.01 - \frac{2204}{T(K)} \tag{2.6b}$$

Hongyi Dang (2001) considered these series of reactions are considered and assumed to be Pseudo First Order Reaction. After considering all the possible equations and reactions involved in membrane-absorption separation process, the final step is to put all the information together in the form of simplified process diagram. However, to simplify the task certain assumptions have to be made in order to make the task more realistic and easier. The assumptions are:

a) The mixture of gases in the feed stream is to be considered perfectly mixed.
b) Natural gas (CH_4) is non-permeable through the membrane pores.
c) The gases flow is counter currently with the amine solution.
d) The delta pressure (P) across the membrane is high enough to prevent from the amine solution permeating through the membrane pores at the liquid side.
e) The overall mass transfer coefficient of the process is independent of gas velocity indicating that the resistance of the gas film is negligible. (Li and Teo, 1996)

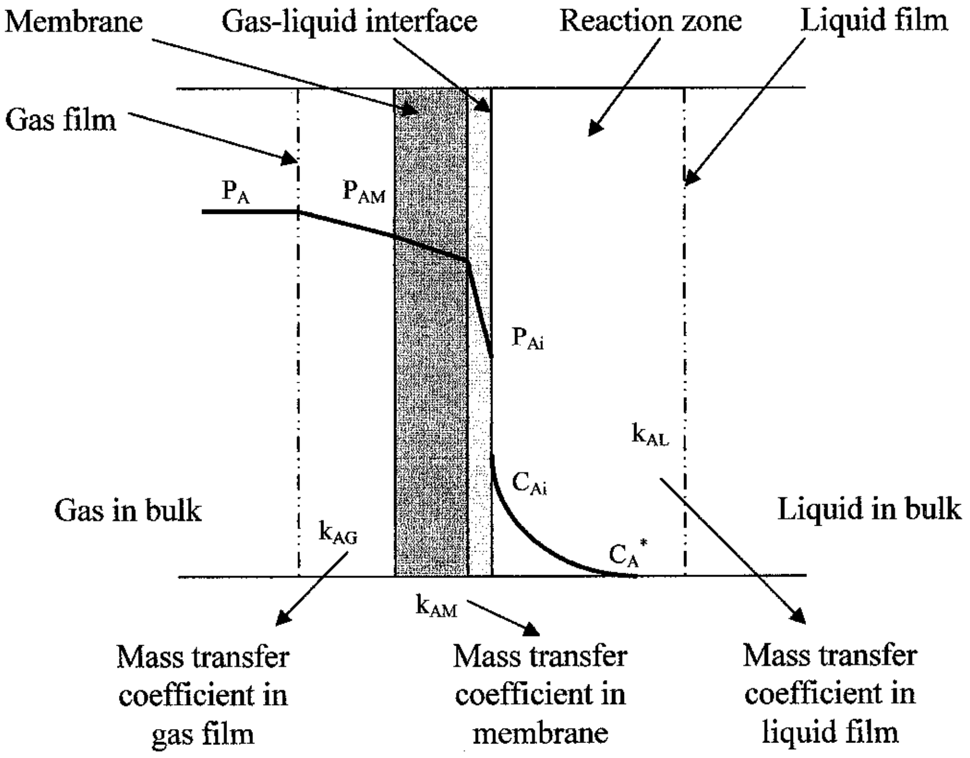


Figure 2.3: Membrane amine separation process concentration gradient profile

Finally, the simplified process diagram showing the concentration gradient of CO_2 across the gas film and membrane as well as the absorbed CO_2 across the liquid film is shown previously.

From Figure 2.3, it can be concluded that the concentration of CO_2 reduces after each resistance in the combination separation system. The resistances are the gas film, the membrane thickness and the liquid film. These resistances contribute highly in the reduction of CO_2 concentration in the feed stream. Because CO_2 permeates faster compared with natural gas, CO_2 is dominantly involved in the separation process.

2.6 Important modelling equations used.

The permeability of gas either pure gas (CH_4 and CO_2) of mixed gases across the membrane is determined using the permeability equations derived from the combination of viscous mechanism, Knudsen mechanism and diffusion mechanism as shown below:

For single species:

$$P = \frac{\varepsilon}{z\tau RT}\left\{\frac{\overline{P}r_P}{8\mu}\left[\left(\frac{1}{\frac{1}{D_i}+\frac{1}{D_K}}\right)+\frac{1}{\varepsilon}\left(D_S\rho_M f\right)\right]\right\} \qquad \textbf{(2.7a)}$$

For multispecies (subscript i indicates the gas species):

$$P_i = \frac{\varepsilon}{z\tau RT}\left\{\frac{\overline{P}r_P}{8\mu}\left[\left(\frac{1}{\frac{1}{D_{ii}}+\frac{1}{D_{Ki}}}\right)+\frac{1}{\varepsilon}\left(D_{S_i}\rho_M f\right)\right]\right\} \qquad \textbf{(2.7b)}$$

This equation constitutes all the three terms consecutively for the mechanism of permeation which are viscous, Knudsen and surface respectively. For further review and analysis, Equation 2.7 is further expanded and separated accordingly. They are referred as the General Gas Permeation Equation across Membrane

(Roslee, 2001). The individual expansion and equations for Equation 2.7 is further mentioned below.

2.6.1 Gas Permeation Equation across Membrane.

Viscous diffusion, $D_V = \frac{\bar{P} r_P}{8\mu}$ **(2.8)**

D_V = Viscous diffusion for species of gas i

$\bar{P}$ = Average pressure in membrane pore

r_P = Pore radius

μ = Viscosity

Knudsen diffusion, $D_K = \frac{2}{3}\frac{\left(r_P - r_{g,A}\right)}{3}\sqrt{\frac{8RT}{\Pi M_A}}$ **(2.9)**

D_K = Knudsen diffusion for species gas i

$r_{g,A}$ = Gas A radius

R = Universal gas constant

T = Temperature

M_A = Molecular weight

Bulk diffusion, $D_B = \frac{1x10^{-7} T^{1.75}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P\left(\upsilon_A^{1/3} + \upsilon_B^{1/3}\right)^2}$ **(2.10)**

D_B = Bulk diffusion for species gas i

υ = Volume diffusion of atom and structure

Surface diffusion, $D_S = 1.6x10^{-2} e\left[\frac{-0.45\left(-\Delta H_{ads}\right)}{mRT}\right]\left(\frac{t_m}{r_P}\right)$ **(2.11)**

D_S = Surface diffusion for species gas i

ΔH_{ads} = Specific enthalpy difference of adsorption

m = Number of moles

t_m = Membrane thickness

Permeability factor, $P_i = \frac{\varepsilon}{zRT\tau}$ **(2.12)**

P_i = Permeability for species gas i

ε = Porosity of membrane

z = Compressibility factor

τ = Tortuosity

Gas diffusivity, $D_g = \frac{1}{\frac{1}{D_K} + \frac{1}{D_B}}$ **(2.13)**

D_g = Gas diffusion

D_K = Knudsen diffusion for species gas i

D_B = Bulk diffusion for species gas i

Viscous permeability, $P_V = P_i D_V$ **(2.14)**

P_V = Permeability for species gas i

P_i = Permeability for species gas i

D_V = Viscous diffusion for species of gas i

Knudsen Permeability, $P_K = P_i D_g$ **(2.15)**

P_K = Permeability for species gas i

P_i = Permeability for species gas i

D_g = Gas diffusion

Surface Permeability, $P_S = P_i \frac{1}{\varepsilon} D_S \rho_M f$ **(2.16)**

Ps = Permeability for species gas i

ρ_M = Membrane density

f = Equilibrium loading factor

As mentioned, there are three general transport mechanism commonly used to describe gas separations using membrane which are Knudsen diffusion, viscous diffusion and surface diffusion. The separation factor from Knudsen is based on the inverse square root ratio of two molecular weights. The process is limited to systems with large values of molecular weight ratio. Knudsen diffusion is expressed in Equation 2.9. The viscous diffusion describes the ideal condition for the separation of vapour compounds of different molecular sizes through a porous membrane meanwhile, surface diffusion occurs in small pore diameter membrane. Both of the mechanism is expressed in Equations 2.8 and 2.11 respectively.

From these three equations, the permeability of the membrane is calculated using the expression in Equations 2.12, 2.14 through 2.16. Three of the equations describe the permeability caused by the different transport mechanisms which are Knudsen, viscous and surface. The fourth equation (Equation 2.12) relates the other three as a factor that effect the other permeability terms. Besides that, knowing that the separation occurs in large volume, the bulk diffusivity (gas) also needs to be identified by using the expression in Equation 2.13. The equation relates the molecular weight of both components improved as well as its volume diffusion of atom and structure. Then, it will be used in calculating the gas diffusivity as described in Equation 2.10. After obtaining all the above calculated value, all the terms will be a product that is expressed in Equation 2.7 which is called the General Gas Permeation Equation across Membrane.

From membrane permeation, CO_2 is then absorbed in the amine solution. The absorption process is actually the combination of reaction of CO_2 with the amine solution and the mass transfer of CO_2 molecules into the amine bulk solution volume. Thus, the liquid mass transfer coefficient is introduced to evaluate the effect of absorption onto the mass transfer of CO_2. The individual expansion and equations for absorption is further mentioned in the next point.

2.6.2 CO_2 Absorption in Amine Solution Liquid.

From Figure 2.3, the rate of CO_2 transfer can be, N_A (mol s^{-1}) at steady state can be expressed as:

$$\begin{aligned} N_A &= k_{AG}(p_A - p_{AM})A_M \\ N_A &= k_{AM}(p_{AM} - p_M)A_M \\ N_A &= k_{AL}(C_{Ai} - C_A)A_M \\ N_A &= K_{AG}(p_A - p^*{}_A)A_M \end{aligned} \qquad \textbf{(2.17)}$$

Where k_{AL}, k_{AM} and k_{AG} are the individual mass transfer coefficient in liquid film, membrane and gas film respectively, while A_M is the surface area of the membrane. The CO_2 partial pressure in equilibrium with the CO_2 concentration is given in terms of Henry's law:

$$p^*{}_A = H_A C^*{}_A \qquad \textbf{(2.18)}$$

H_A = Henry's constant

$p^*{}_A$ = Partial pressure of gas A at equilibrium

$C^*{}_A$ = Concentration of gas A at equilibrium

As the mass transfer of the gas through the gas film, the membrane and the liquid film are in series, the overall mass transfer coefficient, K_{AG} can be expressed as:

Overall mass transfer equation, $\frac{1}{K_{AG}} = \frac{1}{k_{AG}} + \frac{1}{k_{AM}} + \frac{H_A}{k_{AL}}$ **(2.19)**

K_{AG} = Overall mass transfer coefficient

k_{AG} = Mass transfer coefficient on gas side

k_{AM} = Mass transfer coefficient on membrane side

k_{AL} = Mass transfer coefficient on liquid side

Because the overall mass transfer coefficient of the process is independent of gas velocity, this indicates that the resistance of the gas film is negligible (Li and Teo, 1996) as stated in assumptions previously. So, Equation 2.19 can be simplified as:

$$\frac{1}{K_{AG}} = \frac{1}{k_{AM}} + \frac{H_A}{k_{AL}} \qquad \textbf{(2.20)}$$

The liquid mass transfer equation can also be expressed in term of its diffusivity and rate constant as shown in Equation 2.21. However, because the concentration of CO_2 in equilibrium and the solubility of CO_2 in amine solution is not available, Equation 2.21 is not applicable.

Liquid mass transfer term, $k_{AL} = \frac{H_A}{\sqrt{D_A C_A k}}$ **(2.21)**

k_{AL} = Mass transfer coefficient on liquid side (1.55×10^{-4} m.s^{-1} for MEA)

H_A = Henry's law constant

D_A = Diffusion coefficient of gas A

C_A = Concentration of gas A absorbed in liquid

k = Rate constant

Table 2.3: Amine solution constants (Reference: Hongyi Dang, 2001)

Solution	**$H_A \times 10^5$ (atm.m^3.mol^{-1})**	**D_A (m^2.s^{-1})**	**k (m^3.mol^{-1}.s^{-1})**
MEA	4.15	Equation 2.13	Equation 2.6a
MDEA	3.96	Equation 2.13	Equation 2.6b

Equations 2.17 through 2.21 are referred from Li and Teo (1996). In 1998, Li and Teo come up the latest form of Equation 2.20 with the inclusion of permeability of the membrane in the equation. The specific permeability of gases can be expressed as:

$$\left(\frac{P}{\delta}\right)=\left(\frac{N}{\pi d_o Z\Delta p}\right)\left(\frac{273.15}{T}\right) \qquad \textbf{(2.22)}$$

$\left(\frac{P}{\delta}\right)$ = Specific gas permeability

d_o = Outer diameter of hollow fibre

Z = Hollow fibre length

Δp = Pressure difference across the membrane

According to Li and Teo (1998), the overall mass transfer coefficient, K_{AG} can be expressed as:

$$\frac{1}{K_{AG}}=\left(\frac{\delta}{P}\right)_A+\frac{H_A}{k_{AL}} \qquad \textbf{(2.23)}$$

Where, the membrane mass transfer coefficient, k_{AM} is actually the inverse of the specific permeability of gas. The value of δ is the membrane thickness or the change in thickness of the membrane. The agreeable value of k_{AM} is in the magnitude of 10^{-6} according to the model done by Li and Teo (1996).

The objective of the study is to obtain this overall mass transfer coefficient, K_{AG} by manipulating the operating parameters which will affect the permeability or the membrane mass transfer coefficient. From the K_{AG} value, the characteristic of compact hybrid membrane-absorption processes in removing CO_2 from natural gas can be predicted and determined.

CHAPTER 3

METHODOLOGY

3.1 Procedure Identification

The methodology and procedure to conduct the research are:

3.1.1 Mathematical Equation and Modelling Development

After identifying all the required equations to be used, important operating parameters are determined. The equations involved are General Gas Permeation Equation across Membrane (Equation 2.7) together with its associated equations (Equations 2.8 through 2.16), the Overall Mass Transfer Coefficient equation which relates the reaction and absorption of CO_2 with the permeability of the membrane (Equations 2.22 and 2.23). A few examples of the respective operating parameters are temperature and the differential pressure across the membrane. The other parameters which are also studied are the membrane characteristic such as the pore size, thickness, porosity and tortuosity of the membrane.

These operating parameters are then manipulated in order to obtain the characteristic or the properties of the compact hybrid membrane-absorption processes. To obtain these relationships, all the equations are coded in MathCad software which then will calculate all the required variables for the analysis. The sample programming can be obtained from the Appendix 4. This procedure is also known as modelling. Before any modelling is done, an algorithm had to be developed to ensure that the procedure for the modelling in sequential and organized. Besides that, the algorithm will help to detect any miscalculation and mistakes just by referring to the flowcharts. The entire necessary and important algorithm is discussed later.

3.1.2 Modelling Results Analysis and Comparison

The output of the software is in the form of graphs and trends which is tangible and observable. From these graphical outputs, the result can be analyzed by observing the trends with respect to the manipulated operating parameters such as the pore size, porosity and tortuosity of the membrane, temperature and the differential pressure across the membrane. All the results can be obtained in next chapter, from Figures 4.0 through 4.14. There will be an increase in trend when the operating parameters increased and vice versa. From this relationship, the discussion can be derived from theoretical point of view. Comparison can also be made to differentiate certain operating parameters with another. All the results are discussed critically and any disagreement or argument with the theory will be addressed accordingly.

3.2 Tools: MATHCAD

The Mathcad product family allows individual engineers to calculate, graph, and communicate technical ideas in a unified, easy-to-use, visual format. MathCad is the industry standard for applying mathematics. Besides that, Mathcad is an integrated environment for performing and communicating math-related work. In addition, MathCad 2-D and 3-D graphing capabilities give you better insight into the work, and precise control over graphs.

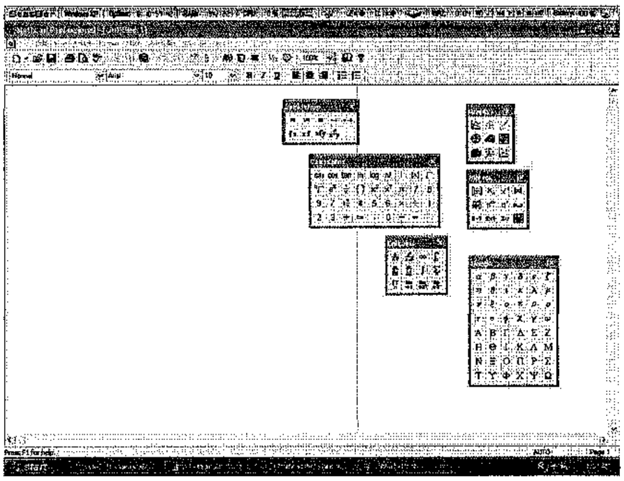
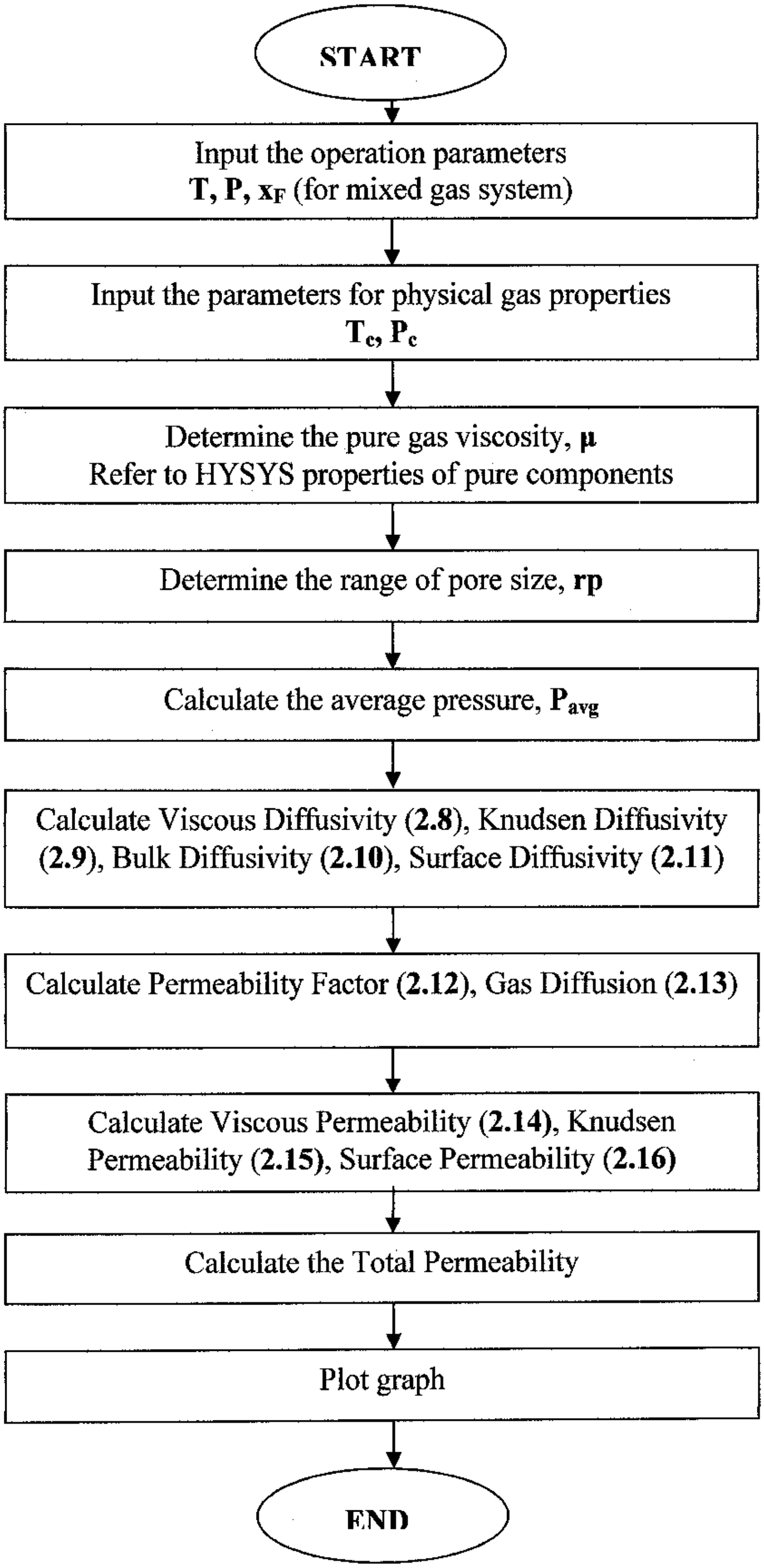
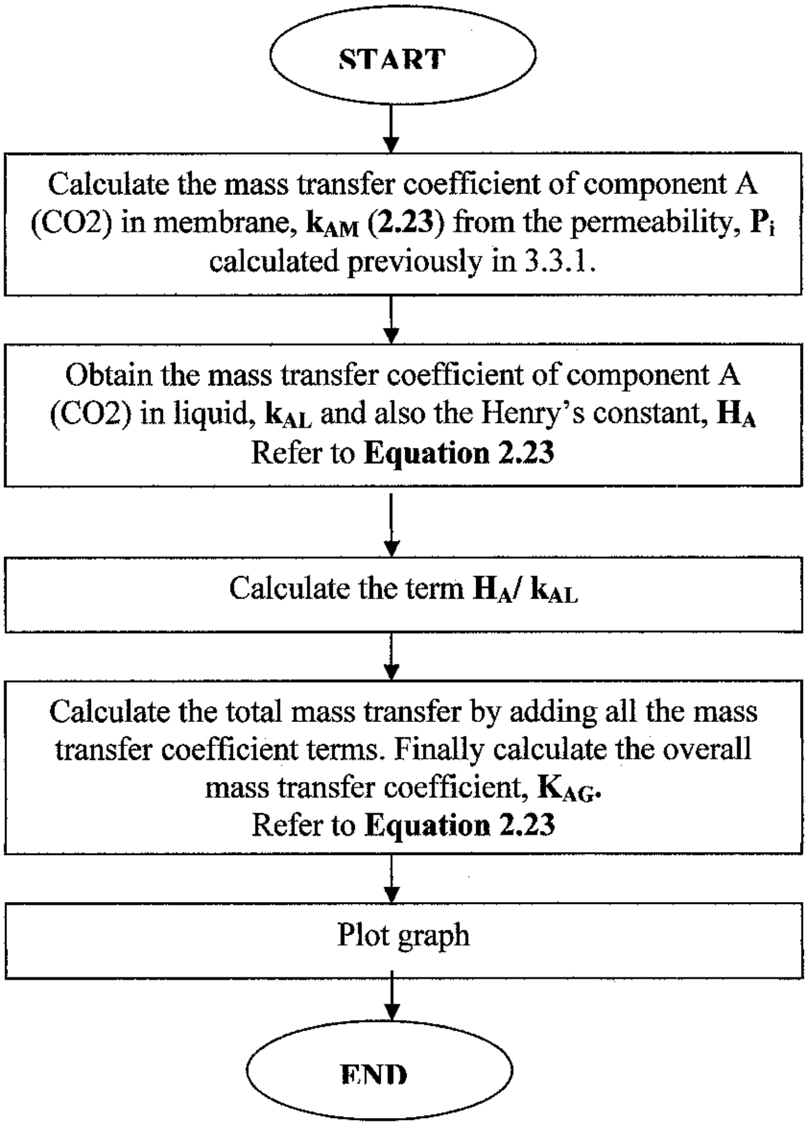


Figure 3.0: MathCad software interface

3.3 Model Development and Algorithm

3.3.1 Algorithm for calculating 'Permeability of pure gas and mixed gas system for compact hybrid membrane-absorption processes'.




START
Calculate the mass transfer coefficient of component A (CO2) in membrane, k_{AM} (2.23) from the permeability, P_i calculated previously in 3.3.1.
Obtain the mass transfer coefficient of component A (CO2) in liquid, k_{AL} and also the Henry's constant, H_A Refer to Equation 2.23
Calculate the term H_A/k_{AL}
Calculate the total mass transfer by adding all the mass transfer coefficient terms. Finally calculate the overall mass transfer coefficient, K_{AG}. Refer to Equation 2.23
Plot graph
END

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results from MathCad Modelling

4.1.1 The permeability of pure CH_4 versus the pore size

Figure 4.0 shows the permeability of methane (CH_4) with a membrane size between 0.2 to 1.6 nm. In the smaller region of pore size, it shows a decrease both for total and surface permeability of pure CH_4. However, for viscous permeability, it shows a stable increment from 0.2 nm to 1.6 nm. The decrease in surface permeability can be explained using the non-polar property of CH_4. At smaller pore size, with same CH_4 volume, the gases are clumped together closely in the pores of the membrane and created weak Van Der Waals bond. However, when the pore size increases, the molecules began to spread out and the intermolecular bond weakens. This resulted in low permeability rate for CH_4 for bigger pore size.

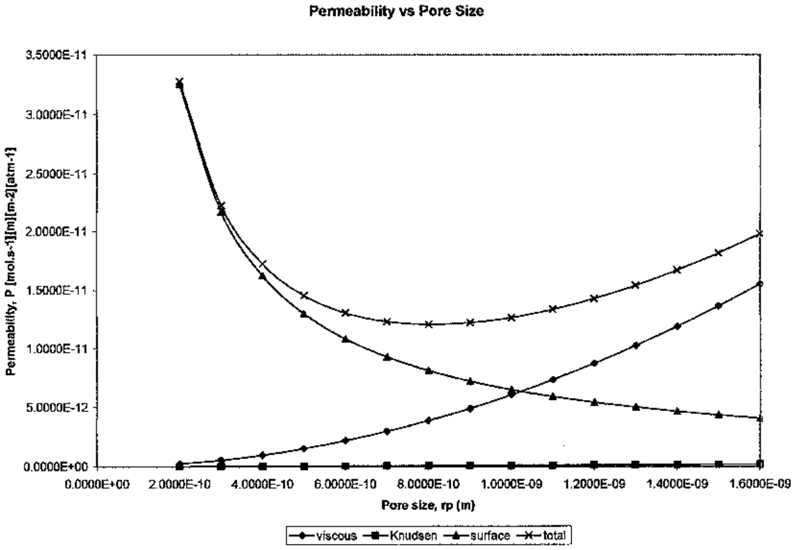


Figure 4.0: Permeability versus pore size of pure methane
$P = 50bar, T = 353K, \varepsilon = 0.272, \tau = 3.676, t_m = 5\mu m$

4.1.2 The permeability of pure CO_2 versus the pore size

Figure 4.1: Generally, the Knudsen and viscous permeability shows an increasing trend with the increase in pore size from 0.2 to 1.6 nm. As pore size increase, the Knudsen diffusion increases since the gas molecules is having more collisions with the pore wall resulting in higher free mean path, λ. The viscous diffusion also increases since this mechanism diffuses at higher rate as the pore size increases.

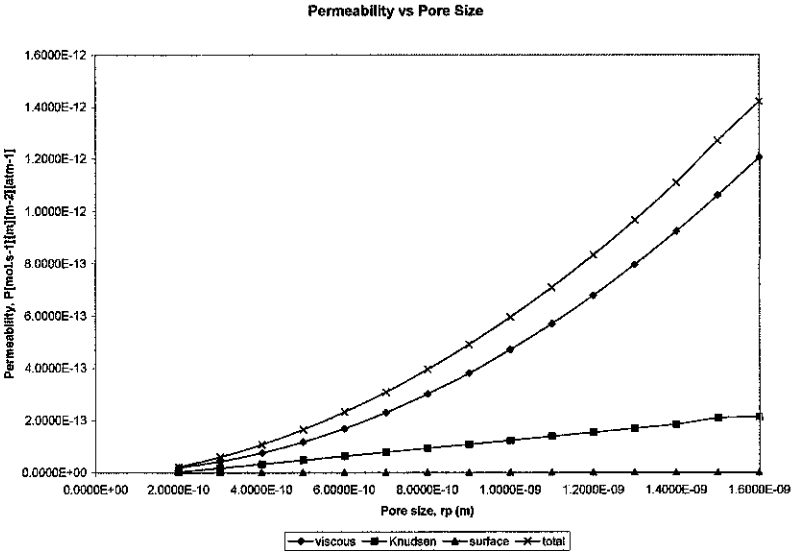


Figure 4.1: Permeability versus pore size of pure CO_2
$P = 50bar, T = 353K, \varepsilon = 0.272, \tau = 3.676, t_m = 5\mu m$

4.1.3 The permeability of mixed gas versus the pore size

Figure 4.2 shows the permeability of mixed gas, CH_4 and CO_2 with a membrane size between 0.2 to 1.6 nm. Similar trending is observed as previous. The difference is that in the degree of deflection between the Knudsen and viscous permeability. This is due to the fact that gas mixture has real physical properties rather that assuming them to be ideal gas. This resulted in minor deviation from actual behavior of either pure CH_4 or CO_2 gas. CH_4 being in abundant (80 wt %) will dominate the result of the permeability in the membrane as per with Figure 4.2.

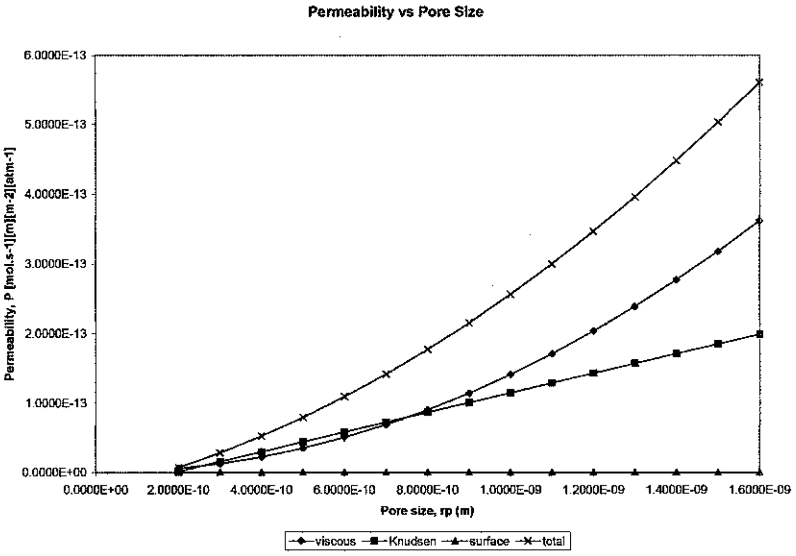


Figure 4.2: Permeability versus pore size of gas mixture
P = 50bar, T = 353K, ε = 0.272, τ = 3.676, t_m = 5μm, 20% CO_2/80% CH_4

4.1.4 The permeability of pure CO_2 versus the temperature

Figure 4.3 shows the permeability of pure CO_2 gas in a membrane with different operating temperature range from 300K to 750K. From Figure 4.3, the trend shows that as temperature is increasing the viscous permeability is slowly decreasing. Viscous mechanism is applicable when λ is less than the pore size in which causes frequent collision between the gas molecules with other molecules rather that the collision with the membrane wall. At higher temperature, molecules will experience a ceaseless random Brownian motion in which the gas molecules move far apart from each other.

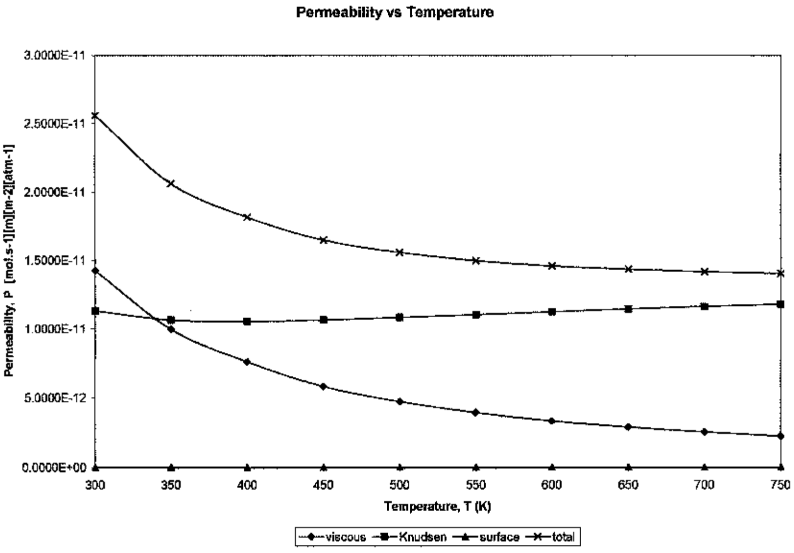


Figure 4.3: Permeability versus temperature of pure CO_2
P = 50bar, r_p = 4nm, ε = 0.272, τ = 3.676, t_m = 5μm

4.1.5 The permeability of pure CO_2 versus the pressure

Figure 4.4 shows the permeability of pure CO_2 gas in a membrane with different operating pressure range from 5 bar to 100 bar. At lower range between 5 to 50 bar, Knudsen permeability shows a gradual decrease until it attained an almost constant value at the range of 60 to 100 bar. However, for viscous permeability, it shows a gradual increase between 5 to 100 bar. At higher pressure, the separation occurs at elevated rate because the pressure difference promotes the mass transfer and permeation of gas through membrane. In addition, a deflection on the graph is detected at the pressure of 35 bar for the total permeability. This can be explained by the back pressure effect in the pores. The pores of the membrane is momentarily clogged and blocked when the pressure is approaching 35 bar. However, at higher pressure approximately 40 bar the pressure is high enough to push all the molecules to the lower pressure side. Thus, the permeability increases. This observation validates the experimental data conducted by Wind, Paul and Koros (2003) on the permeation of gas in polyimide membranes.

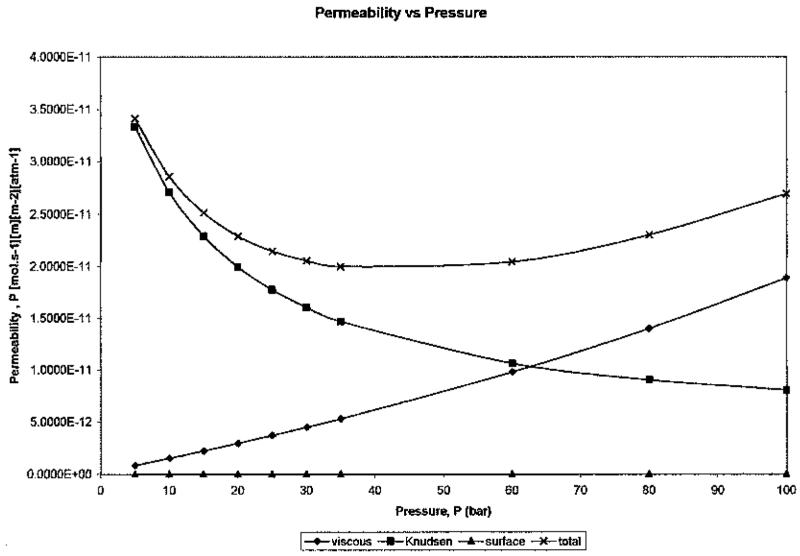


Figure 4.4: Permeability versus pressure of pure CO_2
T = 353K, r_p = 4nm, ε = 0.272, τ = 3.676, t_m = 5μm

4.1.6 The permeability of pure CO_2 versus the porosity

Figure 4.5 shows the trending of different permeability mechanism with respect to the porosity of the membrane. Generally, all mechanism shows increasing relation when the porosity of the membrane increased. Higher porosity will allow larger diffusion volume of CO_2 into the membrane thus increasing the permeability of the separation process.

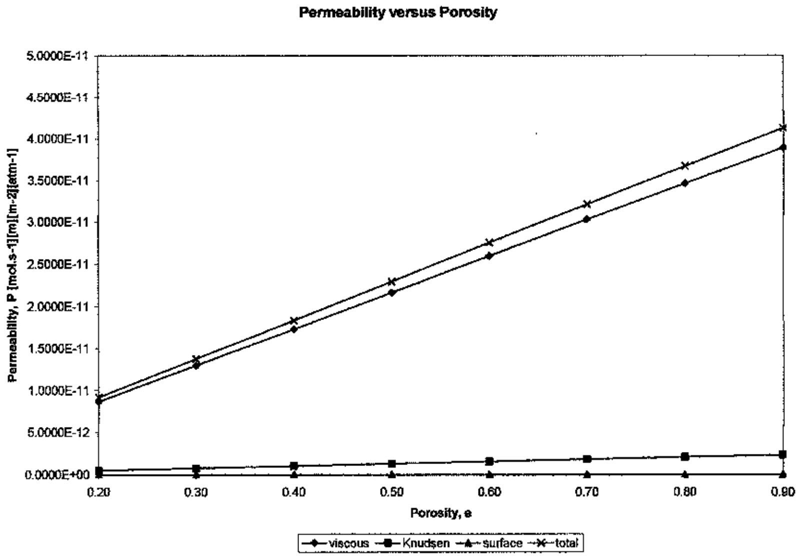


Figure 4.5: Permeability versus porosity of pure CO_2
$P = 50bar$, $T = 353K$, $r_p = 4nm$, $\tau = 3.676$, $t_m = 5\mu m$

4.1.7 The permeability of pure CO_2 versus the tortuosity

Figure 4.6 shows the permeability of different diffusion mechanism in relation with the tortuosity of the membrane. Tortuosity is defined as the ratio between the pore length and the membrane thickness. From the graph, it can be observed that higher tortuosity will give lower permeability of CO_2 across the membrane. This is because the CO_2 molecules had to travel longer time in the pore in order to diffuse at the lower pressure side of the membrane. Besides that, CO_2 that is traveling inside a long pore will be adsorbed on the pore surface thus clogging the pore. This also contribute is reducing the permeability of the membrane.

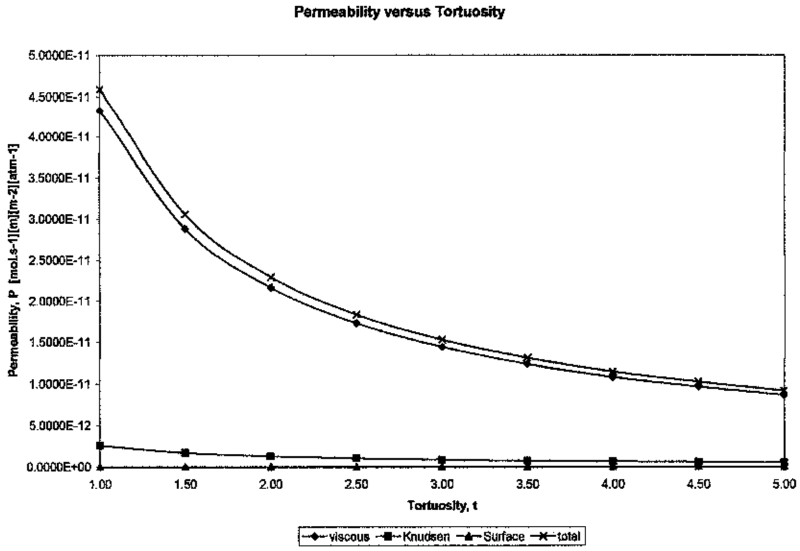


Figure 4.6: Permeability versus tortuosity of pure CO_2
$P = 50bar$, $T = 353K$, $r_p = 4nm$, $\varepsilon = 0.272$, $t_m = 5\mu m$

4.1.8 The Overall mass transfer coefficient versus temperature at different membrane thickness

Figure 4.7 shows the relationship between the overall mass transfer coefficients with temperature for different membrane thickness. This analysis is based on the modelling done previously by manipulating two parameters simultaneously, which are the membrane thickness and the operating temperature. The high and low value of overall mass transfer coefficient signifies the capability of the compact hybrid system in separating CO_2 from the natural gas. The higher the value of the coefficient, the compact hybrid system is favourable and sound. Besides that, the system also implies the usage of high selectivity membrane to ensure that high concentration of CO_2 not natural gas diffuses across the membrane and subsequently into the anime solution.

From the figure below, the overall mass transfer is reduced from higher temperature to lower temperature until it almost reaches a steady state value. This is true as discussed earlier in 4.1.3. As the membrane thickness is increased from 5 to 50 μm, it can be observed that the overall mass transfer is significantly reduced. This is because; the increase in membrane thickness decreases the permeation of CO_2 across the membrane thus affecting the membrane mass transfer coefficient. The same explanation goes with the membrane thickness at 500 μm where the overall mass transfer is approaching zero.

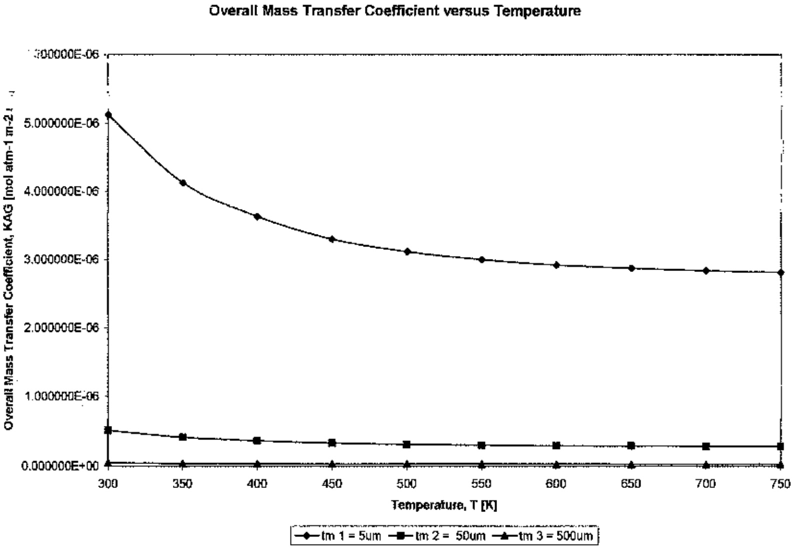


Figure 4.7: Overall mass transfer coefficient versus temperature

$P = 50\text{bar}, r_p = 4\text{nm}, \varepsilon = 0.272, \tau = 3.676$

4.1.9 The Overall mass transfer coefficient versus pressure at different membrane thickness

Figure 4.8 shows the relationship between the overall mass transfer coefficients with pressure for different membrane thickness. The similar method is done as previously by manipulating simultaneously two variables which are the operating pressure and membrane thickness. From Figure 4.8, the overall mass transfer increased as the operating pressure of the process is increased. This is true because at higher pressure, the permeation CO_2 across the membrane is also increasing thus affecting the membrane mass transfer coefficient. However, when the membrane thickness is increased from 5 to 50 μm, the overall mass transfer is reduced especially at the high pressure region around 50 bar. This is due to the back diffusion effect experienced by the membrane. Thicker membrane will prevent the permeation of CO_2. Besides that, high operating pressure will induce back diffusion due to the thick membrane thickness. The same observation goes for the membrane thickness of 500 μm where the overall mass transfer coefficient is approximately zero which means no mass transfer is happening.

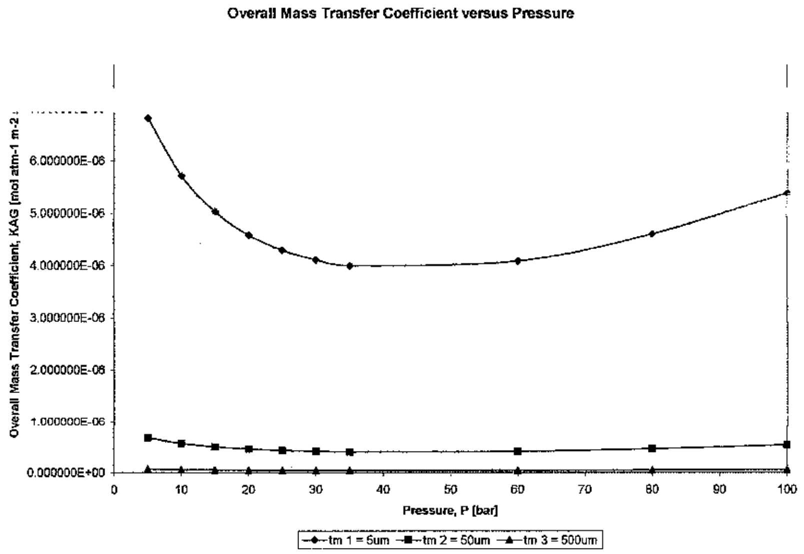


Figure 4.8: Overall mass transfer coefficient versus pressure

$T = 353K$, $r_p = 4nm$, $\varepsilon = 0.272$, $\tau = 3.676$

4.1.10 The Overall mass transfer coefficient versus porosity at different membrane thickness

Figure 4.9 shows the relationship between the overall mass transfer coefficients with porosity for different membrane thickness. From the figure. the overall mass transfer coefficient is increased for every increment of the membrane porosity. This is true because porous membrane will allow more permeation of CO_2 across the membrane thus increasing the membrane mass transfer. Although it seems feasible at high porosity, this is not practiced in industries because too porous membrane will allow the permeation of other gas components. As the membrane thickness is increased 5 to 50 μm, the overall mass transfer coefficient is reduced gradually. Porous and thick membrane will reduced the mean free path for the CO_2 to permeate across the membrane. Thus the membrane mass transfer is reduced.

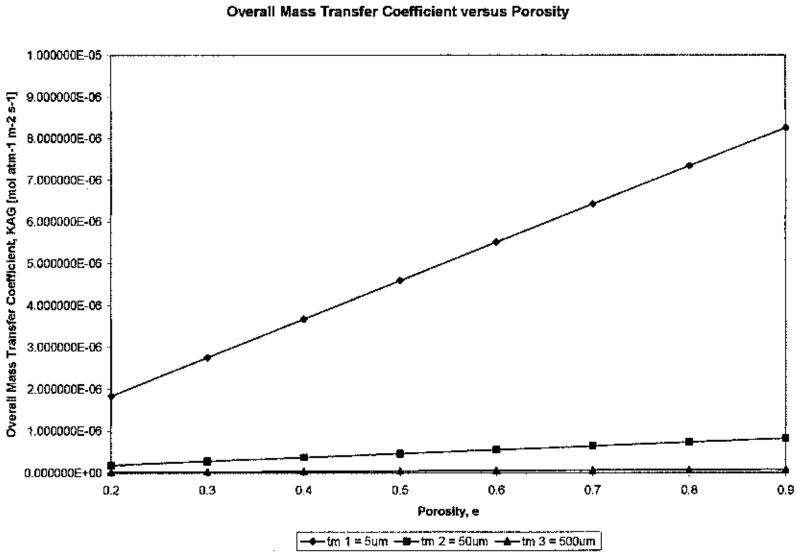


Figure 4.9: Overall mass transfer coefficient versus porosity

P = 50bar, T = 353K, r_p = 4nm, τ = 3.676

4.1.11 The Overall mass transfer coefficient versus tortuosity at different membrane thickness

Figure 4.10 shows the relationship between the overall mass transfer coefficients with tortuosity for different membrane thickness. As previously explained in 4.1.6, the membrane tortuosity is a function of pore length and the membrane thickness. From the figure, the overall mass transfer is reduced for every increment in the tortuosity. High tortuosity means that the pore length is much larger compared to the membrane thickness which means that the permeation of CO_2 is hindered and reduced. With the increase in membrane thickness from 5 to 50 μm, the overall mass transfer coefficient is further reduced due to reduction of mean free path and permeation capability. The overall mass transfer coefficient is approaching zero at membrane thickness of 500 μm.

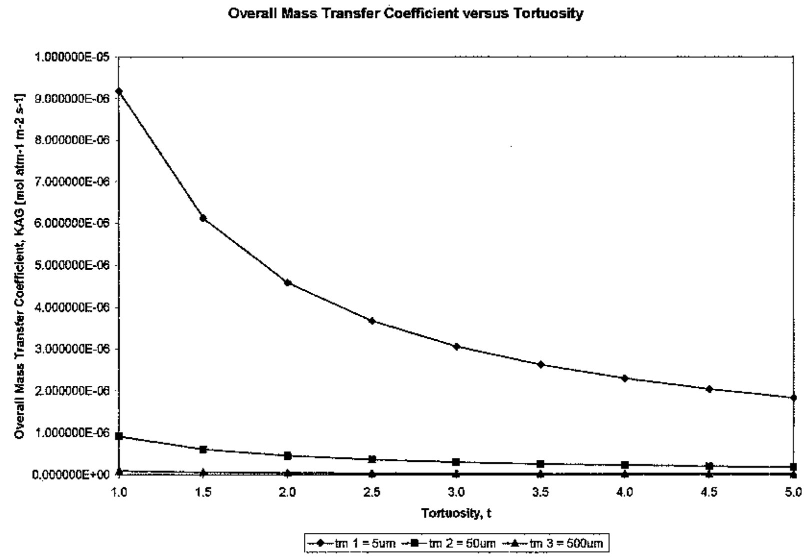


Figure 4.10: Overall mass transfer coefficient versus tortuosity

P = 50bar, T = 353K, r_p = 4nm, ε = 0.272

4.1.12 The Overall mass transfer coefficient versus temperature at different membrane porosity

Figure 4.11 shows relationship between the overall mass transfer coefficients with temperature for different membrane porosity. From the figure, it can be observed that different trend is predicted compared with the previous one in 4.1.7. Here, the magnitude of K_{AG} is between 10^{-5} until 10^{-6}. However, the best operating range in between the porosity of membrane between 0.1 and 0.5. In this range, the overall mass transfer coefficient is in the magnitude of 10^{-6} which is feasible and at its optimum operation according to Li and Teo (1996). Generally, a cascade trend is observed starting from the top trend for more porous membrane and the bottom trend for less porous membrane.

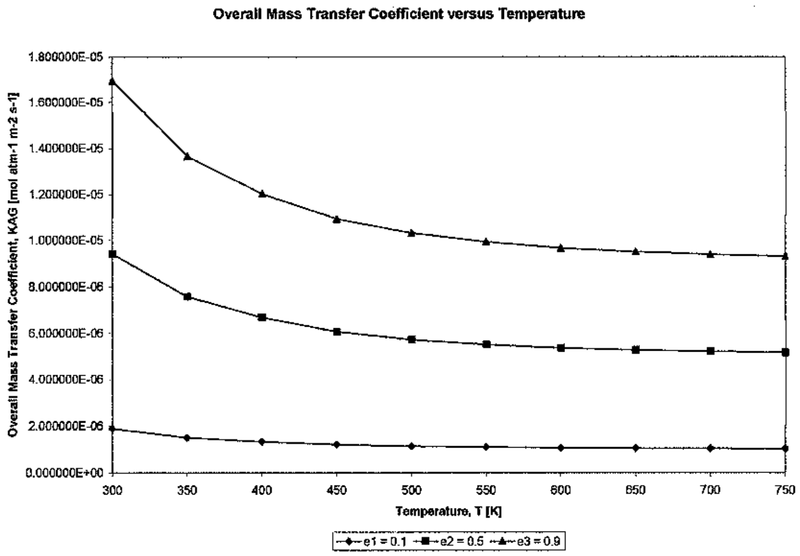


Figure 4.11: Overall mass transfer coefficient versus temperature

$P = 50\text{bar}$, $r_p = 4\text{nm}$, $\tau = 3.676$, $t_m = 5\mu\text{m}$

4.1.13 The Overall mass transfer coefficient versus pressure at different membrane porosity

Figure 4.12 shows relationship between the overall mass transfer coefficients with pressure for different membrane porosity. From the figure, it can be observed that different trend is predicted compared with the previous one in 4.1.8. Generally, the overall mass transfer is increased when the operating pressure of the process is increased. Here, the magnitude of K_{AG} is between 10^{-5} until 10^{-6} which agrees with the model developed by Li and Teo (1996). The best operating pressure for the process is around 0.1 to 0.5. In this range, the overall mass transfer coefficient is in the magnitude of 10^{-6} which is feasible and at its optimum operation. Generally, a cascade trend is observed starting from the top trend for more porous membrane and the bottom trend for less porous membrane.

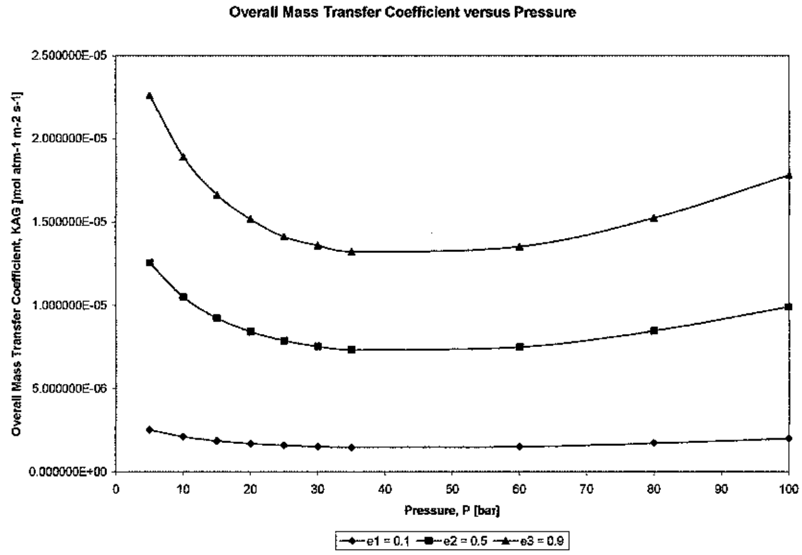


Figure 4.12: Overall mass transfer coefficient versus pressure

$T = 353K$, $r_p = 4nm$, $\tau = 3.676$, $t_m = 5\mu m$

4.1.14 The Overall mass transfer coefficient versus porosity at different operating temperature and pressure

Figure 4.13 shows relationship between the overall mass transfer coefficients with membrane porosity for operating temperature and pressure. In this analysis, three variables are manipulated simultaneously which are porosity, operating temperature and pressure. Here, different trends are obtained with respect to each manipulated variables. For temperature, lower temperature favors the optimum overall mass transfer coefficient which is the magnitude of 10^{-6} which agrees with the model developed by Li and Teo (1996). For pressure, high pressure favors the optimum overall mass transfer coefficient which is the magnitude of 10^{-6}. Generally, all the ranges given in Figure 4.14 are acceptable because it lays in the magnitude 10^{-6}. However, the values of overall mass transfer coefficient favor the operation at temperature between 300K and 400K meanwhile, the pressure between 10 bar to 30 bar for optimum process.

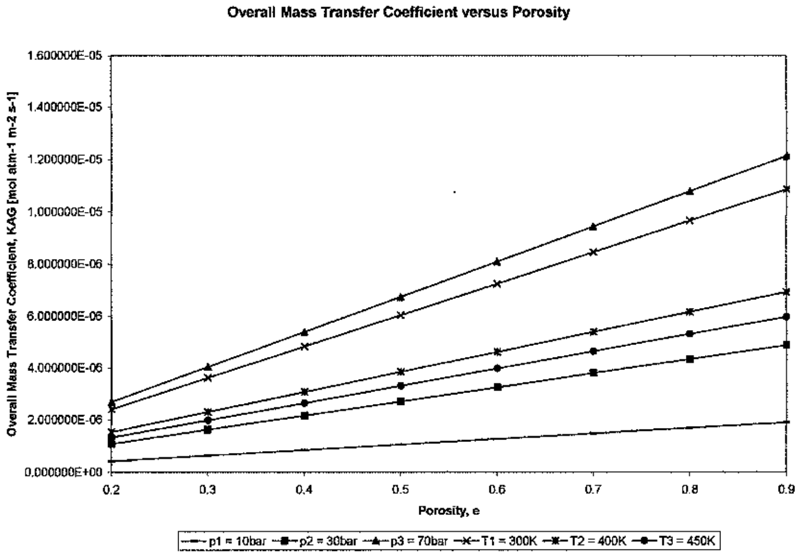


Figure 4.13: Overall mass transfer coefficient versus porosity

$r_p = 4\text{nm}, \tau = 3.676, t_m = 5\mu\text{m}$

4.1.15 The Overall mass transfer coefficient versus tortuosity at different operating temperature and pressure

Figure 4.14 shows relationship between the overall mass transfer coefficients with membrane tortuosity for operating temperature and pressure. In this analysis, three variables are manipulated simultaneously which are tortuosity, operating temperature and pressure. For temperature, lower temperature favors the optimum overall mass transfer coefficient which is the magnitude of 10^{-6} which agrees with the model developed by Li and Teo (1996). For pressure, high pressure favors the optimum overall mass transfer coefficient which is the magnitude of 10^{-6}. Generally, all the ranges given in Figure 4.14 are acceptable because it lays in the magnitude 10^{-6}. However, the values of overall mass transfer coefficient favor the operation at temperature between 300K and 400K meanwhile the pressure is between 10 bar and 30 bar for optimum process.

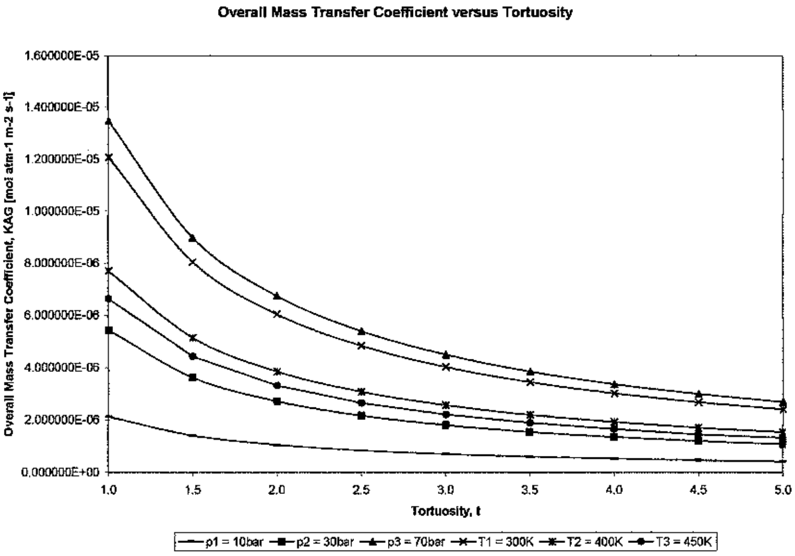


Figure 4.14: Overall mass transfer coefficient versus tortuosity

$r_p = 4\text{nm}, \tau = 3.676, t_m = 5\mu\text{m}$

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Generally, the model developed is able to predict the membrane permeability for CO_2 and CH_4 and subsequently to calculate the overall mass transfer coefficient for the compact hybrid membrane-absorption processes.

There are a few parameters which govern the mass transfer in membrane separation. Generally, the larger the pore size of a membrane the higher will be the permeability of CO_2 in the membrane. This is due to the larger surface area provided by the pore for the gas molecules to permeate and diffuse to the lower pressure side.

The increase in the operating temperature and the tortuosity of the membrane would decrease the permeability of CO_2 in the membrane. This is because at higher temperature, CO_2 molecules collision frequency increases between the molecule itself. Thus, the mean free path is reduced and decreasing the chances of the molecules to diffuse into the pore and permeate. Moreover, at high tortuosity the pore length also increases thus the molecules have to travel more distance into the membrane pore.

Next, the increase in the operating pressure and porosity of the membrane would increase the permeability of CO_2 gas in the membrane. This is because pressure is the driving force of the diffusion of CO_2 in the membrane. If more pressure is applied at the feed, permeation will occur faster thus increasing the permeability. In addition, porous membrane allows more movement and permeation of molecules inside them

For compact hybrid membrane-absorption processes, the overall mass transfer coefficient is found to vary when the operating parameters such as the temperature and pressure are manipulated. Besides that, the same effect is found when the membrane characteristic such as the membrane pore size, porosity, thickness and tortuosity is manipulated.

The overall mass transfer coefficient generally decreased when the operating temperature is increased. The increase in membrane thickness reduces this overall mass transfer coefficient. Besides that when the porosity of the membrane is increased, the overall mass transfer coefficient gradually increased.

When the operating pressure is increased, the overall mass transfer coefficient generally increased. The increase in membrane thickness reduces the overall mass transfer coefficient. In addition, when the porosity of the membrane is increased, the overall mass transfer coefficient would increase.

Lastly, the best operating parameters for the compact hybrid membrane-absorption process is in the region of low temperature between 300K and 400K and in the region of high pressure between 10 bar to 30 bar. In this range, the magnitude of the overall mass transfer is in the magnitude of 10^{-6} which agrees with the study and model developed by Li and Teo (1996). These values also show that separation is favorable for the compact hybrid membrane-absorption process.

5.2 RECOMMENDATION

5.2.1 There are many modes of membrane separation which can be implemented. One of the examples is wetted wall which is studied in this project. In order to obtain accurate and variability in result, the study should take into consideration other mode of membrane separation such as the non-wetted mode or partially wetted mode which definitely gives different results and observation. Besides that, further study can also be conducted by manipulating the contacting mode for the absorption process such as counter-current flow, co-current flow or cross-flow.

5.2.2 The mass transfer for the permeability of the membrane for both pure and mixed gas system has been justified. Three mechanisms which are: Knudsen diffusion, viscous diffusion and surface diffusion are considered throughout the study. Besides that, it is recommended to include the effect of capillary condensation in the membrane. This phenomenon is considered on of the major problem encountered if the operating variables are not attained. The effect of capillary condensation will help people to understand the natural behavior of membrane separation and the aspect of operating it at certain operating values.

5.2.3 Comparative study also can be done by using other types of membrane specifically non-organic membrane such as zeolite and alumina. In addition, different amine solution can also be considered in the study in order to understand the reaction kinetics as well as the order of reaction between the amine solutions with CO_2 and the effect on the membrane-absorption processes.

5.2.4 Further studies can also be conducted by considering the percentage of CO_2 removal from natural gas. This can be achieved by knowing the solubility of CO_2 in the amine solution and the equilibrium concentration of CO_2 during the absorption. By doing this, the effectiveness of using compact hybrid membrane-absorption can be justified.

5.2.5 Experimental work should be considered to prove the validity of the modelling done in this study.

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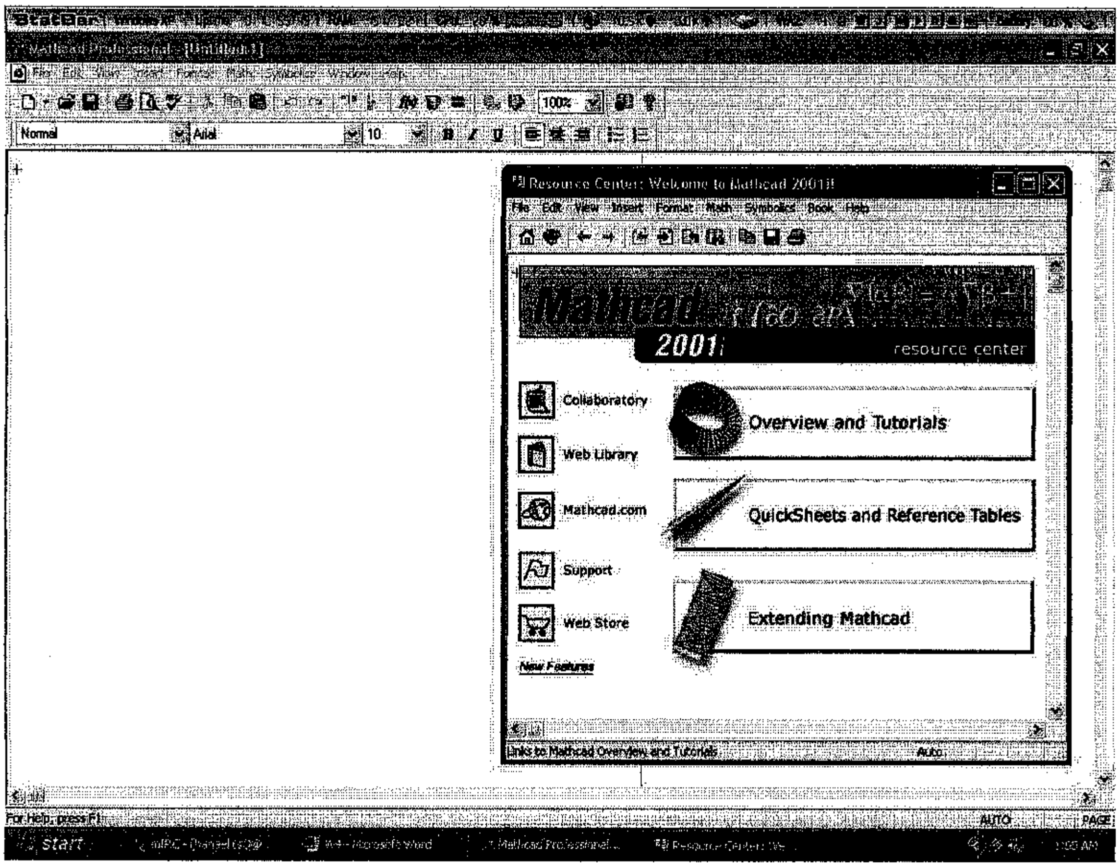
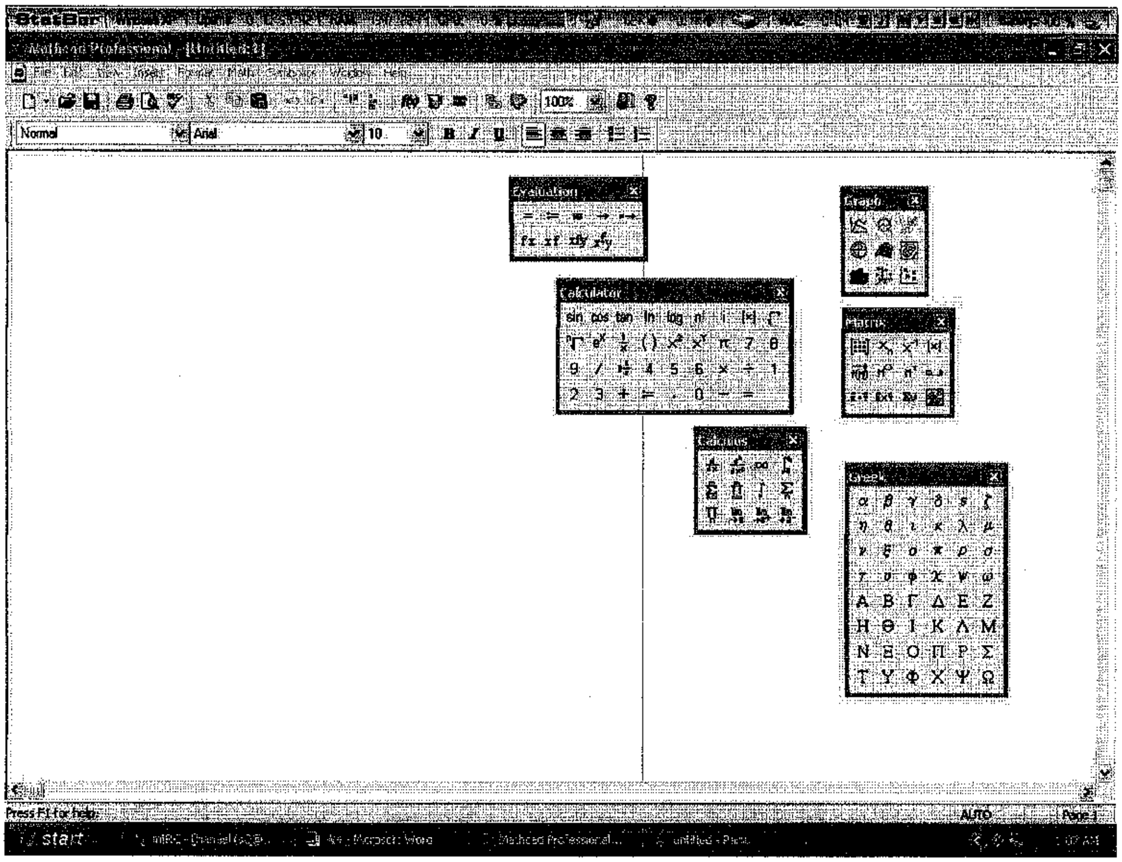
APPENDIX I

		WEEK													
NO	DETAIL	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	**Selection of Project Topic**	▨													
	Propose topic														
	Topic assigned to student														
	FYP briefing by Coordinator	●													
2	**Preliminary Research**		▨	▨											
	First meeting with FYP Supervisor		●												
	Introduction and briefing on topic		●												
	List of references and literature		●	●											
	Project planning			●											
3	**Submission of Preliminary Report**			●											
4	**Project Work**				▨	▨	▨	▨							
	Development of basic equation for mass transfer				●										
	Further literature review on mass transfer					●	●								
	Consulting and training on MATHCAD					●	●								
	First trial on modelling using MATHCAD							●							
	Preparation for Progress Report							●							
5	**Submission of Progree Report**								●						
6	**Project Work continued**								▨	▨	▨	▨			
	Continue on modelling using MATHCAD								●	●	●				
	Analysis of result from MATHCAD										●				
	Consultation with FYP Supervisor								●	●	●	●			
	Dissertation Final Draft preparation											●			
7	**Submission of Dissertation Final Draft**												●		
8	**Oral presentation**													●	
9	**Submission of Project Dissertation**														●

▨ Process
● Milestone



APPENDIX 2



APPENDIX 3

APPENDIX 4

Overall Mass Transfer of Mixed Component (Methane+CO2)
Study of mass transfer as a function of pore size
P = 50 bar
T = 353 K
Tortuosity, τ = 3.676
Porosity, ξ = 0.272

Pressure (Bar)	**Temperature (K)**
$P := 50$	$T := 353$

1 refers to CH4, 20%
2 refers to CO2, 80%

$Tc1 := 190.6$ $\quad$ $Tc2 := 304.1$

$Pc1 := 46.0$ $\quad$ $Pc2 := 73.8$

$\omega1 := 0.007$ $\quad$ $\omega2 := 0.225$

$vc1 := 118$ $\quad$ $vc2 := 93.9$

$zc1 := 0.288$ $\quad$ $zc2 := 0.274$

Reduced Pressure	**Reduced Temperature**
$Pr1 := \frac{P}{Pc1}$	$Tr1 := \frac{T}{Tc1}$
$Pr1 = 1.087$	$Tr1 = 1.852$
$Pr2 := \frac{P}{Pc2}$	$Tr2 := \frac{T}{Tc2}$
$Pc2 = 73.8$	$Tc2 = 304.1$

$$\omega12 := \frac{\omega1 + \omega2}{2} \qquad zc12 := \frac{zc1 + zc2}{2}$$

$\omega12 = 0.116$ $\quad$ $zc12 = 0.281$

$$vc12 := \left(\frac{vc1^{\frac{1}{3}} + vc2^{\frac{1}{3}}}{2}\right)^3 \qquad Tc12 := (Tc1 \cdot Tc2)^{\frac{1}{2}}$$

$vc12 = 105.492$ $\quad$ $Tc12 = 240.752$

$$Pc12 := \frac{zc12 \cdot 82.06 \cdot Tc12}{vc12} \qquad Tr12 := \frac{T}{Tc12}$$

$Pc12 = 52.625$ $\quad$ $Tr12 = 1.466$

Virial Coefficient

$$B11 := \left[\left(0.083 - \frac{0.422}{Tr1^{1.6}}\right) + \omega1\cdot\left(0.139 - \frac{0.172}{Tr1^{4.2}}\right)\right]\cdot\frac{82.06\cdot Tc1}{Pc1}$$

$B11 = -25.005$

$$B22 := \left[\left(0.083 - \frac{0.422}{Tr2^{1.6}}\right) + \omega2\cdot\left(0.139 - \frac{0.172}{Tr2^{4.2}}\right)\right]\cdot\frac{82.06\cdot Tc2}{Pc2}$$

$B22 = -80.761$

$$B12 := \left[\left(0.083 - \frac{0.422}{Tr12^{1.6}}\right) + \omega12\cdot\left(0.139 - \frac{0.172}{Tr12^{4.2}}\right)\right]\cdot\frac{82.06\cdot Tc12}{Pc12}$$

$B12 = -50.169$

$y1 := 0.75 \quad y2 := 0.25$

$$B := \left(y1^2\cdot B11\right) + (2\cdot y1\cdot y2\cdot B12) + \left(y2^2\cdot B22\right)$$

$B = -37.926$

Compressibility Factor

$$z := 1 + \frac{B\cdot P}{82.06\cdot T}$$

$z = 0.935$

Viscosity of Mixed Gas

$M1 := 16.043 \quad M2 := 44.01 \quad \mu1 := 0.000013846 \; \mu2 := 0.000019551$

$$\Phi12 := \frac{1}{\sqrt{8}}\cdot\left(1 + \frac{M1}{M2}\right)^{-0.5}\cdot\left[1 + \left(\frac{\mu1}{\mu2}\right)^{0.5}\cdot\left(\frac{M1}{M2}\right)^{0.25}\right]^2$$

$\Phi12 = 0.828$

$$\mu mix := \frac{y1\cdot\mu1}{y2\cdot\Phi12} + \frac{y2\cdot\mu2}{y2\cdot\Phi12}$$

$\mu mix = 7.379 \times 10^{-5}$

Pore Size

$x := 1, 2 .. 15$

$m_{0,0} :=$ "Pore Size"

$m_{1,0} := 0.2$

$m_{2,0} := 0.3$

$m_{3,0} := 0.4$

$m_{4,0} := 0.5$

$m_{5,0} := 0.6$

$m_{6,0} := 0.7$

$m_{7,0} := 0.8$

$m_{8,0} := 0.9$

$m_{9,0} := 1$

$m_{10,0} := 1.1$

$m_{11,0} := 1.2$

$m_{12,0} := 1.3$

$m_{13,0} := 1.4$

$m_{14,0} := 1.5$

$m_{15,0} := 1.6$

m =

	0
0	"Pore Size"
1	0.2
2	0.3
3	0.4
4	0.5
5	0.6
6	0.7
7	0.8
8	0.9
9	1
10	1.1
11	1.2
12	1.3
13	1.4
14	1.5
15	1.6

$rp_x := m_{(x,0)} \cdot 10^{-9}$

Average Pressure

$$\text{AVEPRESS} := \frac{\left(P \cdot 10^5 + 10^5\right)}{2}$$

$\text{AVEPRESS} = 2.55 \times 10^6$

Viscous Diffusivit

$$\text{viscous}_x := \text{AVEPRESS} \cdot \frac{\left(rp_x\right)^2}{8 \cdot \mu\text{mix}}$$

$\text{viscous}_x =$

$1.728 \cdot 10^{-10}$
$3.888 \cdot 10^{-10}$
$6.912 \cdot 10^{-10}$
$1.08 \cdot 10^{-9}$
$1.555 \cdot 10^{-9}$
$2.117 \cdot 10^{-9}$
$2.765 \cdot 10^{-9}$
$3.499 \cdot 10^{-9}$
$4.32 \cdot 10^{-9}$
$5.227 \cdot 10^{-9}$
$6.221 \cdot 10^{-9}$
$7.301 \cdot 10^{-9}$
$8.467 \cdot 10^{-9}$
$9.72 \cdot 10^{-9}$
$1.106 \cdot 10^{-8}$

Knudsen Diffusivity

$$\mathrm{knudsen}_x := \frac{2}{3}\cdot\left(\mathrm{rp}_x - 1.9\cdot 10^{-10}\right)\cdot\sqrt{8.8314\cdot\frac{T}{\pi\cdot 16.043}}$$

$\mathrm{knudsen}_x =$

$5.243\cdot10^{-11}$
$5.767\cdot10^{-10}$
$1.101\cdot10^{-9}$
$1.625\cdot10^{-9}$
$2.15\cdot10^{-9}$
$2.674\cdot10^{-9}$
$3.198\cdot10^{-9}$
$3.723\cdot10^{-9}$
$4.247\cdot10^{-9}$
$4.771\cdot10^{-9}$
$5.296\cdot10^{-9}$
$5.82\cdot10^{-9}$
$6.344\cdot10^{-9}$
$6.869\cdot10^{-9}$
$7.393\cdot10^{-9}$

Bulk Diffusivity

$$\mathrm{bulk} := 10^{-7}\cdot T^{1.75}\cdot\frac{\left(\frac{1}{16.043}+\frac{1}{44.01}\right)^{0.5}}{P\cdot\left(\sqrt[3]{24.42}+\sqrt[3]{20.96}\right)^{2}}$$

$\mathrm{bulk} = 5.237\times 10^{-7}$

Surface Diffusivity

$\Delta H := 304200$

Membrane Thickness

$\mathrm{tm} := 0.000005$

$$\mathrm{surface} := 0.016\cdot \mathrm{tm}\, e^{-0.45\cdot\frac{\Delta H}{8.314\cdot T}}$$

$\mathrm{surface} = 0\times 10^{0}$

Permeability Factor

$\varepsilon := 0.272$

$\tau := 3.676$

$$\text{Factor} := \frac{\varepsilon}{z \cdot 8.314 \cdot \tau \cdot T}$$

$\text{Factor} = 2.698 \times 10^{-5}$

Gas Diffusion

$$\text{GasDiff}_x := \frac{1}{\dfrac{1}{\text{knudsen}_x} + \dfrac{1}{\text{bulk}}}$$

$\text{GasDiff}_x =$

$5.243 \cdot 10^{-11}$
$5.761 \cdot 10^{-10}$
$1.099 \cdot 10^{-9}$
$1.62 \cdot 10^{-9}$
$2.141 \cdot 10^{-9}$
$2.66 \cdot 10^{-9}$
$3.179 \cdot 10^{-9}$
$3.696 \cdot 10^{-9}$
$4.213 \cdot 10^{-9}$
$4.728 \cdot 10^{-9}$
$5.243 \cdot 10^{-9}$
$5.756 \cdot 10^{-9}$
$6.268 \cdot 10^{-9}$
$6.78 \cdot 10^{-9}$
$7.29 \cdot 10^{-9}$

Viscous Permeability

$\text{vp}_x := \text{Factor} \cdot \text{viscous}_x$

$\text{vp}_x =$

$4.662 \cdot 10^{-15}$
$1.049 \cdot 10^{-14}$
$1.865 \cdot 10^{-14}$
$2.914 \cdot 10^{-14}$
$4.196 \cdot 10^{-14}$
$5.711 \cdot 10^{-14}$
$7.459 \cdot 10^{-14}$
$9.44 \cdot 10^{-14}$
$1.165 \cdot 10^{-13}$
$1.41 \cdot 10^{-13}$
$1.678 \cdot 10^{-13}$
$1.97 \cdot 10^{-13}$
$2.284 \cdot 10^{-13}$
$2.622 \cdot 10^{-13}$
$2.983 \cdot 10^{-13}$

Knudsen Permeability

$\text{kp}_x := \text{Factor} \cdot \text{GasDiff}_x$

$\text{kp}_x =$

$1.414 \cdot 10^{-15}$
$1.554 \cdot 10^{-14}$
$2.964 \cdot 10^{-14}$
$4.371 \cdot 10^{-14}$
$5.776 \cdot 10^{-14}$
$7.177 \cdot 10^{-14}$
$8.576 \cdot 10^{-14}$
$9.972 \cdot 10^{-14}$
$1.137 \cdot 10^{-13}$
$1.276 \cdot 10^{-13}$
$1.414 \cdot 10^{-13}$
$1.553 \cdot 10^{-13}$
$1.691 \cdot 10^{-13}$
$1.829 \cdot 10^{-13}$
$1.967 \cdot 10^{-13}$

Surface Permeability

$$\mathrm{sp}_x := \frac{\mathrm{Factor}\cdot\mathrm{surface}\cdot\frac{1}{\varepsilon}\cdot 1140\cdot 0.0000215\cdot 0.000000006}{\mathrm{rp}_x}$$

$\mathrm{sp}_x =$

$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$
$0\cdot10^{0}$

Total Permeability

$\mathrm{Total}_x := \mathrm{vp}_x + \mathrm{kp}_x + \mathrm{sp}_x$

$\mathrm{Total}_x =$

$6.076\cdot10^{-15}$
$2.603\cdot10^{-14}$
$4.829\cdot10^{-14}$
$7.285\cdot10^{-14}$
$9.971\cdot10^{-14}$
$1.289\cdot10^{-13}$
$1.603\cdot10^{-13}$
$1.941\cdot10^{-13}$
$2.302\cdot10^{-13}$
$2.686\cdot10^{-13}$
$3.093\cdot10^{-13}$
$3.522\cdot10^{-13}$
$3.975\cdot10^{-13}$
$4.451\cdot10^{-13}$
$4.95\cdot10^{-13}$

Amine Solution Properties

$H := 0.0000415$

$kAL := 0.000155$

Specific Gas Permeability

$$invkAM_x := \frac{tm}{Total_x}$$

$invkAM_x =$

822904339.339
192076801.925
103543090.601
68634569.646
50143976.519
38796073.798
31182157.226
25757233.44
21720672.385
18616852.119
16167858.097
14194842.733
12577695.922
11232898.431
10100669.503

Membrane Mass Transfer Term

$$in_x := \frac{1}{invkAM_x}$$

Liquid Mass Transfer Term

$$\frac{H}{kAL} = 0.268$$

Sum of all Mass Transfer Term

$$overall_x := \frac{H}{kAL} + invkAM_x$$

$overall_x =$

822904339.607
192076802.193
103543090.869
68634569.914
50143976.787
38796074.066
31182157.493
25757233.707
21720672.653
18616852.387
16167858.364
14194843.001
12577696.19
11232898.699
10100669.77