Mass Transfer Modelling for Compact Hybrid Membrane-Amine System in Removal of CO_2 from Natural Gas

by

Nguyen Thi Quynh Nga

Dissertation submitted in partial fulfillment
of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

January, 2005

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Mass Transfer Modelling for Compact Hybrid Membrane-Amine System in Removal of CO_2 from Natural Gas

by

Nguyen Thi Quynh Nga

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)

January, 2005

Approved by,

....

(Dr. Hilmi B. Mukhtar)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January, 2005

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 work 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.

NGUYEN THI QUYNH NGA

ABSTRACT

The removal of CO_2 from natural gas down to the pipeline quality is an important step before the natural gas can be sold to the end users. Typical natural gas treatment's specification requires that the composition of CO_2 in the treated gas cannot be more than 2 mole%. Normally amine scrubbing process is extensively used to treat natural gas with low content of CO_2. However, this is not efficient in dealing with natural gas with high CO_2 content. Therefore, there is a proposal of using hybrid system in sequencing of membrane for bulk CO_2 removal followed by amine solution for absorption process. However, there are some disadvantages for the hybrid system such as not applicable in offshore. All the disadvantages of the hybrid system will be overcome if the compact hybrid membrane-absorption column is brought into operation. This system uses the concept in which amine absorption is integrated together with the membrane permeation. The feedgas will flow along the membrane and permeate through the membrane and then will be absorbed into the amine solution.

The main objective of this work is to develop a mathematical model for the removal of CO_2 from natural gas in compact hybrid membrane amine system. The model has analyzed the permeability of CO_2 and methane across membrane followed by absorption of CO_2 in amine solution. The effect of various parameters, which consist of concentration of CO_2 in feed gas, operating pressure of feed gas, flow rate of amine solution and membrane pore size, towards the permeability and separation factor of the compact hybrid membrane-amine system has been analyzed systematically. The model is developed using MATHCAD version 2000i and Microsoft Excel to represent the mass transfer of CO_2 in the compact hybrid membrane-amine system.

The performance of membrane separation is determined by the permeability of each component through the membrane and selectivity of the membrane for each component in the mixture. Based on the mathematical model developed, it was found that the permeability of CO_2 and methane was independent of the concentration of each component in the feed gas. However, the permeability of CO_2 and methane was a strong function of operating pressure at the feed gas and membrane pore size due to the effect of surface diffusion at small pore sizes, but this effect was lost at bigger pore sizes.

For amine absorption, the mathematical model showed that the separation factor for removal of CO_2 from natural gas using compact hybrid membrane-amine system was strongly dependent on concentration of CO_2 in the natural gas as well as flow rate of amine solution due to its effect on the rate of absorption. However, operating pressure of feed gas does not show any effect on the separation factor of CO_2 removal.

The model for compact hybrid membrane-amine absorption system is successfully developed and various operating parameters have been studied and discussed in the later section of this report.

ACKNOWLEDGEMENT

The author deeply feels that the accomplishment of this endeavour would not be so successful without valuable help and support from the following personnel.

First of all, the author would like to express her heartfelt gratitude to Dr. Hilmi Bin Mukhtar, the author's project supervisor in realizing this project. The result of this study would not be so fruitful and meaningful without his supervision, suggestion, motivation and constructive comments to discuss the project proper throughout the four-month project period. Many thanks to him for his time and his patience in showing her the requirements of the project in order to get good outcome.

Next, the author would like to thank Mrs. Suriati Sufian for her help in modeling gas-liquid extraction. Her ideas are valuable to the author in order for her to make progress in modeling the project.

The author would like to thank Mr. Ruslan of the IT department for providing her with the MathCad software as well as the manual in order for her to get familiar with the software.

The author would like to thank Dr. Abdul Huq for his help in MathCad programming. MathCad is new software for the author and she had to learn to get familiarized with the software in order to write a program. When she had problems with programming, Dr. Huq had given ideas which helped her to realize the errors in the program and made correction.

Last but not least, the author would like to thank all her course mates and her friends for their continuous support and suggestion through the project period. They all gave great support to author in accomplishing the project.

Thank you all.

TABLE OF CONTENT

LIST OF ILLUSTRATION

List of Table

List of Figure

List of Equation

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

1. INTRODUCTION

1.1. Background of study

Natural gas, refinery gas or coal gas generates huge quantities of CO_2 when it is employed for industrial and domestic heating and other chemical processes. Emission of CO_2 from these sources is regarded as the most serious potential cause of environment problems such as global warming and acid rain (Sam Wong and Rob Bioletti, 2000).

Carbon dioxide accounts for over 80% of global warming pollution. Atmospheric levels of CO_2 are now higher than at any time in the past 420,000 years. CO_2 comes mainly from the burning of coal, oil and gas. Around 97% of the CO_2 emitted by western industrialized countries comes from the burning of coal, oil and gas for energy. Approximately 23,000,000,000 tones of CO_2 are spewed into the earth's atmosphere every year. That's mkore than 700 tones every second. The average coal-fired power plant wastes twice as much energy heating up the planet as it converts to useful electricity. Each large 1000 Megawatt (MW) coal-fired plant typically emits 5.6 million tones of CO_2 per year. An average car with a fuel consumption of around 7.8 litres/100 km (36 miles per gallon) traveling 16,000 km (10,000 miles) per year emits almost 3 tones (6,500 lbs) of CO_2 per year. That's roughly equal to three times the vehicle's body weight. (UNFCCC, SBI, 1997)

In Table 1.1, it shows the emission of CO_2 per capita in particular countries in 1999, where the emission of CO_2 per capita is in United States with about 19.7 metric tons CO_2 per person and that in Malaysia is 5.4 metric tons CO_2 per person. CO_2 emission per capita is the amount of CO_2 emitted per head of population in a country

Table 1.1: CO_2 emission per capita of many different countries
(World Resources Institute, 1999)

Countries	CO_2 emission per capita (metric tons/ 1000 persons) (1999)
United States	19.7
Australia	18.2
Canada	14.4
Singapore	13.7
Germany	9.7
United Kingdom	9.2
Japan	9.1
Italy	7.3
France	6.1
Hong Kong, China	6.2
Malaysia	5.4
Indonesia	1.2
Viet Nam	0.6

K. Li and W.K. 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 and establishments in the world.

1.2. CO_2 in natural gas

Natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely.

Table 1.2 shows that the composition of carbon dioxide in the natural gas is 0-83%. In enhanced oil recovery (EOR) operation, CO_2 is pumped into depleting oil reserves at high pressures to drive residual oils to existing oil wells. Over an extended period of time, the pumped CO_2 gas mixes with the natural gas associated with the wells and can reach up to 95% (Spillman, 1989).

Table 1.2 : Composition of natural gas Reservoirs (wt %) (Hunt, 1979)

Reservoir	CH_4	C_2 to C_6	CO_2	N_2	H_2	H_2S	He
Sweetwater (Wyo.,USA)	75.60	1.30	2.70	20.20	-	-	0.75
Transylvanian Basin (Romania)	98-99	0.80	0.50	1-2	-	-	-
Krecsegopan (Hungary)	42-47	-	45-83	3-6	0.90	-	-
North German Plain	Up to 95.0	0.3 -12	Up to 60.0	Up to 99.0	Up to 90.0	0-8	-
Cumato, Sakada & other gas reservoirs of Japan	42-98	0.10	0.5 – 4.5	4 - 53	-	-	-
Baden (Germany)	82.10	0.80	10.30	6.80	-	-	-

The composition of CO_2 in the existing natural gas wells varies for different geographical locations. Table 1.3 shows different composition of CO_2 in natural gas in different wells in the world.

Table 1.3: Composition of CO_2 in different natural gas wells (Rojey et al, 1997)

No.	Location	Composition (%)
1	Lacq, France	9.3
2	Frigg, Norway	0.3
3.	Uch, Pakistan	46.2
4	Kapuni, New Zealand	43.8
5	Uthmaniyah, Saudi Arabia	8.9
6	Terrengganu, Malaysia	7.0
7	Krecsegopan, Poland	83.0
8	North German Plain, Germany	60.0
9	Kirkuk, Iraq	7.1
10	Duri, Indonesia	23.0

1.3. Removal of CO_2 from natural gas

Due to its acidic nature and being non-combustible, carbon dioxide must be removed from natural gas before the natural gas can be sold to the customers. In practice, CO_2 content of the natural gas must be reduced down to a permissible level. Typical pipeline quality states that the composition of CO_2 in treated gas stream must not be more than 2% (Spillman, 1989). In Malaysia, Gas Malaysia sets an even more stringent limit where the level of CO_2 is further reduced to about 1.8% maximum. Table 1.4 shows the typical pipeline quality of treated natural gas where the composition of CO_2 is highlighted.

Acid gas removal is a very important industrial operation which has been described in many works such Kohl and Riesenfeld (1985), the report published by the ATG (1988) concerning natural gas processing on the field and the general references already listed (ATG, 1990; Arnold and Stewart, 1989; Kumar, 1987; Mohr; 1984; Maddox, 1982; GPA, 1980; Ikoku, 1980).

1.3.1 Chemical and Physical Absorption

1.3.1.1 Chemical Absorption – Amine absorption process

In the amine gas processing operation, the gas stream and liquid amine solution are contacted by countercurrent flow in an absorption tower. Conventionally, the gas to be scrubbed enters the absorber at the bottom, flows up, and leaves at the top, whereas the solvent enters the top of the absorber, flows down (coming in contact with the gas), and emerges from the bottom.

Alkanolamines can be divided into three groups: (1) primary amines such as monoethanolamine (MEA), diglycolamine (DGA); (2) secondary amines, diethanolamine (DEA), di-isopropylamine (DIPA); and (3) tertiary amines whose include triethanolamine (TEA) and methyl-diethanolamine (MDEA). MEA and DEA are still widely used but other amines, introduced more recently, such as diglycolamine, diisopropanolamine and methyldiethanol amine, are gaining interest.

1.3.1.2 Physical Solvent

For physical absorption, CO_2 is physically absorbed in a solvent according to Henry's Law, which means that they are temperature and pressure dependent, with absorption occurring at high partial pressures of CO_2 and low temperatures. The solvents are then regenerated by either heating or pressure reduction.

The advantage of this method is that it requires relatively little energy; but the CO_2 must be at high partial pressure. Hence, it is suitable for recovering CO_2 from Integrated Gasification Combined Cycle (IGCC) systems where the exhaust CO_2 would leave the gasifier at elevated pressures. Typical solvents used are Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol).

1.3.2 Alkaline Salt – Based Processes

Many processes have been developed for carbon dioxide removal utilizing alkaline salts of various weak acids. Many salts have been proposed such as sodium and potassium salts of carbonate, phosphate, borate arsenite and phenolate (Kohl and Reisenfeld, 1985). The most popular salts in the industry have been sodium carbonate and potassium carbonate.

The primary advantages of this process are low cost and minimal degradation of the solvent. However, solution concentrations are limited by the precipitation of bicarbonate salts and solution temperatures are high. Foaming is also reported to be a concern. Corrosion problems may be severe depending on input gas composition. (Benson, 1954)

1.3.3 Adsorption – Pressure Swing and Temperature Swing Adsorption

The adsorption process consists of two major steps: adsorption and desorption. The technical feasibility of a process is dictated by its adsorption step, whereas the desorption step controls its economic viability. The main advantage of physical adsorption over chemical is its simple and energy efficient operation and regeneration, which can be achieved with a pressure swing or temperature swing cycle. The primary adsorption material under consideration is zeolite. The concerns over this technology are scale up and the need to develop CO_2 specific adsorbent materials.

1.3.4 Low Temperature Distillation (Cryogenic Separation)

Low temperature distillation (cryogenic separation) is a commercial process commonly used to liquefy and purify CO_2 from relatively high purity (> 90%) sources. It involves cooling the gases to a very low temperature so that the CO_2 can be liquefied and separated. Distillation generally has good economies of scale, which is worth considering where there is a high concentration of CO_2 in the waste gas. The advantage is that it produces liquid CO_2 ready for transportation by pipeline. The major disadvantages of this process are the amount of energy required to provide the refrigeration and the necessary removal of components that have freezing points above normal operating temperatures to avoid freezing and eventual blockage of process equipment.

1.3.5 Membranes

Separation membranes are thin barriers that allow selective permeation of certain gases. They are predominately based on polymeric materials. Membranes for gas separation are usually formed as hollow fibers arranged in the tube-and-shell configuration, or as flat sheets, which are typically packaged as spiral-wound modules. The membrane process has many advantages compared to absorption separation, which will be discussed in detail in section 2.1 later.

A number of solid polymer membranes are commercially available for the separation of CO_2 from gas streams, primarily for natural gas sweetening. These membranes selectively transmit CO_2 versus CH_4. The driving force for the separation is pressure differential across the membrane. As such, compression is required for the feed gas in order to provide the driving force for permeation, and the separated CO_2 is at low pressure and requires additional compression to meet pipeline pressure requirements.

The commercial membranes for CO_2 separation are mainly prepared from cellulose acetate, polysulfone, and polyimide. K. Li and W.K. Teo (1997) discussed that membrane separation, although recently discovered, has many advantages due to the properties of the membrane which can be used as separation unit due to the intrinsic selectivity of the membrane between CO_2 and other gases.

1.3.6 Hybrid Membrane-Amine System

It may be desirable to apply amine and membrane technologies in tandem, thereby forming a hybrid process to capture CO_2 from natural gas. Micro-porous hollow fibre membranes are evolving as a new technology for CO_2 separation using amine based chemical absorption processes. Micro-porous membranes are used in the gas-liquid unit where the amine solution is contacted with the CO_2 containing flue gas. The principle advantage of the micro-porous membrane is the reduction in the physical size and the weight of the gas-liquid contacting unit (Sam Wong and Rob Bioletti, 2000)

The feedgas will flow along the membrane and permeate through the membrane and then will be absorbed in the amine solution.

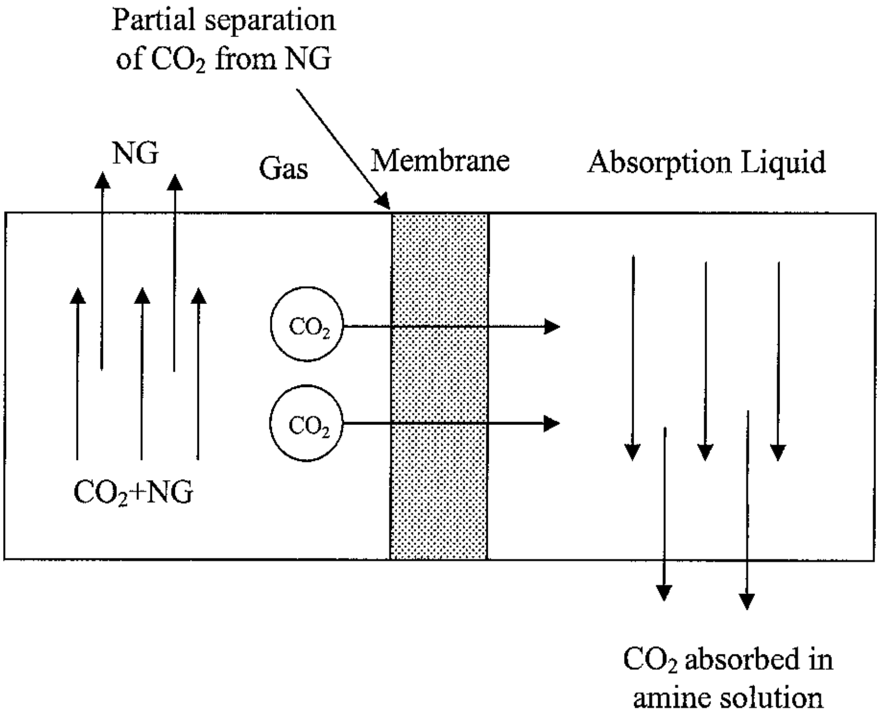


Figure 1.1: Membrane and amine separation system in CO_2 removal

However, there are some disadvantages for such hybrid system, which are large required floor area and high capital cost of installing two units at the same time. Besides that, the system needs to have a reliable control system in place in order to ensure the operation of the hybrid membrane-absorption processes goes well.

1.3.7 Compact Hybrid Membrane Amine System

In order to overcome the weakness of Hybrid Membrane Amine System, Compact Hybrid Membrane-Amine System is proposed. Its advantages over the hybrid membrane–amine system are less floor area required which is suitable to be used in the offshore application and capital expenditure saving by removing the cost of installing two units at the same time (only one unit of compact hybrid membrane-amine system needs to be installed).

Combining membranes with solvents has the potential to increase the advantages of each technology and reduce the disadvantages of each technology. Membranes operate best at high partial pressures of CO_2, while solvents operate best when treating to low CO_2 specifications. Therefore, a high-pressure gas with a high concentration of CO_2 that must be conditioned to pipeline specification is a very good candidate for using a compact hybrid system consisting of a membrane unit followed by a solvent unit. For processing large gas flow rates where two or more trains may be required, a compact hybrid can reduce the system to a single, less expensive train. If an existing solvent system needs to be modified to handle an increase in feed gas CO_2 concentration, adding a membrane upstream can be a very attractive method of expanding the system capacity (William Echt, 2002).

1.4. Problem Statement

The composition of carbon dioxide in natural gas may vary from 2% to 60% depending on the geographical location of the well. The removal of CO_2 is very important and the concentration of CO_2 must be below 2% (or 1.83% for Gas Malaysia) before the gas can be sold. Hybrid system with a sequence column of membrane followed by amine solution for absorption process is recommended for effective removal of CO_2. However, hybrid system is not suitable for offshore application. Therefore, Compact Hybrid Membrane–Amine System, in which amine absorption is integrated together with membrane permeation, is recommended to overcome the problem faced by hybrid system.

Mathematical models are very helpful in understanding the mechanism of membrane process and absorption process for high content CO_2 removal as a function of various process influences. Furthermore, similar empirical study carried out on a pilot plant scale is both time consuming and expensive. Thus mathematical models can generate sets of data concerning the behavior of the system quickly without incurring much cost as compared to experimental study.

1.5. Objectives

The objectives of this study can be summarized as follows:

- To develop mathematical models for removal of high content CO_2 from CH_4 using Compact Hybrid Membrane–Amine System.
- To study and analyze the parameters which influence the permeability of CO_2 and CH_4 and the capability of CO_2 absorption on alkanolamine solution.

The main objective of this work is to develop a mathematical for the removal of CO_2 from methane in compact hybrid membrane amine system. The model will analyze the permeability of CO_2 and methane across membrane followed by absorption of CO_2 in amine solution. The effect of various parameters which consist of concentration of CO_2 in feed gas, operating pressure of feed gas, flow rate of amine solution and membrane pore size, towards the permeability and separation factor of the compact hybrid membrane-amine system has been analyzed systematically. The model is developed using MATHCAD version 2000i and Microsoft Excel to represent the mass transfer of CO_2 in the compact hybrid membrane-amine system.

1.6. Scope of Study

The study involves the development of the mathematical models that could predict the mechanism of gas permeation and gas absorption as a function of pore size, operating pressure, concentration of CO_2 at the feed as well as ratio of flow rate of amine over flow rate of feed gas. The study relates to conduct the mass transfer modeling in membrane separation and amine absorption in order to identify and discuss the optimum operating conditions for compact hybrid membrane-amine process. In addition, the performance of the compact hybrid membrane-absorption process will be studied and analyzed in the following chapter.

CHAPTER 2

2. LITERATURE REVIEW

Transport phenomena in porous solids have been the subject of many studies. However, quantitative solutions are obtained only in a number of limiting cases of generally formulated problems or in relatively simple cases. Transport of mixtures is more complicated especially in compact hybrid membrane-absorption process with a more complex architecture and operated with high pressure gradients. In such cases, the solutions have to be obtained by approximations and by combining solutions of limiting cases.

2.1. Membrane Separation Technology

The membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals across the barrier in a selective manner.

2.1.1 Types of Membranes

2.1.1.1 Micro porous membrane:

The membrane behaves almost like a fibre filter and separates by a sieving mechanism determined by the pore diameter and particle size. Materials such as ceramics, graphite, metal oxides, polymers etc. are used in making such membranes. The pores in the membrane may vary between 1 nm-20 microns.

2.1.1.2 Homogeneous membrane

This is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be separated efficiently when their concentrations differ significantly.

2.1.1.3 Asymmetric membrane

An asymmetric membrane comprises a very thin (0.1-1.0 micron) skin layer on a highly porous (100-200 microns) thick substructure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of membrane material or pore size; and the mass transport rate is determined mainly by the skin thickness. Porous sub-layer acts as a support for the thin, fragile skin and has little effect on the separation characteristics.

2.1.1.4 Electrically Charged Membrane

It is essentially ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges. These membranes are mainly used in electro-dialysis.

2.1.1.5 Liquid Membrane

A liquid membrane utilizes a carrier to selectively transport components such as metal ions at relatively high rate across the membrane interface.

2.1.2 Gas separation with membrane

The separation of gas mixtures with membranes has emerged from being a laboratory curiosity to becoming a rapidly growing, commercially viable alternative to traditional methods of gas separation within the last two decades. Membrane gas separation has become one of the most significant new unit operations to emerge in the chemical industry in the last 25 years. Table 2.1 shows commercial applications and some of the major suppliers of membrane gas separation units.

Table 2.1 Gas membrane applications and suppliers (R.W. Spillman, 1995)

Gas separation	Application	Suppliers
O_2/N_2	Nitrogen generation, oxygen enrichment	A/G technology Permea (Air Products) Medal (Dupont, Air Liquide)
H_2/Hydrocarbons	Refinery hydrogen, recovery	Air Products Air Liquide, Praxair
H_2/CO	Syngas ratio adjustment	Air Products Air Liquide, Praxair
H_2/N_2	Ammonia purge gas	Air Products Air Liquide, Praxair
CO_2/Hydrocarbon	Acid gas treating, enhanced oil recovery, landfill gas upgrading	Kvaerner (Grace Membrane System), Air Products, Ube
H_2O/hydrocarbon	Natural gas dehydration	Kvaerner, Air Products
H_2S/ Hydrocarbon	Sour gas treating	Kvaerner (Grace Membrane System), Air Products, Ube

2.1.3 Materials for Gas Separation Membranes

Organic polymers are the dominating materials for gas separation membranes. Many polymers exhibit sufficient gas selectivity and they can be easily processed into membranes. Palladium alloys are the only inorganic materials which are currently used for gas separation (ultra-pure hydrogen generation) on a commercial scale. However, during the last decade inorganic materials have been developed with exciting unmatched selectivity for certain gas mixtures and some of the inorganic membranes described in the scientific literature seem to be on the brink of commercialization. (Eds. S.P.Nunes and K.-V.Peinemann, 2001). Table 2.2 shows relevant membrane materials for gas separation.

Table 2.2: Materials for gas separation membranes
(S.P.Nunes and K.-V.Peinemann, 2001)

Organic polymers	Inorganic materials
Polysulfone, polyethersulfone	Carbon molecular sieves
Cellulose acetate	Nanoporous carbon
Polyimide, polyetherimide	Zeolites
Polycarbonate (brominated)	Ultramicroporous amorphous silica
Polyphenyleneoxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydimethylsiloxane	
Polyvinyltrimethylsilane	

2.1.4 The mechanism for gas separation

The mechanism for gas separation is independent of membrane configuration and is based on the principle that certain gases permeate more rapidly than others (Figure 2.1).

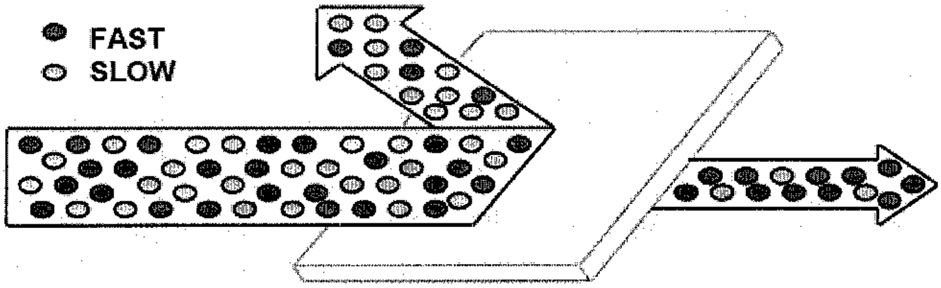


Figure 2.1: Thin Semi-Permeable Barriers that Selectively Separate Some Compounds from Others

"Permeability" is a measure of the rate at which gases pass through the membrane. "Selectivity" refers to the relative rates of permeation among gas components. The permeation rate for a given gas component is determined by the molecule's size, its solubility in the membrane polymer and the operating conditions of the separation. Selectivity allows a gas mixture of two or more components, of varying permeability, to be separated into two streams, one enriched in the more permeable components and the other enriched in the less permeable components. Figure 2.2 shows the relative permeability of the components most common in a natural gas stream.

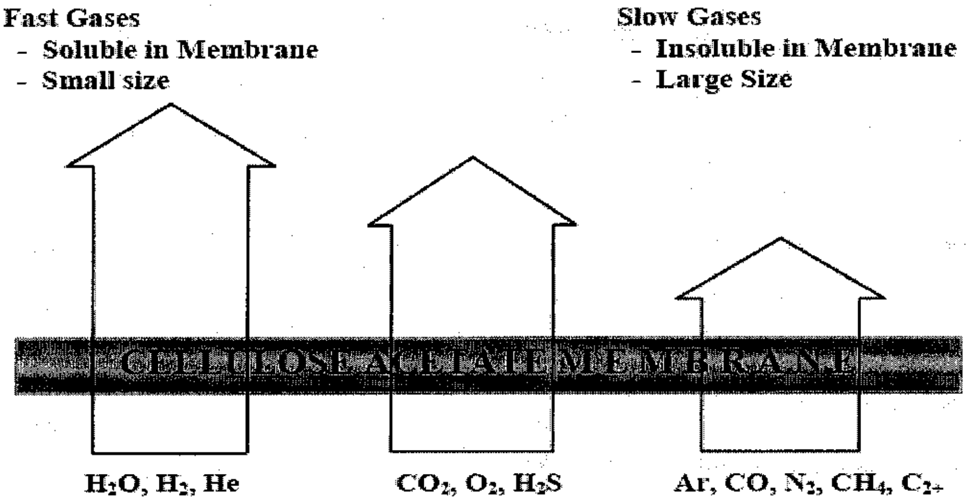


Figure 2.2: Relative Solubility of Some Typical Gas Components

2.1.5 Advantages and disadvantages of membrane separation

2.1.5.1 Advantages of membrane separation

In comparison to absorption separation, membrane process has some advantages, which are (Sam Wong and Rob Bioletti, 2000)

- It does not require a separating agent, thus no regeneration is required;
- The systems are compact and lightweight, and can be positioned either horizontally or vertically, which is especially suitable for retrofitting applications;
- Modular design allows optimization of process arrangement by using multi-stage operation;
- Low maintenance requirements because there are no moving parts in the membrane unit and limited manpower requirements due to simplified operation and maintenance. Therefore, it leads to low capital and energy cost.

- Reduced space requirements, faster delivery time and lower installation costs due to smaller lighter modular design. The technology's compactness makes it the preferred technology for offshore gas treatment.
- Increased adaptability to changing feed flow and composition.

2.1.5.2 Disadvantages of membrane separation

Some of the disadvantages of membrane separation in removal of CO_2 from natural gas (William Echt, 2002)

- Level of hydrocarbon losses depending on the operating conditions (methane loss to the permeate is often 10-15% in one stage plants (Richard W. Baker, 2000). For the methane loss in the permeate, if there is no fuel use for this gas, it must be flared, which represents a significant revenue loss.
- Only suitable for bulk CO_2 removal from natural gas therefore it cannot meet low CO_2 specification of pipeline quality
- Requirement of compression of feed gas because the driving force of separation is the pressure difference cross membrane, which is at less 40 bar

2.1.6 Application of membrane gas separation

Some applications of membrane gas separation in industries (G. Srikanth, 2001)

- hydrogen separation and recovery,
- ammonia purge gas,
- refinery hydrogen recovery;
- 'syngas' separation in petrochemicals industry,
- CO_2 enhanced oil recovery,
- natural gas processing,
- landfill gas upgrading,
- air separation,
- Nitrogen production, etc.

The gas separation technology may enjoy the following applications in the near future:

- N_2 enrichment of air
- Low level O_2 enrichment of air
- H_2 and acid gas separation from hydrocarbons
- Helium recovery
- Natural gas dehydration

2.1.7 Membrane process in CO_2 removal

Membranes have shown promise in a variety of applications related to the processing of natural gas streams. Some natural gas contains impurities such as carbon dioxide and hydrogen sulfide, which are corrosive to pipeline. Hydrogen sulfide is also toxic. Therefore they must be removed prior to delivery to a pipeline. Membrane is an attractive option in this type of application since the feed gas is already at high pressure; the gas impurities readily permeate membranes and the methane stream exits as the high pressure residue which means no recompression is necessary (R.D. Noble and S.A.Stern, 1995)

2.1.7.1 Membrane Configuration

The new membrane is called asymmetric and is first cast into a flat sheet. The major portion of the asymmetric membrane is an open-pore, sponge-like support structure through which the gases flow without restriction. All the selectivity takes place in the thin, non-porous polymer layer at the top (Figure 2.3).

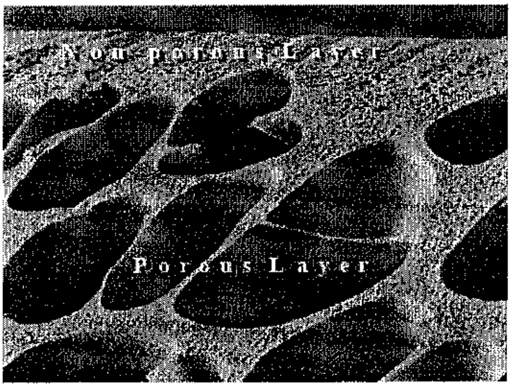


Figure 2.3: Asymmetric Membranes Use a Single Polymer with a Thin Selective Layer

2.1.7.2 Types of membrane elements

The most common types of membrane elements in use today for natural gas separation are of the spiral-wound type and the hollow-fiber type (William Echt, 2002)

a. Spiral-wound membrane

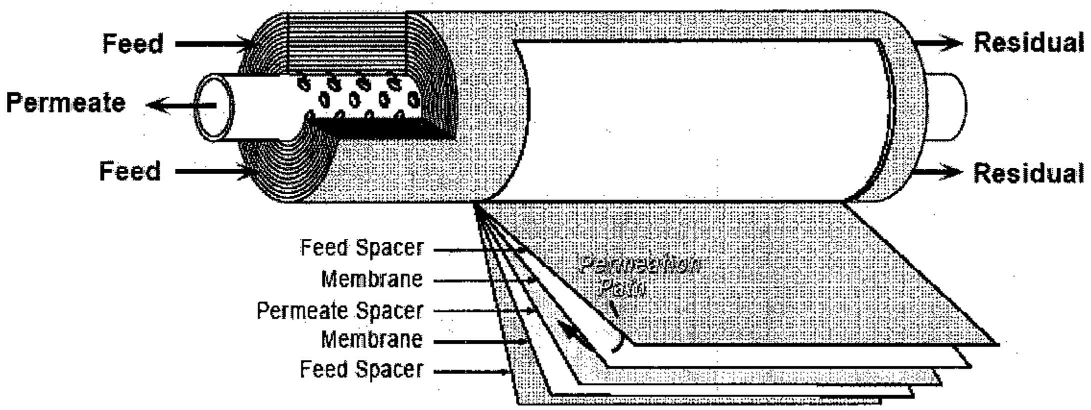


Figure 2.4: Spiral-Wound Membrane Element

In order to separate carbon dioxide from natural gas, the feed mixture enters the pressure vessel (tube) at high pressure and is introduced into the element via the feed spacer. The more permeable CO_2 and H_2O rapidly pass through the membrane into the permeate spacer, where they are concentrated as a low pressure gas stream. This low pressure CO_2 gas stream flows radially through the element in the permeate spacer channel and is continuously enriched by additional CO_2 entering from other sections of the membrane. When the low pressure CO2 reaches the permeate tube at the center of the element, the gas is removed in one or both directions. The high pressure residual gas mixture remains in the feed spacer channel, losing more and more of the carbon dioxide and being enriched in hydrocarbon gases as it flows through the element, and exits at the opposite end of the element.

b. Hollow fiber membrane

To construct hollow fiber elements, very fine hollow fibers are wrapped around a central tube in a highly dense pattern. The feed natural gas flows over and between the fibers and the fast components permeate into the middle of the hollow fiber. The wrapping pattern used to make the element is such that both open ends of the fiber terminate at a permeate pot on one side of the element. The permeate gas travels within the fibers until it reaches the permeate pot, where it mixes with permeate gas from other fibers. A permeate pipe allows the collected gases to exit the element.

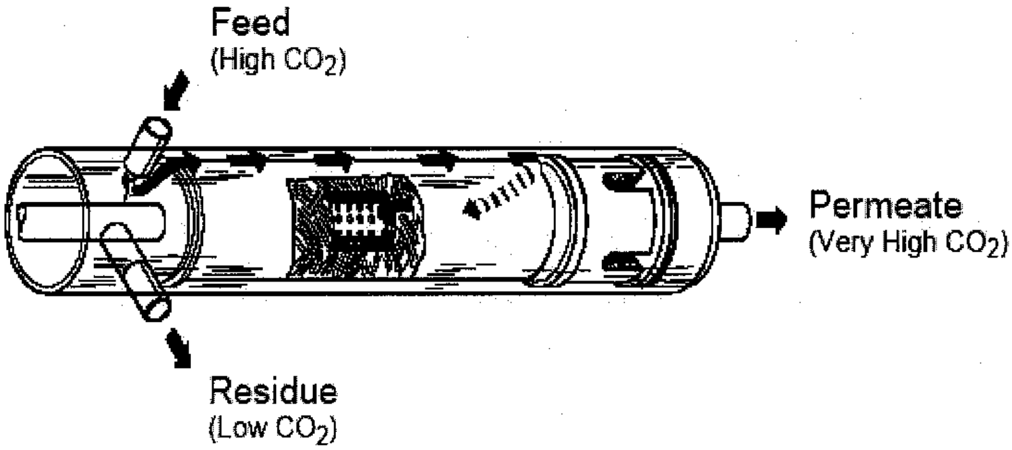


Figure 2.5: Hollow Fiber Membrane Element

2.2. Principle of Absorption Process

Many chemical process materials and biological substances occur as mixtures of different components in the gas, liquid or solid phase. In order to separate or remove one or more of the components from its original mixture, it must be contacted with another phase. The two phases are brought into more or less intimate contact with each other so that a solute or solutes can diffuse from one to the other. The two bulk phases are usually only somewhat miscible in each other. Absorption occurs when the two contacting phases are gas and liquid.

The removal of CO_2 from natural gas using amine solution involves molecular and turbulent diffusion or mass transfer of CO_2 solute through a stagnant non-diffusing natural gas into a stagnant liquid, which is amine solution. Usually the exit CO_2-amine solution then goes to stripping section to recycle the amine solution.

Types of amine solution used to sweeten natural gas:

- Monoethanolamine (MEA)
- Diethanolamine (DEA),
- Diglycolamine (DGA),
- Diisopropanolamine (DIPA)
- Methyldiethanolamine (MDEA)

The prefix “mono”, “di”, or “tri” indicates the degree of substitution around the nitrogen atom. Thus, if R denotes the functional group $HOCH_2CH_2$-, monoethanolamine has the chemical formula RNH_2, diethanolamine R_2NH and triethanolamine R_3N.

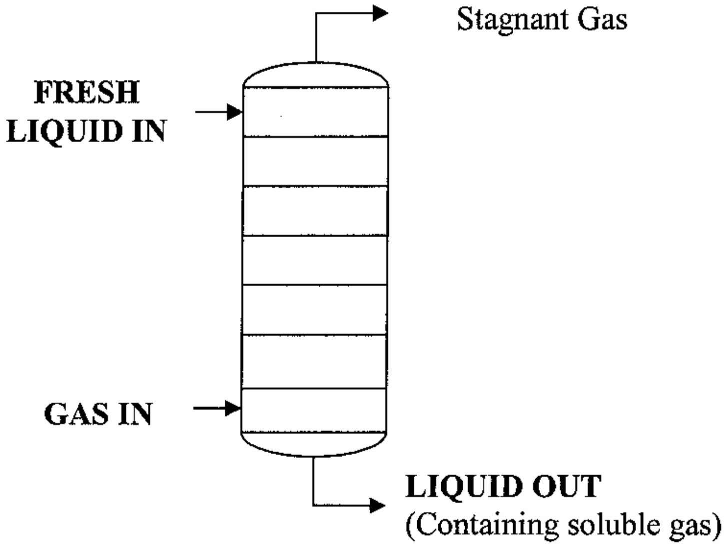


Figure 2.6: Industrial equipment for absorption of CO_2

Triethanolamine, which was the first amine used, is the least active amine and has gradually been supplanted by MEA and DEA.

Amines also react with carbon dioxide by two types of reaction.

Formation of carbonate and bicarbonate:

$$2RNH_2 + CO_2 + H_2O \Leftrightarrow (RNH_3)_2CO_3$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \Leftrightarrow 2RNH_3HCO_3$$

Formation of carbamate:

$$2RNH_2 + CO_2 \Leftrightarrow RNHCOONH_3R$$

The formation of carbonate and bicarbonate reactions is slow because carbon dioxide must form carbonic acid with water (slow reaction) before reacting with the amine. The formation of carbamate which predominates with MEA, is relatively fast.

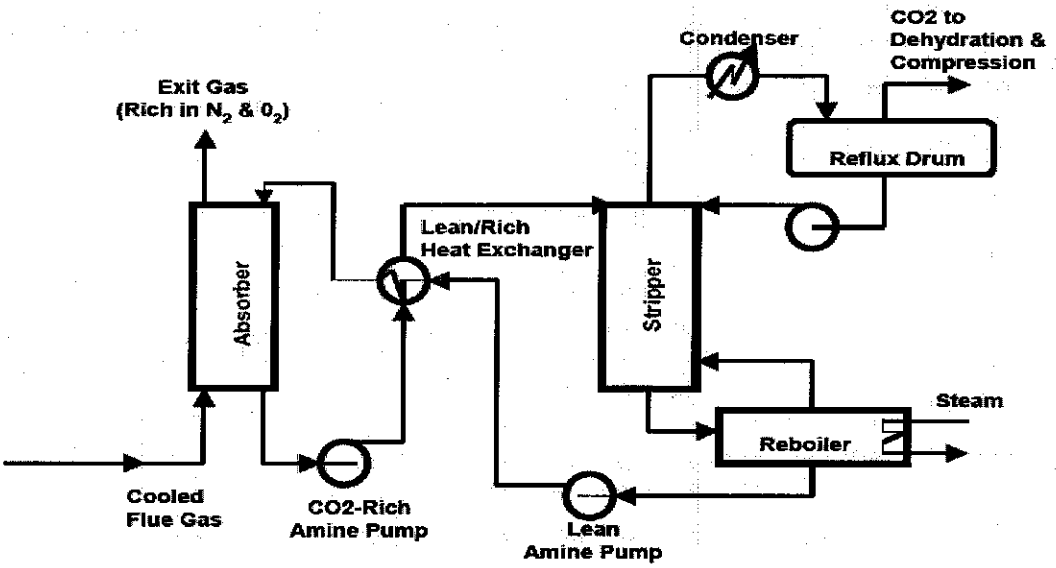


Figure 2.7: Typical Amine Absorption Unit for CO_2 Recovery from Flue Gas

Monoethanolamine (MEA), considered to be the state-of-the-art technology, gives fast rates of absorption and favorable equilibrium characteristics. Secondary amines, such as diethanolamine (DEA), also exhibit favorable absorption characteristics.

Although alkanolamines have proven to be commercially successful, there is still room for process improvement. The promotion of potassium carbonate (K_2CO_3) with amines appears to be a particularly effective way to improve overall solvent performance. K_2CO_3 in solution with catalytic amounts of piperazine (PZ) has been shown to exhibit a fast absorption rate, comparable to 30 wt% MEA. (Scott M. Klara, John Litynski, Gary T. Rochelle, 2004)

However, nowadays, the most selected absorbent for absorption of CO_2 is amine-based solution because of its high loading factor as well as its less contribution to the corrosion of the pipe lines. During early 90's, the chemical industry have come up with an alternative absorbent which is less corrosive. They are amine-based absorbent or commonly known as amine solution. Each of this amine absorbent has different properties and usage especially during absorbing CO_2.

Table 2.3: Different types of amine absorbent and its application
(Reference: www.chemicalland21.com)

Amine Solution	Usage and properties
DEA	Neutralizing acid gases to make them non-irritating
MDEA	Scrubbing H_2S and CO_2 from petroleum gas stream as well as dispersing agent and corrosion inhibitor
MEA	Scrubbing H_2S and CO_2 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

Monoethanolamine (MEA)

Among the primary amines, MEA has been the traditional solvent of choice for CO_2 absorption and acid gas removal in general. MEA is the least expensive of the alkanolamines and has the lowest molecular weight, so it possesses the highest theoretical absorption capacity for carbon dioxide. This theoretical upper absorption capacity of MEA is not realized in practice due to corrosion problems. In addition, MEA has the highest vapor pressure of any of the alkanolamines and high solvent carryover can occur during carbon dioxide removal from the gas stream and in the regeneration step.

There is considerable industrial experience with MEA and most systems at present use an aqueous solution with only 15-25 wt % MEA, mainly due to corrosion issues (GPSA, 1998). Corrosion inhibitor may be added to MEA solution, which results in an increase in solution strength. In a commercial process, concentration of MEA up to 30% has been employed successfully to remove 80-90% CO_2 from the feed gas (Mariz, 1998).

Diethanolamine (DEA)

The application of DEA to natural gas processing was described for the first time by Berthier in 1959 (Kohl and Riesenfeld, 1985). DEA helps to overcome the limitation of MEA and can be used in the presence of COS and CS_2. Moreover DEA has advantage over primary amines – their heat of reaction with CO_2 is lower, 360 cal/gm (650BTU/lb) vs. 455 cal/gm (820BTU/lb). This means that the secondary amines require less heat in the regeneration step. From an energy consumption point of view, this is an important consideration when the primary objective is the isolation of CO_2 from flue gas.

Triethanolamine (TEA)

TEA reacts slower with CO_2 than MEA and DEA thus require higher circulation rate of liquid to remove CO_2 compared to MEA and DEA. A major advantage of TEA is their lower heat requirements for CO_2 liberation from CO_2 containing solvent.

Table 2.4: The heat of reaction between the three amine and CO_2 (Skinner et al 1995)

Amine	MEA	DEA	MDEA
ΔH_f for CO_2 (cal/gm)	455	360	320
ΔH_f for CO_2 (BTU/lb)	820	650	577

2.3. The compact hybrid membrane absorption

The compact hybrid membrane-absorption model that will be used in this study is a hollow fiber module with dense ultra thin skinner layer. Micro porous hollow fibre membrane modules used for gas absorption or stripping process are known to possess much larger interfacial areas than those of conventional absorbers such as packed column. Furthermore, it has other advantages such as independent control of gas and liquid flow rates without flooding, loading, foaming etc. and known gas-liquid interfacial area. The dense outer layer prevents amine solution from leaching into the micro porous membrane structure to ensure that no absorption process happen prior to membrane separation. Moreover, it has two advantages. Firstly operating pressure at the gas phase side may be more flexible and higher than those at the liquid side may be operated, as long as no bubble formation is observed in the liquid. Secondly, the dense skin layer of the fibre will eliminate the possibility of filling the membrane pores with the liquid thus preventing the dramatic reduction of the CO_2 transfer rate.

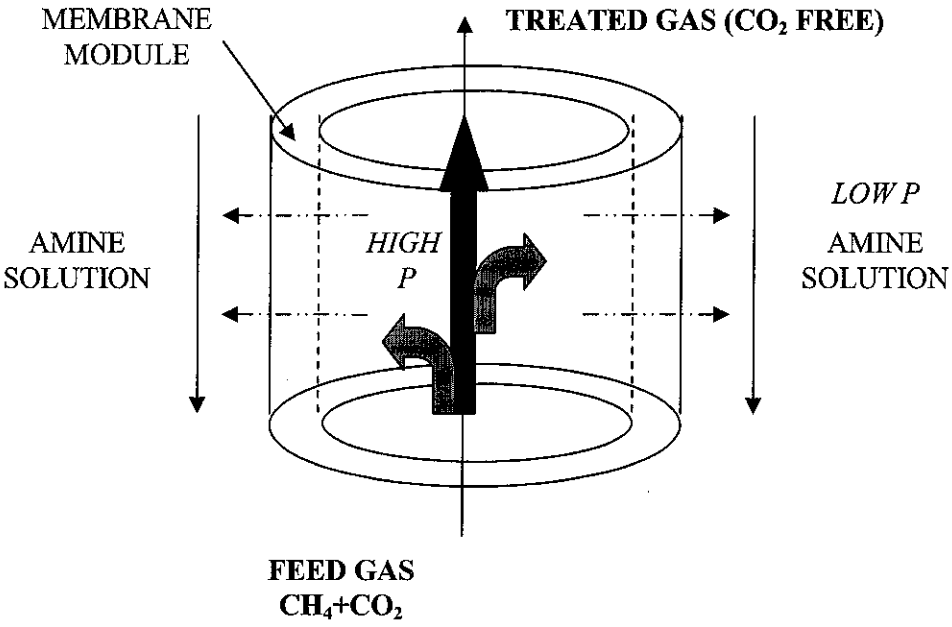


Figure 2.8: Typical hybrid membrane amine separation process system

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 CO_2 component will permeate into the membrane and later absorbed by the amine solution. The rich amine solution is then sent to downstream equipment for the recovery of solute absorbed. Meanwhile, the treated gas (CO_2-free natural gas) will then be used for other purposes. The schematic of the process is shown in Figure 2.8.

In membrane system, the separation is based on the permeation mechanism of gas molecules 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.

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, which consists of 3 important components: the mass transfer coefficient of CO_2 in bulk 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 are also called the overall mass transfer coefficient, K_{AG} in the compact hybrid membrane-amine system. In other words, each of this term makes the individual resistance of CO_2 in gas phase, membrane and liquid phase respectively.

The amine absorption process is 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.

There are a number of advantages of using gas-liquid membrane contactors, including (Sam Wong and Rob Bioletti, 2000):

- High gas/ liquid contact area due to the high packing density of the hollow fibers (500 to 1500 m^2/m^3 versus 100~250 m^2/m^3 for a conventional column)
- Foaming is eliminated because the gas flow does not impact the solvent and there is no connective dispersion of gas in the liquid.
- The membrane acts as a partition between the gas and liquid, and the gas/liquid flow rate ratio may vary in a wide range without causing flood problems
- The available gas/liquid contact area is not disturbed by variations in flow rates. This means the process can tolerate a wider range of process condition variations.
- Solvent degradation is minimized as oxygen (a degradation agent to amines) is prevented from intimate contact with the solvents.
- Unlike the absorption column that can only be operated vertically, the hollow fibre membrane contactor may be operated in any orientation to suit the overall plant layout.
- Increase the productivity of plant production by reducing the time to remove CO_2 from the natural gas.
- The system is robust and reliable since it is using membrane which is considered the preferred medium of separation in the future.
- The advancement in the hybrid membrane-absorption processes is tangible and flexible because it can be used in many applications.

CHAPTER 3

3. THEORY

Hongyi Dang (2001) experimented in vapour-liquid equilibrium (VLE) model, one-phase equilibrium and five chemical equilibria in the liquid phase were considered for $CO_2/MEA/H_2O$ system.

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

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

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

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

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

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

The mass transfer in the compact hybrid membrane-absorption system is divided into 2 sections: membrane separation and absorption process.

The overall rate of CO_2 transfer through compact hybrid membrane-amine system can be expressed by equation 3.1

$$N_A = K_{AG}\left(p_A - p^*_A\right)A_M \tag{3.1}$$

The overall transfer of CO_2 through compact hybrid membrane-amine system can be expressed into three parts: through bulk gas (Equation 3.1a), followed by membrane (Equation 3.1b) and finally through bulk liquid (Equation 3.1c).

$$N_A = k_{AG}\left(p_A - p_{AM}\right)A_M \tag{3.1a}$$

$$N_A = k_{AM}(p_{AM} - p_M)A_M \tag{3.1b}$$
$$N_A = k_{AL}(C_{Ai} - C_A)A_M \tag{3.1c}$$

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 can be expressed by equation 3.2.

$$\frac{1}{K_{AG}} = \frac{1}{k_{AG}} + \frac{1}{k_{AM}} + \frac{H_A}{k_{AL}} \tag{3.2}$$

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. Therefore equation 3.2 can be simplified to 3.2a.

$$\frac{1}{K_{AG}} = \frac{1}{k_{AM}} + \frac{H_A}{k_{AL}} \tag{3.2a}$$

The mechanism of mass transfer in the compact hybrid membrane-absorption process is indicated by the Figure 3.1.

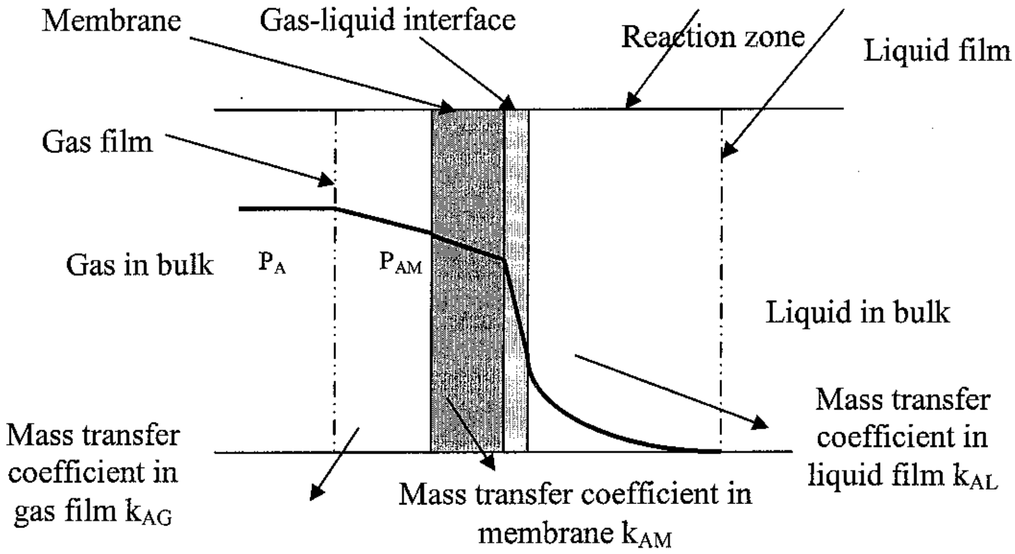


Figure 3.1: Membrane amine separation process concentration gradient profile

3.1. Transport mechanism across Membrane

Permeability is an important parameter in membrane characterization. It gives an overview of permeation behavior of a certain gas through a particular type of membrane, either highly permeable or less permeable. The permeability of gas consists of three types of diffusion, which predominate the transport of gas molecules through the pores. They are viscous diffusion, Knudsen diffusion and surface diffusion.

3.1.1 Knudsen 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 (Equation 3.3). 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.

$$\mathrm{D_K} = \frac{2}{3}\frac{\left(r_P - r_{g,A}\right)}{3}\sqrt{\frac{8RT}{\Pi M_A}} \qquad (3.3)$$

D_K = Knudsen diffusion for species gas i

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

R = Universal gas constant

T = Temperature

M_A = Molecular weight

3.1.2 Viscous diffusion

The viscous diffusion mechanism describes the ideal condition for the separation of vapour compounds of different molecular sizes through a porous membrane. The assumption that the pore resembles a perfect cylinder is necessary to model the viscous flow in the pore (Bird et at., 1960). This assumption is practical for a piece of thin membrane with pore size ranging from 1 – 7 mm, as the gas molecules will collide against each other more frequently than their collision with the cylinder wall, under this condition. 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.

$$D_V = \frac{\overline{P} r_P}{8\mu} \tag{3.4}$$

D_V = Viscous diffusion for species of gas i

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

r_P = Pore radius

μ = Viscosity

3.1.3 Surface diffusion

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. With gas mixtures, enhancement of the separation factor can be obtained by preferential sorption of mobile species of one of the components of the gas mixture. In a mixture of light non adsorbing molecules and heavy molecules, the heavy molecules move slower than the lighter ones but in many cases are preferentially absorbed. Consequently, the flux of the heavier molecules is better enhanced by surface diffusion and the separation factor increases. This occurs, e.g. in CH_4/CO_2 mixtures, in Vycor glass membrane (Burggraaf and Cot, 1996). With two adsorbing molecular species, competition for the absorption sites may exist and sorption isotherms for single gas species are no longer valid (Uhlhorn et at.,1989)

$$D_S = 1.6x10^{-2} e\left[\frac{-0.45(-\Delta H_{ads})}{mRT}\right]\left(\frac{t_m}{r_P}\right) \tag{3.5}$$

D_S = Surface diffusion for species gas i

ΔH_{ads} = Specific enthalpy difference of adsorption

m = Number of moles

t_m = Membrane thickness

$$D_B = \frac{1x10^{-7}T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}}{P\left(\upsilon_A{}^{1/3}+\upsilon_B{}^{1/3}\right)^2} \tag{3.6}$$

D_B = Bulk diffusion for species gas i

υ = Volume diffusion of atom and structure

$$P_i = \frac{\varepsilon}{zRT\tau} \tag{3.7}$$

P_i = Permeability for species gas i

ε = Porosity of membrane

z = Compressibility factor

τ = Tortuosity

$$D_g = \frac{1}{\frac{1}{D_K}+\frac{1}{D_B}} \tag{3.8}$$

D_g = Gas diffusion

D_K = Knudsen diffusion for species gas i

D_B = Bulk diffusion for species gas i

$$P_V = P_i\, D_V \tag{3.9}$$

P_V = Viscous permeability for species gas i

P_i = Permeability for species gas i

D_V = Viscous diffusion for species of gas i

$$P_K = P_i\, D_g \tag{3.10}$$

P_K = Permeability for species gas i

P_i = Permeability for species gas i

D_g = Gas diffusion

$$P_S = P_i \frac{1}{\varepsilon} D_S \rho_M f \tag{3.11}$$

Ps = Permeability for species gas i

ρ_M = Membrane density

f = Equilibrium loading factor

The total permeability of species gas i will be the sum of three permeability components

$$P_i = P_{Ki} + P_{Vi} + P_{Si} \tag{3.12}$$

In 1998, Li and Teo came up with the latest form of Equation 2.23 with the inclusion of permeability of the membrane in the equation. The specific permeability of gases can be expressed as:

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

$\left(\frac{P}{\delta}\right)$ = Specific gas permeability (3.13)

d_o = Outer diameter of hollow fibre

Z = Hollow fibre length

Δp = Pressure difference across the membrane

3.1.4 Separation factor:

Separation factor is a measurement of the enrichment of a gas component after it has passed the membrane. It is a parameter to describe the separation efficiency for a binary mixture. Vieth (1991) suggested that the ideal separation factor for a binary system can be written as,

$$\alpha^* = \frac{P_A'}{P_B'} \tag{3.14}$$

P'_A, P'_B: permeability of component A, B in the mixture

Typical separation factors for some industrial membranes are indicated in the table below.

Table 3.1: Typical separation factors for some industrial membranes (Geankoplis,1993)

Gas separated	**Separation factor**
H_2O/CH_4	500
He/CH_4	5-44
H_2/CO	35-80
H_2/N_2	3-200
H_2/O_2	4-12
H_2/CH_4	6-200
O_2/N_2	2-12
CO_2/CH_4	3-50
CO_2/O_2	3-6
CH_4/C_2H_6	2

3.2. CO_2 Absorption in Amine solution

From Figure 3.1, the rate of CO_2 transfer, N_A (mol s^{-1}) at steady state, can be expressed as in equation 3.1c.

$$k_{AL} = \frac{H_A}{\sqrt{D_A C_A k}} \tag{3.15}$$

k_{AL} = Mass transfer coefficient on liquid side

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, which can be calculated as below

$$\log_{10}(0.001 k_{MEA}) = 10.99 - \frac{2152}{T} \tag{3.15a}$$

The partial pressure of carbon dioxide in the mixture can be determined by using the phase equilibrium.

$$p_{CO2} = y_{CO2} P_{total} = x_{CO2} P^0_{CO2} \tag{3.16}$$

where x_{CO2}: mole fraction of CO_2 in liquid phase (amine solution)

y_{CO2}: mole fraction of CO_2 in vapor phase.

3.3. Complete Mixing Model

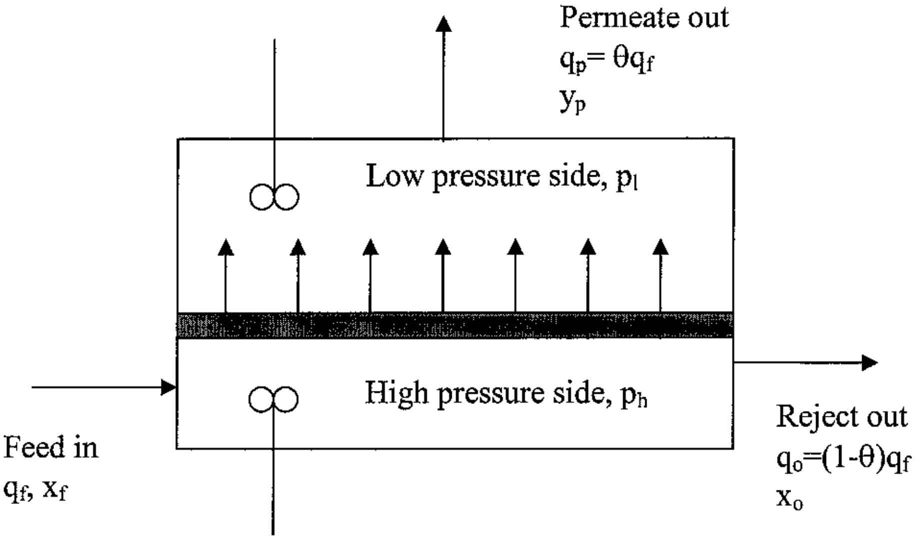


Figure 3.2: Complete mixing model

A detailed process flow diagram for complete mixing model is shown in Figure 3.2. When a separator element is operated at low recovery (i.e., where the permeate flow rate is a small fraction of the entering feed rate), there is a minimal change in composition. The results derived from using the complete-mixing model provides reasonable estimates of permeate purity (Weller and Steiner, 1950).

The overall material balance through membrane can be expressed by Equation 3.17

$$q_f = q_o + q_p \tag{3.17}$$

The stage cut of the membrane is defined as

$$\theta = \frac{q_p}{q_f} \tag{3.18}$$

Rate of diffusion or permeation of species A (in a binary of A and B) will be

$$\frac{q_A}{A_m} = \frac{q_{pA} y_{pA}}{A_m} = \left(\frac{P_A'}{t}\right)\left(p_h x_{oA} - p_l y_{pA}\right) \tag{3.19a}$$

Rate of diffusion or permeation of species B

$$\frac{q_B}{A_m} = \frac{q_{pB} y_{pB}}{A_m} = \left(\frac{P_A'}{t}\right)\left(p_h x_{oB} - p_l y_{pB}\right) \tag{3.19b}$$

$$y_{pA} = \frac{p_h x_{fA}/(1-\theta)}{q_p t/(P_A' A_m) + \theta p_h/(1-\theta) + p_l}$$
$$y_{pB} = \frac{p_h x_{fB}/(1-\theta)}{q_p t/(P_B' A_m) + \theta p_h/(1-\theta) + p_l} \quad (3.20)$$

Outlet reject composition for component A and B

$$x_{oA} = \frac{1}{1-\theta} x_{fA} - \frac{\theta}{1-\theta} y_{pA}$$
$$x_{oB} = \frac{1}{1-\theta} x_{fB} - \frac{\theta}{1-\theta} y_{pB} \quad (3.21)$$

3.4. Model development

3.4.1 Membrane properties

The membrane used in this study is 2-polyether-polyamide copolymers (trade name PEBAX). The physical properties of the membrane are shown in Table 3.2.

Table 3.2: The physical properties of the membrane

Membrane	**Pore size, rp**	**Thickness, tm**	**Tortuosity, τ**	**Porosity ξ**
PEBAX	1nm	$1\mu m$	3.676	0.272

3.4.2 MEA properties

Table 3.3: MEA properties (www.chemicalland21.com)

Name	Monoethanolamine
Formula	$(CH_2)_2OHNH_2$
Molecular weight	61.06
Melting point	10-11°C
Boiling point	170 - 171°C
Specific gravity	1.015 – 1.020
Vapor density	2.1
Flash Point	93 °C
Henry's constant	4.15×10^5 atm.m^3/mol

3.4.3 Assumptions for model development

Few assumptions need to be made before the mathematical model was developed. These assumptions are divided into two parts: membrane separation and absorption separation.

3.4.3.1 Assumptions for Membrane separation

1. The membrane is assumed to be operated isothermally with negligible pressure drop in the feed and retentate side. The effect of Joule-Thomson expansion of gas will not be considered in this study.

2. Complete mixing occurs in both the feed and permeate chamber and that the bulk gas phase is moving in a plug flow manner.

3. The axial pressure drop in the module is negligible for both the shell and the tubes sides. The effect of total pressure and/or composition of the gas are negligible and the permeability of each component is constant (i.e. no interactions between different components).

4. No reactions occurs in the membrane barrier

5. Monolayer adsorption is assumed to take place in the membrane material. As obtained from Burggraaf and Cot (1996), capillary condensation (multilayer adsorption) is possible in the membrane material at high pressures and temperatures well below the critical temperature of the adsorbed molecule, which is not applicable in this study. This is due to monolayer assumption in surface diffusion.

6. The surface diffusion, which comprises the adsorption of gas molecules onto the surface of the pores and then glide along the pores upon the pressure gradient through the membrane, would behave as ideally as predicted by Henry's law.

7. Another phenomenon on surface science, which is the capillary condensation, was not considered in this study due to the monolayer adsorption assumption made earlier.

8. 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)

3.4.3.2 Assumptions for Absorption process

1. Natural gas is essentially insoluble in the MEA solution, which means natural gas will not be absorbed in the liquid phase.

2. MEA does not vaporize to the gas phase, which means the gas phase will be CO_2 and natural gas and liquid phase will be MEA and CO_2 absorbed.

3. The CO_2 concentration in the liquid is negligible, which is admissible as the concentration of NaOH used in this study is high.

The objective of the study is to obtain the overall mass transfer coefficient, K_{AG}, the mass transfer coefficient at the liquid side; as well as the overall amount of CO_2 removed from natural gas with respect to operating parameters such as operating pressure, flow rate of amine solution and concentration of CO_2 in the feed gas as well as membrane's pore size. The detailed method will be discussed in the following chapter.

CHAPTER 4

4. METHODOLOGY

4.1. Procedure identification

All the required equations to be used have been identified. In addition, important operating parameters also need to be determined. The equations involved are the Overall Mass Transfer Coefficient equation which relates the reaction and absorption of CO_2 with the permeability of the membrane (Equations 3.2 and 3.2a), General Gas Permeation Equation across Membrane (Equation 3.12) together with its associated equations (Equations 3.3 through 3.11), the liquid mass transfer coefficient equation (Equation 3.15) together with its associated equations (Equations 3.15a through 3.21). Other parameters which are also studied are the membrane characteristics such as differential pressure across the membrane, pore size, concentration of feed gas and flow rate of amine solution.

These operating parameters are then manipulated in order to obtain the characteristics or the properties of the compact hybrid membrane-absorption processes. To obtain these relationships, all the equations are coded in MathCAD and Microsoft Excel which then will calculate all the required variables for the analysis.

4.2. Tools used: MATHCAD 2000i and Microsoft Excel

MathCAD 2001i version is required to perform sensitivity analysis on models developed. MathCAD is a software program that uses a unique method to manipulate formulas, numbers, text and graphs. It is used to see the effects of some of parameters such as pore size, operating pressure and temperature etc. on the permeability of CO_2

and also absorbability of amine solution. Unlike other programming languages such as Pascal, C++, etc. the equations are written as they appear in a mathematics reference book. Moreover, the descriptive text may be places arbitrarily as long as all the variables are defined before they are used. The equations may be solved analytically or numerically. The combination of equations, text and diagrams in an open screen environment makes application development easy.

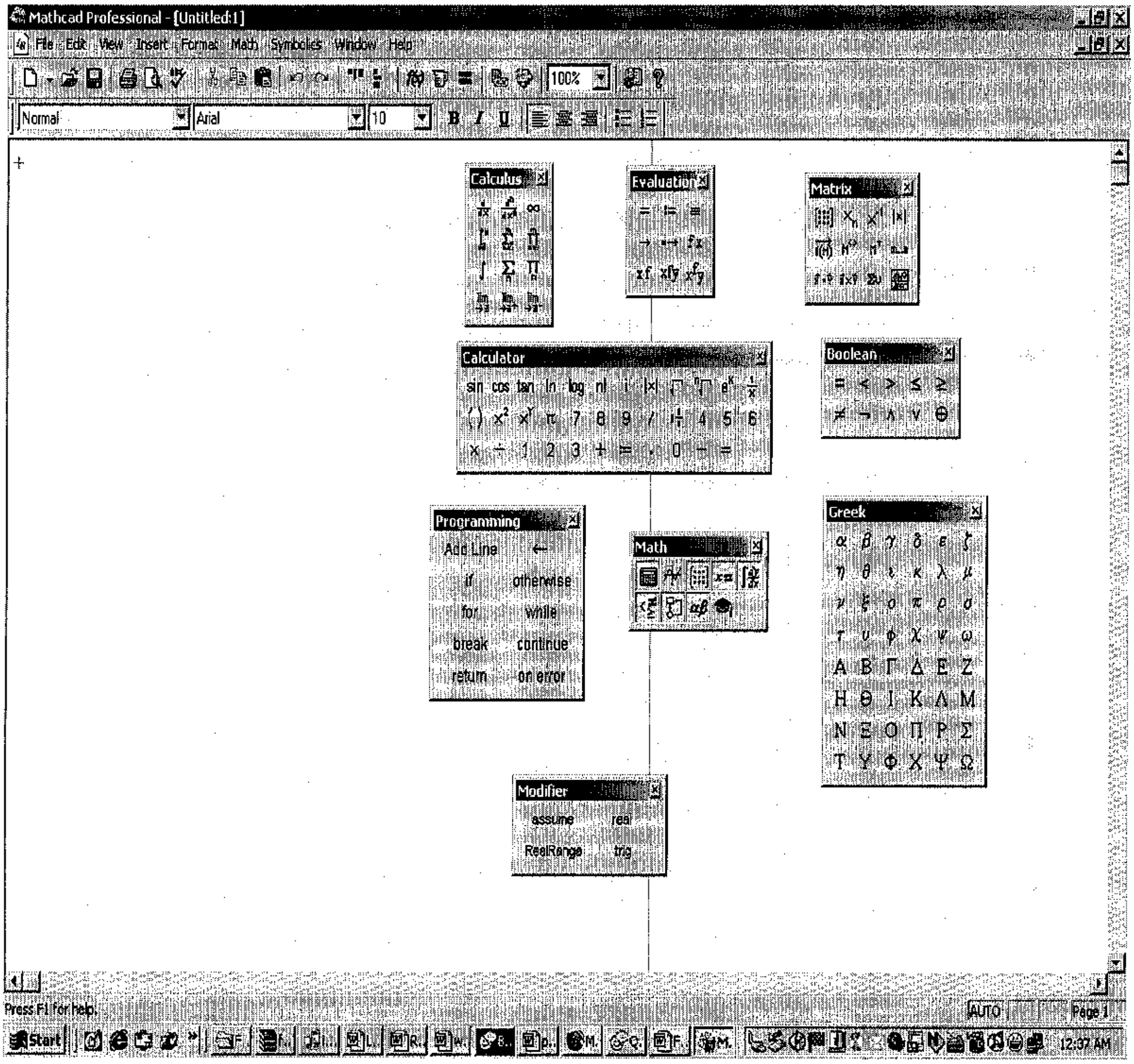
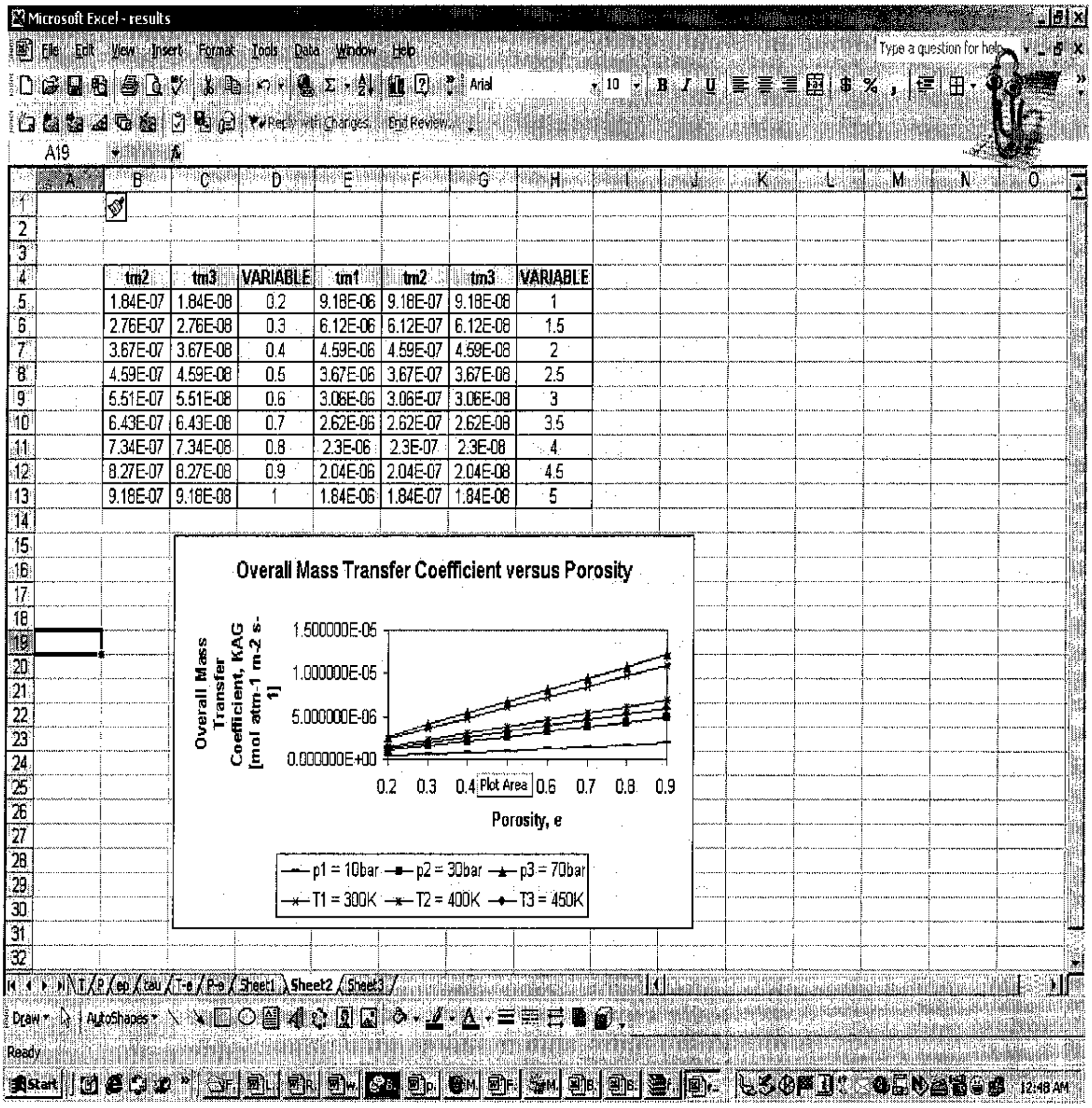


Figure 4.1: MathCAD software interface

Microsoft Excel will extract and analyze data generated by MathCAD. Analysis of trending of data will be done by this tool in order to plot multiple set of data on the same graph representation.



tm2	tm3	VARIABLE	tm1	tm2	tm3	VARIABLE
1.84E-07	1.84E-08	0.2	9.18E-06	9.18E-07	9.18E-08	1
2.76E-07	2.76E-08	0.3	6.12E-06	6.12E-07	6.12E-08	1.5
3.67E-07	3.67E-08	0.4	4.59E-06	4.59E-07	4.59E-08	2
4.59E-07	4.59E-08	0.5	3.67E-06	3.67E-07	3.67E-08	2.5
5.51E-07	5.51E-08	0.6	3.06E-06	3.06E-07	3.06E-08	3
6.43E-07	6.43E-08	0.7	2.62E-06	2.62E-07	2.62E-08	3.5
7.34E-07	7.34E-08	0.8	2.3E-06	2.3E-07	2.3E-08	4
8.27E-07	8.27E-08	0.9	2.04E-06	2.04E-07	2.04E-08	4.5
9.18E-07	9.18E-08	1	1.84E-06	1.84E-07	1.84E-08	5

Figure 4.2: Microsoft software interface

4.3. Mathematical model development and Algorithm

4.3.1 Algorithm for calculation of Permeability of pure gas and mixed gas system and mass transfer coefficient at membrane side for compact hybrid membrane-absorption processes

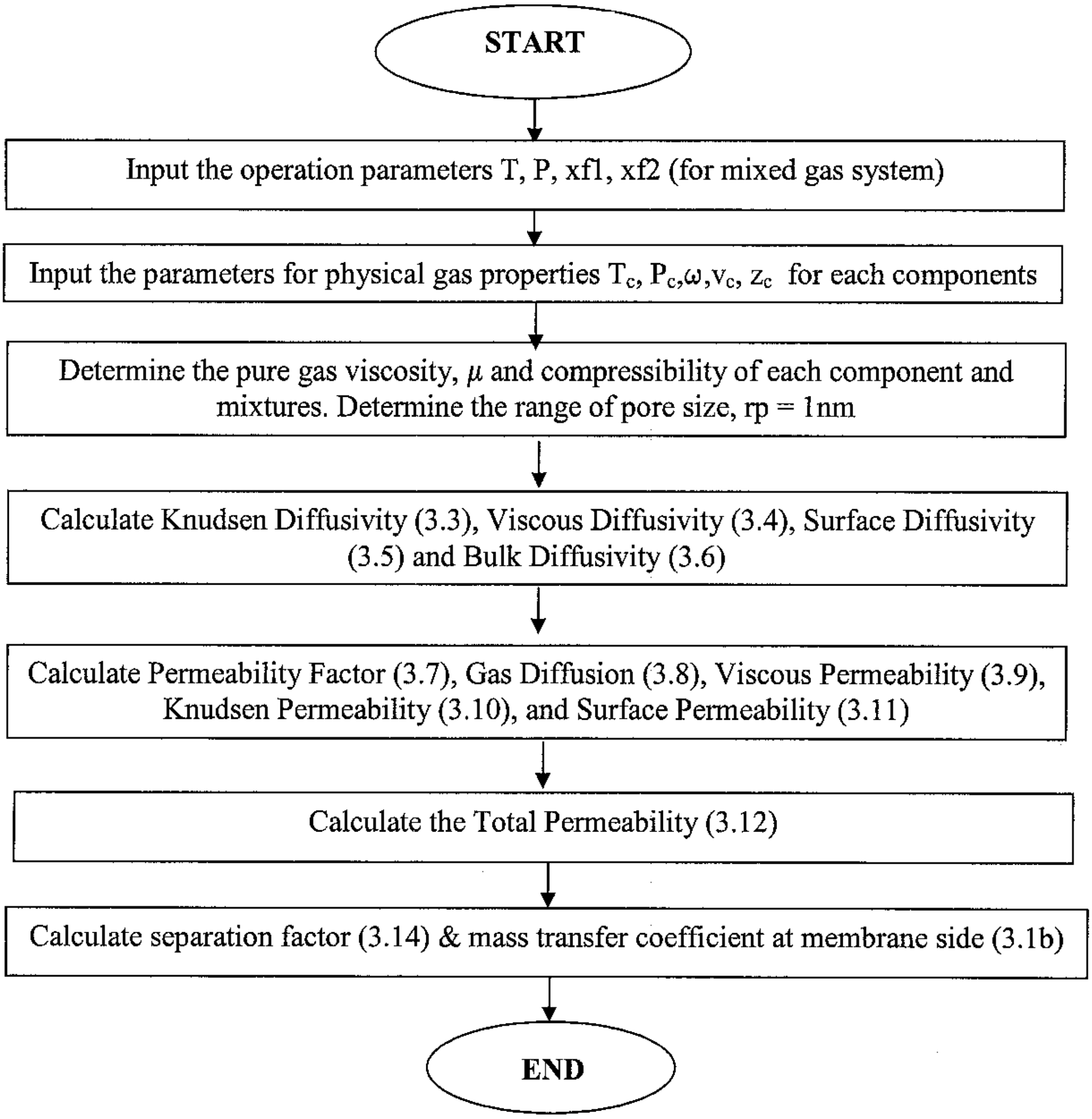


Figure 4.3: Algorithm for calculation of Permeability of pure gas and mixed gas system and mass transfer coefficient at membrane side

4.3.2 Algorithm for calculating Mass Transfer at liquid film for compact hybrid membrane-absorption processes

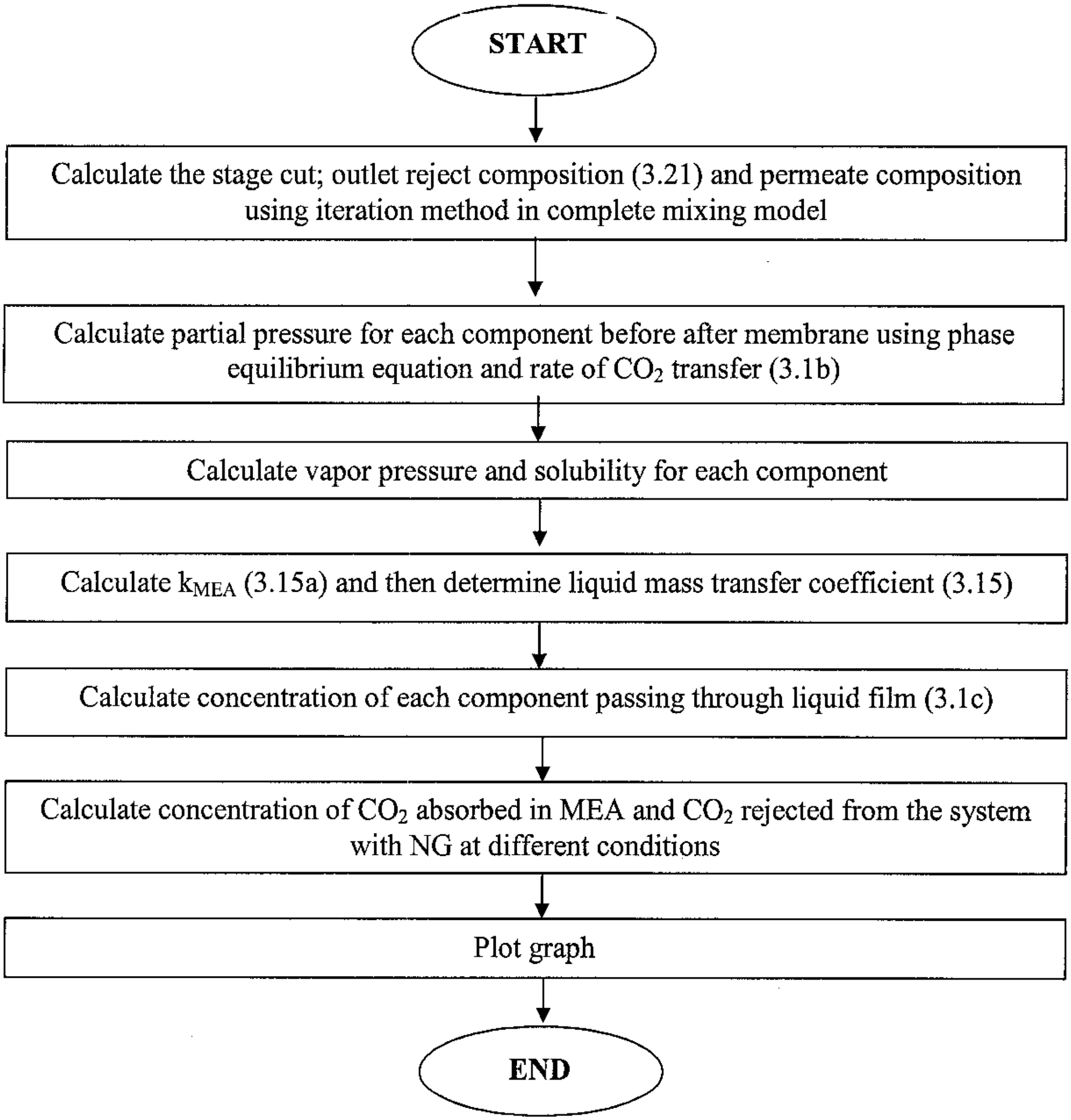


Figure 4.4: Algorithm for calculating Mass Transfer at liquid film

CHAPTER 5

5. RESULTS AND DISCUSSIONS

The study of CO_2 removal from natural gas by using compact hybrid membrane absorption system requires good understanding of mass transfer flow of each component through membrane, liquid film and finally absorbed in amine solution. The mass transfer flow is a function of many parameters which are the combination of parameters for membrane separation and parameters for gas absorption. These parameters may either affect both membrane separation and gas absorption or affect only membrane separation or gas absorption. Due to the time constraint, only three parameters were studied and analyzed, which are concentration of feed gas, operating pressure at the feed and the ratio of flow rate of MEA over flow rate of feed gas.

5.1. Effect of concentration of CO_2 in feed gas on CO_2 absorption

A study was carried out to observe the trend of CO_2 absorbed in MEA in the range of concentration of feed gas. The concentration of CO_2 in feed gas will be varied from 10% mole fraction to 80% mole fraction, which is the range of CO_2 content in natural gas at different well locations (Rojey et. Al, 1997).

Figure 5.1 shows the percentage of CO_2 removal versus mole fraction of CO_2 in the feed gas at different L/G ratio (L/G is ratio of MEA flow rate over natural gas flow rate) at T = 298 K, P = 50 bar. The percentage of CO_2 removal is calculated by amount of CO_2 absorbed in amine divided by the initial amount of CO_2 in the feed gas.

The results show that CO_2 removal is strongly dependent on concentration of feed. The increase in the concentration of CO_2 in feed will lead to the decrease in CO_2 absorbed at the same operating condition of pressure, temperature and L/G ratio. At a certain temperature and pressure, MEA solution has a certain limitation for CO_2 to be absorbed in solution, which is indicated by Henry constant. According to Henry's Law, the partial pressure of component A in the mixture at certain temperature and pressure is proportional to the solubility of that component in the solution at that temperature and pressure. At the same L/G ratio, the rate of absorption will be reduced when increasing the concentration of CO_2 in feed gas as the solution approaches to saturation.

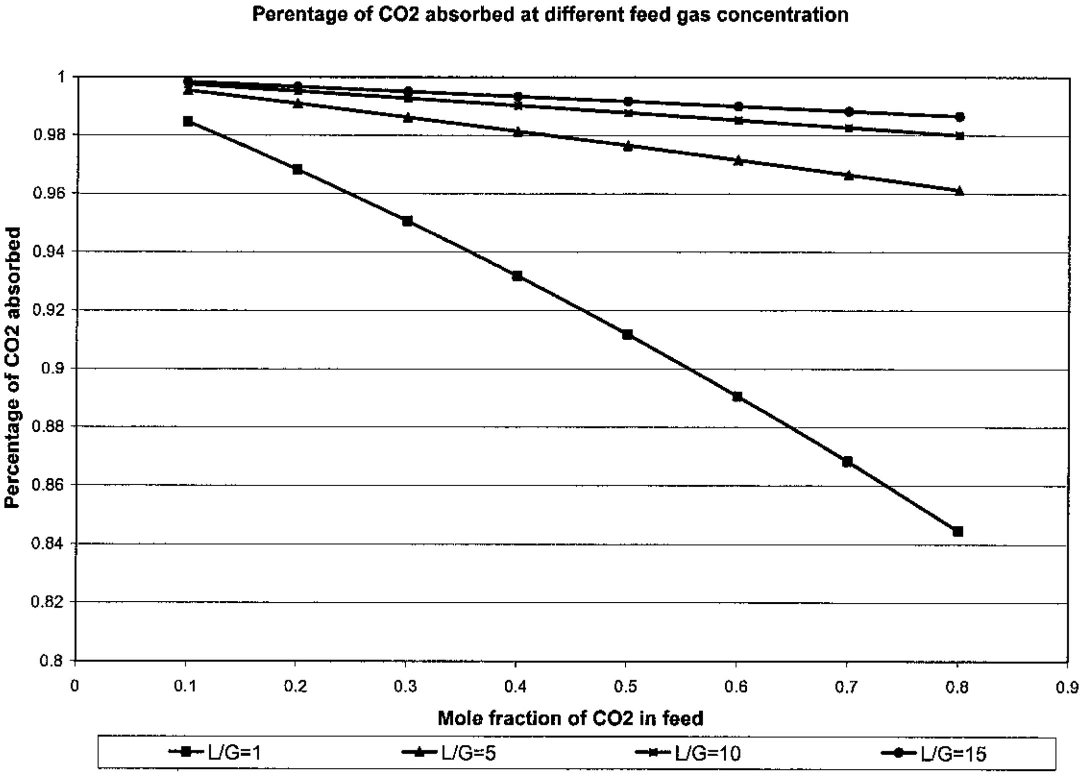


Figure 5.1: Effect of feed gas composition on CO_2 absorption at different L/G ratio (L/G is ratio of MEA flow rate over Natural Gas flow rate) at T = 298 K, P = 50 bar.

Moreover, increasing amount of CO_2 in the feed gas will not cause any effect on separation factor at the membrane side because the membrane in this study does not act as a separator, which means no separation between CO_2 and natural gas when the mixture passes through membrane barrier. In contrast, membrane barrier is acting as a packing material in the separation, which means all the gas will be allowed to pass through the membrane. CO_2 removal is accomplished by means of gas absorption and membrane is employed as a fixed interface for CO_2 transfer. In this case the membrane is acting to increase the area contact between CO_2 and MEA, which will enhance the absorbability of CO_2 of MEA.

Moreover, changing the operating conditions of L/G ratio affects the amount of CO_2 removed. The increase in L/G ratio will lead to increase in rate of absorption as more MEA molecules are available for the neutralization reaction. This will explain why there is an increase in percentage of CO_2 absorbed at the same feed gas composition when increasing the L/G ratio. This is indicated clearly in Figure 5.1. For example, at the mole fraction of CO_2 in feed gas of 0.2 (20% CO_2 and 80% CH_4), when L/G =1, percentage of CO_2 removed will be around 97%, when L/G = 5, percentage of CO_2 removed will be increased to 99% and so on. This characteristic will be a big deal when the flow rate of feed gas increases as the amount of CO_2 removed will increase dramatically.

5.2. Effect of operating pressure on CO_2 removal

The study is carried out in varying the operating pressure of feed gas stream within a range of 50 bar to 100 bar at 298K and pore size of PEBAX membrane of 1 nm. Figure 5.2 shows the permeability of CO_2 versus operating pressure at T= 298K and PEBAX membrane pore size at 1nm. The results show that the permeability of CO_2 as well as permeability of CH_4 are a strong function of operation pressure. The effect of operating pressure on permeability of CH_4 is more clearly observed in Figure 5.3, which is the permeability of CH_4 versus operating pressure at T= 298K and pore size of PEBAX membrane of 1 nm. This can be explained by the fact that the surface diffusion is the dominant contributor to total permeability of CO_2 at small pores size and it decreases with increasing pore size (Hsieh 1996). At small pore sizes, the movement of the gas molecules have higher tendency to diffuse from the bulk stagnant gas film to the pore surface due to concentration gradient between bulk gas phase and pore phase. At the pore surface, adsorption of CO_2 molecules (strong adsorbing gas) takes place and thus contributes to the high total permeability of CO_2. Due to the hindered pathways of travel at small pore sizes, viscous diffusion and Knudsen diffusion are not apparent. Moreover, surface diffusion increases at increasing operating pressure because adsorption processes are favored at high pressure due to increased molecular density. The same trend is observed for CH_4, which is more clearly indicated in Figure 5.3.

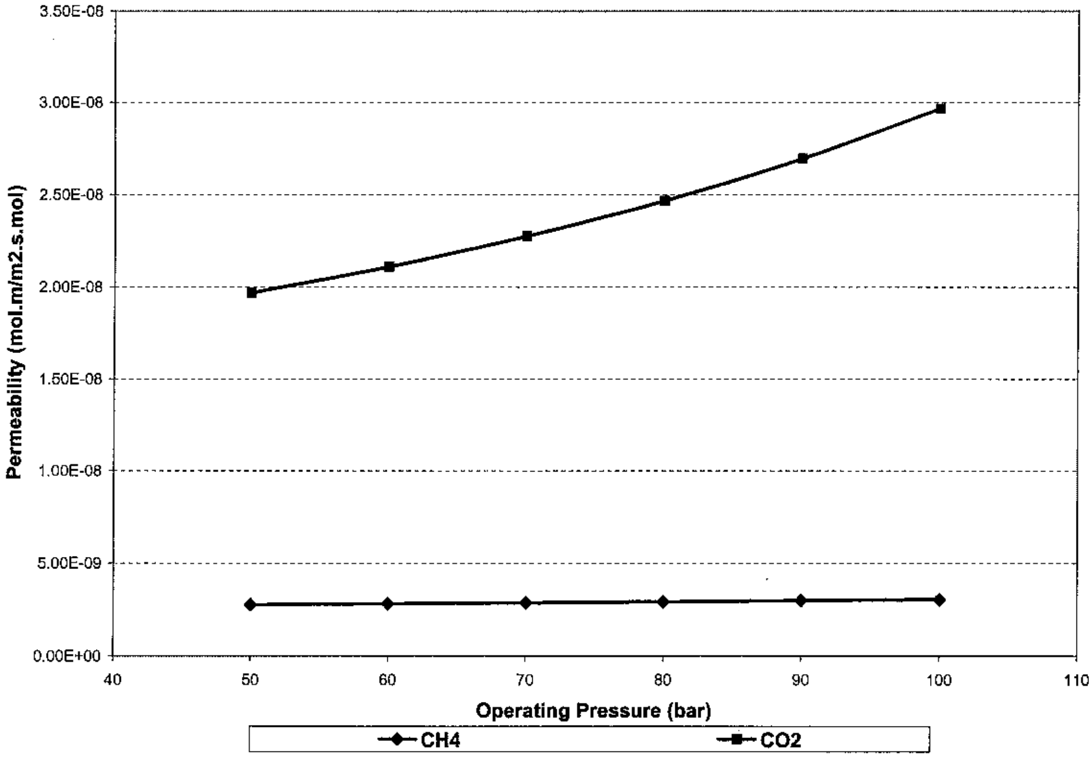


Figure 5.2: Effect of operating pressure on permeability of CO_2 and CH_4 at T = 298K, pore size = 1nm of PEBAX membrane

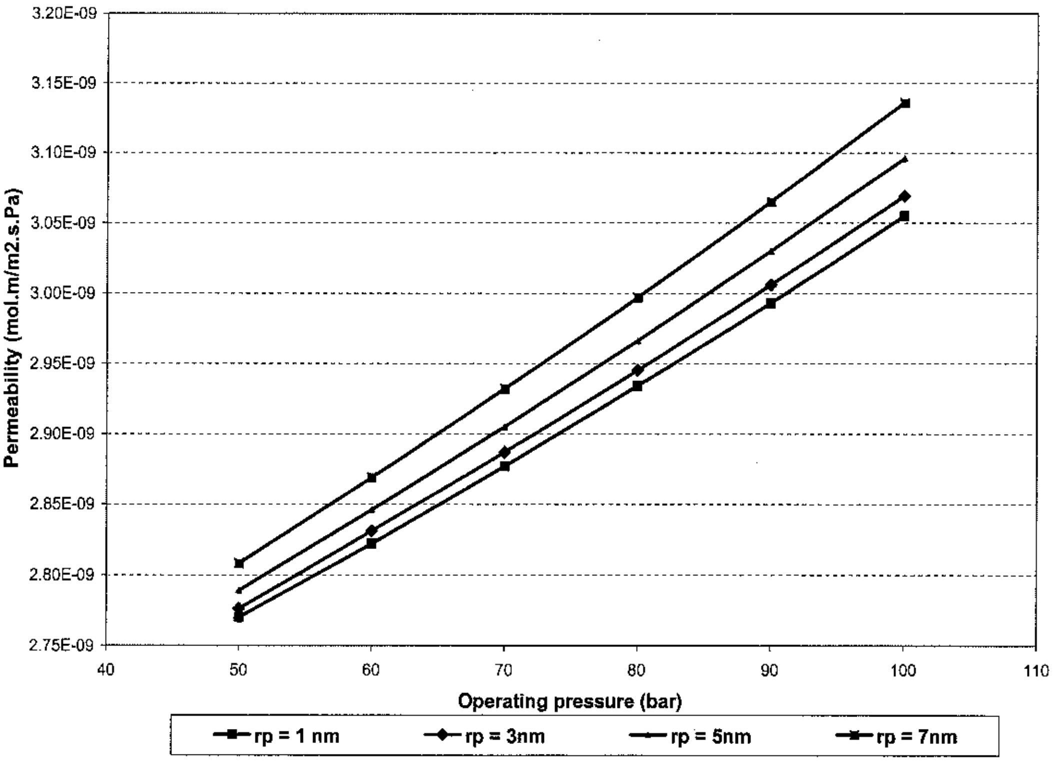


Figure 5.3: Effect of operating pressure on permeability of CH_4 at different pore size at 298 K in PEBAX membrane

However, the operating pressure at the feed gas does not have any effect on the overall CO_2 absorbed in the membrane-absorption system. Figure 5.4 shows the independence of operating pressure on the removal of CO_2 from natural gas. Although the operating pressure has a strong effect on the membrane side, membrane does not act as a gas separator, but just a packing material for CO_2 transfer. Therefore, it does not affect the amount of CO_2 absorbed as long as there is sufficient membrane area and sufficient L/G ratio in order for the absorption to occur. Because the membrane is acting as a fixed interface for CO_2 removal, all CO_2 and CH_4 will pass through the membrane. The operating pressure only has effect on the membrane side but no effect on the liquid side as increase in operating pressure does not affect the liquid (liquid is relatively uncompressed). Therefore the overall percentage of CO_2 removed is not affected by the change in operating pressure.

Figure 5.4 shows the effect of concentration of CO_2 in the feed gas on the removal of CO_2 efficiency. Increase in concentration of CO_2 in feed gas will lead to increase in percentage of removal as explained in part 5.1.

As the operating pressure does not show any effect on the overall removal of CO_2 from natural gas in this case, we can choose to operate at pressure that is more economical with respect to the overall plant layout and requires the least energy supplied to the system.

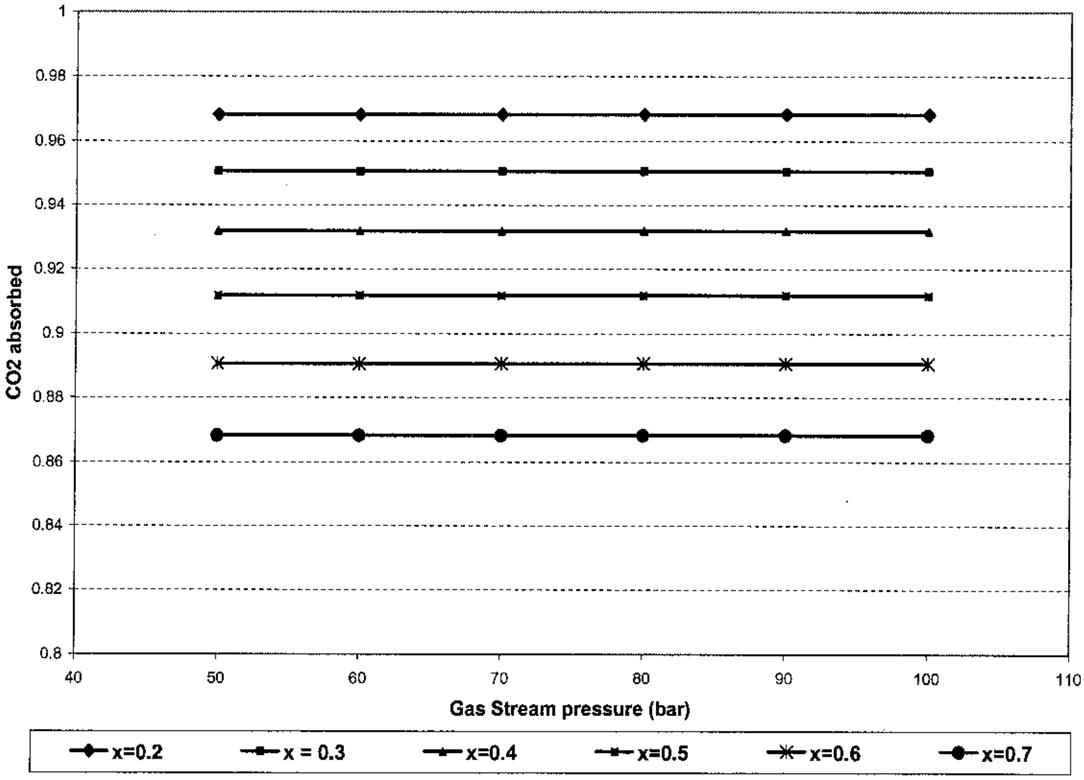


Figure 5.4: Effect of operating pressure on CO_2 absorption at T = 298 K and P = 50 bar for different composition of CO_2 in feed gas. (x is the mole fraction of CO_2 in feed gas)

5.3. Effect of MEA flow rate on CO_2 removal

Figure 5.5 is the percentage of CO_2 removal versus the ratio of flow rate of MEA solution over the flow rate of feed gas (L/G ratio) at T = 298 K and P = 50 bar at different CO_2 concentration in the feed at 298K and 50 bar. The results show that the increase in MEA flow rate leads to the increase in amount of CO_2 absorbed by MEA. The slope of the graph is very steep at low L/G ratio, which indicates a sharp increase in amount of CO_2 absorbed when L/G increases from 1 to around 10; most of CO_2 has been absorbed in MEA. When L/G increases further, the amount of CO_2 absorbed increases slowly with the increase of L/G above 10 to further 15 to 20, depending on the amount of CO_2 in the feed gas.

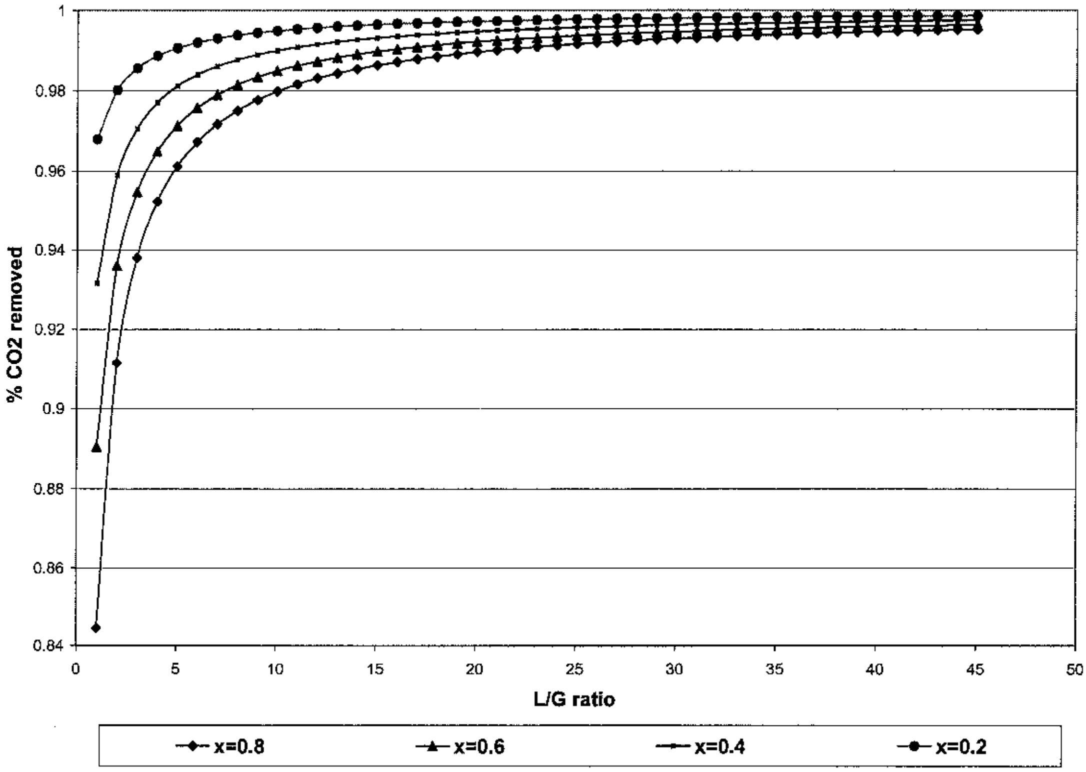


Figure 5.5: Effect of MEA flow rate on removal of CO_2 in natural gas at different CO_2 concentration in the feed at 298K and 50 bar. (x is the mole fraction of CO_2 in feed gas)

The sharp increase in CO_2 removal at low L/G ratio is due to the amount of MEA is not sufficient enough for the removal of CO_2 at low L/G ratio, which means MEA solution became saturated before all CO_2 is absorbed. Therefore amount of CO_2 that is not absorbed is still high. This amount is reduced when the L/G ratio is increased. When L/G ratio reaches a certain limit, the rate of absorption will reduce due to surplus of MEA for reaction between MEA and CO_2.

At higher concentration of CO_2 in natural gas, higher L/G ratio is required to maintain the required percentage of CO_2 removal. The amount of CO_2 absorbed depends on the rate of absorption, which is a function of amount of absorbent and amount of contacting time between CO_2 and natural gas. At a certain contacting time between CO_2 and natural gas, increase in L/G ratio leads to increase in amount of MEA solution at fixed natural gas flow rate. This will cause the increase in contacting between CO_2 and MEA, leading to more CO_2 absorbed by amine at a certain concentration of CO_2 in feed gas. Therefore the required L/G ratio for the amount of CO_2 absorbed to reach saturation is less for lower concentration of CO_2 in feed gas than that at higher concentration of CO_2 in feed gas. Figure 5.5 shows that for the condition of CO_2 concentration in feed gas is 80% mole fraction, about 84.5% of CO_2 will be removed at L/G = 1; at mole fraction of CO_2 in feed of 20%, 97 % of CO_2 is absorbed at L/G =1.

Moreover, contacting time between CO_2 and MEA is also an important factor in absorption, which determines the amount of CO_2 absorbed in the solution. Therefore if high purity of natural gas is required, the plug flow reactor or recycling of feed gas should be used in order to increase the efficiency of absorption of CO_2. However, it will be an economic justification in determining whether to operate at high L/G ratio or recycle the feedgas.

5.4. Effect of Operating Pressure and Pore Size on Separation Factor

Separation factor is the most important aspect in membrane separation for binary gas mixture. It is a measure of the enrichment of a gas component after it has passed the membrane. It is also the measurement of effectiveness of membrane separation. High separation factor would result in a sharper separation between the species in the binary mixture. In this study, the separation factor of CO_2/CH_4 separation for high CO_2 concentration in feedgas is studied based on the complete mixing model, which will predict the separation factor by assuming the gas species in the feed and permeate chamber are completely mixed, which is true in real application.

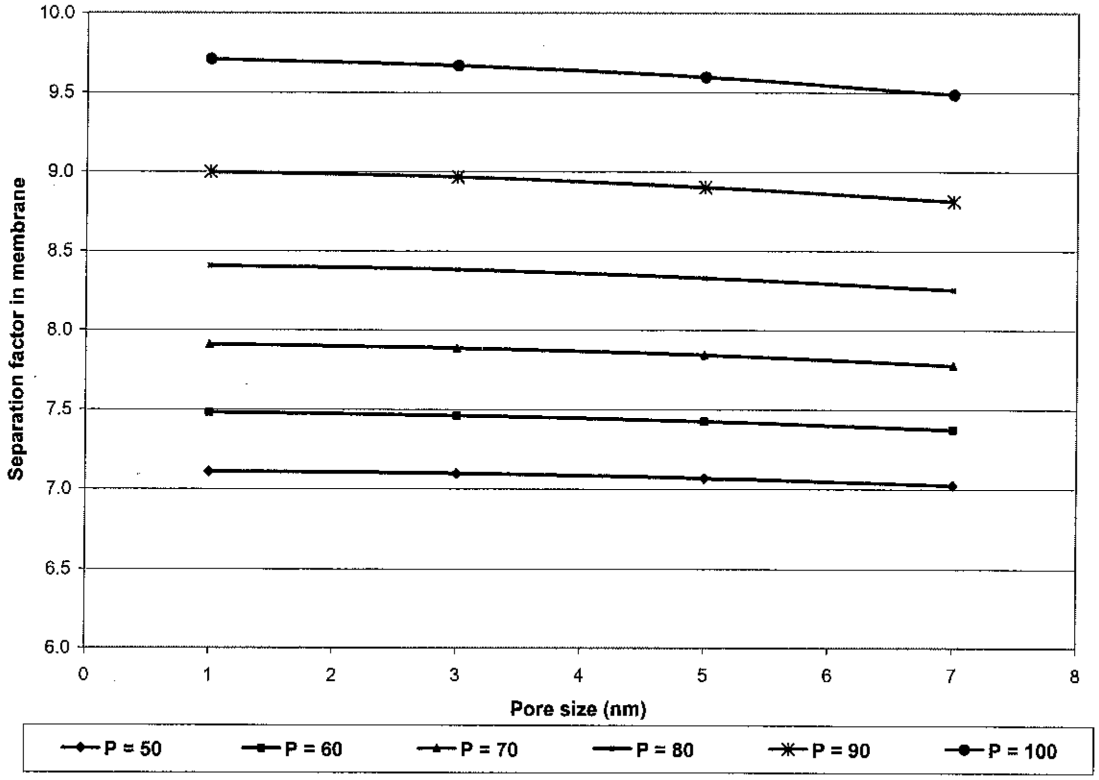


Figure 5.6: Effect of Operating Pressure and Pore Size on Separation Factor at 298K

Figure 5.6 is the separation factor in membrane versus pore size at 298 K for different operating pressure at the feed gas. The results show that the separation factor slightly decreases when increasing pore sizes at certain operating condition of temperature and pressure. This is because at higher pore sizes, the separation is no longer predominated by surface diffusion, which is more selectivity in gas separation due to the difference in adsorptivity of different gas species. When the pore size is larger than the molecular size of CO_2 and CH_4, both gases can pass through the porous membrane easily and membrane selectivity separation will lose its efficiency hence resulting in a lower separation factor.

Hwang and Kammermeyer (1975) reported that the economically justified separation factors in the industry for CO_2 removal is 3 – 50, depending on the types of membrane used as indicated in Table 3.1 above. As indicated in Figure 5.6, the separation factor for CO_2 is within the range of 7 to 10, which satisfies the requirement of economically separation factors in the industry for CO_2 removal.

Figure 5.6 also shows the increase in separation factor when increasing the operating pressure of feed gas. This is a result of increasing of surface diffusion due to adsorption at the membrane surface, which is favored at high pressure as discussed in section 5.2.

However, operating at high pressure in the feed gas requires a large compressor in order to compress the gas to the required pressure. This would not be economically sound. In addition, it will be more dangerous to operate high pressure without any safety measure.

CHAPTER 6

6. CONCLUSIONS AND RECOMMENDATIONS

In general, the mathematical models to study the removal of CO_2 from natural gas in Compact Hybrid Membrane-Amine System have been developed successfully. The effect of various parameters such as operating pressure of feedgas, concentration of CO_2 in natural gas, flow rate of MEA fed to system as well as membrane pore size have been studied and analyzed systematically.

The mathematical models developed are able to predict the transport of CO_2 and CH_4 in the compact hybrid membrane-amine system. It is used to study the behavior of permeation of both CO_2 and CH_4, the separation behavior of this binary system as well as the absorption of CO_2 for removal of CO_2 from natural gas by using the compact hybrid membrane-amine system. The membrane does not act as a separator for binary gas system in this study but rather as a packing material in the separation, which means all the gas will be allowed to pass through the membrane and CO_2 removal is accomplished by the gas absorption and membrane is employed as a fixed interface for CO_2 transfer. In this case the membrane is acting to increase the area contact between CO_2 and MEA, which will enhance the absorbability of CO_2 of MEA.

This chapter will conclude the findings from various studies done by using the mathematical model. A few recommendations will also be presented at the end of this chapter for improvement in future works.

6.1. Conclusion

The first part of the study dealt with the effect of concentration of CO_2 on removal of CO_2 from natural gas. The concentration of CO_2 in natural gas varies from 0.2% to 80% depending on the location of natural gas well. It is noticed that increasing the concentration of CO_2 in feed will lead to decrease in CO_2 absorbed at the same operating condition of pressure, temperature and L/G ratio. This is due to limitation of CO_2 molecules contact with MEA molecules in a certain contacting time between gas and liquid and limitation of absorption capability of MEA at certain conditions.

The effect of operating pressure at the feed gas was also analyzed in this study. Operating pressure has a strong effect on permeability of both CO_2 and CH_4. Increasing operating pressure would increase the permeability of CO_2 and CH_4 due to the effect of pressure on the surface diffusion, which predominates at small pore sizes. At bigger pore sizes, operating pressure does not have much effect on the permeability as both gases are allowed to pass through the membrane pore due to increase in free path and surface diffusion loses its effect. However, the overall mass transfer of CO_2 in the system is relatively insensitive with operating pressure because increasing operating pressure does not have effect on the liquid side and the function of membrane in this study is a packing material for CO_2 transfer.

The removal of CO_2 from natural gas depends on the rate of absorption of CO_2 by MEA, which is a function of flow rate of MEA into the system and the time contacting of gas and liquid. Therefore increasing flow rate of MEA to the system will lead to increase percentage of CO_2 removal due to the increase in contacting between CO_2 and MEA at given contacting time. The rate of removal increases sharply when increase the flow rate at low L/G ratio (ratio of MEA flow rate over flow rate of natural gas fed in the system). Depending on the concentration of CO_2 in feed gas, it will have its own optimum L/G ratio to achieve the best removal of CO_2 from natural gas.

Last but not least, the effect of operating pressure and pore size on the separation factor at the membrane side was investigated. The separation factor decreases slightly when pore sizes increases at certain operating condition of temperature and pressure due to the decrease in effect of surface diffusion at large pore size. It also shows the increase in separation factor when increasing the operating pressure of feed gas as the result of increase in surface diffusion due to adsorption at the membrane surface.

6.2. Recommendation

The mathematical models developed in this project have helped to study the behavior of gas permeation in ultra thin skinned hollow fiber membrane as well as the absorption of CO_2 from natural gas by using MEA solution. However, there are many more studies that can be extended to improve the performance of the models developed. Few of extended studied recommended are illustrated below:

1. Series of experiment can be carried out to study the validity of the mathematical models developed in this study. Further tuning of the models should be done in order to improve the reliability of the models.

2. The model developed was based on the basis that the membrane is not acting as a gas separator but it is actually a packing material for CO_2 transfer. It is recommended in the future work, further study should be carried out to study and analyze the case that membrane is acting as a packing material in order to compare the effectiveness of removal CO_2 from natural gas using compact hybrid membrane amine system.

3. As in the assumptions made in section 3.1, the complete mixing model was assumed in this project to study the performance of the compact hybrid membrane-absorption process. For further study on this model, it is recommended to study on other three types of pattern flow, i.e. counter current flow model, cross flow model as well as co-current flow model to compare the effectiveness of removal of CO_2 from natural gas.

4. In order to improve the purity of natural gas to satisfy the requirement of quality of natural gas with composition of CO_2 in natural gas must be lower than 2% (Spillman 1989) or 1.8% (Gas Malaysia 2003), it is recommended for future work to study the various sequencing separation columns to derive a suitable model for effective gas separation with required purity of natural gas out of system.

5. In this project, the capillary condensation was not taken into account due to the assumption of monolayer surface diffusion. However, at a relatively low temperature and high pressure, some gases will undergo capillary condensation (multilayer adsorption) where there is a blockage of the membrane pores due to the formation of layers of adsorbed molecules on top each other. Therefore it is recommended for future study on the effect of capillary condensation as it has an important role under certain operating condition

6. It was assumed an isothermal operation in the membrane module. Heating and cooling can occur in the membrane module due to Joule-Thompson expansion effect. It is recommended that this effect should be taken into account in future works.

7. REFERENCES

1. Geankoplis, "Transport Processes and Unit Operations", third edition.
2. J. D. Seader, Ernest J. Henley, 1998, Separation Process Principles, 1st Edition, John Wiley & Sons Inc.
3. K. Li, W. K. Teo, 1998, "Use of permeation and absorption methods for CO_2 removal in hollow fibre membrane modules", Separation and Purification Technology 13.
4. K. Li, Dongliang Wang, C. C. Ko, W. K. Teo, 1997, "Use of asymmetric hollow fibre modules for elimination of H_2S from gas streams via a membrane absorption method", Chemical Engineering Science, Vol. 53, No. 6.
5. K. Li, Jianfeng Kong, Xiaoyao Tan, 2000,"Design of hollow fibre membrane modules for soluble gas removal", Chemical Engineering Science 55.
6. Sam Wong and Rob Biolettie, Carbon and Energy Management, Carbon Dioxide Separation Technologies, Alberta Research Council, Edmontion, Alberta, T6N 1E4, Canada.
7. Yoshihito Osada, Tsutomu Nakagawa, 1992, Membrane Science and Technology, QP159.M4M447, USA
8. George Wypych, 2001, Handbook of Solvents, ISBN, Canada.
9. H.Ohya, V.V. Kudryavtsev, S.I.Semenova, 1996, Polyamide Membrane, Applications Fabrications and Properties, Tokyo.

10. Hwang, S.T., and Kammermeyer, K. 1975, Membranes in Separations. New York: John Wiley & Sons, Inc.,

11. Kurz, J.E., and Narayan, R.S., “New Developments and Applications in Membrane Technology”.

12. A. Rojey, C.Jaffret, S.Cornot-Gandolphe B.Durand, S. Jullian, M.Valais, Natural Gas Production Processing Transport, France 1997.

13. William Echt, 2002, Hybrid Systems: Combining Technologies leads to more efficient gas conditioning UOP LLC, 2002 Laurance Reid Gas Conditioning Conference.

14. R.W. Splillman, 1995, Membrane separation technology. Principles and applications, Ed. :R.D.Noble, S.A. Stern, 1995, Elsevier Science.

15. Scott M. Klara, John Litynski, Gary T. Rochelle, Carbon Dioxide Capture by Absorption with Potassium Carbonate, 2/2004, US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory.

16. G. Srikanth, Membrane Separation Processes- Technology and Business Opportunities, 2001

17. Richard W Baker, 2000, Membrane Technology and Applications, McGraw-Hill

18. Ed. S.P.Nunes and K.-V.Peinemann, 2001, Membrane Technology in the Chemical Industry, Wiley-Vch Verlag GmnH, D-69469 Weinheim.

19. R.D.Noble, S.A.Stern, 1999, Membrane Separation Technology, Principles and Applications, Elsevier Science B.V.

20. www.chemicalland21.com

21. http://dataranking.com/English/ee02-2.html

LIST OF APPENDICES

Appendix 1: GANTT CHART FOR FINAL YEAR RESEARCH PROJECT

No	Activities / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	Selection of Project Topic	▨														
2.	Preliminary research on project	▨	▨													
3.	Writing on Preliminary Report			▨	▨											
4.	Submission of Preliminary Report				●											
5.	Getting familiar with Mathcad software					▨	▨									
6.	Modeling on different parameters							▨	▨	▨						
7.	Writing on Progress Report										▨					
8.	Submission of Progress Report										●					
9.	Analysis and Discussion on Modeling Results										▨	▨	▨	▨		
10	Writing on the final report												▨	▨	▨	
11	Submission first draft of project dissertation														▨	
12.	Oral Presentation														▨	
13.	Submission of Project Dissertation															▨

Appendix 2: Properties of CO_2 and CH_4

Properties	CO_2	CH_4
Molecular weight	44.01	16.04
Molecular radius A^o	1.7	1.94
T_c (K)	304.1	190.6
P_c (bar)	73.8	46.0
T_{nbp} (K)	194.5	111.6
V_c cc/mol	93.9	99.0
ω	0.23	0.01
Z_c	0.27	0.29
ΔH_{ads} at standard kJ/mol	25.24	8.18
Density kg/m^3	1.80	0.66

AIR LIQUIDE

Safety Data Sheet

Product : **Carbon dioxide** Page :1/4

MSDS Nr : 018A_AL Version : 1.01 Date : 31/07/2002

IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

MSDS Nr	018A_AL
Product name	Carbon dioxide
Chemical formula	CO2
Company identification	see heading and/or footer see paragraph 16 "OTHER INFORMATION"
Emergency phone numbers	see heading and/or footer see paragraph 16 "OTHER INFORMATION"

COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation	Substance.
Components/Impurities	Contains no other components or impurities which will influence the classification of the product.
CAS Nr	00124-38-9
EEC Nr (from EINECS)	204-696-9

HAZARDS IDENTIFICATION

Hazards identification	Liquefied gas In high concentrations may cause asphyxiation.

FIRST AID MEASURES

Inhalation	In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. Low concentrations of CO2 cause increased respiration and headache. Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
Skin/eye contact	Immediately flush eyes thoroughly with water for at least 15 minutes. In case of frostbite spray with water for at least 15 minutes. Apply a sterile dressing. Obtain medical assistance
Ingestion	Ingestion is not considered a potential route of exposure.

FIRE FIGHTING MEASURES

Specific hazards	Exposure to fire may cause containers to rupture/explode. Non flammable
Hazardous combustion products	None

Suitable extinguishing media	All known extinguishants can be used.
Specific methods	If possible, stop flow of product. Move away from the container and cool with water from a protected position.
Special protective equipment for fire fighters	In confined space use self-contained breathing apparatus.

ACCIDENTAL RELEASE MEASURES

Personal precautions	Evacuate area. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Ensure adequate air ventilation.
Environmental precautions	Try to stop release. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.
Clean up methods	Ventilate area.

HANDLING AND STORAGE

Handling and storage	Suck back of water into the container must be prevented. Do not allow backfeed into the container. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt. Refer to supplier's container handling instructions. Keep container below 50°C in a well ventilated place.

EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure limit value -TLV(ACGIH)	5000 ppm (2000 edition)
Exposure limit value for country	Great Britain: STEL: 15000 ppm; LTEL: 5000 ppm (EH 40/97) Germany: MAK= 5000 ppm
Personal protection	Ensure adequate ventilation.

PHYSICAL AND CHEMICAL PROPERTIES

Molecular weight	44
Melting point	-56.6 °C
Boiling point	-78,5(s) °C
Critical temperature	30 °C
Relative density, gas	1.52 (air=1)
Relative density, liquid	0.82 (water=1)

Vapour Pressure 20°C	57.3 bar
Solubility mg/l water	2000 mg/l
Appearance/Colour	Colourless gas
Odour	No odour warning properties.
Other data	Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.

STABILITY AND REACTIVITY

Stability and reactivity	Stable under normal conditions.

TOXICOLOGICAL INFORMATION

General	In high concentrations cause rapid circulatory insufficiency. Symptoms are headache, nausea and vomiting, which may lead to unconsciousness.

ECOLOGICAL INFORMATION

General	When discharged in large quantities may contribute to the greenhouse effect.
Global warming factor	1

DISPOSAL CONSIDERATIONS

General	Do not discharge into any place where its accumulation could be dangerous. To atmosphere in a well ventilated place. Discharge to atmosphere in large quantities should be avoided. Contact supplier if guidance is required.

TRANSPORT INFORMATION

Proper shipping name	Carbon dioxide
UN Nr	1013
Class/Div	2.2
ADR/RID Classification code	2, 2°A
ADR/RID Hazard Nr	20
Labelling ADR	Label 2: non flammable non toxic gas
Other transport information	Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured and:

- cylinder valve is closed and not leaking
- valve outlet cap nut or plug (where provided) is correctly fitted
- valve protection device (where provided) is correctly fitted
- there is adequate ventilation.
- compliance with applicable regulations.

REGULATORY INFORMATION

Number in Annex I of Dir 67/548	Not included in Annex I.
EC Classification	Not classified as dangerous preparation.
EC Labelling (Symbols, R&S phrases)	No EC labelling required.

OTHER INFORMATION

Asphyxiant in high concentrations.

Keep container in well ventilated place.

Do not breathe the gas.

Contact with liquid may cause cold burns/frost bite.

Ensure all national/local regulations are observed.

The hazard of asphyxiation is often overlooked and must be stressed during operator training.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

This MSDS is for information purposes only and is subject to change without notice. [Prior to purchase of products, please contact your local Air Liquide office for a complete MSDS (with Manufacturer's name and emergency phone number).]

End of document.
Number of pages :4

AIR LIQUIDE

Safety Data Sheet

Product : **Methane**

MSDS Nr : 078A_AL Version : 1.01 Date : 31/07/2002

IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

MSDS Nr	078A_AL
Product name	Methane
Chemical formula	CH_4
Company identification	see heading and/or footer see paragraph 16 "OTHER INFORMATION"
Emergency phone numbers	see heading and/or footer see paragraph 16 "OTHER INFORMATION"

COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation	Substance.
Components/Impurities	Contains no other components or impurities which will influence the classification of the product.
CAS Nr	00074-82-8
EEC Nr (from EINECS)	200-812-7

HAZARDS IDENTIFICATION

Hazards identification	Compressed gas Extremely flammable

FIRST AID MEASURES

Inhalation	In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. In low concentrations may cause narcotic effects. Symptoms may include dizziness, headache, nausea and loss of co-ordination. Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

FIRE FIGHTING MEASURES

Specific hazards	Exposure to fire may cause containers to rupture/explode.
Hazardous combustion products	Incomplete combustion may form carbon monoxide.
Suitable extinguishing media	All known extinguishants can be used.
Specific methods	If possible, stop flow of product. Move away from the container and cool with water from a protected position.

	Do not extinguish a leaking gas flame unless absolutely necessary. Spontaneous/explosive re-ignition may occur. Extinguish any other fire.
Special protective equipment for fire fighters	In confined space use self-contained breathing apparatus.

ACCIDENTAL RELEASE MEASURES

Personal precautions	Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe. Evacuate area. Ensure adequate air ventilation. Eliminate ignition sources.
Environmental precautions	Try to stop release.
Clean up methods	Ventilate area.

HANDLING AND STORAGE

Handling and storage	Ensure equipment is adequately earthed. Suck back of water into the container must be prevented. Purge air from system before introducing gas. Do not allow backfeed into the container. Use only properly specified equipment which is suitable for this product, its supply pressure and temperature. Contact your gas supplier if in doubt. Keep away from ignition sources (including static discharges). Segregate from oxidant gases and other oxidants in store. Refer to supplier's container handling instructions. Keep container below 50°C in a well ventilated place.

EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protection	Ensure adequate ventilation. Do not smoke while handling product.

PHYSICAL AND CHEMICAL PROPERTIES

Molecular weight	16
Melting point	-182 °C
Boiling point	-161 °C
Critical temperature	-82 °C
Relative density, gas	0.6 (air=1)
Relative density, liquid	0.42 (water=1)
Vapour Pressure 20°C	Not applicable.

Solubility mg/l water	26 mg/l
Appearance/Colour	Colourless gas
Odour	None
Autoignition temperature	595 °C
Flammability range	5-15 vol% in air.

STABILITY AND REACTIVITY

Stability and reactivity	Can form explosive mixture with air. May react violently with oxidants.

TOXICOLOGICAL INFORMATION

General	No known toxicological effects from this product.

ECOLOGICAL INFORMATION

General	No known ecological damage caused by this product.
Global warming factor	21

DISPOSAL CONSIDERATIONS

General	Do not discharge into areas where there is a risk of forming an explosive mixture with air. Waste gas should be flared through a suitable burner with flash back arrestor. Do not discharge into any place where its accumulation could be dangerous. Contact supplier if guidance is required.

TRANSPORT INFORMATION

Proper shipping name	Methane, compressed
UN Nr	1971
Class/Div	2.1
ADR/RID Classification code	2, 1°F
ADR/RID Hazard Nr	23
Labelling ADR	Label 3: flammable gas
Other transport information	Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers ensure that they are firmly secured and: - cylinder valve is closed and not leaking

- valve outlet cap nut or plug (where provided) is correctly fitted
- valve protection device (where provided) is correctly fitted
- there is adequate ventilation.
- compliance with applicable regulations.

REGULATORY INFORMATION

Number in Annex I of Dir 67/548	601-001-00-4.
EC Classification	F+;R12
-Symbols	F+: Extremely flammable
-Risk phrases	R12 Extremely flammable.
-Safety phrases	S9 Keep container in well ventilated place. S16 Keep away from ignition sources - No smoking. S33 Take precautionary measures against static discharges.

OTHER INFORMATION

Ensure all national/local regulations are observed.

Ensure operators understand the flammability hazard.

The hazard of asphyxiation is often overlooked and must be stressed during operator training.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

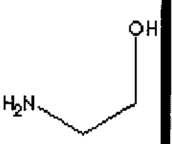
This MSDS is for information purposes only and is subject to change without notice. [Prior to purchase of products, please contact your local Air Liquide office for a complete MSDS (with Manufacturer's name and emergency phone number).]

End of document.
Number of pages :4

OFFER TO SELL
OFFER TO BUY

RODUCTS >INDUSTRIAL CHEMICALS >□ORGANIC CHEMICALS >

MONOETHANOL AMINE



RODUCT IDENTIFICATION

AS NO.	141-43-5
INECS NO.	205-483-3
ORMULA	$(CH_2)_2OHNH_2$
AOL WT.	61.06
I.S. CODE	2922.12
OXICITY	Oral rat LD50: 1720 mg/kg
YNONYMS	Aminoethyl Alcohol; Beta-Aminoethanol;

-Amino-ethanol; Ethanolamine; 1-Amino-2-hydroxyethane; 2-Amino-1-Ethanol; -Aminoaethanol German); 2-Aminoetanolo (Italian); 2-Aminoethanol; ethanolamin (German); Beta-Aminoethyl Alcohol; Beta-ethanolamine; Beta-ydroxyethylamine; Colamine; Etanolamina (Italian); Ethylolamine; Glycinol; AEA; Monoaethanolamin (German);

ERIVATION	□
LASSIFICATION	□

HYSICAL AND CHEMICAL PROPERTIES

HYSICAL STATE	clear liquid
AELTING POINT	10 - 11 C
OILING POINT	170 - 171 C
PECIFIC GRAVITY	1.015 - 1.020
OLUBILITY IN WATER	Miscible
H	12.0 (0.1N aq sol.)
APOR DENSITY	2.1
UTOIGNITION	365 C
IFPA RATINGS	Health: 2 ; Flammability: 2; Reactivity: 0
EFRACTIVE INDEX	1.4539
LASH POINT	93 C
TABILITY	Stable under ordinary conditions

PPLICATIONS

is compound is used in scrubbing hydrogen sulfide (H_2S) and carbon dioxide CO_2) from petroleum gas streams. It is a family of surfactants or solvents useful produce emulsion paints, dispersing agent for agricultural chemicals,□ light-uty detergents and personal care product.□ It is used aa s chemical itermediate for resins, plasticizers, corrosion inhibitor, rubber chemicals, bricants; cutting fluids for pharmaceuticals and textile softnening agents.

ALES SPECIFICATION

PPEARANCE	clear liquid
SSAY	99.0% min
OLOR, APHA	20 max
IOISTURE	0.3% max

ANSPORTATION

Appendix 6: Sample Mathcad Modeling

Overall Mass Transfer of Mixed Component (Methane+CO2)

Study of mass transfer as a function of pore size

P = 50 bar T = 298 K Tortuosity, τ = 3.676 Porosity, ξ = 0.272

$P := 5$

$T := 29$

1 refers to CH4, 20%

2 refers to CO2, 80%

$Tc1 := 190.$ $Tc2 := 304.$

$Pc1 := 46.$ $Pc2 := 73.$

$\omega 1 := 0.00$ $\omega 2 := 0.22$

$vc1 := 11$ $vc2 := 93.$

$zc1 := 0.28$ $zc2 := 0.27$

Reduced Pressure and Reduced Temperature

$Pr1 := \frac{P}{Pc1}$ $Tr1 := \frac{T}{Tc1}$

$Pr2 := \frac{P}{Pc2}$ $Tr2 := \frac{T}{Tc2}$

$$\omega 12 := \frac{\omega 1 + \omega 2}{2}$$

$$zc12 := \frac{zc1 + zc2}{2}$$

$$vc12 := \left(\frac{vc1^{\frac{1}{3}} + vc2^{\frac{1}{3}}}{2} \right)^{3}$$

$$Tc12 := (Tc1 \cdot Tc2)^{\frac{1}{2}}$$

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

$$Tr12 := \frac{T}{Tc12}$$

Virial Coefficient

$$z1 := 1 + \frac{Pr1}{Tr1} \cdot \left[\left(0.083 - \frac{0.422}{Tr1^{1.6}} \right) + \omega 1 \cdot \left(0.139 - \frac{0.172}{Tr1^{4.2}} \right) \right]$$

$$B11 := \left[\left(0.083 - \frac{0.422}{Tr1^{1.6}} \right) + \omega 1 \cdot \left(0.139 - \frac{0.172}{Tr1^{4.2}} \right) \right] \cdot \frac{82.06 Tc1}{Pc1}$$

$$z2 := 1 + \frac{Pr2}{Tr2} \cdot \left[\left(0.083 - \frac{0.422}{Tr2^{1.6}} \right) + \omega 2 \cdot \left(0.139 - \frac{0.172}{Tr2^{4.2}} \right) \right]$$

$$B22 := \left[\left(0.083 - \frac{0.422}{Tr2^{1.6}} \right) + \omega 2 \cdot \left(0.139 - \frac{0.172}{Tr2^{4.2}} \right) \right] \cdot \frac{82.06 Tc2}{Pc2}$$

$$B12 := \left[\left(0.083 - \frac{0.422}{Tr12^{1.6}} \right) + \omega 12 \cdot \left(0.139 - \frac{0.172}{Tr12^{4.2}} \right) \right] \cdot \frac{82.06 Tc12}{Pc12}$$

$y1 := 0.2$

$y2 := 0.8$

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

Compressibility Factor

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

Viscosity of Mixed Gas

$M1 := 16.043$

$M2 := 44.01$

$\mu 1 := 0.00001384$

$\mu 2 := 0.00001955$

$$\Phi 12 := \frac{1}{\sqrt{8}} \cdot \left(1 + \frac{M1}{M2} \right)^{-0.5} \cdot \left[1 + \left(\frac{\mu 1}{\mu 2} \right)^{0.5} \cdot \left(\frac{M1}{M2} \right)^{0.25} \right]^{2}$$

$$\mu mix := \frac{y1 \cdot \mu 1}{y2 \cdot \Phi 12} + \frac{y2 \cdot \mu 2}{y1 \cdot \Phi 12}$$

Average Pressure

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

Pore Size

$$rp := 1\cdot 10^{-9}$$

Viscous Diffusivity

$$viscous\_dif1 := AVEPRESS\frac{rp^{2}}{8\cdot \mu 1}$$

$$viscous\_dif2 := AVEPRESS\frac{rp^{2}}{8\cdot \mu 2}$$

Knudsen Diffusivity

$$knudsen1 := \frac{2\cdot\left(rp - 1.9\cdot 10^{-10}\right)\cdot\sqrt{8\cdot 8.314\frac{T}{3.14\cdot 16.042}}}{3}$$

$$knudsen2 := \frac{2\cdot\left(rp - 0.5\cdot 0.33\cdot 10^{-9}\right)\cdot\sqrt{8\cdot 8.314\frac{T}{3.14\cdot 44.01}}}{3}$$

Bulk Diffusivity

$$bulk\_dif := 10^{-7}\cdot T^{1.75}\cdot\frac{\left(\frac{1}{44.01}+\frac{1}{16.042}\right)^{\frac{1}{2}}}{P\cdot\left(24.42^{\frac{1}{3}} + 20.96^{\frac{1}{3}}\right)}$$

Surface Diffusivity

$$\Delta H1 := -2100$$

$$Ds1 := 1.6\cdot 10^{-2}\cdot e^{\left[-0.45\cdot\frac{(-\Delta H1)}{8.314\cdot T}\right]}$$

$$\Delta H2 := -1711$$

$$Ds2 := 1.6\cdot 10^{-2}\cdot e^{\left[-0.45\cdot\frac{(-\Delta H2)}{8.314\cdot T}\right]}$$

Permeability Factor

$$\xi := 0.27$$

$$Factor1 := \frac{\xi}{z1\cdot 8.314T\cdot 3.676}$$

$$\text{Factor2} := \frac{\xi}{z2\cdot 8.314\,T\cdot 3.676}$$

Viscous Permeability

$\text{Pv1} := \text{Factor1}\cdot \text{viscous\_dif1}$

$\text{Pv2} := \text{Factor2}\cdot \text{viscous\_dif2}$

Knudsen Permeability

$$\text{Dg1} := \frac{1}{\dfrac{1}{\text{knudsen1}} + \dfrac{1}{\text{bulk\_dif}}}$$

$$\text{Dg2} := \frac{1}{\dfrac{1}{\text{knudsen2}} + \dfrac{1}{\text{bulk\_dif}}}$$

$\text{Pk1} := \text{Factor1}\cdot \text{Dg1}$

$\text{Pk2} := \text{Factor2}\cdot \text{Dg2}$

Surface Permeability

$\rho m := 3040$

$f1 := 2.15\cdot 10^{-5}$

$f2 := 6.18\cdot 10^{-5}$

$$\text{Ps1} := \text{Factor1}\cdot \frac{1}{\xi}\cdot \text{Ds1}\cdot \rho m\cdot f1$$

$$\text{Ps2} := \text{Factor2}\cdot \frac{1}{\xi}\cdot \text{Ds2}\cdot \rho m\cdot f2$$

Overall Permeability

$P1 := \text{Pv1} + \text{Pk1} + \text{Ps1}$

$P2 := \text{Pv2} + \text{Pk2} + \text{Ps2}$

$tm := 0.1\cdot 10^{-6}$

$$k1M := \frac{tm}{P1}$$

$$k2M := \frac{tm}{P2}$$

Fraction Permeated

$\text{Phigh} := 50$

$\text{Plow} := 1$

$$Am := 10($$

$$q\_feed := 10($$

$$\alpha := \frac{P2}{P1}$$

$$xf1 := 0.2$$

$$xf2 := 0.8$$

$$Cf1 := q\_feed \cdot xf1$$

$$Cf2 := q\_feed \cdot xf2$$

Stage cut can be calculated based on the following equation

$$Am := \frac{(\theta \cdot q\_feed \cdot yp1 \cdot tm)}{P1 \cdot \left[Phigh \cdot \frac{(xf1 - \theta \cdot yp1)}{1 - \theta} - Plow \cdot yp1 \right]}$$

$$q\_permeate := \theta \cdot q\_feed$$

$$q\_retentate := (1 - \theta) \cdot q\_feed$$

$$yp1 := 0.2$$ from iteration by guessing the initial value of yp1

$$yp2 := 0.8$$

$$xo1 := \frac{xf1 - \theta \cdot yp1}{1 - \theta}$$

$$xo2 := \frac{xf2 - \theta \cdot yp2}{1 - \theta}$$

$$Cp1 := q\_permeate \cdot yp1$$

$$Cp2 := q\_permeate \cdot yp2$$

$$p1M := 4.9 \cdot 10^{6} \cdot Cf1$$

$$p2M := 0.156 \cdot 10^{6} \cdot Cf2$$

$$p1ML := 4.9 \cdot 10^{6} \cdot yp1$$

$$p2ML := 0.156 \cdot 10^{6} \cdot yp2$$

$$N1 := k1M \cdot (p1M - p1ML) \cdot Am$$

$$N2 := k2M \cdot (p2M - p2ML) \cdot Am$$

Mass Transfer Coefficient of Mixed Component through liquid side (Methane+CO2)

Study of mass transfer as a function flowrate

P =1 bar

T = 298 K

$$k := \frac{10^{\left(10.99-\frac{2152}{298}\right)}}{0.001}$$

$H := 4.2\cdot 10^{7}$ kPa.m3/mol

Vapor Pressure

$$Po2 := 10^{\left(9.81066-\frac{1347.786}{25+273}\right)}$$

$$Po2 := \frac{Po2\cdot 1.0132510^{2}}{760}$$

$$S2 := \frac{Po2\cdot yp2}{\left(0.15610^{6}\right)^{2}}$$

$$Po1 := 10^{\left(6.69561-\frac{405.42}{25+267.78}\right)}$$

$$Po1 := \frac{Po1\cdot 1.0132510^{2}}{760}$$

$$S1 := \frac{Po1\cdot yp1}{\left(4.9\cdot 10^{6}\right)^{2}}$$

$$k2L := \frac{H}{\sqrt{Dg2\cdot S2\cdot k}}$$

$$k1L := \frac{H}{\sqrt{Dg1\cdot S2\cdot k}}$$

$$C1i := Cp1 - \frac{N1}{k1L\cdot Am}$$

$$C2i := Cp2 - \frac{N2}{k2L\cdot Am}$$

$Ci := C1i + C2$

Overall Mass Transfer of Mixed Component through liquid side (Methane+CO2)

Study of mass transfer as a function flowrate

P =1 bar

T = 298 K

A for CH4 20%

B for CO2 80%

$$yA2 := \frac{C1i}{C2i + C1i}$$

$$yB2 := \frac{C2i}{C1i + C2i}$$

Input various flow rate of MEA

$i := 1, 2 .. 13$

$L(i) := m_{(i,0)}$

m =

	0
0	"Flow rate"
1	100
2	150
3	200
4	250
5	300
6	350
7	400
8	450
9	500
10	550
11	600
12	650
13	700

$$C\_total := \frac{Po2}{H}$$

$$w := \frac{44}{61.06}$$

$w = 0.721$

$$x3 := \frac{c3}{c3\cdot(1000\,1.015995.5 - c3\cdot 44)\cdot\left[\frac{(1-w)}{18.02} + \frac{w}{61.06}\right]}$$

$$H1 := H\cdot\frac{C\_total}{10^2}$$

Given

$V1(i) + L1(i) = V2 + L(i)$

$(1 - x(i))\cdot L1(i) = L(i)$

$x(i)\cdot L1(i) + y3(i)\cdot V1(i) = yB2\cdot V2$

$y3(i) = H1\cdot x(i)$

$Find(x(i), V1(i), L1(i), y3(i)) = \blacksquare$