CERTIFICATION OF APPROVAL

Study of Carbon Dioxide (CO₂) Absorption in Single MEA and Mix MEA & DEA

By Mardziah Ismail

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Pn.Azlin Suhaida Azmi)

Main Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2005

t QC 297 , m298 2005 (.Specific heaf 2. Gases .— thermal

properties
3. Call - Thoris

i

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 reference and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MARDZIAH BT ISMAIL

TABLE OF CONTENTS

CERTIFICATION (OF APP	PROVA	L	•	•	•	•	i
CERTIFICATION (OF OR	[GINA]	LITY	•		•		ii
ABSTRACT .				6	•	•	•	iii
ACKNOWLEDGEN	1ENT	•		•		•		iv
LIST OF FIGURES				•	•	•	•	V
LIST OF TABLES	•	•	•	5	•	•	•	vi
ABBREVIATION A	ND NC)TATI(ON		•	•	•	vi
CHAPTER 1:	INTRO	ODUCT	ΓΙΟΝ		•			1
	1.1	Backgr	ound o	f Study	ě	•	•	1
	1.2	Proble	m State	ment	•		•	3
	1.3	Object	ive and	Scope of	of Study	'•	•	3
CHAPTER 2:	LITE	RATUR	E REV	IEW &	k THEO	ORY		4
	2.1	Absorp	otion Th	eory	•		•	4
	2.2	Proces	s Chem	istry	•			8
	2.3	Amine	Blends		•		•	10
	2.4	Foami	ng	•	•	•	•	11
CHAPTER 3:	METH	IODOI	JOGY /	PROJ	ECT W	ORK	•	12
	3.1	Metho	dology	of Stud	y			12
	3.2	Experi	mental	Procedi	ıre	•		16

CHAPTER 4	:	RESU	LT & I	DISCU	SSION	•	•	•	19
		4.1	Experi	imental	Result	•	•	•	19
		4.2	Discus	ssion	•	•	•	•	25
CHAPTER 5	:	CONC	CLUSIC	ONS &	RECO	MMEN	DATIO	ONS	36
		5.1	Conclu	usions	•	•	•	•	36
		5.2	Recon	nmenda	tions	•	•	•	37
REFERENC	ES	•	•			•	•	•	39
APPENDICE	S	•	•	•	•	•			41
Appendix 1:	Sampl	e recalc	ulation	for sen	ior's pro	oject			41
Appendix 2:	Data fo	or recald	culation	of sen	ior's pro	ject	•		43
Appendix 3:	Sampl	e calcul	ation fo	or this p	roject	•			48
Appendix 4:	Experi	mental	data			•	•		50

ABSTRACT

Increasing amount of carbon dioxide (CO₂) in the atmosphere has lead to growing interest in research for new methods to reduce it because of the global warming effect. Fossil fuel combustion for energy generation is the main source of carbon dioxide emissions. Alkanolamine is one of the commercial solvent in removing CO₂ from flue gas. The objective of this study is to study the CO2 absorption in monoethanolamine (MEA) and to determine the optimum percentage of mix amines for optimum absorption. From previous research, mixed amine has been found can improve the CO₂ absorption and great savings in regeneration energy requirement. The experiment is conducted in experimental setup which is almost similar to gas bubbler method with various MEA concentrations (15wt%, 20wt% and 28wt%), varying solvent speed (2rpm and 5rpm), and varying mixtures of amines (MEA-15wt% + DEA-5wt%, MEA-20wt% + DEA-10wt%, and MEA-25wt% + DEA-10wt%). From the experiment that has been done, the higher the solvent speed the higher the CO₂ removal efficiency. The CO₂ removal efficiency also increase when the concentration of amine increases. The reaction temperature is higher for higher concentration of MEA and for higher solvent speed. The optimum blend of amines is MEA-20wt% and DEA-10wt% which has high CO₂ removal efficiency, no significant corrosion problem, and low regeneration energy. Foaming is a bad phenomenon to the absorption process unit. It might cause the equipment damage and loss of production time. From this study it also has been found that the foaming increase when the speed of the solvent increase from 2rpm to 5rpm. It is also expected that the higher the MEA concentration, the higher the foaming height and the higher the collapse time.

ACKNOWLEDGEMENT

Alhamdulillah, thanks to Allah SWT for His blessing, give me the strength to start and finish this project. My deepest gratitude is dedicated to my main supervisor, Puan Azlin Suhaida bt Azmi for her supervision and guidance throughout this project. Her knowledge, patience and support to me is greatly appreciated.

My deepest gratitude is also dedicated to my co-supervisors, Mr. Azry Borhan and also Pn Yuliana Yuhana, FYP Coordinator who has given much needed guidance and advice on the Final Year Research Project (FYP).

I also would like to thank the technician for Final Year Research Project (FYP), Mr Zaaba and the other technicians of the Chemical Engineering Department of Universiti Teknologi PETRONAS especially Mr. Jaamal, Mr Jailani, Mr Fauzi, Mr Yusoff and Mr Mahathir for their willingness to provide technical support and assistance to conduct the experiment required. Thanks also to my laboratory partner, Husna Fairuz for helping and accompany me throughout the experiment.

Last but not least, I would like to thank my parent, family and friends who support and motivate me a lot in completion of this project.

LIST OF FIGURES

Figure 2.1:	Simplified Process Flow Diagram in Amine Treating Process.	4
Figure 2.2:	Structures of common amines used in gas treating.	9
Figure 3.1.1:	Graph of mol CO ₂ absorbed/mol solvent for Foo Lee Lian's	
	data.	13
Figure 3.1.2:	Graph of mol CO ₂ absorbed/mol solvent for Foo Lee Lian's	
	and Khalid's data	13
Figure 3.1.3:	Schematic diagram of absorption experimental setup	15
Figure 3.2.1:	Equipment setup for CO ₂ absorption in amines	16
Figure 3.2.2:	Schematic diagram of foam test setup	17
Figure 3.2.3:	Equipment setup for foaming test	18
Figure 4.1.1:	Graph of exit CO ₂ vol% from the conical flask as a function	
	of time	19
Figure 4.1.2:	Graph of CO ₂ vol% absorbed as a function of time for single	
	MEA at solvent speed of 2rpm and 5 rpm	21
Figure 4.1.3:	Graph of CO ₂ vol% absorbed as a function of time for mix	
	MEA and DEA at solvent speed of 5rpm	22
Figure 4.1.4:	Graph of reaction temperature as a function of time	23
Figure 4.2.1:	Graph of CO ₂ vol% absorbed as a function of time for single	
	MEA at solvent speed of 2rpm and 5rpm	25
Figure 4.2.2:	Graph showing effect of MEA solvent concentration at 15wt%,	
	20wt% and 28wt% to CO ₂ removal efficiency	27
Figure 4.2.3:	Graph of CO ₂ vol% absorbed as a function of time for single	
	MEA at solvent speed of 5rpm	28
Figure 4.2.4:	Graph of CO ₂ vol% absorbed as a function of time for mix	
	MEA and DEA and single MEA-28wt% at solvent speed of	
	5rpm	29
Figure 4.2.5	Graph of reaction temperature as a function of time	31

LIST OF TABLES

Table 2.1:	Heat of Reaction Between Amines and CO ₂	6
Table 4.1.1:	Summary of experiment for CO ₂ absorption in amine	
	solvents	20
Table 4.1.2:	Foaming test results	24
Table 4.2:	Effect of amine solvent concentration to CO ₂ removal	
	efficiency	30

ABBREVIATION AND NOTATION

$\alpha \alpha$	\sim 1	1, , ,
CO_2	(arbon	dioxide
	1.01118111	UHIANE

DEA Diethanolamine

IR Infra Red

MEA Monoethanolamine

N₂ Nitrogen

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND OF STUDY

Carbon dioxide (CO₂) is one of the most abundant gasses in the atmosphere. It plays an important part in vital plant and animal process, such as photosynthesis and respiration. Hundreds of millions of years ago, CO₂ content of the air stabilized at 0.03 percent. Natural sources of CO₂ released into the air by wildfires and the decomposition and respiration of plants and animals balanced with the amount of carbon removed into long-term storage in the oceans and on the land.

Due to human activity, the amount of CO₂ released into the atmosphere has been rising extensively during the latest 150 years. As a result it has exceeded the amount sequestered in biomass, the oceans, and other sinks. There has been a climb in carbon dioxide concentrations in the atmosphere of about 280 ppm in 1850 to 364 ppm in 1998, mainly due to human activities during and after the industrial revolution, which began in 1850. Humans have been increasing the amount of carbon dioxide in air by burning of fossil fuels, by producing cement and by carrying out land clearing and forest combustion. Of these activities fossil fuel combustion for energy generation causes about 70-75% of the CO₂ emissions, being the main source of carbon dioxide emissions. The remaining 20-25% of the emissions is caused by land clearing and burning and by emission from motor vehicle exhausts.

The increasing concentration of CO₂ in atmospheric has result in increasing of greenhouse gasses, because CO₂ is one of it. As amount of greenhouse gasses grew extensively, the earth climate also change because the temperatures are rising or it is known as global warming. Increasing CO₂ emissions cause about 50-60% of the global warming. It is suspected that global warming may cause increases in storm activity, melting of ice caps on the poles, which will cause flooding of the inhabited continents, and other environmental problems. Carbon dioxide remains in the troposphere about fifty up to two hundred years.

The growing evidence that links the CO₂ and global climate change highlights the need to develop economically feasible technology to capture CO₂ from fossil fuel burning power plant and from process stream.

There are many methods that may be employed to remove carbon dioxide (CO₂) from hydrocarbon streams. The methods are divided into chemical reaction processes, physical reaction processes, combination processes (chemical and physical reaction processes) and alkaline salt processes.

Chemical absorption with alkanolamines has been used commercially for the removal of acid gas impurities (CO₂ and H₂S) from process gas stream. It gives better CO₂ removal and less energy utilization. Amines used in aqueous alkanolamine processes are triethanolamine (TEA), monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), diglycolamine (DGA) and methyldiethanolamine (MDEA). The alkanolamine processes are particularly applicable when acid gas partial pressures are low and/or low levels of acid gas are desired in the residue gas.

Another process for removal CO₂ is alkaline salt process or hot carbonate employs an aqueous solution of potassium carbonate (K₂CO₃). The most popular of the carbonate processes is Benfield Process. It is an old proven technology. To compare with alkanolamine, it is less effect to environment and easy to get the solution. However this process encounter corrosion, crystallization, require long time passivation for start up and need regeneration after shut down. Numerous improvements have been made to the potassium carbonate process resulting in significant reduction in capital and operating costs. At the same time, lower acid gas concentration in the treated acid gas can now be achieved.

1.2 PROBLEM STATEMENT

CO₂ is the primary green house gas representing roughly 83% of anthropogenic effect. One way to reduce CO₂ is to remove CO₂ from process stream before it goes out to atmosphere. CO₂ from stream process can be removed by absorption process using amine.

Aqueous alkanolamine solutions are frequently used for removal of acidic gases such as CO₂ and H₂S from gas stream in natural gas, synthetic, and refinery industries. Aqueos monoethanolamine (MEA) has been used extensively because of its high reactivity and low solvent cost. However, the maximum CO₂ loading in the MEA is limited by stoichiometry to 0.5 mol of CO₂ per mole of amine. The mixed amine system in gas treating processes is of increasing interest today. The mixed amine systems can bring considerable improvement in gas absorption and great savings in regeneration energy requirement (Hagewiesche, Ashor, Al-Ghawas, & Sandal, 1995).

1.3 OBJECTIVE AND SCOPE OF STUDY

The objectives of this project are:

- i. To determine amount of CO₂ absorb in amines
- ii. To determine the best amines and the optimum percentage of mix amines for optimum absorption.

This study is an experiment based project. This project requires some experiments to be carried out to achieve all the objectives stated above. The experiment is absorption in an experimental setup which is almost similar to gas bubbler method. The amines that will be used are MEA and DEA.

CHAPTER 2

LITERATURE REVIEW & THEORY

2.1 ABSORPTION THEORY

Absorption is a separation process involving the transfer of a substance from a gaseous phase to a liquid phase through the phase boundary. In this study, CO₂ is in the gaseous phase while amine in the liquid phase. CO₂ is a solute that absorbed into amine that acts as an absorbent. The reverse of absorption is called stripping or desorption. Stripping is used to regenerates the amine solution in the amine regenerator. Figure 2.1 shows the simplified flow diagram for amine treating process.

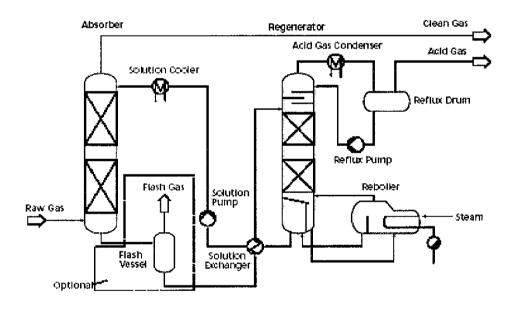


Figure 2.1: Simplified Process Flow Diagram in Amine Treating Process

Alkanolamines remove CO₂ from the gas stream by the exothermic reaction of CO₂ with the amine. Different amines have different reaction rates with respect to the various acid gases. In addition, different amines vary in their equilibrium absorption characteristics for the various acid gases and have different sensitivities with respect to the solvent stability and corrosion factors. Alkanolamines can be divided into three groups: (1) primary amines whose members include monoethanol amine (MEA), diglycolamine (DGA); (2) secondary amines whose members include diethanolamine

(DEA), di-isopropylamine (DIPA); and (3) tertiary amines whose members include triethanolamine (TEA) and methyl-diethanolamine (MDEA).

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 leave at the top, whereas the solvent enters the top of the absorber, flows down (contacting the gas), and emerges at the bottom. Dilution the circulating amine with water is done to reduce viscosity of the circulating fluid. The liquid amine solution containing the absorbed gas is then flowed to a regeneration unit where it is heated and the acid gases liberated. The solvent regeneration can be carried out at low pressures to enhance desorption of CO₂ from the liquid. Some amine solution is typically carried over in the acid gas stream from the regeneration step and the amine solution is recovered using a condenser. The hot lean amine solution then flows through a heat exchanger where it is contacted with the rich amine solution from the contact tower and from there the lean amine solution is returned to the gas contact tower.

Among the primary amines, MEA has been the traditional solvent of choice for CO₂ absorption and the acid gas removal in general. MEA is the least expansive of the alkanolamines and has the lowest molecular weight, so it possesses the highest theoretical absorption capacity for CO₂. 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 CO₂ removal from the gas stream and in the regeneration step. To reduce solvent losses, a water wash of the purified gas stream is usually required. In addition, MEA reacts irreversibly with minor impurities such as carbonyl sulfide (COS) and carbon disulfide (CS₂) resulting in solvent degradation. Foaming of the absorbing liquid MEA due to the build-up of impurities can also be concern.

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 the corrosion issues (GPSA, 1998). Corrosion inhibitors may be added to MEA solution, and this results in an increase in solution strength. In a commercial process, concentration of MEA up to 30 wt% has been employed successfully to remove 80% - 90% of the

CO₂ from the feed gas (Mariz, 1998). The process has been used to treat flue gas, however, some cooling and compression of the gas is required to operate the system. The solvent composition is proprietary, so royalty costs may be significant. Another commercial process, which uses 20% MEA with inhibitors, is also offered for flue gas treatment (Barchas, 1992).

Secondary amines have advantage over primary amines – their heat of reaction with carbon dioxide is lower, 360 calorie/gm (650 BTU/lb) versus 455 calorie/gm (820 BTU/lb). This means that the secondary amines require less heat in the regeneration step than primary amines. From an energy consumption point of view, this is an important consideration when the primary objective is the isolation of CO₂ from flue gas.

Tertiary amines react slower with carbon dioxide than primary and secondary amines thus require higher circulation rate of liquid to remove CO₂ compared to primary and secondary amines. A major advantage of tertiary amine is their lower heat requirements for CO₂ liberation from the CO₂ containing solvent. The table below displays data for the heat of reaction between the three amine and CO₂ (Skinner et al., 1995).

Table 2.1: Heat of Reaction Between Amines and CO₂

Amine	MEA	DEA	MDEA
ΔHf for carbon dioxide in Calorie/gm	455	360	320
(BTU/lb)	820	650	577

Tertiary amines show a lower tendency to form degradation products in use the primary and secondary amines, and are more easily generated. In addition, tertiary amines have lower corrosion rates compared to primary and secondary amines.

It may be pointed out that corrosion has been a serious issue in amine process. In general, alkanolamines themselves are not corrosive to carbon steel; the dissolved CO_2 is the primary corroding agent. As such, the alkanolamines indirectly influence corrosion rate due to their absorption of CO_2 . The observed corrosivity of alkanolamines to carbon steel is generally in the order:

Primary Amines > Secondary Amines > Tertiary Amines

Specialty amines are also being formulated for specific purpose, for example, hindered amines. Hindered amine concept is based on the reaction rates of the acid gases with different amine molecules. In the case of CO₂ removal, the capacity of the solvent can be greatly enhanced if one of the intermediate reactions, i.e. the carbamate formation reaction can be slowed down by providing steric hindrance to the reacting CO₂. This hindrance effect can be achieved by attaching a bulky substitute to the nitrogen atom of the amine molecule. In addition to slowing down the overall reaction, bulkier substitutes give rise to less stable carbamates. By making the amine carbamate unstable, one cans theoretically double the capacity of the solvent (Chakma, 1994).

Since 1990, an industrial company and an electric power company in Japan have been working together to develop the KS-1 solvent absorption process (Iijima, 1998). It uses a proprietary sterically hindered amine KS-1 for recovering CO₂ from flue gas. The first commercial plant using the newly develop solvent KS-1 has been in operation in Malaysia since October 1999.

2.2 PROCESS CHEMISTRY

H₂S and CO₂ are "acid gases" because they dissociate to form a weak acidic solution when they come in contact with water or an aqueous medium. The amines are weak organic bases. The acid gases and the amines base will combine chemically to form an acid base complex or "salt" in the treating solution. In the absorber column the acid gas absorption of H2S is based only on "acid-based-reaction". For CO2 removal the basis of the chemistry is a combination of indirect "acid-base-reaction" and direct "carbamate-reaction". The acid base reaction may occur with any of the alkanolamines regardless of the amine structure but it is kinetically slow because the carbonic acid dissociation step to the bicarbonate is relatively slow. The second reaction for CO2, which results in the formation of the carbamate, is called the carbamate formation reaction and may only occur with the primary and secondary amines.

CO2-reaction: Acid-base-reaction

Relative kinetics: slow

CO₂ + H₂O \Leftrightarrow H₂CO₃

 $H_2CO_3 + [Amine] \Leftrightarrow HCO_3^T + [Amine]^T$

CO₂-reaction: Carbamate-reaction

Relative kinetics: fast

 $CO_2 + 2[Amine] \Leftrightarrow [Amine]^+ + [Amine]COO^-$

The rate of CO₂ absorption via the carbamate reaction is rapid, much faster than the CO_2 hydrolysis reaction, but somewhat slower than the H_2S absorption reaction. The stoichiometry of the carbamate reaction indicates that the capacity of the amine solution for CO₂ is limited to 0.5 mole of CO₂ per mole of amine if the only reaction is the amine carbamate. However, the carbamate can undergo partial hydrolysis, as shown below in equation below, to form bicarbonate, regenerating free amine. Hence, CO₂ loading greater than 0.5 is possible through the hydrolysis of the carbamate intermediate to bicarbonate.

[Amine]COO † + H₂O \Leftrightarrow [Amine] + HCO₃

The alkanolamines are classified by the degree of substitution on the central nitrogen; a single substitution denoting a primary amine, a double substitution, a secondary amine, and a triple substitution, a tertiary amine. Each of the alkanolamines has at least one hydroxyl group and one amino group. In general the hydroxyl group serves to reduce the vapor pressure and increase water solubility, while the amino group provides the necessary alkalinity in water solutions to promote the reaction with acid gases. It is readily apparent looking at the molecular structure that the non-fully substituted alkanolamines have hydrogen atoms at the non-substituted valent sites on the central nitrogen. This structural characteristic plays an important role in the acid gas removal capabilities of the various treating solvents. Figure 2.2 shows the commonly used alkanolamines in the gas treating industry (LRGCC, 2003; Kohl and Nielsen, 1997).

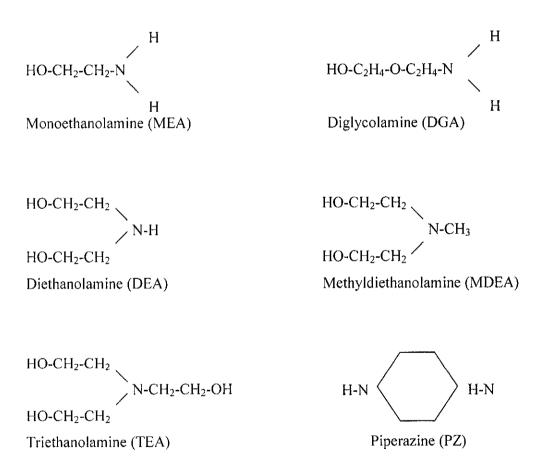


Figure 2.2: Structures of common amines used in gas treating

2.3 AMINE BLENDS

2.3.1 Praxair's Advanced Amine Technology

Praxair has been granted a patent that describes CO_2 recovery using amine blends. MEA based systems tend to have higher steam consumption due to high heat of reaction of MEA with CO_2 . Corrosion with MEA-based systems becomes significant at concentration above 30 wt%. Therefore, this patent recommends the use of concentrated amine blends, as high as 50 wt%. Higher concentrations imply less water to be heated resulting in lower steam consumption rates. Use of another amine such as MDEA potentially allows for greater capacity and reaction rates without the operational problems that arise due to corrosion. Examples of such amine blends are solutions containing 10 - 20 wt% MEA and 20 - 40 wt% MDEA. Detailed simulations have confirmed the feasibility of the use of such amines blends for CO_2 recovery from flue gases. Pilot tests are underway to demonstrate that use of concentrated amine blends can reduce steam consumption from today's value of 4 - 5 MMBtu/mT of CO_2 to around 3 MMBtu/mT of CO_2 recovered.

2.3.2 Investigation on MDEA/MEA and AMP/MEA

The absorption of CO₂ into aqueous solutions of mixture of small amount of fast reacting MEA, a primary amine, and much larger amounts of MDEA, a tertiary amine, and small amount of MEA, and much larger amounts of sterically hindered amine AMP were studied experimentally and theoretically by B.P. Mandal, M. Guha, A.K. Biswas and S.S. Bandyepadhyay from Indian Institute of Technology, Kharagpur, India. From their work it has been found that the addition of a small amount of MEA to an aqueous solution of MDEA or AMP significantly enhances the enhancement factor and rate of absorption for both solvents, while the enhancement has been found to be relatively higher for CO₂ absorption for CO₂ absorption into (AMP+MEA+H₂O) than into (MDEA+MEA+H₂O). This establishes the importance of the blended amine solvent AMP/MDEA as a potential alternative besides MDEA/MEA for CO₂ absorption.

2.4 FOAMING

A clean amine solution exhibits no foaming tendencies. Foaming is encountered when contaminants are introduced. Particulates, heavy hydrocarbons, oils and grease left behind from inadequate prestart-up washing or introduced with the feed gas usually are the cause of foaming.

Particulates can be either produced internally or introduced into the system. Internal sources include; degradation products or bicarbonate precipitates. External sources are introduced through the feed gas or through the make up water (make up water and water used for mixing the solution should be boiler feed quality).

Liquid hydrocarbons also present a problem with foaming. These are introduced into the system from the feed gas if the feed gas separator is not properly functioning. This problem can sometimes be detected when there is a separation of liquid layers in the rich solution in the absorber bottom. To avoid any condensation of liquid hydrocarbons the feed gas is preheated before entering the absorber. At high pressures certain natural gas composition when checked at the absorber inlet and outlet conditions will show no possibility of hydrocarbons condensation. But at some intermediate point condensation can take place due to shrinkage in volume of the gas.

Proper filtration of solution is important to prevent the buildup of particulates. A 10% slipstream of lean solution should be passed through a 10 micron filter continuously (a micron filter can be used during start-up). Pressure drop across the filter should be checked frequently especially during the commissioning stage.

The anti-foam agent is used to treat the foaming condition and is not the solution to the problem. When a foaming problem is detected the source of the problem should be sought by analysis of the solution. Excessive levels of anti-foam agent in the solution can cause a foaming problem in itself. Antifoam agent also slows down the rate of reaction of CO₂ with the solution.

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1 METHODOLOGY OF STUDY

In doing this project, the first stage is to get information on the application of amines in CO₂ removal process. Literature research has been conducted from various sources such as books, research articles, online journals via Internet access and information from process plant engineer. Besides that the data from the previous students is studied. At the first place, the experiment is planned to be conducted by using wetted wall column, same as the seniors. However because of late arrival and limited amount of amines, the experiment is conducted in the backup experiment for this project which is almost similar to gas bubbler method. From this work the trend of the solution can be analyzed. The Yokogawa IR Gas Analyzer IR 200 is attached to quantify the amount of CO₂ leaving the setup.

3.1.1 Study on seniors' project

Data from the previous students, Foo Lee Lian and Khalid, are recalculated and converted from mol CO₂ absorbed/mL solvent to mol CO₂ absorbed/mol solvent. See Appendix 1 for the sample recalculation and Appendix 2 for data from the previous student. Graphs obtained are as shown in Figure 3.1.1 and Figure 3.1.2.

From Foo Lee Lian's data (Figure 3.1.1), the mixture of DEA-25wt% and MEA-10.2 wt% gave the highest moles of CO_2 absorbed per mol of solvent. However, the next mixture of DEA-25 wt% and MEA-6.4 wt% did not yield a good result as compared to MEA-30wt%. This mixture has been determined not to be the optimum mix for CO_2 effective removal.

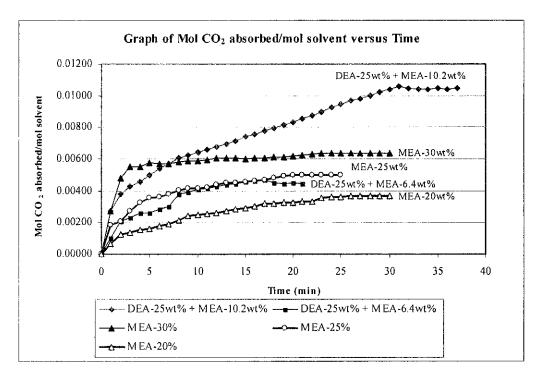


Figure 3.1.1: Graph of mol CO₂ absorbed/mol solvent for Foo Lee Lian's data.

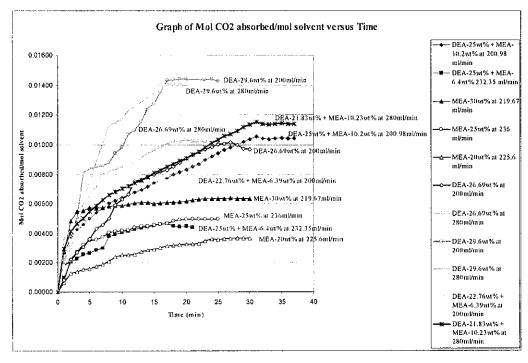


Figure 3.1.2: Graph of mol CO₂ absorbed/mol solvent for Foo Lee Lian's and Khalid's data.

When the result is compared to Khalid's data (Figure 3.1.2), the DEA-29.6wt% at 200ml/min gave the highest moles of CO₂ absorbed per mol of solvent. The mixture of DEA-21.83wt% + MEA-10.23wt% at 280ml/min gave the third highest CO₂ absorbed per mol of solvent. However it is the first mixture that gave the highest CO₂ absorbed per mol of solvent compared to the other mixtures. MEA-20wt% at 225.6ml/min gave the lowest CO₂ absorbed per mol of solvent. When compared the DEA and MEA at approximately 25 wt%, DEA result in double absorption capacity compared to MEA.

The mixture of DEA-21.83wt% and MEA-10.23wt% at 280ml/min can be an optimum mixture for CO₂ removal when the cost is taken into account. DEA is about triple higher cost compared to MEA. I liter DEA is about RM 380 compared to RM 132 for 1 liter MEA. By using this mixture cost can be reduced compared to just using DEA alone for the desired CO₂ absorbed per mol of solvent.

3.1.2 Experimental method

The experiments for absorption in alkanolamines were performed to study the following parameters:

- 1. Effect of constant concentration of primary amine (MEA) with varying stirrer rate on the total moles of CO₂ absorbed.
- 2. Effect of varying concentration of primary amine (MEA) on the absorption capacity of solvent.
- 3. Comparison between performance of single primary amines (MEA) and mixed amines (MEA + DEA) on the total moles of CO_2 absorbed.
- 4. Comparison of foaming tendency for amines solvent.

3.1.3 Experimental setup

The schematic diagram of experimental set up is as shown in Figure 3.1.3. The setup is the modified experimental setup from Yeh (1999) in study of reaction between CO₂ and NH₃ solvent. The equipment required to perform the experiment are the Yokogawa IR Gas Analyzer IR 200, conical flask, stirrer, magnetic stirrer, throttle valve, purified CO₂ gas cylinder, pure N₂ gas cylinder, cylinder pressure regulator and temperature probe. The nitrogen is added as a carrier gas to reduce the overall CO₂ volume% so that the IR gas analyzer can be used because the range of the IR gas analyzer is 0 to 20 volume% CO₂. Because of higher pressure in the tank and only small volume of CO₂ need to be introduced to the setup, the CO₂ and N₂ gas flow is controlled by gas regulator and the throttle valve. All connection is sealed to avoid leaking. The concentration of CO₂ at the inlet and the outlet of the flask are measured by IR gas analyzer. All solutions were prepared with distilled water.

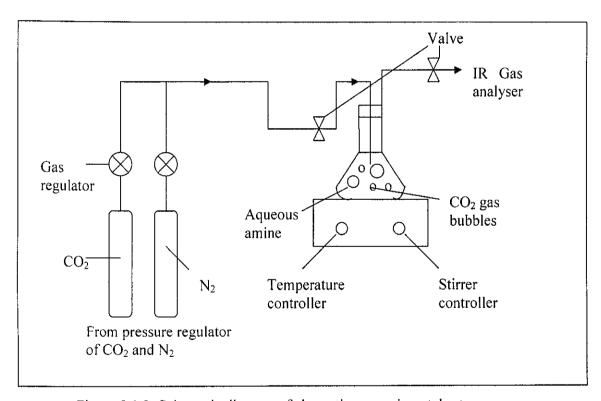


Figure 3.1.3: Schematic diagram of absorption experimental setup

The first run of the experiment is performed for MEA-15wt% with water. Initially the stirrer or speed for the amine solvent is set at 2rpm. The initial CO_2 vol% was recorded from the display panel of IR Gas Analyzer. After that the stopwatch is started and the CO_2 vol% value is subsequently recorded from the panel on a 1 minute interval basis. The experiment is stopped when the CO_2 vol% values remains about the same value over time. This can be considered as the steady state value of CO_2 vol% in the system. Subsequently, the experiment is repeated with differing speed which is 5rpm.

The absorption experiment is then repeated for the next MEA solvent concentration by using the best speed obtained in the first experiment.

3.2.3 Foaming tendency test

Apparatus as shown in Figure 3.2.2 is setup. The setup is the modified experimental setup for foaming test use in Benfield Process. 50 ml solution to be tested is added in the 200 ml beaker with 10 ml of petrol (liquid hydrocarbon) as a source of contaminant that can cause foaming. The solution is heated at 25°C with constant stirring at 5rpm, and the air is bubbled into the beaker. The foam height is measured after 10 seconds of bubbling. The air bubbled and stirrer is shut off, and the collapse time of the foam is measured.

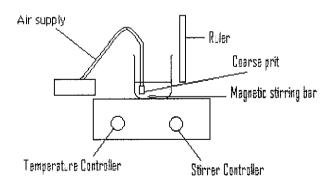


Figure 3.2.2: Schematic diagram of foam test setup

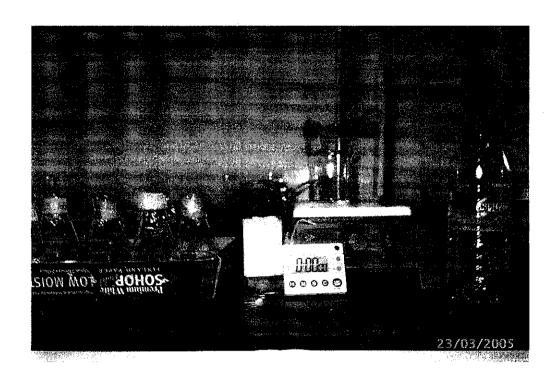


Figure 3.2.3: Equipment setup for foaming test

CHAPTER 4 RESULT AND DISCUSSION

4.1 EXPERIMENTAL RESULTS

The experiments performed were for MEA-15wt% at speed 2rpm, MEA-15wt% at speed 5rpm, MEA-20wt% at speed 5rpm, MEA-28wt% at speed 5rpm, mixture of MEA-15wt% and DEA-5wt% at speed 5rpm, mixture of MEA-20wt% and DEA-10wt% at speed 5rpm, and mixture of MEA-25wt% and DEA-10wt% at speed 5rpm. The experimental data are shown in Appendix 4. The data recorded for each run of the experiment are the entering CO₂ vol% into the conical flask, exiting CO₂ vol% from the conical flask as well as the temperature of the conical flask during the absorption process at a one-minute interval. The data obtained from the experiments are further analyzed by plotting a graph.

4.1.1 Determination of CO₂ gas flow absorbed

The experimental data collected is initially used to generate plots of the exiting CO₂ vol% from the conical flask as a function of time.

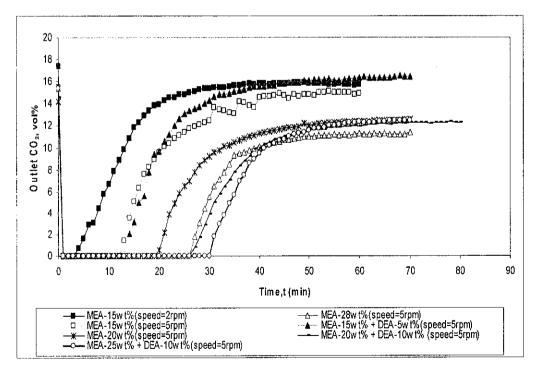


Figure 4.1.1: Graph of exit CO₂ vol% from the conical flask as a function of time

From the Figure 4.1.1, it can be observed the general trend is of decreasing exiting CO_2 vol% from the conical flask to 0 vol% and then increasing back to the stable value. This corresponds to the absorption process occurring in the conical flask, with amine solvent removing CO_2 from the entering gas. At first the CO_2 vol% decrease to 0% because of the total inlet CO_2 is absorbed by the amine solvent. The CO_2 vol% is then start increasing which shown that the amine solvent has absorbed a large volume of CO_2 and not all the inlet CO_2 can be absorbed by the amine solvent any more. The CO_2 vol% increases until it comes to the stable vol% which is the point in time when the experiment is stopped.

However there is a limitation to observe the actual amount of CO_2 moles entering the conical flask which occurs due to the different values of entering CO_2 vol% into the conical flask at time=0 as seen from the Figure 4.1.1. It was difficult to maintain a constant same value of CO_2 vol% entering the conical flask. During the experiment, the ratio of N_2 to CO_2 in the entering gas to the column was controlled manually by regulating the pressure of the gases for both cylinders. This contributes to the different flow of gas introduced to the column for each respective run of absorption with varying concentration of amines.

Table 4.1.1: Summary of experiment for CO₂ absorption in amine solvents

Solvent	M	EA	MEA	MEA	MEA	MEA	MEA
	(15-	wt%)	(20-wt%)	(28-wt%)	(15-wt%)	(20-wt%)	(25-wt%)
					+	+	+
					DEA	DEA	DEA
					(5-wt%)	(10-wt%	(10-wt%)
Stirrer setting	2	5	5	5	5	5	5
CO2 vol% inlet	17.41	15.5	14.25	15.42	17.44	14.57	15.4
Total time for maximum CO ₂ vol% absorbed (min)	3	12	19	26	13	26	30
Stable CO ₂ vol% outlet	15.79	14.94	12.6	11.37	16.5	12.33	12.53

As seen from the Table 4.1.1, the effect of increasing the speed and increasing solvent concentration can be observed. As both of these parameters are increased, the effect on the total time for CO₂ absorbed at 100vol% or IR gas analyzer reading at 0vol% is longer which indicate the higher moles of CO₂ absorbed. This will be discussed further in Section 4.2.

4.1.2 Determination of amount of CO₂ absorbed

To determine the amount of CO₂ absorbed, the volume% of CO₂ absorbed at each time interval must be calculated. It is assumes that all the entering CO₂ into the conical flask is absorbed into amine with no losses of CO₂ to atmosphere. However, there might be release of CO₂ into atmosphere due to leaks or gaps in the installation of piping from the gas cylinders to the conical flask and from the conical flask to the IR gas analyzer.

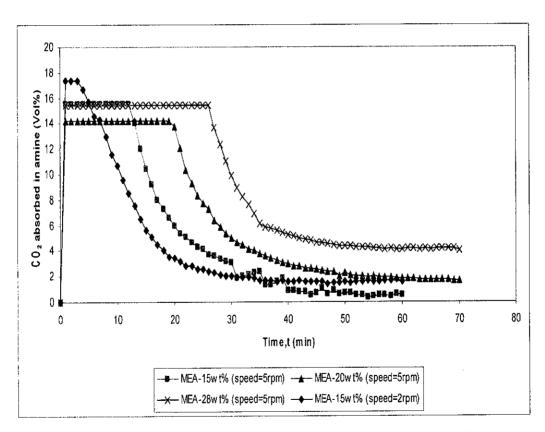


Figure 4.1.2: Graph of CO₂ vol% absorbed as a function of time for single MEA at solvent speed of 2rpm and 5 rpm

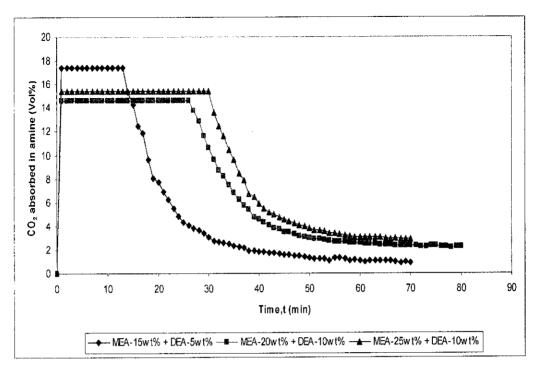


Figure 4.1.3: Graph of CO₂ vol% absorbed as a function of time for mix MEA and DEA at solvent speed of 5rpm

Figure 4.1.2 and Figure 4.1.3 are obtained by subtracting the initial inlet of CO₂ vol% with the outlet CO₂ vol% at each interval. This will be discussed further in Section 4.2.

4.1.3 Determination of absorption capacity of amines

The other method to describe the effectiveness of amine in removing CO_2 is the determination of the absorption capacity of a solvent in removing CO_2 . The absorption capacity of a solvent in removing CO_2 is given by:

Absorption capacity = $\frac{\text{kg CO}_2 \text{ removed}}{\text{kg solvent used}}$

The mass of solvent used in kilogram was found by multiplying the volume of solvent used with the density for that particular amine.

Mass of solvent used (kg) = Volume of solvent used x Density of solvent (kg/m 3).

However the kg CO₂ removed cannot be determine because the flow rate of the gas cannot be measured as there is no portable rotameter or flow meter available in the

laboratory to be detach to this experimental setup. The discussion part of this project is only discussed on the vol% of CO₂ absorbed in the amines.

4.1.4 Determination of CO₂ removal efficiency

In order to compare the performance of the solvents, the CO_2 removal efficiency is calculated. It is expressed as an average percentage of vol% CO_2 absorbed per percentage vol% of CO_2 entering the system at each interval time.

$$CO_2$$
 removal efficiency (%) = $\underline{CO_2 \text{ vol}\% \text{ inlet} - CO_2 \text{ vol}\% \text{ outlet}}$ x 100% $CO_2 \text{ vol}\% \text{ inlet}$

The effect of MEA solvent concentration on the CO₂ removal efficiency is discussed further in Section 4.2.

4.1.5 Determination of reaction temperature

Although the operating temperature was kept constant at 25°C, temperature variations in the conical flask were unavoidable. Figure 4.1.4 shows the temperature variations in the conical flask as a function of operating time.

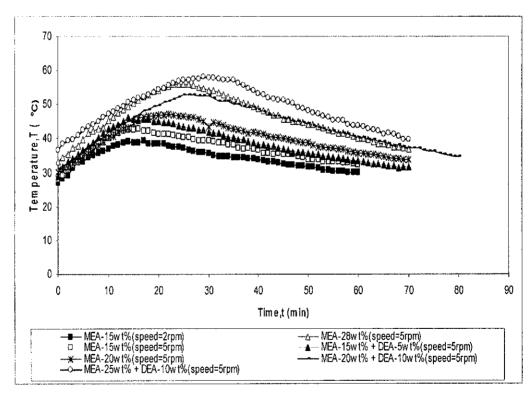


Figure 4.1.4: Graph of reaction temperature as a function of time

The trend of the graph is the sharp increase in the temperature and then sharp incline until reach the temperature remains to about constant with slight fluctuations. This effect of reaction temperature will be discussed further in section 4.2.

4.1.6 Determination of foaming tendency

The last experiment was to determine the tendency of the solvent to "foaming". The results from the experiment are as shown in the Table 4.1.2 below:

Table 4.1.2: Foaming test results

Solution	Foam height (cm)	Collapse time (sec)
MEA-15wt% (speed=2rpm)	2	5
MEA-15wt% (speed=5rpm)	3	6
MEA-20wt% (speed=5rpm)	3.5	6
MEA-28wt% (speed=5rpm)	2	5
MEA-15wt% + DEA-5wt% (speed=5rpm)	3.5	6
MEA-20wt% + DEA-10wt% (speed=5rpm)	4	6
MEA-25wt% + DEA-10wt% (speed=5rpm)	2	3

From the result it can be seen that foam height and collapse time increase with the increasing speed of the solution. However an increasing in concentration of MEA did not exactly increase the foam height or collapse time. This will be discussed further in the Section 4.2.

4.2 DISCUSSION

4.2.1 Effect of solvent speed

Two setting of stirrer or speed of the solvent is used which are 2rpm and 5rpm. The higher the speed the higher the solvent in the conical flask circulate. This circulation rate will affect the CO₂ absorbed in the amine solvent because at higher speed the CO₂ is mix and absorbed well in the solvent and give more space for absorption to take place. As observed from the Figure 4.2.1, MEA-15wt% at speed 5rpm can maintain maximum vol% CO₂ absorbed longer, over 12 minutes compared to MEA-15wt% at speed 2rpm which is only 3 minutes.

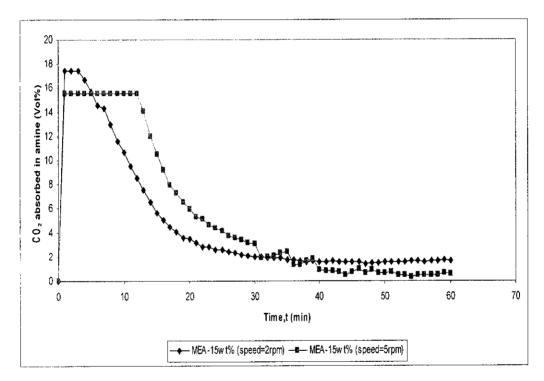


Figure 4.2.1: Graph of CO₂ vol% absorbed as a function of time for single MEA at solvent speed of 2rpm and 5rpm

However due to the difficulty in maintaining the same entering CO₂ vol% into the conical flask at time=0, the maximum vol% CO₂ absorbed is different for the two solvent. At speed 2 rpm the inlet CO₂ vol% is higher which is 17.41 vol% and gave the higher maximum vol% CO₂ absorbed which is 17.41 vol%. At maximum vol% CO₂ absorbed the IR Gas Analyzer shows 0% reading which indicate that all the CO₂ that entering the conical flask is absorbed and no outlet CO₂ detected. At speed 5

rpm the inlet CO_2 vol% is lower which is 15.5 vol% and gave the lower maximum vol% CO_2 absorbed which is 15.5 vol%.

Due to this limitation, the result is compared using the area under the graph. This area indicates the volume of the CO₂ absorbed in the amine solvents. The exact area cannot be calculated as there is another limitation of this experiment which is the flow of the gas cannot be measured because no portable flow meter available to attached to the setup. From the estimation using the vol% CO₂ absorbed versus time graph (Figure 4.2.1), the area under the graph for solvent at speed 5 rpm is larger which indicates that the higher volume of CO₂ has been absorbed. In the next sub section, there will be a discussion on CO₂ removal efficiency which also indicates that solvent at 5rpm gave higher CO₂ removal efficiency as shown in Table 4.2. Therefore, the stirrer has been maintained at high speed which is 5rpm for the other experiments run to gain higher CO₂ absorption capacity.

4.2.2 Effect of solvent concentration

The variations are done for the single amine concentrations which are MEA-15wt%, MEA-20wt% and MEA-28wt%. In order to compare the performance of the solvents, the CO₂ removal efficiency for each solvent is calculated. It is expressed as an average percentage of vol% CO₂ absorbed per vol% of CO₂ entering the system at each interval time.

The CO_2 removal efficiency at each interval is calculated as follow: CO_2 removal efficiency (%) = $\underline{CO_2}$ vol% inlet - $\underline{CO_2}$ vol% outlet x 100% $\underline{CO_2}$ vol% inlet

From work previously done by Yeh et. al. (1999) it was reported that with MEA solvent concentration of greater than 28% would not yield any improvement in CO₂ removal efficiency. This is because the CO₂ removal efficiency at 28% has been reported to be quite high, at a value of 92%. However industrial experience with MEA and most systems at present use an aqueous solution with only 15-25 wt% MEA, mainly due to the corrosion issues (GPSA, 1998). MEA-28wt% may have significant problem with corrosion. Due to that, concentration of MEA-28wt% and lower in the range of 15-25wt% MEA has been studied in this project to find the

ideal concentration of MEA with higher CO₂ loading and do not have significant problem with corrosion.

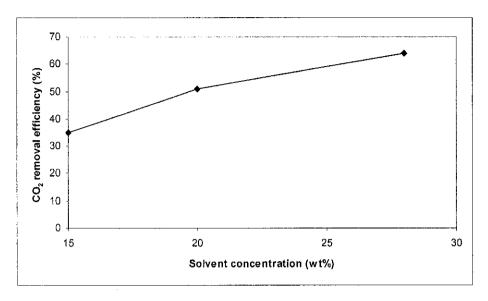


Figure 4.2.2: Graph showing effect of MEA solvent concentration at 15wt%, 20wt% and 28wt% to CO₂ removal efficiency

The maximum CO₂ removal efficiency for this single MEA experiment was obtained at 64.14% using MEA solvent concentration of 28wt%. This result is lower than the CO₂ removal efficiency at 28% that has been reported by Yeh et. al. (1999) which is 92%. This low value could be contributed by loss of CO₂ to the atmosphere due to the limitation of the setup which is not under tight experimental control.

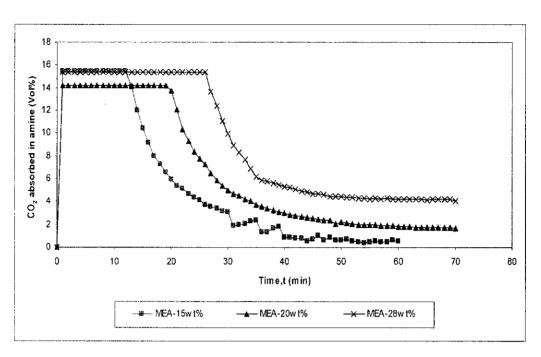


Figure 4.2.3: Graph of CO₂ vol% absorbed as a function of time for single MEA at solvent speed of 5rpm

The solvent absorption capacity could not be determine in this study because the flow rate of the gas cannot be measured as there is no portable rotameter or flow meter available in the laboratory to be detach to this experimental setup. Due to this limitation, the result is compared using the area under the graph of vol% CO_2 absorbed versus time graph (Figure 4.2.3) above. This area indicates the volume of the CO_2 absorbed in the amine solvents. However the exact volume also cannot be calculated due to no reading of gas flow rate. The estimated area under the graph for solvent of MEA-28wt% is the largest, followed by MEA-20wt% and then MEA-15wt%. The largest area of MEA-28wt% indicates that the highest volume of CO_2 has been absorbed.

4.2.3 Effect of single amines and mixture of amines

Theoretically, the mixture of primary and secondary amines will give better performance to remove CO_2 as compared to single primary amines. However, optimum mixture of amines is crucial to ensure the benefits of the primary and secondary amine can be maximized to produce a solvent far superior in removing CO_2 from natural gas.

The mixtures of amine studied in this project are MEA-15wt% + DEA-5wt%, MEA-20wt% + DEA-10wt% and MEA-25wt% + DEA-10wt%. Figure 4.2.4 below shows the CO₂ vol% absorbed for mix MEA and DEA compared to single MEA-28wt% at same solvent speed of 5rpm. The area under the graph is hard to compare and the absorption capacity cannot be determined due to the experimental limitation. The result is discussed further to the CO₂ removal efficiency.

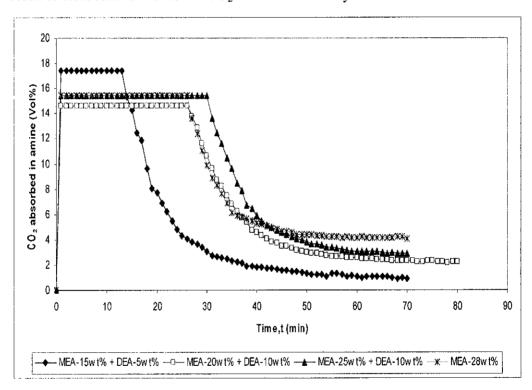


Figure 4.2.4: Graph of CO₂ vol% absorbed as a function of time for mix MEA and DEA and single MEA-28wt% at solvent speed of 5rpm

Table 4.2: Effect of amine solvent concentration to CO₂ removal efficiency (Solvent speed at 5 rpm for all except the first MEA-15wt%)

Mixture	CO ₂ removal efficiency (%)
MEA-15wt%	26.46
MEA-15wt%	34.92
MEA-20wt%	51.05
MEA-28wt%	64.14
MEA-15wt% + DEA-5wt%	37.82
MEA-20wt% + DEA-10wt%	62.76
MEA-25wt% + DEA-10wt%	67.49

From Table 4.2 above, the mixture of MEA and DEA gave higher CO₂ removal efficiency compared to single MEA at same concentration. This shows that adding DEA to MEA will result in increasing CO₂ removal efficiency. The maximum CO₂ removal efficiency for this experiment was obtained at 67.49% using MEA-25wt% + DEA-10wt% solvent concentration. This result is higher compared to the other mixture of MEA and DEA and also to single MEA-28%.

The performance of the solvents can be summarized as below. Solvent speed at 5 rpm for all except the final MEA-15wt% which is at 2rpm.

MEA-25wt% + DEA-10wt%

MEA-28wt%

MEA-20wt% + DEA-10wt%

MEA-20wt%

MEA-15wt% + DEA-5wt%

MEA -15wt%

MEA -15wt%

The advantage of use with MEA is that the active group in MEA reacts faster compared to other secondary amines and also the lower cost of solvent. However, the main issue with use of MEA is its highly corrosive nature, which can affect downstream equipment in a natural gas processing plant. Its other disadvantages are its low loadings and high regeneration cost. Therefore a blend of amine is a right choice as a solvent.

4.2.3 Effect of reaction temperature

Although the operating temperature was kept constant at 25°C, temperature variations in the conical flask were unavoidable. Figure 4.2.5 shows the temperature variations in the conical flask as a function of operating time. As can be seen, the temperature variation of MEA–28wt% gradually increases from 33.2°C to its maximum temperature of 56.1°C and decreases to 36.9°C after 70 minutes. The sharp increase in the temperature of the conical flask indicates that the amine and CO₂ reacts in an exothermal manner. After the sharp incline, the temperature remains to about constant with slight fluctuations that could be contributed by the ambient effect on the temperature of the conical flask. The room temperature is 24°C.

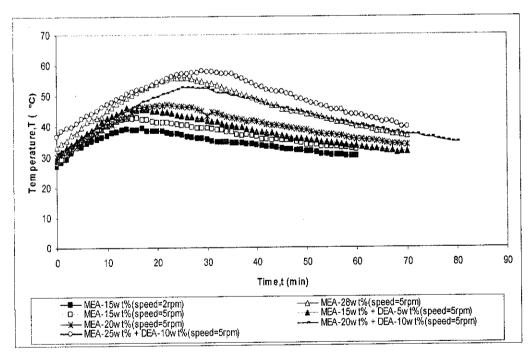


Figure 4.2.5: Graph of reaction temperature as a function of time

The maximum temperature for this experiment is obtained for mixture of MEA-25 wt% and DEA-10wt% which is 58.3 °C. For the other concentration the trend of the

graph is the same, the different is the temperature is lower then the MEA-28wt%. The effect of reaction temperature for the concentrations that has been studied is shown below:

MEA-25wt% + DEA-10wt%

MEA-28wt%

MEA-20wt% + DEA-10wt%

MEA-20wt%

MEA-15wt% + DEA-5wt%

MEA -15wt%

MEA -15wt%

Decreasing reaction temperature

The results show that the reaction temperature is higher for higher concentration of MEA and for higher solvent speed. The higher the temperature indicates that the heat released in the solution absorption process will require more heat during regeneration. As a result the energy requirement for the whole absorption and regeneration process should be higher for the MEA-25wt% + DEA-10wt% process as compared to the MEA-28wt%. From this point of view, MEA-25wt% + DEA-10wt% is not the economical mixture if compared to MEA-28wt%. MEA-20wt% and DEA-10wt% will be the right choice because the reaction temperature is lower where the maximum temperature is only 53°C compared to MEA-28wt% at 56.1°C which require lower energy for regeneration process.

4.2.4 Foaming tendency for the amine solvents

Foaming is a bad phenomenon to the absorption process unit. It might cause the equipment damage and loss of production time. From this foaming tendency test (Table 4.1.2), the foaming height and collapse time increase with the increasing speed of the solvent. MEA-15wt% at speed 5rpm has higher foaming height and collapse time which is compared to MEA-15wt% at speed 2rpm. However an increasing in concentration of MEA did not exactly increase the foam height or collapse time. MEA-28wt% has lower foaming height and collapse time compared to MEA-20wt% and MEA-15wt%. From these experimental results, it shows that foaming tendency did not depend on the concentration of the MEA. Since there is no

similar study on the foaming test for CO₂ absorption in alkanolamines, the result obtained is discussed from my point of view. From my expectation the higher the MEA concentration the higher the foaming height and the higher the collapse time. This is because the higher the concentration the higher the amount of degradation products or bicarbonate precipitates which the internal source of contaminant that causes foaming is. The higher the foaming will take longer time to collapse.

However these results may be having some error because the time the samples solution has been stored after the experiment is not the same. Some of the solution that has been stored for a long time before the foaming test take place at the end of this project may be has contain more internal sources of contaminants to cause foaming such as degradation products and bicarbonate precipitates. More contaminants will result in higher foaming height.

4.2.5 Optimum blend of amines

Throughout this study of amines, it has been found that MEA-20wt% + DEA-10wt% is the choice for optimum blend of amines. The reason is first it gave the higher CO_2 removal efficiency compared to MEA-20wt% alone. From Table 4.2 it can be clarified that MEA-20wt% only gave value of 51.05% for CO_2 removal efficiency compared to MEA-20wt% + DEA-10wt% which is 62.76%.

Although MEA-28wt% gave higher CO_2 removal efficiency compared to MEA-20wt% + DEA-10wt% which is 64.14% and possible lower price but this 28wt% solvent will gave higher rate of corrosion. It is because the observed corrosivity of alkanolamines to carbon steel is generally in the order:

Primary Amines > Secondary Amines > Tertiary Amines

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 the corrosion issues (GPSA, 1998). It may be pointed out that corrosion has been a serious issue in amine process. For a long term planning it shown that MEA-20wt% + DEA-10wt% gave better profit compared to MEA-28wt% from the view of maintenance of equipment and piping due to corrosion problem. The mixture of MEA-20wt% +

DEA-10wt% will give lower corrosion rate because the quantity of MEA (primary amine) is lower that MEA-28wt%. The addition of DEA (secondary amine) 10wt% will result in lower corrosion rate compared to 8wt% MEA because the corrosion rate for secondary amine is lower compared to primary amine. However this is only the approximation and the exact corrosion rate of these solvents should be studied further. Besides that the CO_2 removal efficiency different between MEA-28wt% and MEA-20wt% + DEA-10wt% is only 1.38% and it can be considered quite same.

Another comparison is on the reaction temperature. MEA-20wt% + DEA-10wt% gave lower maximum temperature which is only 53°C compared to MEA-28wt% at 56.1°C. The lower the reaction temperature the lower the energy required for regeneration process. From Figure 4.2.5 it can be seen that the reaction temperature for MEA-20wt% and DEA-10wt% is lower throughout the experiment compared to MEA-28wt%. From the research it has been found that secondary amines have advantage over primary amines – their heat of reaction with carbon dioxide is lower, 360 calorie/gm (650 BTU/lb) versus 455 calorie/gm (820 BTU/lb). This means that the secondary amines require less heat in the regeneration step than primary amines. From an energy consumption point of view, this is an important consideration when the primary objective is the isolation of CO₂ from flue gas. However the exact energy required for this mixture of amine should be further studied to justify the result.

Foaming tendency is also expected lower in mixture of MEA-20wt% + DEA-10wt% compared to MEA-28wt% because the lower concentration will give lower height of foaming and collapse time. From some research it has been found that MEA reacts irreversibly with minor impurities such as carbonyl sulfide (COS) and carbon disulfide (CS₂) resulting in solvent degradation. Foaming of the absorbing liquid MEA due to the build-up of impurities can also be concern. From this research it can be accepted that the lower the concentration of the MEA will be better to reduce the foaming tendency.

MEA-25wt% + DEA-10wt% is also not selected as the optimum mixture although it gave higher CO₂ removal efficiency compared to single MEA-20wt% + DEA-10wt% because the price, corrosion rate, energy required for regeneration and foaming tendency are higher as the concentration of MEA is higher.

Based on the corrosisivity, heat requirement in regeneration step and foaming tendency it can be conclude that mixture of MEA-20wt% + DEA-10wt% is the right choice for optimum mixture compared to the other solvents. The higher the price of it compared to MEA-28wt% will become more profitable in the long term planning.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Alkanolamines is widely used in gas treating process for acid removal in the natural gas and petroleum processing industries. Many researches have been done to find the ideal amines and to improve this alkanolamines process. The mixed amine systems can bring considerable improvement in gas absorption and great savings in regeneration energy requirement.

The study on absorption of CO₂ with amines has been performed with varying effect of solvent speed, amine concentration and mixtures of amines. From the experiment that has been conducted, the reaction between CO₂ and amines is determined to be an exothermic reaction. This is indicated by the increase of reaction temperature as a function of time.

The result from the experiment showed that the CO₂ removal efficiency is higher for higher solvent speed. Increase amine concentration of MEA from 15wt% to 28wt% will increase the CO₂ removal efficiency. However MEA-28wt% will give significant corrosion problem.

Mixture of MEA-25wt% and DEA-10wt% give higher CO₂ removal efficiency compared to single MEA-28wt%. However, this mixture is not an economical mixture if compared to MEA-28wt% because the energy required for regeneration is higher as the reaction temperature is higher. Besides that from my point of view, the corrosion may be significant problem by using this mixture as the MEA-25wt% is already the highest concentration in the range reported use in the plant due to the corrosion problem. By adding 10wt% DEA it will increase the corrosion rate.

The mixture of MEA-20wt% and DEA-10wt% give a trend of absorption nearly same as MEA-28wt%. This shown that this mixture can get the capacity of absorption as near as MEA-28wt%. From my expectation the corrosion for mixture

of MEA-20wt% and DEA-10wt% will be in the safe range of the plant. This mixture also requires lower energy for regeneration as compared to MEA-28wt% and also mixture of MEA-25wt% + DEA-10wt%. From this project MEA-20wt% + DEA-10wt% will be the right choice for the absorption with high CO₂ removal efficiency, no significant corrosion problem, and low regeneration energy.

Foaming is a bad phenomenon to the absorption process unit. It might cause the equipment damage and loss of production time. From this study it has been found that the foaming increase when the speed of the solvent increase. From my expectation the higher the MEA concentration the higher the foaming height and the higher the collapse time.

5.2 **RECOMMENDATIONS**

The recommendations to be made are based on several aspects to further improve the current research. This study of absorption is very interesting and it can be conduct further for the other types of amines such as AMP and MDEA because from the research, mix of primary and tertiary amine or sterically hindered amine can enhance the CO₂ absorption.

For preparation of aqueous alkanolamines, instead of using distilled water, double distilled water that degassed by boiling should be used. It will leads to more accurate result as the amount of air in the water is discharged and minimized. Besides, the preparation of aqueous alkanolamines should be done in Nitrogen Flushed Box to create CO₂ free environment. CO₂ in the environment effect the result as it is absorbed in the amine solvent during the solvent preparation.

The experimental setup should be improved by adding a flow meter to measure the flow rate of the gas entering the setup. By knowing the flow rate of the gas, the result can be further discuss in determining the exact amount of the CO₂ absorbed in the amine solvents.

It is also recommended to have the amines as early as possible so that the experiment can be started earlier. Because of late arrival of the amines, it causes time constraint to the experiment.

REFERENCES

- 1. Aina Suharny Abdul Rahman, 2005, Study on Carbon Dioxide (CO₂)

 Absorption into Several Types of Amines, Degree Dissertation, University

 Teknologi Petronas, Malaysia
- 2. Al-Juaied M.A., 2004, Carbon Dioxide Removal from Natural Gas by Membranes in the Presence of Heavy Hydrocarbons and by Aqueous Diglycolamine®/Morpholine, Degree Dissertation, University of Texas, Austin
- 3. Chakravarti S., Gupta A., Hunek B., 2001, Advanced Technology for the Capture of Carbon Dioxide from Flue Gases, Praxair, Inc., Tonawada, USA
- Geankoplis C.J., 2005, Transport Process and Separation Process Principles,
 New Jersey, Prentice Hall Professional Technical Reference
- 5. Hagewiesche D.P., Ashour S.S., Al-Ghawas H.A. and Sandall O.C., 1994, Absorption of Carbon Dioxide into Aqueous Blends of Monoethanolamine and N-Methyldiethanolamine, Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, U.S.A
- 6. Lian F.L., 2005, Study on CO₂ Absorption in Single MEA and Mixed MEA & DEA, Degree Dissertation, University Teknologi Petronas, Malaysia
- 7. Lunsford K.M. and Bullin J.A., Copyright 2001, Optimization of Amine Sweetening Units, Bryan Research & Engineering, Inc. Bryan, Texas
- 8. Lurgi Oel. Gas. Chemie Gmbh. Lurgiallee5. D-60295 Frankfurt am Main, 2005, Gas Sweetening with Alkanolamines, http://www.lurgi.com
- 9. Mandal B.P., Guha M., Biswas A.K. and Bandyepadhyay S.S., 2005, Removal of Carbon Dioxide by absorption in mix amines: modeling of absorption in aqueous MDEA/MEA and AMP/MEA solutions, Indian Institute of Technology, Kharagpur, India
- 10. Polasek J.C., Iglesias-silva G.A., Bullin J.A., 2001, *Using Mixed Amine Solutions for Gas Sweetening*, Bryan Research & Engineering, Inc., Texas.
- 11. Rameshni M., P.E, 2000, State-of-the-Art in Gas Treating, Parsons Energy & Chemicals Group, Inc.,125 West Huntington Drive, Arcadia, USA
- Wong S., Bioletti R., 2005, Carbon Dioxide Separation Technologies,
 Carbon & Energy Management, Alberta Research Council, Edmonton,
 Alberta, T6N 1E4, Canada

13. Yeh A.C., Bai H., 1999, Comparison of ammonia and momoethanolamine solvents to reduce CO2 greenhouse gas emissions, Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan

APPENDIX 1: Sample recalculation for senior's project.

Chemical Name	Chemical Formula	Molecular Weight,	Density, ρ (kg/m ³)
		MW (kg/kmol)	
MEA	HOCH ₂ CH ₂ NH ₂	61.08	1020
DEA	(HOCH ₂ CH ₂) ₂ NH	105.14	1090
Water	H ₂ O	18.016	1000

Table 1: Properties of amines.

DEA-25wt% + MEA-10.2wt%

 CO_2 flow rate = 1517.72 cm³/min

Solvent flow rate = $200.98 \text{ cm}^3/\text{min}$

Density $CO_2 = 1.83 \text{ kg/m}^3$

Molecular Weight CO₂ = 44.01 kg/kmol

$$\begin{aligned} \text{MW}_{\text{solvent}} &= 0.25 \text{ (MW}_{\text{DEA}}) + 0.102 \text{ (MW}_{\text{MEA}}) + 0.648 \text{ (MW}_{\text{H2O}}) \\ &= 0.25 \text{ (105.14)} + 0.102 \text{ (61.08)} + 0.648 \text{ (18.016)} \\ &= 44.19 \text{ kg/kmol} \end{aligned}$$

$$\begin{split} \rho_{\text{solvent}} &= 0.25 \; (\rho_{\text{DEA}}) + 0.102 \; (\rho_{\text{MEA}}) + 0.648 \; (\rho_{\text{H2O}}) \\ &= 0.25 \; (1090) + 0.102 \; (1020) + 0.648 \; (1000) \\ &= 1024.54 \; \text{kg/m}^3 \end{split}$$

Convert CO_2 flow rate from cm³/min to mol/min, (1517.72 cm³/min) x (1.83 kg/m³) x (1x10⁻⁶ m³/cm³) / (44.01 kmol/kg) x (1000 mol/kmol) = 0.0631 mol CO_2 /min

at t = 1 min, [(14.6-11.67)/14.6] x (0.0631 molCO₂/min) / (200.98 cm³ solvent/min) = 0.000063 molCO₂/mLsolvent Convert molCO₂/mLsolvent to mol CO₂/mol solvent, (mol CO₂/mL solvent) x (1/ $\rho_{solvent}$) x (1000000 mL/m³) x (MW_{solvent}) x (1 x 10⁻³ kmol/mol)

= $(0.000063 \text{ mol CO}_2/\text{mL solvent}) \times (1/1024.54 \text{ kg/m}^3 \text{ solvent}) \times (1000000 \text{ mL/m}^3) \times (1/1024.54 \text{ kg/m}^3 \text{ solvent}) \times (1/1024.54 \text{ kg/m$ $(44.19 \text{ kg/kmol solvent}) \times (1 \times 10^{-3} \text{ kmol/mol})$

= 0.0027 mol CO₂/mol solvent

APPENDIX 2: Data for recalculation of senior's project.

DEA-25wt% + MEA-10.2wt%

CO₂ mol CO2 / mol CO2 / t/min vol% mL solvent mol solvent 0.00000 0 14.600 0.000000 0.00272 1 11.670 0.000063 2 10.500 0.00380 0.000088 10.010 0.00426 3 0.000099 4 9.660 0.000106 0.00458 5 9.210 0.000116 0.00500 6 8.790 0.000125 0.00539 7 0.00572 8.430 0.000133 8 8.080 0.000140 0.00605 7.900 0.00621 9 0.000144 10 7.680 0.000149 0.00642 11 7.500 0.000153 0.00659 12 7.310 0.000157 0.00676 13 7.110 0.000161 0.00695 14 6.890 0.00715 0.000166 15 6.610 0.000172 0.00741 16 6.460 0.000175 0.00755 17 6.210 0.000180 0.00778 18 6.010 0.000185 0.00797 19 0.00815 5.810 0.000189 20 5.640 0.000193 0.00831 21 5.400 0.000198 0.00853 22 5.200 0.000202 0.00872 23 4.930 0.000208 0.00897 0.00924 24 4.640 0.000214 4.410 0.000219 0.00945 25 26 4.180 0.000224 0.00966 27 4.030 0.000227 0.00980 28 3.840 0.000231 0.00998 29 3.580 0.000237 0.01022 30 3.420 0.000240 0.01037 0.000245 0.01055 31 3.230 32 3.350 0.000242 0.01043 33 0.01039 3.400 0.000241 34 3.380 0.000241 0.01041 35 3.310 0.000243 0.01047 36 3.370 0.000241 0.01042 37 0.01043 3.350 0.000242

DEA-25wt% + MEA-6.4wt%

t/min	CO2 vol%	mol CO2 / mL solvent	mol CO2 / mol solvent
0	14.000	0.0000000	0.00000
1	12.740	0.0000238	0.00099
2	11.360	0.0000499	0.00207
3	11.080	0.0000552	0.00229
4	10.710	0.0000622	0.00259
5	10.640	0.0000635	0.00264
6	10.360	0.0000688	0.00286
7	10.180	0.0000722	0.00300
8	9.150	0.0000917	0.00381
9	9.000	0.0000945	0.00393
10	8.790	0.0000985	0.00409
11	8.680	0.0001006	0.00418
12	8.550	0.0001030	0.00428
13	8.430	0.0001053	0.00438
14	8.300	0.0001078	0.00448
15	8.210	0.0001095	0.00455
16	8.130	0.0001110	0.00461
17	8.060	0.0001123	0.00467
18	8.250	0.0001087	0.00452
19	8.300	0.0001078	0.00448
20	8.270	0.0001083	0.00450
21	8.350	0.0001068	0.00444

MEA-30%

mol CO2 / CO₂ mol CO2 / t/min vol% mol solvent mL solvent 0 17.00 0.0000000 0.00000 11.20 0.0000895 0.00275 1 2 6.80 0.0001573 0.00484 3 5.40 0.0001789 0.00550 4 5.30 0.0001805 0.00555 5 4.90 0.0001866 0.00574 4.93 0.00572 6 0.0001862 7 0.00573 4.92 0.0001863 8 4.68 0.0001900 0.00584 9 4.62 0.0001910 0.00587 10 4.57 0.0001917 0.00590 4.43 0.00596 11 0.0001939 12 4.28 0.0001962 0.00603 13 4.17 0.0001979 0.00609 14 4.20 0.0001974 0.00607 0.00602 15 4.30 0.0001959 16 4.25 0.0001967 0.00605 17 4.19 0.0001976 0.00608 18 4.12 0.0001987 0.00611 19 4.05 0.0001997 0.00614 20 3.96 0.0002011 0.00618 21 3.81 0.0002034 0.00626 22 0.00628 3.75 0.0002044 23 3.66 0.0002058 0.00633 24 3.64 0.0002061 0.00634 25 0.00635 3.62 0.0002064 26 3.57 0.0002071 0.00637 0.00637 27 3.56 0.0002073 28 3.62 0.0002064 0.00635 0.00635 29 3.61 0.0002065 30 3.66 0.0002058 0.00633

MEA-25%

	CO2	mol CO2 /	mol CO2 /
t/min	vol%	mL solvent	mol solvent
0	14.670	0.0000000	0.00000
11	10.450	0.0000639	0.00183
2	9.830	0.0000733	0.00210
3	8.320	0.0000961	0.00275
4	7.110	0.0001144	0.00328
5	6.420	0.0001249	0.00358
6	6.310	0.0001265	0.00362
7	5.930	0.0001323	0.00379
8	5.310	0.0001417	0.00406
9	5.110	0.0001447	0.00414
10	5.010	0.0001462	0.00419
11	4.890	0.0001480	0.00424
12	4.520	0.0001536	0.00440
13	4.320	0.0001566	0.00449
14	4.270	0.0001574	0.00451
15	4.110	0.0001598	0.00458
16	4.030	0.0001610	0.00461
17	3.890	0.0001632	0.00467
18	3.520	0.0001688	0.00483
19	3.320	0.0001718	0.00492
20	3.170	0.0001741	0.00498
21	3.180	0.0001739	0.00498
22	3.190	0.0001738	0.00498
23	3.200	0.0001736	0.00497
24	3.210	0.0001734	0.00497
25	3.210	0.0001734	0.00497

MEA-20%

	· · · · ·	1	1
	CO2	mol CO2 /	mol CO2 /
t/min	vol%	mL solvent	mol solvent
0	16.73	0.000000	0.00000
1	14.73	0.000025	0.00066
2	12.89	0.000048	0.00127
3	12.52	0.000053	0.00139
4	12.04	0.000059	0.00155
5	11.93	0.000060	0.00159
6	11.42	0.000066	0.00176
7	10.98	0.000072	0.00190
8	10.32	0.000080	0.00212
9	9.45	0.000091	0.00241
10	9.11	0.000095	0.00252
11	9.04	0.000096	0.00255
12	8.91	0.000098	0.00259
13	8.45	0.000103	0.00274
14	8.04	0.000108	0.00288
15	7.91	0.000110	0.00292
16	7.53	0.000115	0.00305
17	7.12	0.000120	0.00318
18	7.04	0.000121	0.00321
19	6.94	0.000122	0.00324
20	6.80	0.000124	0.00329
21	6.72	0.000125	0.00331
22	6.59	0.000127	0.00336
23	6.05	0.000133	0.00353
24	5.72	0.000137	0.00364
25	5.83	0.000136	0.00361
26	5.69	0.000138	0.00365
27	5.64	0.000138	0.00367
28	5.62	0.000139	0.00368
29	5.62	0.000139	0.00368
30	5.63	0.000139	0.00367

DEA 26.69wt% at 200ml/min

DEA 26.69wt% at 280ml/min

DEA 29.6wt% at 200ml/min

t/min mol CO2 / mol solvent 0 0 1 0.000799849 2 0.00224402 3 0.00268838 4 0.003077195 5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.00654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889		
0 0 1 0.000799849 2 0.00224402 3 0.00268838 4 0.003077195 5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.006298807 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426		
1 0.000799849 2 0.00224402 3 0.00268838 4 0.003077195 5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.00654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.0107587 27 0.010153633 28 0.009975889 29 0.0097426	t/min	
2 0.00224402 3 0.00268838 4 0.003077195 5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.00654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426		· · · · · · · · · · · · · · · · · · ·
3 0.00268838 4 0.003077195 5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.006298807 11 0.00654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426		
4 0.003077195 5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426		0.00224402
5 0.003643755 6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.00976059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	3	0.00268838
6 0.004343622 7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	4	0.003077195
7 0.004576911 8 0.005021272 9 0.005909992 10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.0097426	5	0.003643755
8 0.005021272 9 0.005909992 10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	6	0.004343622
9 0.005909992 10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.0097426	7	0.004576911
10 0.006298807 11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.00976059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	8	0.005021272
11 0.006654296 12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	9	0.005909992
12 0.007565234 13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.0097426	10	0.006298807
13 0.007654106 14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	11	0.006654296
14 0.007854069 15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.00976059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	12	0.007565234
15 0.007965159 16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	13	0.007654106
16 0.008198448 17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	14	0.007854069
17 0.008298429 18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	15	0.007965159
18 0.008520609 19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	16	0.008198448
19 0.008787225 20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	17	0.008298429
20 0.009076059 21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	18	0.008520609
21 0.00929824 22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	19	0.008787225
22 0.009531529 23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	20	0.009076059
23 0.009675946 24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	21	0.00929824
24 0.009864799 25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	22	0.009531529
25 0.010020325 26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	23	0.009675946
26 0.01007587 27 0.010153633 28 0.009975889 29 0.0097426	24	0.009864799
27 0.010153633 28 0.009975889 29 0.0097426	25	0.010020325
28 0.009975889 29 0.0097426	26	0.01007587
29 0.0097426	27	0.010153633
29 0.0097426	28	0.009975889
		0.0097426
	30	

t/min	mol CO2 /
	mol solvent
0	0
1	0.002234891
2	0.003033067
3	0.004789053
4	0.006026225
5	0.006624856
6	0.00714367
7	0.008013681
8	0.008181298
9	0.008340933
10	0.008540477
11	0.008580386
12	0.008819839
13	0.009139109
14	0.009458379
15	0.009618014
16	0.00987343
17	0.010080956
18	0.010216646
19	0.010264536
20	0.010320409
21	0.010272518
22	0.010216646
23	0.010256554

mol CO2 /
mol solvent
0
0.00263555
0.0036678
0.00509539
0.00810431
0.0083459
0.00854357
0.00858749
0.00880712
0.00944405
0.00981741
0.01071789
0.01098145
0.01157445
0.01247493
0.01273848
0.01357307
0.01434177
0.0143857
0.01442962
0.01440766
0.0143857
0.01440766
0.01427588

DEA 29.6wt% at 280ml/min

22.76wt% DEA + 21.83wt% DEA + 6.39wt% MEA at 200ml/min 10.23wt% MEA at 280ml/min

	mol CO2 /
t/min	mol solvent
0	0
1	0.00367194
2	0.00425039
3	0.00412464
4	0.00596061
5	0.00746963
6	0.00890319
7	0.01008525
8	0.01129246
9	0.01149367
10	0.01174517
11	0.01224817
12	0.01254998
13	0.01287693
14	0.01320388
15	0.01348054
16	0.01388294
17	0.01408414
18	0.01405899
19	0.01408414
20	0.01403384

	mol CO2 /
t/min	mol solvent
0	0
1	0.001673169
2	0.003505688
3	0.003877504
4	0.004368831
5	0.004461785
6	0.0048336
7	0.005072625
8	0.006440374
9	0.006639561
10	0.006918423
11	0.007064493
12	0.007237121
13	0.007396471
14	0.0075691
15	0.007688612
16	0.00755582
17	0.007887798
18	0.007635495
19	0.0075691
20	0.007608937
21	0.007502704

A/matin	mol CO2 /
t/min	mol solvent
0	0
1	0.00297438
2	0.0041621
3	0.00465952
4	0.00501482
5	0.00547164
6	0.005898
7	0.00626345
8	0.00661875
9	0.00680148
10	0.00702481
11	0.00720754
12	0.00740041
13	0.00760344
14	0.00782677
15	0.00811101
16	0.00826329
17	0.00851707
18	0.0087201
19	0.00892313
20	0.00909571
21	0.00933934
22	0.00954237
23	0.00981646
24	0.01011085
25	0.01034434
26	0.01057782
27	0.01073009
28	0.01092297
29	0.01118691
30	0.01134933
31	0.01154221
32	0.01142039
33	0.01136963
34	0.01138994
35	0.011461
36	0.01140009
37	0.01142039
	0.01112000

APPENDIX 3: Sample calculation for this project

Sample calculation for MEA

$$V_{\text{solvent}} = 200 \text{ mL} = 0.2 \text{ L} = 0.0002 \text{ m}^3$$

$$\rho_{H2O} = 1000 \text{ kg/m}^3$$

$$\rho_{MEA} = 1020 \text{ kg/m}^3$$

$$x\% = (V_{MEA} \times \rho_{MEA}) / [(V_{MEA} \times \rho_{MEA}) + (V_{H2O} \times \rho_{H2O})]$$

$$x\% = (V_{MEA} \times 1020) / [(V_{MEA} \times 1020) + [(0.0002 - V_{MEA}) + 1000]]$$

$$x\% = (1020V_{MEA}) / [(1020V_{MEA}) + (0.2 - 1000V_{MEA})]$$

$$x\% = (1020V_{MEA}) / (20V_{MEA} + 0.2)$$

$$x\% (20V_{MEA} + 0.2) = 1020V_{MEA}$$

15wt% MEA

$$0.15 (20V_{MEA} + 0.2) = 1020V_{MEA}$$

$$3 V_{MEA} + 0.03 = 1020 V_{MEA}$$

$$0.03 = 1017V_{MEA}$$

$$V_{MEA} = 2.95 \times 10^{-5} \text{ m}^3$$

$$V_{MEA} = 2.95 \times 10^{-2} L$$

$$V_{MEA} = 29.5 \text{ mL}$$

$$V_{H2O} = 200 - 29.5 = 170.5 \text{ mL}$$

Sample calculation for mixture of MEA and DEA

MEA-15wt% and DEA-5wt%

 $V_{MEA} = 29.63 \text{ mL}$

$$\begin{split} &V_{\text{Solvent}} = 200 \text{ mL} = 0.2 \text{ L} = 0.0002 \text{ m}^3 \\ &V_{\text{DEA}} = 10 \text{ mL} = 0.01 \text{ L} = 0.00001 \text{ m}^3 \\ &\rho_{\text{H2O}} = 1000 \text{ kg/m}^3 \\ &\rho_{\text{MEA}} = 1020 \text{ kg/m}^3 \\ &\rho_{\text{DEA}} = 1090 \text{ kg/m}^3 \\ &x\% = \left(V_{\text{MEA}} \times \rho_{\text{MEA}}\right) / \left[\left(V_{\text{MEA}} \times \rho_{\text{MEA}}\right) + \left(V_{\text{DEA}} \times \rho_{\text{DEA}}\right) + \left(V_{\text{H2O}} \times \rho_{\text{H2O}}\right) \right] \\ &x\% = \left(V_{\text{MEA}} \times 1020\right) / \left[\left(V_{\text{MEA}} \times 1020\right) + \left(V_{\text{DEA}} \times 1090\right) + \left[\left(0.0002 - V_{\text{DEA}} - V_{\text{MEA}}\right) + 1000\right] \right] \\ &15\% = \left(1020 \text{ V}_{\text{MEA}}\right) / \left[\left(1020 \text{V}_{\text{MEA}} + \left(0.00001 \times 1090\right) + \left[\left(0.0002 - 0.00001 - V_{\text{MEA}}\right) + 1000\right] \right] \\ &0.15 = \left(1020 \text{ V}_{\text{MEA}}\right) / \left(1020 \text{V}_{\text{MEA}} + 0.0109 + 0.19 - 1000 \text{V}_{\text{MEA}}\right) \\ &0.15 = \left(1020 \text{ V}_{\text{MEA}}\right) / \left(20 \text{V}_{\text{MEA}} + 0.2009 - 1000 \text{V}_{\text{MEA}}\right) \\ &0.15 \left(20 \text{V}_{\text{MEA}} + 0.2009\right) = 1020 \text{V}_{\text{MEA}} \\ &3 \text{V}_{\text{MEA}} + 0.030135 = 1020 \text{V}_{\text{MEA}} \\ &0.030135 = 1017 \text{V}_{\text{MEA}} \\ &V_{\text{MEA}} = 2.963 \times 10^{-5} \text{ m}^3 \\ &V_{\text{MEA}} = 2.963 \times 10^{-2} \text{ L} \end{aligned}$$

APPENDIX 4: Experimental data

CO₂ absorption in MEA-15wt% Operating Temperature = 25 °C (Speed=2rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	17.41	27	0
1	0	28.3	17.41
2	0	29.4	17.41
3	0	31.4	17.41
4	0.7	33.2	16.71
5	1.67	33.4	15.74
6	2.88	34.4	14.53
7	3.11	35.2	14.3
8	4.47	35.7	12.94
9	5.82	36.4	11.59
10	6.74	37.1	10.67
11	7.87	38.1	9.54
12	8.91	38.3	8.5
13	9.9	38.9	7.51
14	10.9	39.1	6.51
15	11.82	38.9	5.59
16	12.35	38.8	5.06
17	12.97	39.4	4.44
18	13.4	38.7	4.01
19	13.87	38.6	3.54
20	13.96	38.6	3.45
21	14.27	38.5	3,14
22	14.57	38.1	2.84
23	14.6	37.8	2.81
24	14.87	37.6	2.54
25	14.88	37.4	2.53
26	15	36.7	2.41
27	15.11	36.4	2.3
28	15.3	36.1	2.11
29	15.38	36	2.03
30	15.39	35.8	2.02
31	15.45	35.3	1.96
32	15.5	34.9	1.91
33	15.5	34.9	1.91
34	15.53	34.8	1.88
35	15.7	34.6	1.71
36	15.7	34.5	1.71
37	15.74	34.4	1.67
38	15.82	34.1	1.59
39	15.77	34.1	1.64
40	15.82	33.8	1.59
41	15.81	33.5	1.6
42	15.78	33.4	1.63
43	15.84	33.2	1.57
44	15.8	32.9	1.61

44	15.8	32.9	1.61
45	15.83	32.6	1.58
46	15.82	32.4	1.59
47	15.97	32.3	1.44
48	15.89	32.1	1.52
49	15.9	31.9	1.51
50	15.82	31.8	1.59
51	15.88	31.6	1.53
52	15.86	31.5	1.55
53	15.86	30.8	1.55
54	15.75	30.8	1.66
55	15.79	30.6	1.62
56	15.82	30.4	1.59
57	15.72	30.4	1.69
58	15.73	30.3	1.68
59	15.69	30.3	1.72
60	15.79	30.1	1.62

CO₂ absorption in MEA-15wt%
Operating Temperature = 25 °C (Speed=5rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	15.5	27.9	0
1	0	29.3	15.5
2	0	30.8	15.5
3	0	32.5	15.5
4	0	33.1	15.5
5	0	35.1	15.5
6	0	36	15.5
7	0	37.3	15.5
8	0	37.8	15.5
9	0	38.8	15.5
10	0	40.1	15.5
11	0	41	15.5
12	0	41.6	15.5
13	1.48	42.4	14.02
14	3.52	42.5	11.98
15	5.04	42.6	10.46
16	6.31	42.8	9.19
17	7.56	42.3	7.94
18	8.22	42.2	7.28
19	8.94	41.6	6.56
20	9.56	41.5	5.94
21	10.17	41.4	5.33
22	10.38	41.3	5.12
23	10.86	41.1	4.64
24	11.16	40.8	4.34
25	11.36	40.6	4.14
26	11.79	40.4	3.71
27	11.92	39.9	3.58
28	12.13	39.6	3.37
29	12.32	39.6	3.18
30	12.46	39.4	3.04
31	13.64	39.1	1.86
32	13.5	38.8	2
33	13.42	38.8	2.08
34	13.18	38.3	2.32
35	13.12	38.3	2.38
36	14.18	37.4	1.32
37	14.15	37.1	1.35
38	13.88	37.1	1.62
39	13.65	36.9	1.85
40	14.61	36.8	0.89
41	14.66	35.9	0.84
41	14.7	35.9	0.8
	 	35.7	0.76
43	14.74	+	0.76
44	14.97	35.7	
45	14.77	35.4	0.73
46	14.48	35.4	1.02
47	14.87	35.4	0.63

48	14.62	34.8	0.88
49	14.86	34.4	0.64
50	14.84	33.8	0.66
51	14.78	33.8	0.72
52	14.98	33.8	0.52
53	15.01	33.4	0.49
54	15.13	33.3	0.37
55	15.04	33.4	0.46
56	14.98	33.3	0.52
57	15	32.9	0.5
58	15.04	32.9	0.46
59	14.88	32.7	0.62
60	14.94	32.4	0.56

CO₂ absorption in MEA-20wt% Operating Temperature = 25 °C (Speed=5rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	14.25	30.2	0
1	0	30.7	14.25
2	0	31.4	14.25
3	0	32.8	14.25
4	0	33.5	14.25
5	0	34.9	14.25
6	0	35.7	14.25
7	0	36.8	14.25
8	0	37.9	14.25
9	0	39.3	14.25
10	0	40.3	14.25
11	0	40.9	14.25
12	0	42.1	14.25
13	0	43	14.25
14	0	43.4	14.25
15	0	44.6	14.25
16	0	45.9	14.25
17	0	46.3	14.25
18	0	46.6	14.25
19	0	46.8	14.25
20	0.51	46.9	13.74
21	2.16	47	12.09
22	3.91	47.2	10.34
23	4.93	47	9.32
24	5.89	46.8	8.36
25	6.54	46.6	7.71
26	7.01	46.4	7.24
27	7.81	46.3	6.44
28	8.41	45.7	5.84
29	8.89	45	5.36
30	9.27	43.7	4.98
31	9.61	44.8	4.64
32	9.77	44.4	4.48
33	10.1	43.8	4.15
34	10.25	43.3	4
35	10.51	42.9	3.74
36	10.68	42.6	3.57
37	10.86	42.3	3.39
38	11.04	41.6	3.21
39	11.15	42.1	3.1
40	11.27	41.6	2.98
41	11.4	41.3	2.85
42	11.48	40.7	2.77
43	11.59	40.4	2.66
44	11.64	40.3	2.61
45	11.73	40.1	2.52
46	11.82	39.7	2.43
47	11.89	39.4	2.36

48	11.91	39.1	2.34
49	12.2	39	2.05
50	12	38.9	2.25
51	12.14	38.3	2.11
52	12.22	37.8	2.03
53	12.25	37.5	2
54	12.31	37.3	1.94
55	12.27	37.2	1.98
56	12.31	36.9	1.94
57	12.36	36.9	1.89
58	12.32	36.4	1.93
59	12.39	36	1.86
60	12.42	35.8	1.83
61	12.44	35.8	1.81
62	12.41	35.4	1.84
63	12.48	35.4	1.77
64	12.5	35.1	1.75
65	12.53	34.9	1.72
66	12.51	34.4	1.74
67	12.53	34.3	1.72
68	12.52	34.3	1.73
69	12.54	33.9	1.71
70	12.6	33.8	1.65

CO₂ absorption in MEA-28wt%
Operating Temperature = 25 °C (Speed=5rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	15.42	33.2	0
1	0	34.4	15.42
2	0	35.4	15.42
3	0	37.4	15.42
4	0	38.1	15.42
5	0	39.8	15.42
6	0	41.6	15.42
7	0	42.2	15.42
8	0	42.8	15.42
9	0	43.2	15.42
10	0	45.5	15.42
11	0	46.5	15.42
12	0	47.5	15.42
13	0	48.6	15.42
14	0	49.6	15.42
15	0	50.3	15.42
16	0	51.4	15.42
17	0	52.4	15.42
18	0	52.9	15.42
19	0	53.8	15.42
20	0	54.2	15.42
21	0	55	15.42
22	0	55.3	15.42
23	0	56.1	15.42
24	0	56.1	15.42
25	0	56	15.42
26	0	56	15.42
27	1.77	55.8	13.65
28	3.04	55.2	12.38
29	4.4	54.8	11.02
30	5.51	54	9.91
31	6.5	54	8.92
32	7.15	53.4	8.27
33	7.76	52.8	7.66
34	8.52	52.4	6.9
35	9.3	51.5	6.12
36	9.54	51.3	5.88
37	9.63	50.5	5.79
38	9.78	50	5.64
39	9.96	49.4	5.46
40	10.13	48.9	5.29
41	10.23	48.3	5.19
42	10.38	47.9	5.04
43	10.52	47.1	4.9
44	10.62	46.9	4.8
45	10.74	45.8	4.68
46	10.79	45.6	4.63
47	10.83	45.1	4.59

48	10.99	45	4.43
49	11	44.9	4.42
50	11.01	44.3	4.41
51	11.06	44.1	4.36
52	11.1	43.6	4.32
53	11.13	43.3	4.29
54	11.16	42.7	4.26
55	11.2	42.4	4.22
56	11.17	41.8	4.25
57	11.26	41.6	4.16
58	11.17	41.5	4.25
59	11.26	40.9	4.16
60	11.27	40.2	4.15
61	11.21	40	4.21
62	11.25	39.9	4.17
63	11.27	39.1	4.15
64	11.25	38.7	4.17
65	11.3	38.6	4.12
66	11.23	38.4	4.19
.67	11.24	37.8	4.18
68	11.21	37.5	4.21
69	11.22	37.3	4.2
70	11.37	36.9	4.05

CO₂ absorption in MEA-15wt% + DEA 5% Operating Temperature = 25 °C (Speed=5rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	17.44	28.8	0
1	0	31.8	17.44
2	0	33.3	17.44
3	0	34.3	17.44
4	0	35.4	17.44
5	0	36.8	17.44
6	0	37.9	17.44
7	0	38.8	17.44
8	0	40.4	17.44
9	0	41.8	17.44
10	0	42.8	17.44
11	0	43.6	17.44
12	0	44.3	17.44
13	0	45.2	17.44
14	2.1	46.2	15.34
15	3.2	45.8	14.24
16	5	45.5	12.44
17	5.6	45.8	11.84
18	7.81	45.7	9.63
19	9.4	45.2	8.04
20	9.71	45.1	7.73
21	10.55	44.8	6.89
22	11.24	44.8	6.2
23	12	44.5	5.44
24	12.63	43.8	4.81
25	13.12	43.5	4.32
26	13.39	43.4	4.05
27	13.6	43.1	3.84
28	13.8	42.7	3.64
29	14.03	42.6	3.41
30	14.34	41.9	3.1
31	14.7	41.8	2.74
32	14.81	41.6	2.63
33	14.87	41	2.57
34	14.95	40.6	2.49
35	15.14	40.3	2.3
36	15.2	39.9	2.24
37	15.25	39.8	2.19
38	15.5	39.3	1.94
39	15.53	38.8	1.91
40	15.6	38.4	1.84
41	15.61	38.4	1.83
42	15.67	38.1	1.77
43	15.69	37.9	1.75
44	15.81	37.4	1.63
45	15.84	36.9	1.6
46	15.9	36.8	1.54
47	15.91	36.2	1.53
			1,75

48	15.93	36.2	1.51
49	16.07	36	1.37
50	16.1	35.9	1.34
51	16.16	35.4	1.28
52	16.18	35.4	1.26
53	16.23	34.9	1.21
54	16.33	34.8	1.11
55	16.14	34.4	1.3
56	16.13	34.4	1.31
57	16.16	34.2	1.28
58	16.33	33.9	1.11
59	16.3	33.6	1.14
60	16.4	33.5	1.04
61	16.48	33.3	0.96
62	16.39	32.9	1.05
63	16.35	32.8	1.09
64	16.35	32.6	1.09
65	16.36	32.4	1.08
66	16.35	32.1	1.09
67	16.44	31.9	1
68	16.56	31.5	0.88
69	16.44	31.8	1
70	16.5	31.6	0.94

CO₂ absorption in MEA-20wt%+DEA-10% Operating Temperature = 25 °C (Speed=5rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	14.57	31.2	0
1	0	32.1	14.57
2	0	32.9	14.57
3	0	33.8	14.57
4	0	35.3	14.57
5	0	36.3	14.57
6	0	37.5	14.57
7	0	38.8	14.57
8	0	39.5	14.57
9	0	40.6	14.57
10	0	41.9	14.57
11	0	42.6	14.57
12	0	43.8	14.57
13	0	44.6	14.57
14	0	45.1	14.57
15	0	46.2	14.57
16	0	47.1	14.57
17	. 0	48.2	14.57
18	0	48.6	14.57
19	0	49.4	14.57
20	0	49.9	14.57
21	0	50.6	14.57
22	0	51.1	14.57
23	0	51.8	14.57
24	0	52.3	14.57
25	0	53	14.57
26	0	52.9	14.57
27	0.79	52.8	13.78
28	1.68	52.5	12.89
29	2.94	52.6	11.63
30	3.93	52.6	10.64
31	4.94	52.1	9.63
32	5.83	51.1	8.74
33	6.39	51	8.18
34	7.08	50.9	7.49
35	7.76	50.1	6.81
36	8.36	50	6.21
37	8.81	49.4	5.76
38	9.21	49.2	5.36
39	9.82	49.2	4.75
40	9.98	48.4	4.59
41	10.29	47.9	4.28
42	10.51	47.4	4.06
43	10.75	46.7	3.82
44	10,84	46.6	3.73
45	11.06	46.1	3.51
46	11.12	45.9	3.45
47	11.29	45.2	3.28

48	11.4	45.1	3.17
49	11.47	44.9	3.1
50	11.59	4 4.5	2.98
51	11.66	43.9	2.91
52	11.68	43.2	2.89
53	11.71	43	2.86
54	11.81	42.4	2.76
55	11.89	42.3	2.68
56	11.9	41.8	2.67
57	11,94	41.6	2.63
58	11.97	41.3	2.6
59	12	40.9	2.57
60	11.97	40.5	2.6
61	12.06	40.4	2.51
62	12.11	39.9	2.46
63	12.11	39.8	2.46
64	12.19	39.3	2.38
65	12.18	39.3	2.39
66	12.16	38.5	2.41
67	12.21	38.1	2.36
68	12.27	38.2	2.3
69	12,25	37.7	2.32
70	12.28	37.2	2.29
71	12.28	37.2	2.29
72	12.29	37.2	2.28
73	12.29	36.6	2.28
74	12.25	36.3	2.32
75	12.28	36.3	2.29
76	12.31	35.9	2.26
77	12.34	35.6	2,23
78	12,39	35.3	2.18
79	12.3	34.9	2.27
80	12.33	34.8	2.24

CO₂ absorption in MEA-25wt%+DEA-10% Operating Temperature = 25 °C (Speed=5rpm)

Time,t (min)	CO ₂ Vol% out	Temp, T (°C)	CO ₂ Vol% absorbed
0	15.4	36.6	0
1	0	38.6	15.4
2	0	39.6	15.4
3	0	39.9	15.4
4	0	41.1	15.4
5	0	42.5	15.4
6	0	43.5	15.4
7	0	44.1	15.4
8	0	45.2	15.4
9	0	46.3	15.4
10	0	47.4	15.4
11	0	47.8	15.4
12	0	48.9	15.4
13	0	49.6	15.4
14	0	50.8	15.4
15	0	51.2	15.4
16	0	52.1	15.4
17	0	52.4	15.4
18	0	52.8	15.4
19	0	53.5	15.4
20	0	54.4	15.4
21	0	54.9	15.4
22	0	55.8	15.4
	0		15.4
23		56.2 56.9	15.4
24	0	57.3	15.4
25	0	57.4	15.4
26	0		15.4
27	0	57.5	15.4
28	0	57.7	15.4
29	0	58.3	15.4
30	0	57.8	
31	1.79	57.8	13.61
32	2.98	57.6	12.42
33	3.79	57.4	11.61
34	4.91	57.4	10.49
35	5.74	57.2	9.66
36	6.93	56.3	8.47
37	7:55	55.6	7.85
38	8.64	54.7	6.76
39	8.94	54.1	6.46
40	9.47	53.1	5.93
41	9.96	53	5.44
42	10.24	52	5.16
43	10.41	51.8	4.99
44	10.67	51.3	4.73
45	10.81	51.3	4.59
46	11.02	50.6	4.38
47	11.19	50.3	4.21

48	11.32	49.1	4.08
49	11.41	48.7	3.99
50	11.59	48.3	3.81
51	11.76	47.6	3.64
52	11.74	47.3	3.66
53	11.85	46.8	3.55
54	12.02	46.5	3.38
55	12.03	45.5	3.37
56	12.12	45.3	3.28
57	12.2	45.3	3.2
58	12.27	44.3	3.13
59	12.3	43.8	3.1
60	12.36	43.8	3.04
61	12.34	43.6	3.06
62	12.34	42.8	3.06
63	12.31	42.6	3.09
64	12.36	42.3	3.04
65	12.42	41.3	2.98
66	12.46	41.8	2.94
67	12.45	41.3	2.95
68	12.47	40.8	2.93
69	12.46	39.9	2.94
70	12.53	39.8	2.87