VLE data of CO2 and Monoethanolamine (MEA)

by

Syafiqa binti Mohd Saleh

Dissertation submitted in partial fulfillment of
the requirements for the
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niversiti Teknologi PETRONAS
andar Seri Iskandar
1750 Tronah
erak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Assoc. Prof. Ir Abdul Aziz bin Omar)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SYAFIQA BINTI MOHD SALEH

ABSTRACT

A major application of technology is the removal of CO_2 from natural gas or synthesis gas by absorption in solutions of amines. The accurate knowledge of VLE for each of pure components and multicomponent mixtures is required for the design purpose of separation process. Since modeling VLE data is mostly only justified for ideal case, experimental method will be used to obtain VLE data for this study.

Monoethanolamine (MEA) is chosen as the amine for this study due to its many advantages: higher capacity, lower heat or reaction and low corrosion problems. The physical properties and hazards of the chemicals involved are taken into consideration.

The process flow on how the experiments will be done has been identified, along with the problems and constraints expected. Simulation on HYSYS was carried out to provide a general idea of the experiment. For the initial test run done, more research and discussions need to be done to overcome the problems faced.

ACKNOWLEDGEMENT

First and foremost, praise to God the Almighty for His guidance. Though difficulties occurred, through His guidance, this challenging project and report have been completed.

This project would not have been possible without the assistance and guidance of the numerous individuals whose contributions have helped in its completion.

Deepest appreciation goes to the project supervisor, Assoc. Prof. Ir Abdul Aziz Omar, who has given guidance and moral support throughout the project. His inputs and advice have helped in carrying out the tasks, and his method of teaching has helped to inculcate the spirit of independency and hard work.

A special thanks to the laboratory technicians of the Chemical Department, especially Mr Firdaus, for all their assistance and help throughout the project. Also, thank you to all the lecturers who had given feedbacks throughout the Final Year Project through seminars and presentations. Their comments were very much welcomed.

On the whole, all the help and feedbacks that had been given are truly appreciated. Thank you to everyone that has contributed to the task directly or indirectly. Completing this project has been a very valuable experience.

Thank you.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Gases containing H_2S or both H_2S and CO_2 are commonly referred to as sour gases or acid gases in the hydrocarbon processing industries. Removal of these acidic gases is an important industrial operation. Its presence in natural gas will reduce the heating value of the gas. Furthermore, as an acidic component, it has the potential to cause corrosion in pipes and process equipments (Ma'mun, et al., 2006). FIGURE 1 below shows a typical natural gas processing unit, where acid gas removal is one of the most important part of gas processing.

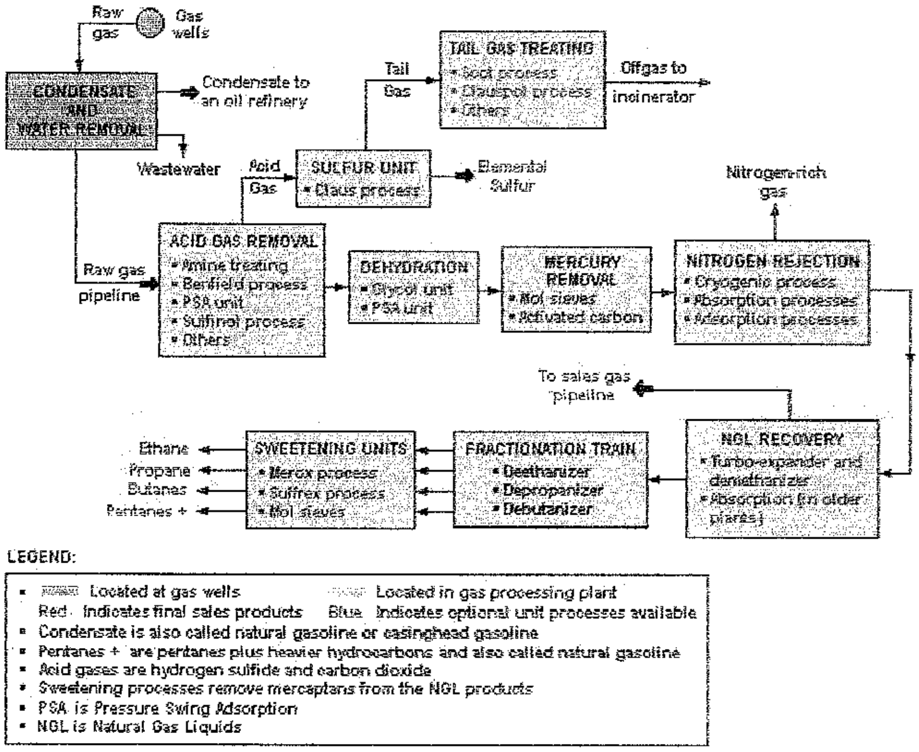

FIGURE 1: Natural gas processing unit

The usage of amine solutions to remove the acid gas is also known as Girdler process, and is used in 95 percent of U.S. gas sweetening operations. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status.

The removal of carbon dioxide (CO_2) is also important to both ammonia and ethylene glycol production. In ammonia production, the first purification step is carbon dioxide removal, which is accomplished through one of a variety of processes that are available, such as Benfield and activated MDEA. Typically, these processes reduce the carbon dioxide content from about 20 percent to less than 0.1 percent (Nexant Inc., 2007). The presence of carbon dioxide (CO_2) can cause catalyst poisoning in ammonia synthesis (Ma'mun, et al., 2006).

In recent years, interest in the development of new materials and technologies for the 'capture' of carbon dioxide (CO_2) has increased significantly. This development appears to be driven largely by increasing concerns about the impact of rising CO_2 emissions on climate change (specifically global warming).

A research body, known as CAPRICE was set up to encourage international cooperation and exchange in the area of CO_2-capture using amine processes. They aim to implement post-combustion capture using amine processes since it is generally considered to be the leading capture technology. Their long-term aim is to contribute to the implementation of these technologies on a large scale.

In addition, the CO_2 Capture Project (CCP), which is a partnership of eight of the world's leading energy companies and three government organizations, are also undertaking research and developing technologies for CO_2 capture.

1.2 PROBLEM STATEMENT

i. Problem Identification

The accurate knowledge of VLE for each of pure components and multicomponent mixtures is required for the design purpose of separation process. Most research to determine the vapor-liquid equilibrium of CO_2-Amine systems, however, is done through modeling. The problem arises since modeling data is only justified for ideal state. The inaccuracy of the thermodynamic model is a very important reason for deviation of CO_2 absorber model from pilot plant experimental data.

Moreover, Chunxi and Furst (1999) cited that the modeling of such systems is difficult for several reasons. The first one is related to the fact that the various published data sets are not always consistent. The second reason is related to the high number of ionic and molecular species produced by the absorption mechanism, these species being also engaged into many chemical equilibria. Faramzi, et al. (2008) has also noted on the fact that there are very few experimental data available in the open literature on the binary vapor-liquid equilibria of alkanolamine plus water systems.

ii. Significance of Project

The lack of reliable and accurate vapor-liquid equilibrium data hinders the maximization usage of alkanolamine such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) in the industry. Accurate and reliable VLE data are critically needed to develop more energy-efficient amine systems for the purification process.

Previous Final Year Projects (FYP) on similar topic had carried out the experiments in developing VLE data for CO_2-Amine system using MEA (C.L. Marcitah, 2006; Nurullainy, 2008) and aqueous mixture of MEA and MDEA (Zahrah, 2008).

1.3 OBJECTIVES AND SCOPE OF WORK

The main objective of this project is to develop the vapor-liquid equilibrium (VLE) data for CO_2-Amine system through experimental method. The amine of choice for this study is monoethanolamine (MEA). The scope of work proposed for this study is as follows:

i. To carry out experiments in order to develop the VLE data for CO_2 and MEA system.
ii. To analyze and compare the VLE data obtained through the experimental method, through modeling or simulation; and from published journals and articles available.
iii. Indirectly, this project hopes to improve on the results obtained by the previous students involved with this topic.

The focus of this project would be to determine the vapor-liquid equilibrium at varying temperature.

CHAPTER 2

LITERATURE REVIEW

2.1. VAPOR-LIQUID EQUILIBRIUM (VLE)

Vapor/liquid equilibrium (VLE) is the state of coexistence of liquid and vapor phases. The VLE relationships (as well as other interphase equilibrium relationships) are needed in the solution of many engineering problems. Although the required data can be found by experiment, such measurements are seldom easy, even for binary systems. Moreover, they become rapidly more difficult as the number of constituent species increases (Perry & Green, 1997).

Thermodynamics is applied to vapor/liquid equilibrium with the goal to find the temperatures, pressures, and compositions of phases in equilibrium through calculation. Models, such as the Raoult's law and Henry's law are often used for the behavior of systems in vapor/liquid equilibrium.

The vapor liquid equilibrium relations are often represented as the common T-x-y or P-x-y diagram. As shown in FIGURE 2.1 below, the upper line represents the saturated vapor line (i.e. dew point line), while the lower line is the saturated liquid line (i.e. bubble point line).The region between those two lines is of two-phase condition. The x-axis shows the concentration of a specific component in the solution.

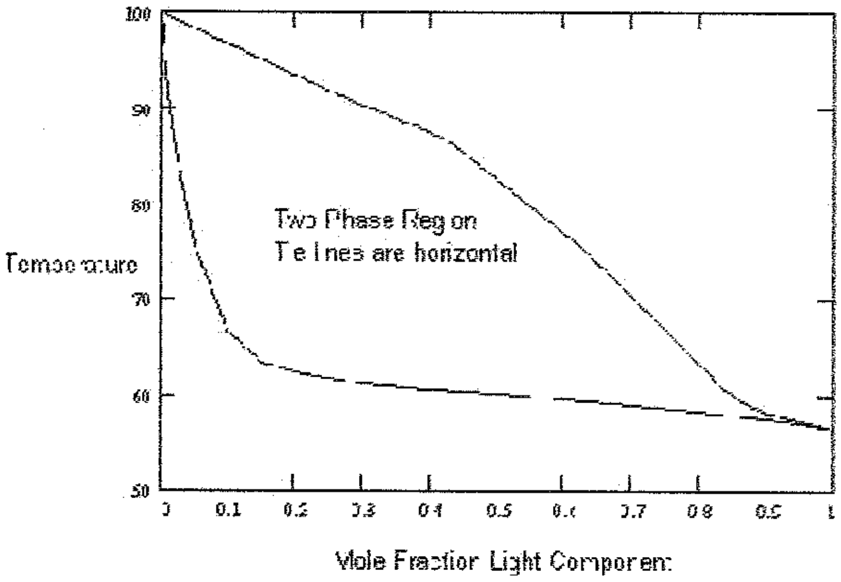

FIGURE 2.1: T-x-y diagram

2.2. SEPARATION PROCESS: GAS ABSORPTION

The use of basic solutions to remove CO_2 and other acid gases is categorized under '*Absorption with Chemical Reaction*' (Perry & Green, 1997; McCabe, et. al, 2005). Absorption followed by reaction is often used to get a more complete removal of solute from a gas mixture. Many present-day commercial gas absorption processes involve systems in which chemical reactions take place in the liquid phase. FIGURE 2.1 below shows the common CO_2 absorption process in a plant.

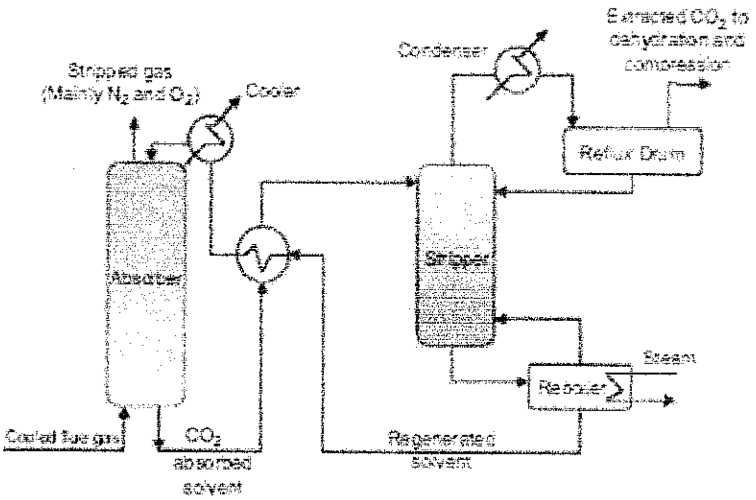

FIGURE 2.2: Process flow sheet for common CO_2 recovery plant (Mofarahi, et. al, 2006).

Reaction in the liquid phase reduces the equilibrium partial pressure of the solute over the solution, which greatly increases the driving force for mass transfer. It enhances the rate of absorption and increases the capacity of the liquid solution to dissolve the solute, when compared with physical absorption systems.

Although absorbing CO_2 in NaOH solution gives high rates of mass transfer, reagent costs and disposal problems make this approach impractical for large-scale use. Instead, CO_2 is removed by using aqueous solutions of amines or potassium carbonate where the chemical reaction is reversible. Absorption in amine solutions can be carried out at 20°C to 50°C and the spent solutions regenerated with steam at 100°C to 130°C (McCabe, et. al, 2005).

2.3. MONOETHANOLAMINE (MEA)

Monoethanolamine (MEA) is a primary amine that has been used extensively as chemical absorbent, especially for removal of CO_2. Unlike monodiethanolamine (MDEA), MEA reacts with both H_2S and CO_2 nonselectively.

The chemical reactions that take place between aqueous MEA and CO_2 help for a complete removal of the gas. The reactions are as follows::

$2MEA + CO_2 \leftrightarrow MEACOO^- + MEAH^+$

$MEA^+ + H_20 \leftrightarrow MEA + H_30^+$

$MEACOO^- + H_20 \leftrightarrow MEA + HCO_3^-$

MEA has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, low molecular weight and, thus, high absorbing capacity on a mass basis and reasonable thermal stability and thermal degradation rate (Ma'mun. et al., 2006).

Comparison done by an ISO 9001:2000 certified company called Amines & Plasticizers Limited (APL) provides the data in TABLE 2.1. It compares between MEA and other amines, and shows that only small concentration of MEA is required compared to others. In general practice, MEA is generally used as a 10 to 20 weight % solution in water.

Solvent	**MEA**	**DEA**	**MDEA**
Concentration (%)	15	30	35 - 50
Solvent Circulation (GPM)	100	100	100
Acid Gas Removal Capacity (mol/hr)	49.8	58.6	87.5

TABLE 2.1: General characteristics of amines (Amines & Plasticizers Limited, APL)

Amines	**Capacity**	
	Mol H_2S/ Mol Amine	**Mol CO_2/ Mol Amine**
MDEA	0.10	0.12
DEA	0.09	0.32
MEA	0.07	0.50

TABLE 2.2: Comparison of amines' capacity (Amines & Plasticizers Limited, APL)

Since MEA is a primary amine, it has a high pH which enables MEA solutions to produce a sweetened gas product containing less than 1/4 grain H_2S per 100 SCF at very low H_2S

partial pressures. When MEA is used, essentially all of the CO_2 must be absorbed to produce gas which meets the quarter grain H_2S specification. Based on TABLE 2.2, it proves that MEA has a high capacity to absorbing CO_2.

However, Ma'mun, et. al. (2006) has described that there are several disadvantages regarding MEA too. Monoethanolamine (MEA) has a high enthalpy of reaction with CO_2 which leads to higher desorber energy consumption. In addition, it has the inability to remove mercaptans.

Most importantly, MEA is considered more corrosive than many other alkanolamines. Although MEA itself is not considered to be particularly corrosive, its degradation products are extremely corrosive. MEA reacts with oxidizing agents such as COS, CS_2, SO_2, SO_3, and oxygen to form the soluble products which must be removed from the circulating system to avoid serious corrosion problems. Degradation or deactivation of MEA also lowers the effective amine concentration. Fortunately, according to Polasek and Bullin (1999) a reclaimer can recover most of the deactivated amine and corrosion inhibitors can be used for higher concentration of MEA. The data in the table below proves the corrosiveness of MEA:

Solvent	**Corrosion rate (mili-inch per year, MPY)**
30% wt MEA	32
50% wt DEA	25
15% wt MEA	13
20% wt DEA	8
50% wt MDEA	3

TABLE 2.3: Corrosion rate of the amines (Amines & Plasticizers Limited, APL)

However, these disadvantges can be overcomed slightly by enforcing a certain limit range to its application. Based on study by M. Mofarahi, et al. (2006), due to the corrosion problems of MEA solvent, the acid gas loading is usually limited to 0.3–0.35 mol acid gas per mole of amine for carbon steel equipment. The study also claimed that loadings as high as 0.7–0.9 mol/mol have been used in stainless steel equipment with no corrosion problems.

Moreover, Romeo, et al. (2007) has also noted that applications of MEA must not overcome 122°C, value above which degradation of MEA and corrosion becomes intoleratable.

2.5. PHYSICAL AND CHEMICAL PROPERTIES

There is the need to know the properties of the chemicals that will be used for the experiments; as well as their hazards and handling requirements. Based on the material safety datasheet (MSDS) of these chemicals, the hazards are summarized as follows:

	Monoethanolamine (MEA)	**CO_2**
Physical state	Viscous liquid	Gas
Color	Colorless or light yellow	Colorless
Boiling point	158°C at 760mmHg	-78.5°C
Freezing point	-4.5°C	-56.6°C
Solubility in water	> 10%	Very soluble
Hazards identification	Corrosive- causes eye and skin burns. Harmful or fatal if swallowed. Irritant - may cause dizziness, drowsiness and cause respiratory tract irritation.	CO_2 exposure can cause nausea and respiratory problems. High concentrations may cause vasodilation leading to circulatory collapse.
Handling	Minimum feasible handling temperatures should be maintained. Eye wash and safety shower should be available nearby when this chemical is handled or used. Period of exposure to high temperatures should be minimized. Water contamination should be avoided.	Use only in well-ventilated areas. CO_2 vapor is heavier than air and will accumulate in low areas. Do not heat cylinder by any means to increase the discharge rate of CO_2. Use a check valve or trap in the discharge line to prevent hazardous back flow into the system.
Materials to avoid	Incompatible with oxidizing agents..	Certain reactive metals, hydrides, moist cesium monoxide, or lithium acetylene carbide diammino may ignite. Passing CO_2 over a mixture of sodium peroxide and aluminum or magnesium may explode.
Hazardous reactions	Toxic levels of ammonia, combustion products of nitrogen, carbon monoxide, carbon dioxide, irritating aldehydes and ketones may be formed when burning in a limited air supply.	CO and O_2 will form when heated above 1700°C. Carbonic acid is formed in the presence of moisture.

TABLE 2.4: Properties and hazards Monoethanolamine (MEA) and CO_2

2.4 REFRACTIVE INDEX

Refractive index is a fundamental physical property of a substance. It is often used to identify a particular substance, confirm its purity, or measure its concentration. Refractive index is used to measure solids (glasses and gemstones), liquids and gases. Most commonly it is used to measure the concentration of a solute in a aqueous solution. A refractometer is used to measure the refractive index.

For this study, the refractive index value is needed to determine the vapor and liquid compositions.

CHAPTER 3

METHODOLOGY

In this project, different approaches are used and compared to determine the best result. The following experiments are carried out:

3.1. SIMPLE SIMULATION WITH HYSYS

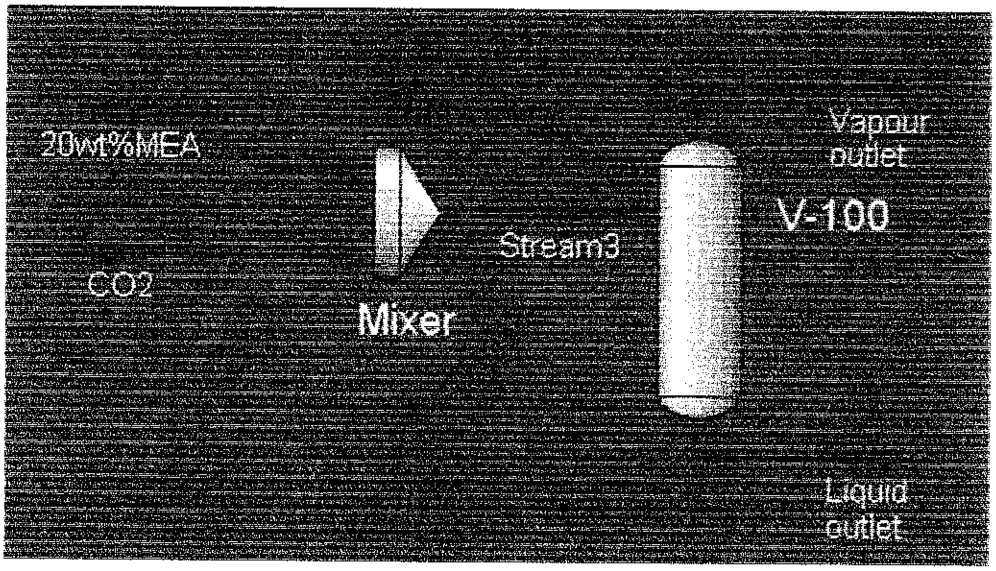

FIGURE 3.1: Simulation done with HYSIS

In attempting to understand better the experiment, simulation on HYSYS is done to give a general idea. The overall streams and equipments involved are as shown in FIGURE 3.1. Column V-100 is used to simulate the VLE Unit (Model BP 16) used in the experiment; where the vapor phase will exit from the overhead, while liquid phase exits in the bottom stream.

The data on the composition of the vapor and liquid phase from the HYSYS simulation would be compared with the experiment's results.

3.2. EXPERIMENT WITH VLE UNIT

The VLE Unit (Model: BP 16), as shown in FIGURE 3.2, can be used to study any binary system as well as multicomponent system. Based on the operating manual, a liquid mixture with known composition is initially fed into the evaporator. When the heater is switched on, the mixture would start to boil. The mixture vapor would rise up and would be cooled down by the condenser at the top of the evaporator. As the vapor starts to condense, the liquid falls back into the evaporator.

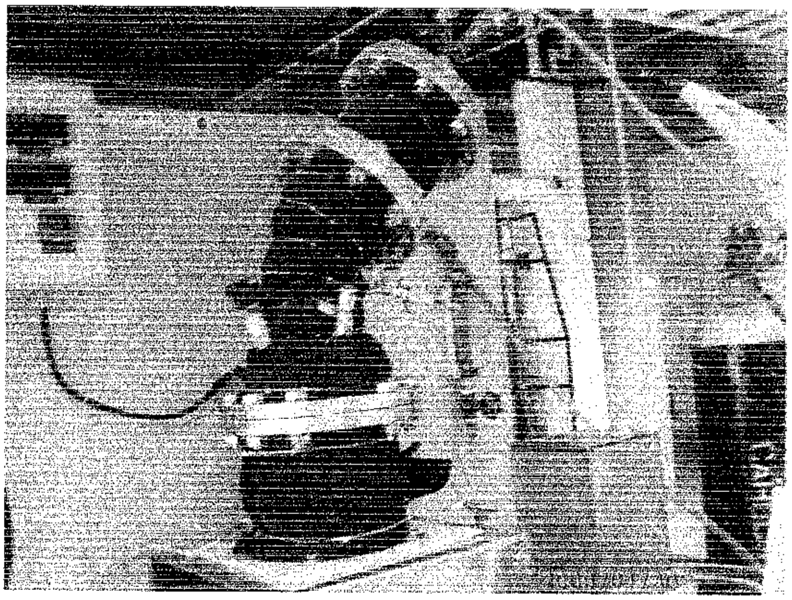

FIGURE 3.2: The VLE unit (Model BP16)

A little modification needed to be made since CO_2 gas is also used for this project. Therefore, 20wt% solution would be fed initially into the evaporator with continuous flow of CO_2 through the unit throughout the experiment.

The system would stabilize and finally reach an equilibrium state when the temperature remains constant. Samples of vapor and liquid are taken to determine their compositions. However, based on the study by Nurullainy (2008), fluctuated reading is to be expected instead of constant temperature reading at equilibrium state.

The data obtained from the VLE Unit would be compared with the available refractive index (RI) data. This is to determine the vapor and liquid compositions. VLE data and graph will be produced based on this.

The summary of this experiment is represented in the figure below:

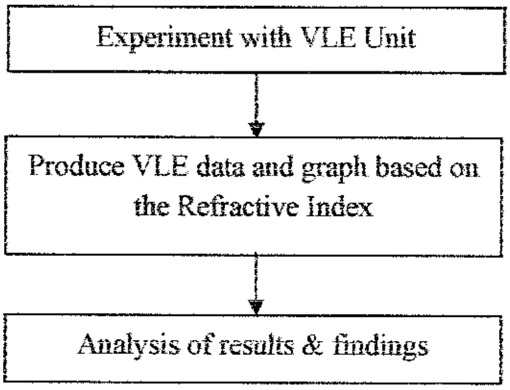

FIGURE 3.3: Experiment process flow

3.3. EXPERIMENT WITH HOT PLATE

Since using amine to absorb CO_2 involves chemical reaction (refer to Section 2.3), this experiment attempts to detect the difference in the MEA and CO_2 mixture at different temperature.

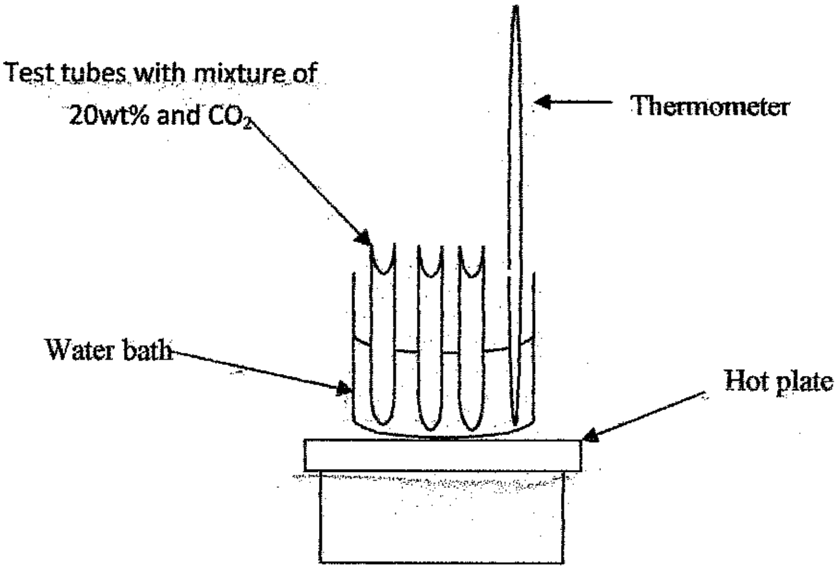

FIGURE 3.4: Experiment apparatus and set up using the hot plate

The set up for the experiment is as shown in FIGURE 3.4 above. The test tubes are filled with 10ml of 20wt% MEA and CO_2 is left to flow into each tube for a minute. The mixtures are heated to the desired temperature and its composition checked by the refractometer.

As an added precaution, the tubes are covered with aluminum foil to reduce the exposure to the air (to completely prevent exposure is however impossible). Besides that, three tubes are used for each temperature reading in order to obtain a more acceptable result.

Attempts are made to get the readings from the room temperature until the highest temperature possible (at boiling point of water, i.e. 100°C) with 10°C-intervals.

3.4. GANTT CHART

The research and project work have been done according to the following schedule:

No	TASK	SEMESTER I						SEMESTER II					
		JULY	AUG.	SEPT.	OCT.	NOV.	DEC.	JAN.	FEB.	MAR.	APR.	MAY	JUNE
1	Selection Of Project Topic	▨											
2	Submission of Preliminary Report		▨										
3	Literature Review & Research Work		▨	▨	▨	▨	▨						
4	Submission of Progress Report			▨									
5	Seminar			▨									
6	Submission of Interim Report				▨								
7	Purchase chemical					▨	▨						
8	Experiment using VLE Unit							▨	▨	▨			
9	Experiment using Hot Plate									▨	▨		
10	Simulation with HYSYS										▨		
11	Review on results & findings										▨		
12	Poster exhibition & Oral presentation											▨	
13	Submission of Project Dissertation												▨

FIGURE 3.5: Gantt chart for the overall Final Year Project (Semester I and II)

CHAPTER 4

RESULTS AND DISCUSSION

4.1. SIMPLE SIMULATION WITH HYSYS

The operating conditions to the simulation are set as closely as possible to the actual settings to the experiment using the VLE unit. Pressure is kept constant while the temperature is manipulated. The following settings are done:

i. Pressure at atmospheric pressure (i.e. 101.3 kPa)
ii. Feed into the column is 5 liter of MEA solution and 1 liter of CO_2.
iii. Amine Package with Li-Mather thermodynamic model is used.

The flow diagram of the simulation can be seen in FIGURE 3.1. The results of the simulation are as follows:

Total mass at column inlet = 5.834 kg/h		
Temperature (°C)	**Overhead (kg/h)**	**Bottom (kg/h)**
60	0	5.834
70	0	5.834
80	0	5.834
86.43	0.7661	5.0668
90	0.9104	4.9234
95	1.3490	4.4849
96	1.5133	4.3206
97	1.7260	4.1080
98	2.0020	3.8320
99	2.3472	3.4867

TABLE 4.1: Separation of phases based on HYSYS simulation

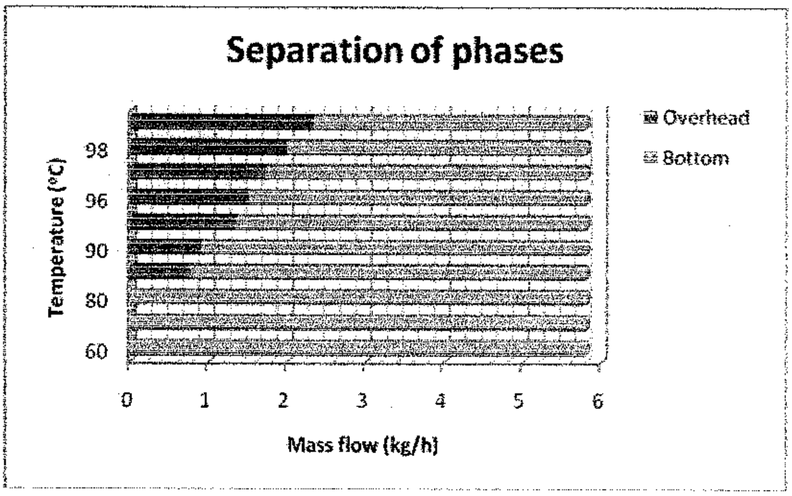

FIGURE 4.1: Separation of phases based on HYSYS simulation

Based on the result above, it is clearly shown through the HSYS simulation that separation of phases would not take place until it reach the temperature of 86.43°C. Therefore, before this temperature, vapor phase would not be expected to form.

In TABLE 4.2 and TABLE 4.3, the result based on separation by components is shown. TABLE 4.2 provides the result in mass flow amount (kg/h); while TABLE 4.3 presents it in mass fraction.

Temperature (°C)	Overhead		Bottom	
	MEA (kg/h)	CO_2 (kg/h)	MEA (kg/h)	CO_2 (kg/h)
86.43	5.3365	0.4975	5.5061	0.3279
90	5.3176	0.5164	5.5241	0.3099
95	5.2803	0.5537	5.5623	0.2717
96	5.2702	0.5638	5.5724	0.2616
97	5.2587	0.5753	5.584	0.2500
98	5.2455	0.5885	5.5971	0.2369
99	5.2308	0.6032	5.6119	0.2221

TABLE 4.2: Separation of components in mass flow (kg/h)

Temperature (°C)	Overhead		Bottom	
	MEA	CO_2	MEA	CO_2
86.43	0.3507	0.6493	0.9353	0.0647
90	0.4329	0.5671	0.9372	0.0628
95	0.5896	0.4104	0.9394	0.0606
96	0.6275	0.3725	0.9395	0.0605
97	0.6670	0.3330	0.9391	0.0609
98	0.7061	0.2939	0.9382	0.0618
99	0.7430	0.2570	0.9363	0.0637

TABLE 4.3: Separation of components in mass fraction

Based on the result in TABLE 4.2, it shows that the amount of CO_2 gas in the overhead increases with the increase of temperature. This can be easily explained by the fact that although the MEA solution does absorb the CO_2; however, the solution itself vaporizes at high temperature causing it to flow to the overhead stream as well. This can be seen clearly in TABLE 4.3 where the mass fraction of MEA increases in the overhead stream as the temperature is increased.

A graph representation in terms of mol fraction is as follows:

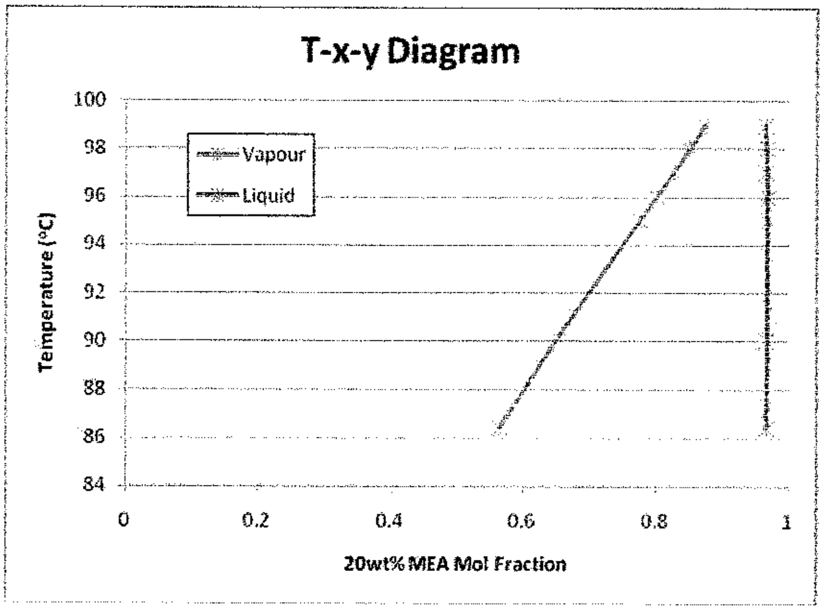

FIGURE 4.2: T-x-y diagram of 20wt% MEA and CO_2 based on HYSYS simulation

A note to be taken as reminder, however, the result of the simulation above does not represent how good the amine MEA is to absorbing the CO_2 with respect to temperature. Instead, it shows the effect of temperature to the equilibrium of phases of the system.

In addition, the simulation is bounded by limitations of the Amine Package and the Li-Mather thermodynamics model used. The limitations are:

- Amine wt% concentration for any stream must be within range of 0/0 – 30.0.
- Streams that contain amine must be within temperature range of 25°C – 125°C.

Although, the result above is simulation-based, the advanced thermodynamic Li-Mather electrolyte model on HYSYS is said to achieve more reliable results than empirical models, especially for blended amines. The technology is based on the AMSIM engine from the Oilphase-DBR division of alliance partner Schlumberger. Therefore, it gives a good idea on the expected result for the experiments.

4.2. EXPERIMENT WITH VLE UNIT

The test run is done using 4 liter of 20wt% MEA and continuous flow of carbon dioxide, CO_2. The temperature of the reboiler was set at 100°C. Records were taken at 10-minutes intervals. Result of experiments gave the following result:

Time (min)	Temperature (°C)	Pressure (bar)	Liquid RI	Vapor RI
10	25.3	0.45	Samples taken	No condensate available
20	25.9	1.05		
30	36.1	0.55		
40	38.0	0.72		
50	42.7	1.53		
60	53.0	1.09		

TABLE 4.4: Result of experiment VLE unit

Based on the result of the test runs, the following discussions are made:

1. The ***temperature could not reach high enough***, even though the reboiler temperature is set at 100°C. Based on the HYSYS simulation result in section 4.1, the general idea obtained is that the temperature needs to be at least about 86°C for the vapor phase to form. Since the highest temperature attained by the unit so far is 53°C, therefore, the vapor-liquid equilibrium could not be determined.

2. Throughout the experiment, it was attempted to ***maintain constant pressure in the vessel*** at 1 atm (i.e. 1.013 bar). However, every time samples were taken, a small amount of loss in the pressure took place. Furthermore, there is a potential leakage at the feed inlet which could result in slight reduction of the pressure.

   Pressure reducing could cause for the temperature to reduce as well. During the test run, in order to maintain the pressure constant, CO_2 is fed into the vessel whenever a drop in pressure value is detected.

3. The third issue above has caused to raise the question on that there is ***no limit to the*** ***CO_2 fed in.*** Continuously feeding CO_2 could possibly give a different result from feeding it in only once at the beginning of the experiment. However, this could not be avoided since it is more desirable to maintain the constant pressure.

4. Since at that temperature no condensate is available, the experiment is terminated. However, based from this, it can be concluded that the data from HYSYS is valid where no vapor would form at such temperature.

Therefore, based on the experiment with VLE Unit, the data obtained is insufficient to create the VLE graph.

4.3. EXPERIMENT WITH HOT PLATE

The set up of the experiment can be seen in the diagram in FIGURE 3.4. Refractive index reading is measured for the samples and average result is taken. The result obtained is as follows:

Note: Room temperature = 26°C	
Temperature (°C)	**Refractometer reading (RI)**
26	1.3737
70	1.3712
80	1.3783
90	1.3784
95	1.3727
96	1.3687

TABLE 4.5: Result of experiment with hot plate

The result above is measured against the available *Refractive index versus Composition of CO_2 Calibration Curve for 20wt% MEA* (as shown in FIGURE 4.3). From this, the composition of the samples in liquid phase can be determined directly by applying the linear equation of the line (i.e. $y = 0.034x + 1.343$) or interpolating and extrapolating the calibration curve.

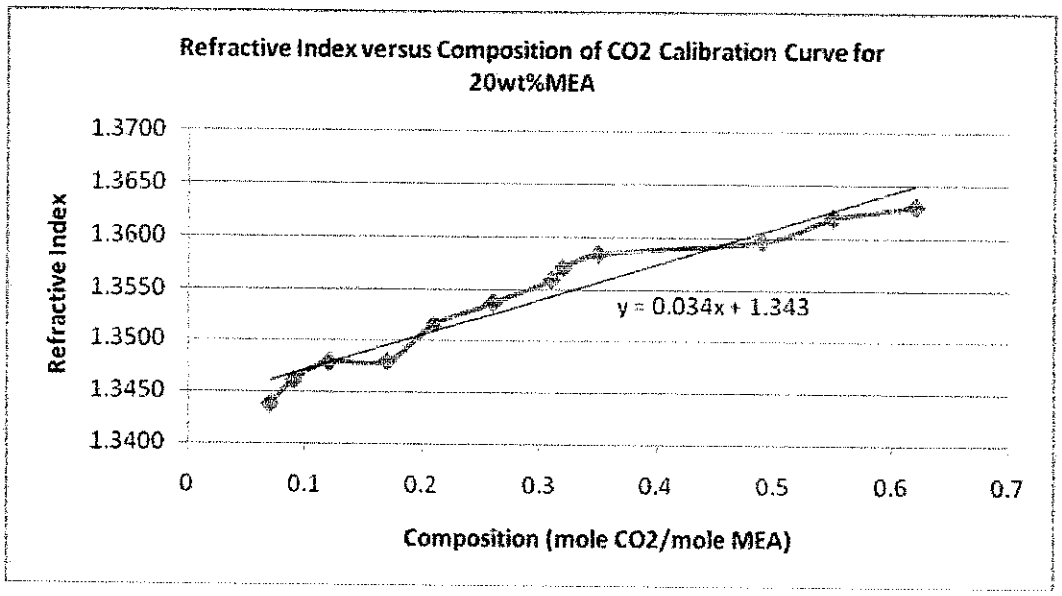

FIGURE 4.3: Graph refractive index vs CO_2 vol% absorbed in 20wt% MEA (Source: Nurullainy, 2008)

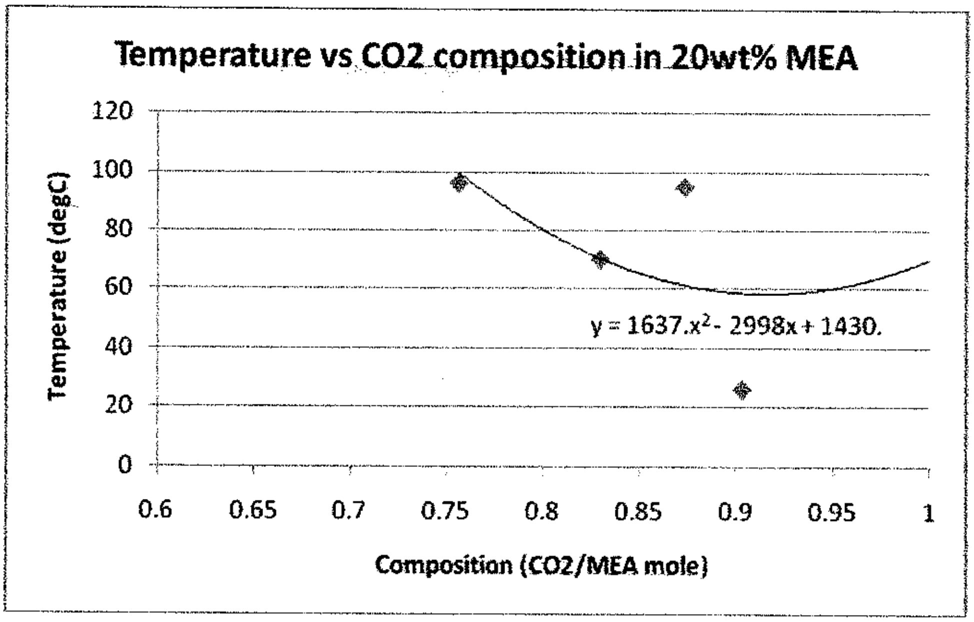

FIGURE 4.4: Temperature vs CO_2 composition in 20wt% MEA for liquid phase

The result in TABLE 4.5 is plotted into a T-x-y diagram as shown above. Comparing the graph from this experiment with the diagram in FIGURE 4.2, the obvious difference in the graph's shape can be seen. Second-order polynomial trend line is used. However, similarity between the two exist, where at high temperature (i.e. about 60°C and above), the equilibrium is as such where the composition of 20wt% MEA by mol% is more and close to 1.

The difference is mainly due to the fact that FIGURE 4.2 is simulation-based and takes ideal condition to obtain the result; while this T-x-y diagram is the real condition and has the potential to be exposed to all sorts of errors while carrying the experiment.

Care was taken by ensuring the meniscus level of the liquid while measuring and carrying out the experiments with multiple samples (where the average reading is taken) in order to gain a more acceptable result. However, there are certain issues that need to be discussed regarding the experiment:

1. The experiment takes into consideration only the equilibrium of the liquid phase, while assuming the vapor phase is neglected. However, by closing the mouth of each test tube with aluminum foil, there is the possibility of the vapor phase forming and condenses back into the tube. This has the potential to alter the result of the experiment.

2. Referring to FIGURE 3.4, a water bath is used to ensure all the samples have reached the same temperature at the same time (i.e. thermal equilibrium). The hot plate used is not of the digital type; therefore a thermometer is used to measure the temperature of the water. This method of setting and measuring temperature is acceptable since the temperature of the samples is of more concern. If digital electric heater is to be used (where the hot plate temperature is set), there is still the concern of heat loss to surrounding.

3. Closing the mouth of the test tubes with aluminum foil is meant to minimize the samples' exposure to the surrounding air. Since air naturally contains CO_2, this action was taken to reduce as much as possible outside air from coming in. However, it is impossible to completely eliminate the surrounding air.

4. From the result obtained, this experiment might not be the best option to determining liquid equilibrium of the system. This experiment was mainly meant as support to the previous two activities (refer Section 4.1 and 4.2). Since using MEA to absorb CO_2 does employ a chemical reaction (refer to Section 2.3), this experiment expects to see the difference in equilibrium of the system due to the reaction and the temperature.

5. The amount of CO_2 gas in every test tube could not be determine accurately since there is no flow meter along the line. Therefore, assumption is used that the same amount is fed when a slow flow is directed for one minute into each tube. Using three test tubes, instead of one, hopes to eliminate this error and achieve an average and reasonable result.

4.4. OVERALL DISCUSSION

Although the result in experiment with hot plate seems to deviate away from simulation result; and the experiment with VLE Unit had to be terminated, the followings are found to be the common ground among those three activities:

i. Vapor phase for the system would not form at any temperature below 80°C. This is shown through simulation and proven through experiment with VLE Unit where no condensate was available.

ii. At high temperature (i.e. at 60°C and above), the liquid equilibrium of the system demonstrate that the mol fraction of 20wt% MEA is more. This is the basic idea grasp from the simulation and experiment with hot plate.

With the objective to improve on the results of research done by previous students on similar topic, comparison against the result of Nurullainy (2008) is done. The result obtained from her research, particularly on the effects of temperature on equilibrium, is as follows:

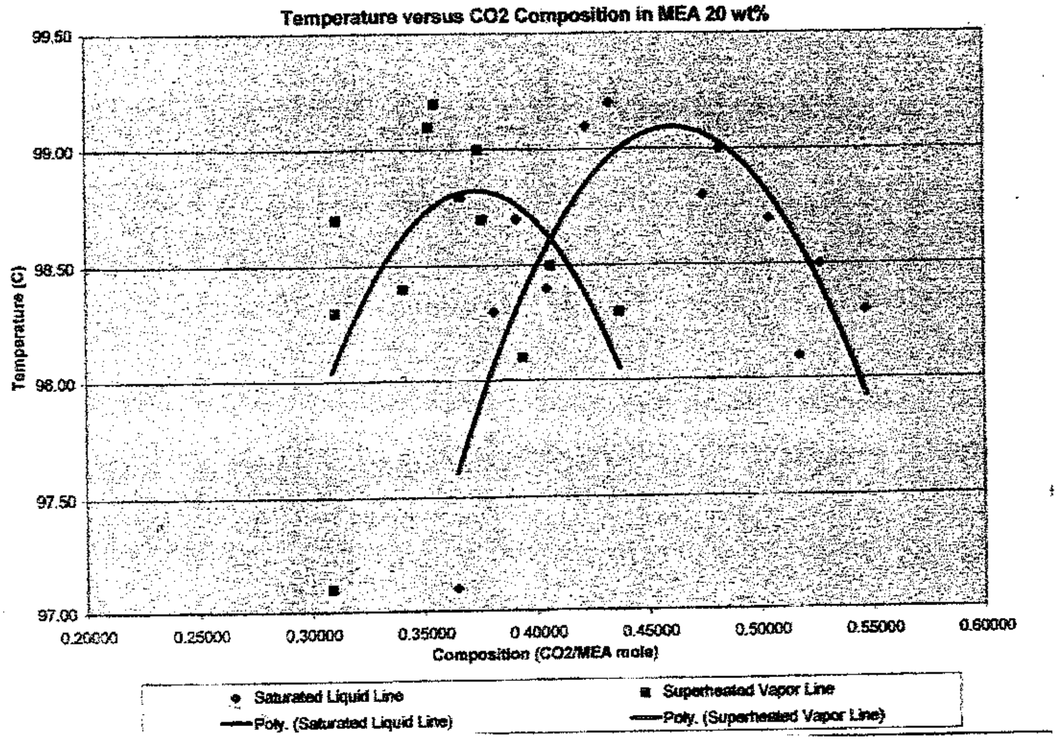

FIGURE 4.5: Temperature vs CO_2 composition in 20wt% MEA by Nurullainy (2008)

From the comparison, the obvious difference is on the shape of the graph and the composition axis. The component of 20wt% MEA (in mol%) in her research does not seem to be as much as what was found in this project. Furthermore, her result also seems to deviate away from HYSYS result.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

Monodiethanolamine (MEA) is chosen as the amine-of-choice for this study. The aim of this study is to produce a vapor-liquid equilibrium (VLE) data on the CO_2-MEA system. Based on literature review, constraint is on the lack of accurate VLE data that obstruct it from being used more in the industry.

This study focused on the effect of temperature on 20wt% MEA-CO_2 system at atmospheric pressure. Both concentration and pressure are hoped to be maintained constant in order to help further improve data from previous studies done.

As a conclusion, the objectives of the project are fulfilled (i.e. to produce VLE data of CO_2-MEA system). Comparison has also been made against the previous projects to see the effectiveness and improvements. The HYSYS simulation done is to set the standard of result expected, while two other experiments were carried out. VLE data has been obtained; however, the reliability of the data can be further researched on in the future.

5.2. RECOMMENDATION

The following recommendations are made for the purpose of further research in this topic:

1. Carry out servicing and maintenance work on the VLE Unit to ensure its smooth operation and obtain a more accurate data.
2. Add a flow meter to the CO_2 line in order to determine exact amount of gas used.
3. Explore on the effects of varying the pressure and concentration of the amine

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