Flowsheet Design and Simulation of Carbon Dioxide Removal System via Reactive Absorption Using Mixed (AMP + MEA) Solvent

by

Irene Ling Fun Yen

Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

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TRONOH, PERAK

January 2014

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

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(Irene Ling Fun Yen)

ABSTRACT

Currently, around 90 % of the world's primary energy requirement is supplied by fossil fuels in which causes rising in the emission of greenhouse gases (GHGs) that contributes to global warming effects and climate change. Carbon dioxide gas is the largest component of greenhouse gas. Moreover, carbon dioxide lowers the heating value of natural gas as well as is corrosive to pipelines and equipments. Therefore, removal of carbon dioxide from natural gas stream is crucial. There are several technologies for carbon dioxide removal available commercially. Chemical solvent absorption is the most common and extensively used in existing natural gas processing and liquefaction plants nowadays. However, the commercially available amines have limitations such as slow rate of reactions, lower loading capacity, subject to degradation and high regeneration energy of solvent. Hence, sterically hindered amine known as 2–amino–2–methyl–1-propanol (AMP) is proposed with the addition of Monoethanolamine (MEA) solvent, commercially attractive to replace existing solvent in carbon dioxide removal process. Due to there is no information found in the open literature for the plant data of chemical absorption process with the mixed (AMP + MEA) solvent. This project aims to study the effects of temperature, pressure and concentration of solvent on the performance of carbon dioxide removal process prior applying into the real plant. The simulation flowsheet is developed using Aspen HYSYS software and the results show that chemical reactive absorption favors low temperature and high pressure. For mixed solvent of 20 wt% AMP + 10 wt% MEA, CO_2 loading is higher for temperature at 30 ℃ (0.3662 mole CO_2/mole amine) than at 55 ℃ (0.2452 mole CO_2/mole amine); and the CO_2 loading is higher for pressure at 70 bar (0.3814 mole CO_2/mole amine) compared to that at 10 bar (0.0587 mole CO_2/mole amine). From the simulation, at temperature of 30 ℃ and pressure of 68.6 bar, the CO_2 loading of 30 wt% AMP (0.4068 mole CO_2/mole amine) is higher than that in 30 wt% MEA (0.3112 mole CO_2/mole amine). Hence, sterically hindered amine, AMP is a solvent that is worth to be invested in industrial for more efficient carbon dioxide removal.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1. Background

Carbon dioxide, CO_2, or formerly known as carbonic acid is a natural component of Earth in which it is largely present in fossil fuels such as natural gas. It is a nonflammable inert gas which will lower the heating value of natural gas as well as it will corrode pipelines and equipment through forming of weak corrosive acid in the presence of water. (Ahmed & Ahmada, 2011; Belloni, Ahner, & Häring, 2008) Besides, carbon dioxide is also the largest component of greenhouse gas (GHG) which leads to 60 % of global warming effects. (Mondal, 2009) Hence, carbon dioxide should be removed from natural gas stream to acceptable level before natural gas is sold or transported in pipelines.

There are several available technologies for the removal of carbon dioxide from natural gas, which are chemical solvent absorption, physical solvent absorption, hybrid solvent absorption, cryogenic fractionation, solid adsorption, and membrane separation. (Kidnay & Parrish, 2006; Kohl & Nielsen, 1997; Sohbi, Meakaff, Emtir, & Elgarni, 2007) However, according to Sohbi et al. (2007), removal of carbon dioxide through chemical solvent absorption process is the most common and most extensively used in existing natural gas processing and liquefaction plants nowadays. Chemical solvent absorption process has the advantage of lower hydrocarbon losses compared to membrane separation process and physical solvent absorption process as well as having lower energy requirement than cryogenic fractionation process in which makes it the most economical and efficient among the available carbon dioxide removal technologies.

For chemical solvent absorption, there are three basic types of alkanolamine solvents, which are primary amine (e.g. MEA), secondary amine (e.g. DEA, DIPA)

and tertiary amine (e.g. MDEA). For the conventional alkanolamine solvents mentioned above, each of them contains advantages of their own characteristic in terms of reactivity, carbon dioxide loading capacity and solubility with limitations. For example, MEA solvent which has high reactivity with carbon dioxide, low solvent cost and ease of reclamation is most commonly used but highly concentrated MEA solvent has the disadvantage of corrosive to equipment whereas MDEA solvent known with its high loading capacity, lower energy of regeneration of solvent and resistant to thermal and chemical degradation is having a slow reactivity with carbon dioxide.

Therefore, sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP) which was originally developed by Exon is proposed to be used in mixture with Monoethanolamine (MEA) solvent. The sterically hindered amine AMP is an amine in which bulky alkyl group is attached on the amino group. (Gupta, Coyle, & Thambimuthu, 2003) AMP is commercially attractive for carbon dioxide removal compared to conventional alkanolamine solvent because AMP has the advantage of high carbon dioxide loading capacity, higher thermal degradation temperature and lower heat of regeneration. According to Ali, Al-Rashed, and Merchant (2010), reaction of carbon dioxide with AMP takes place faster than the reaction of carbon dioxide with MDEA. This is also supported by Jamal, Meisen, and Jim Lim (2006) where it stated that the carbon dioxide absorption rate in 1M aqueous AMP solvent is four times of the reaction rate in the same concentration of MDEA solvent. Besides, the addition of MEA solvent to AMP was used because addition of primary amine into a sterically hindered amine will enhance the rate of absorption of carbon dioxide largely and retaining the characteristic of lower desorption energy by AMP. (Xiao, Li, & Li, 2000) Hence, mixed (AMP + MEA) solvent exhibit higher performance compared to the conventional or commercially available amine in which should be commercialized and applied in industrial for better removal of carbon dioxide.

However, before applying the mixed (AMP + MEA) solvent into plant, the optimum operating condition of the system is required to be determined. Thus, this project will focus on simulating a carbon dioxide removal system with mixed (AMP+MEA) solvent by using Aspen HYSYS software and investigate the effects of parameters on the performance of carbon dioxide removal. Simulation of the carbon dioxide is important because it enables the performance of the carbon dioxide

removal process to be justified without testing at industrial scale, which is very expensive. Furthermore, simulation software is vital in process development nowadays as the feasibility of the process can be assessed, economics can be estimated and evaluated as well as optimization and increasing the yield can be achieved. (Mohamadirad, Hamlehdar, Boor, Monnavar, & Rostami, 2011; Sohbi et al., 2007)

1.2. Problem Statement

The major impact of carbon dioxide is global warming problem which is caused by the emission of greenhouse gases into the atmosphere where carbon dioxide contributes to the largest amount of greenhouse gases. As a result, the study on carbon dioxide removal processes has gained much interest globally in order to reduce the carbon dioxide emission. However, the major challenge in carbon dioxide removal processes used in industrial is the limitation of conventional alkanolamine solvent used. This lead to the invention of sterically hindered amine solvent whereby it is not yet implemented in industry due to there is no information found in the open literature for the plant data of chemical absorption process with the mixed (AMP + MEA) solvent. Although the kinetic, solubility, thermodynamic and physiochemical properties of chemical absorption with mixed (AMP + MEA) solvent has been studied and proven having better performance of carbon dioxide removal in the literatures (Ali et al., 2010; Alper, 1990; Mandal & Bandyopadhyay, 2006; Saha, Bandyopadhyay, & Biswas, 1995; Vázquez, Alvarez, Navaza, Rendo, & Romero, 1997; Xiao et al., 2000), the effects of parameters such as temperature, pressure and concentration of the mixed solvent on the dynamic performance of carbon dioxide removal is still yet to be discovered. Therefore, simulation of the whole process of carbon dioxide removal through chemical absorption is required to obtain the optimum condition prior applying into the real plant.

1.3. Objectives

The purpose of this project is focusing on simulating and designing a flow sheet for the removal of carbon dioxide from natural gas by mixed (AMP + MEA) solvent. Aspen HYSYS software simulator is used as it enables optimization of the design process to be done easily and economically. The main objectives of project are as follows:

- To design and simulate a flowsheet for carbon dioxide removal system through chemical absorption via mixed (AMP + MEA) solvent
- To investigate the effects of parameters (temperature, pressure, concentration and flow rate) on the performance of carbon dioxide removal
- To compare with other conventional amine solvent (MEA)

1.4. Scope of Study

The scope of study for this project will be:

- Design and flow sheeting of carbon dioxide removal unit using Aspen HYSYS software
- Simulate and design a flowsheet of removal of carbon dioxide through chemical absorption via mixed (AMP + MEA) solvent with different parameters
- Compare the performance of mixed (AMP + MEA) solvent in carbon dioxide removal with other conventional amine solvents such as MEA solvent

CHAPTER 2

LITERATURE REVIEW

2.1   Chemical Reactive Absorption Process

Absorption is a type of separation process that occurs between gas and liquid where the solute in the gas is absorbed into liquid solvent whereas desorption is the opposite of absorption where the solute in the liquid phase is stripped into gas phase by using heat. Absorption process can be divided into two groups, physical and chemical absorption. Chemical absorption is the separation process which chemical reactions occur whereas physical absorption is without chemical reaction. (Geankoplis, 2003; Richardson, Harker, & Backhurst, 2002) In this case, carbon dioxide will be the solute that required to be removed from the natural gas with the liquid mixed (AMP + MEA) solvent through chemical reaction that will be discuss in section 2.1.2.

Chemical absorption process contains two stages which are:

- Absorption of carbon dioxide into the mixed solvent in an absorber
  The mixed solvent captures and removed the carbon dioxide from natural gas stream by forming unstable carbamate ions.

- Regeneration or desorption of mixed solvent
  1.   Partially of carbon dioxide is flashed off at low pressure in a flash vessel.
  2.   Carbon dioxide is stripped off in a regenerator with the aid of a reboiler.

2.1.1   Primary, Secondary and Tertiary Alkanolamine Solvent

There are three basic conventional amines which are commonly used in industries for chemical solvent absorption, which is shown in Figure 1.
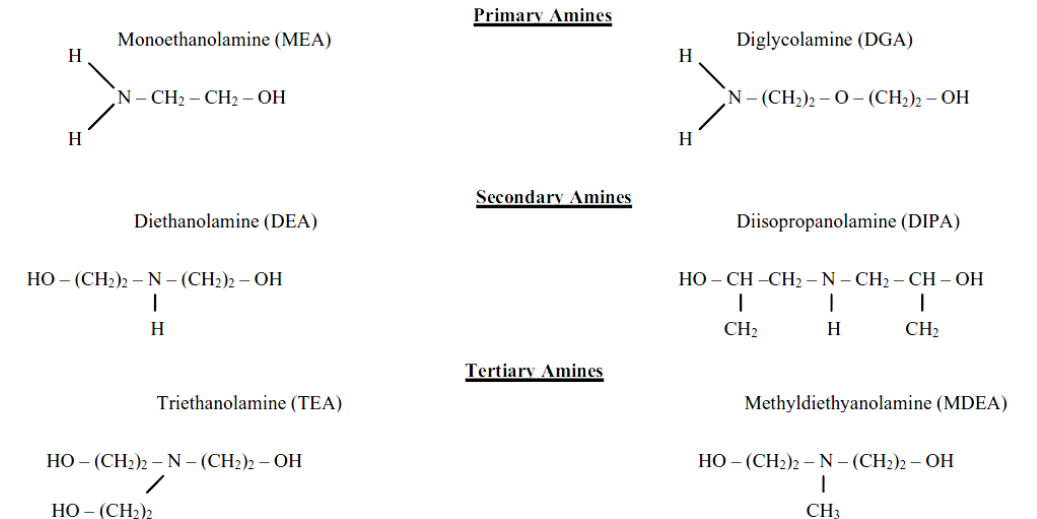
Figure 1: Structures of amines (Kohl & Nielsen, 1997)

The chemistry of the solvents react with carbon dioxide determined the maximum theoretical loading of carbon dioxide by the solvent in which will be discussed below. The following equations are using the symbol R to denote C_2H_4OH for simplicity.

- The chemical reactions of primary amine based solvents with CO_2 are

$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+ \text{(Carbamate reaction)} \qquad (1)$$

$$CO_2 + H_2O + RNH_2 \leftrightarrow HCO_3^- + RNH_3^+ \text{(Bicarbonate reaction)} \qquad (2)$$
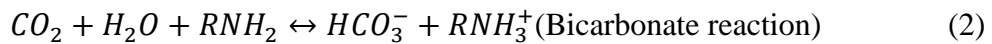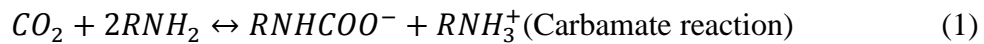
Carbamate reaction is the fastest among the reactions in absorbing CO_2 so the absorption rate of CO_2 in primary amine is determined by the carbamate reaction. From the equations, 1 molecule of CO_2 reacts with 2 molecules of primary amine. This means that the maximum theoretical loading of CO_2 is 0.5 mole CO_2/mole primary amine.

- The chemical reactions of secondary amine based solvents with CO_2 are

$$CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH_2^+ \text{ (Carbamate reaction)} \qquad (3)$$

$$CO_2 + H_2O + R_2NH \leftrightarrow HCO_3^- + R_2NH_2^+ \text{(Bicarbonate reaction)} \qquad (4)$$
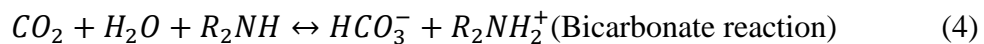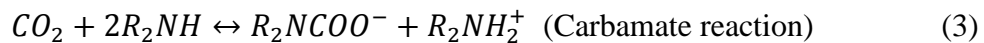
Similar to primary amine, the carbamate reaction will determine the absorption rate of CO_2 in secondary amine. From the equations, 1 molecule of CO_2 reacts with 2 molecules of secondary amine. This means that the maximum theoretical loading of CO_2 is 0.5 mole CO_2/mole secondary amine.

- The chemical reaction of tertiary amine based solvents with CO_2 is

$$CO_2 + H_2O + R_3N \leftrightarrow HCO_3^- + R_3NH^+ \text{(Bicarbonate reaction)} \qquad (5)$$

Due to tertiary amine does not have a hydrogen atom attached directly to the nitrogen atom, the carbamate reaction which is important in primary and secondary amines is inhibited and the bicarbonate reaction becomes the only important reaction. From the equations, 1 molecule of CO_2 reacts with 1 molecule of tertiary amine. This means that the maximum theoretical loading of CO_2 is 1 mole of CO_2 / mole tertiary amine.

2.1.2 Sterically Hindered Amine

Recently, the use of sterically hindered amines has become of great interest as potential carbon dioxide removal absorbent. A sterically hindered amine is defined structurally as a primary amine in which the amino group is attached to a secondary or a tertiary carbon atom. (Le Tourneux, 2007) The sterically hindered amine that is selected to be used in this project is 2-Amino-2-methyl-1-propanol (AMP) with the structure as below.
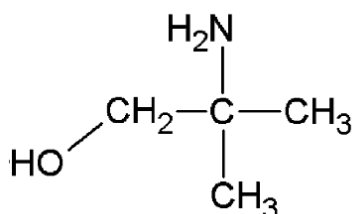
Figure 2: Molecule structure of AMP (Bougie & Iliuta, 2009)

The properties of AMP are as below:

Table 1: Properties of AMP (Yildirim, Kiss, Hüser, Leßmann, & Kenig, 2012)

Formula	$C_4H_{11}NO$
Normal boiling point (°C)	165
Density (g/cm$_3$)	0.934
Molecular weight	89.14

The chemical reaction of AMP with carbon dioxide is suggested by Chakraborty, Astarita, and Bischoff (1986) which is shown in the equation below.

$$RR'NH + CO_2 + H_2O \leftrightarrow RR'NH_2^+ + HCO_3^- \qquad (6)$$
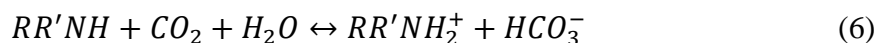
The absorption reaction of AMP with carbon dioxide above is similar with the reaction of tertiary amine, MDEA with carbon dioxide where AMP has the theoretical loading of 1 mole of CO_2 per mole of amine.

2.2 Benefits of Using Mixed (AMP+ MEA) Solvent

As discussed before that conventional amine solvents, either MEA solvent, DEA solvent or MDEA solvent, all contain limitations whereby all of these can be solved by using AMP solvent. This is because AMP is a primary sterically hindered amine obtained from substituting two methyl groups into the original two hydrogen atoms which is attached to α-carbon atom of the amino group in MEA.(Bougie & Iliuta, 2012) As the consequence of the substitution, the properties of the amine and the absorption capacity is influenced.

Gupta et al. (2003) states that the sterically hindered amine, AMP offers better carbon dioxide absorption capacity, faster absorption rate, higher thermal degradation and lower heat of absorption/regeneration compared to the conventional amines. Due to its hindrance of the bulky group adjacent to the amino group, AMP will form unstable carbamate in which hydrolysis of the carbamate leads to preferential of bicarbonate reaction, causing the theoretical carbon dioxide loading to achieve 1.0 mole per mole of AMP. (Saha et al., 1995) With high carbon dioxide loading, less circulation rate of solvent will be required for the same amount of carbon dioxide removal in which it will reduce the cost for solvent. Moreover, with same reaction equation of bicarbonate reaction with MDEA solvent, AMP exhibit faster reaction rate with carbon dioxide compared to MDEA. Ali et al. (2010) stated that the carbon dioxide absorption rate in 1.0M aqueous AMP solvent is four times of the reaction rate in the same concentration of MDEA solvent. Hence, AMP is a new solvent that is commercially attractive to be used in replace of the conventional amine.

The addition of MEA solvent into AMP solvent as a mixed solvent because mixed (MEA+AMP) solvent have higher carbon dioxide loading than MEA and a higher reaction rate than AMP. Hence, the use of blend of solvents has the combination of each amine advantage which is the fast reactivity of the primary amine (MEA) with the high absorption capacity and low solvent regeneration cost from the sterically hindered amine (AMP). (Bougie & Iliuta, 2012; Choi, Seo, Jang, Jung, & Oh, 2009) Therefore, this project will focus on the study of the performance of carbon dioxide removal by mixed (AMP + MEA) solvent through simulation using Aspen HYSYS software.

2.3 Process Simulation

Process simulation software are programs that are configured to calculate material balances, energy balances and equilibrium condition in chemical process units as well as in the whole flow sheet containing the units. One of the widely used process simulation software is Aspen HYSYS.

2.3.1 Simulation with Aspen HYSYS

The main objective of using simulation in this project is because there is no plant data available for the carbon dioxide removal system using mixed (AMP + MEA) solvent and testing the solvent in industrial scale will be costly. Thus, Aspen HYSYS is used to validate the different conditions such as temperature, pressure and concentration on the performance of carbon dioxide removal, prior applying the system in industrial.

Besides, Aspen HYSYS provides accurate simulation as it addresses a wide range of models from distillation, reaction, heat transfer operation, rotating equipment, controller as well as logical operation in both steady state and dynamic environment. (Hysys, 2008) And Aspen HYSYS can provide easy and time saving way to achieve the objectives compared to manual calculations. Moreover, one of the important advantage is Aspen HYSYS has a large number of models for vapor/liquid equilibrium, for example, Extended- Non Random Two Liquid (e-NRTL) and also different calculation tools for unit operations are also available and reliable. Therefore, Aspen HYSYS is selected to be used in this project.

CHAPTER 3

METHODOLOGY

3.1. Main Project Flow

The main flow for whole project work will be as follows:

Preliminary project work

Background study and literature review was done for chemical absorption process and mixed solvent.

Familirize with software simulator, Aspen HYSYS

The functions and procedure to run simulation using HYSYS is studied.

Study on design and flowsheeting of carbon dioxide removal unit

The process flow for carbon dioxide removal with chemical absorption is understood.

Simulate and design a flowsheet of removal of carbon dioxide through chemical absorption via mixed (AMP + MEA) solvent with different parameters

A flowsheet of carbon dioxide removal with mixed solvent is simulated and designed by using HYSYS simulator and the effects of changing in the parameters such as temperature, pressure, concentration and flow rate will be investigated through the simulation

Compare the design with other commercially available amine solvent

The performance of carbon dioxide removal with mixed (AMP + MEA) solvent is compared with other conventional solvent such as MEA.

Presentation

Proposal defense and oral presentation are done in FYP I and FYP II respectively.

Report writing

The reports that are written are progress report, final report and technical paper.

The Gantt chart for entire project including FYP I and FYP II is planned and shown in Figure 3.

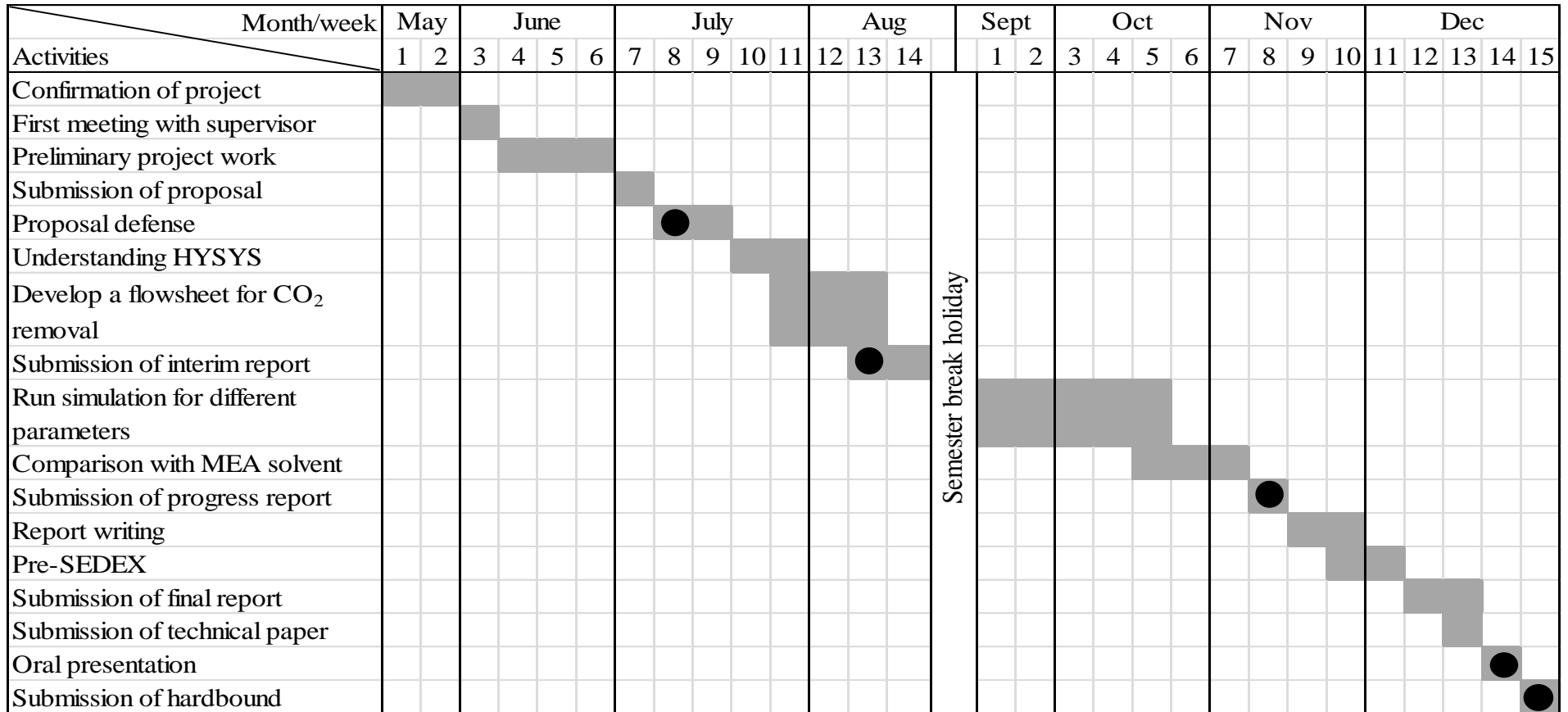| Month/week Activities	May		June				July					Aug			Semester break holiday	Sept		Oct				Nov				Dec				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Confirmation of project	█																													
First meeting with supervisor		█																												
Preliminary project work			█	█																										
Submission of proposal							█																							
Proposal defense								●																						
Understanding HYSYS										█	█																			
Develop a flowsheet for CO_2 removal												█	█																	
Submission of interim report														●																
Run simulation for different parameters																█	█	█	█											
Comparison with MEA solvent																				█	█									
Submission of progress report																							●							
Report writing																								█	█					
Pre-SEDEX																										█	█			
Submission of final report																												█		
Submission of technical paper																														
Oral presentation																													●	
Submission of hardbound																														●

Figure 3: Project Gantt chart

The important milestones are marked as ●

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3.2. Process Simulation of CO_2 Removal

3.2.1. Simulating an Actual CO_2 Removal Using Mixed (AMP + MEA) Solvent

The feed natural gas to the system is used based on composition of natural gas reserves in Malaysia (Ahmed & Ahmada, 2011). The composition is shown in table below.

Table 2: Compositions of natural gas reserves in Malaysia

Components	Mole %
Nitrogen	0.16
Carbon dioxide	**70**
Hydrogen sulfide	1.72
Methane	21.05
Ethane	3.93
Propane	0.93
i-butane	0.26
n-butane	0.29
n-pentane	0.14
i-hexane	0.12
n-hexane	0.18
n-heptane	0.72
water	0.5
Total	**100**

The specifications as below are used as inlet or feed for the system.

Inlet natural gas flow rate	= 6225 kmol/h
Inlet liquid flow rate	= 332.4 m^3/h
Carbon dioxide inlet gas composition	= 70 mole%
Inlet gas pressure	= 68.6 bar
Inlet solvent pressure	= 68.6 bar
Inlet gas temperature	= 30 °C
Inlet solvent temperature	= 30 °C

3.2.2. Process Description and Process Flow Diagram

Figure below presents a simplified process flow diagram representing the configuration of proposed carbon dioxide removal system via chemical reactive absorption process by using mixed (AMP + MEA) solvent.
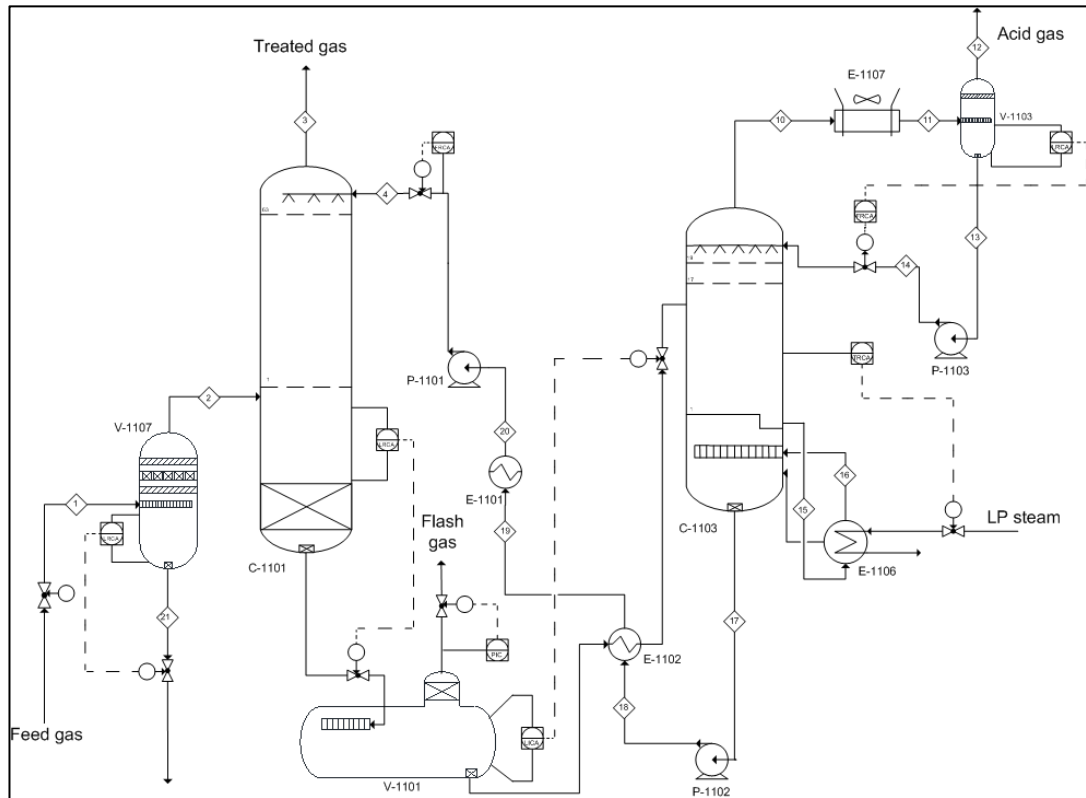

Figure 4: Process Flow Diagram of carbon dioxide removal system

The natural gas will be feed into a feed gas knockout vessel to removed heavy hydrocarbons to prevent the contamination of the solvent prior entering into the absorber column. In the absorber, the gas is inlet at bottom and liquid is sprayed from top of the column where the carbon dioxide is absorbed from the gas into the countercurrent liquid solvent. Then, this solvent is saturated with carbon dioxide and is called rich solvent in which it is flowed to the flash vessel to partially flash off the carbon dioxide. Then, the rich solvent is passed through a lean and rich heat exchanger to recover heat from lean solvent to the rich solvent. Pressure is dropped and the rich solvent is inlet into a regenerator whereby the carbon dioxide is approximately total stripped off from the solvent with the aid of a reboiler. And the lean solvent regenerated is cooled down through exchangers and then recirculate back to the absorber.

According to Sohbi, et al., for the success of simulation and design of flow sheet for carbon dioxide removal using chemical reactive absorption, several major equipments necessary are discussed in table below.

Table 3: Functions of major equipment for simulation using HYSYS

Equipment	Function
Feed gas knockout vessel	To knockout carry over water and heavy hydrocarbon
Absorber column	To remove carbon dioxide by contacting counter current feed with lean solvent to meet the product specification
Regenerator column	To regenerate mixed (AMP + MEA) solvent
Lean solvent cooler	To cool down lean solvent
Lean and rich heat exchanger	To recover heat from lean solvent to rich solvent
Regenerator overhead condenser	To cool down wet carbon dioxide stream in order to condensed water
Regenerator reboiler	To produce enough steam for stripping of carbon dioxide from solvent
Charge pump	To pump lean solvent into absorber
Booster pump	To pump hot lean solvent to lean and rich heat exchanger
Reflux pump	To pump water reflux back to regenerator column
Flash vessel	To flash off entrained light hydrocarbon and partial of the carbon dioxide
Reflux drum	To separate liquid water and carbon dioxide

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Flowsheet Simulation

A flowsheet for carbon dioxide removal system through chemical absorption via AMP solvent has been carried out by using Aspen HYSYS software. The fluid package used in this simulation is Extended Non Random Two Liquid (E-NRTL) package. This is because E-NRTL is more accurate for systems with a wide boiling point range between components and simultaneous solution of vapour-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) are required. The HYSYS simulation is converged and the flowsheet is shown in Figure 5.
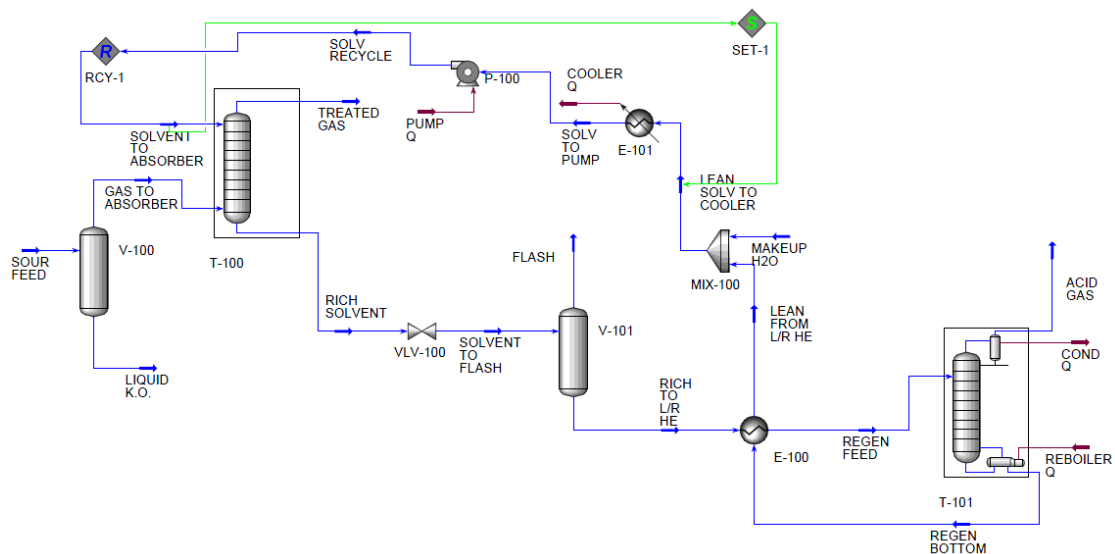
Figure 5: Flowsheet for simulation of CO_2 removal system

In Figure 5, the blue lines denote converged material streams, red lines denote energy streams whereas green line stand for set operation and R stands for recycle operation.

Natural gas which is untreated is contained with carbon dioxide impurities where denote here as sour gas. This sour gas will enter V-100 which is the feed gas knockout vessel in order to removed water and heavy hydrocarbon in the gas stream to prevent contamination of the solvent before entering into the absorber column (T-100). At T-100, sour gas is entered at the bottom of the column and lean liquid solvent is sprayed from top of the column in which the carbon dioxide is absorbed from the gas into the countercurrent liquid solvent.

Then, this solvent is saturated with carbon dioxide and is called rich solvent where it is flowed to the flash vessel (V-101) to partially flash off the carbon dioxide. After that, the rich solvent is passed through a lean and rich heat exchanger (E-100) to recover heat from lean solvent to the rich solvent. Pressure is dropped and the rich solvent is inlet into a regenerator (T-101) whereby the carbon dioxide is approximately total stripped off from the solvent with the aid of a reboiler. And the lean solvent regenerated is cooled down through exchangers (E-100 and E-101) and then recirculate back to the absorber.

4.2 Effect of parameters on Performance of Carbon Dioxide Removal

For the second part of the project, the effects of parameters including temperature, pressure and concentration of AMP in the solvent, on the performance of carbon dioxide removal have been investigated. The performance of carbon dioxide removal has been quantified in terms of carbon dioxide loading which is calculated by dividing molar flow rate of carbon dioxide absorbed into the solvent by the molar flow rate of amine solvent.

$$CO_2 \ loadings = \frac{molar \ flow \ rate \ of \ CO_2 \ absorbed}{molar \ flow \ rate \ of \ amine} \qquad (7)$$

The unit for CO_2 loading is mole of CO_2/mole of amine.

4.2.1 Effect of different temperature of solvent on CO_2 loadings

In this part, simulations have been carried out for different temperature from 30 ℃ to 55 ℃ with different concentration of mixed solvent between AMP and MEA. The pressure of absorber was kept constant and the solvent weight percent is kept constant at a total of 30 wt% of total amine. The flow rate of each mixed solvent concentration inserted into the HYSYS software is shown in Table 4.

Table 4: Flow rate of AMP and MEA in the mixed solvent

	Solvent wt%			
AMP	30	20	10	0
MEA	0	10	20	30
	Amine in solvent, kmol/h			
AMP	476.90	320.74	161.80	0
MEA	0	234.03	472.23	714.70
Total amine	476.90	554.77	634.03	714.70
Total Solvent flow rate	5983	6109	6238	6369

Then, the result which is the amount of carbon dioxide absorbed by each mixed solvent at different temperature is obtained and shown in the Table 5.

Table 5: Amount of carbon dioxide removed at different temperature and concentrations of mixed solvent

	Concentration of solvent (wt%)			
AMP	30	20	10	0
MEA	0	10	20	30
Temperature (℃)	CO_2 Removed (kmol/h)			
30	194.02	203.15	212.61	222.42
35	176.60	184.95	193.62	202.61
40	161.86	169.52	177.52	185.79
45	149.38	156.50	163.87	171.53
50	138.81	145.43	152.30	159.42
55	129.85	136.05	142.48	149.15

After obtaining the amount of carbon dioxide being absorbed into the mixed solvent, the carbon dioxide loadings are calculated with Equation (7) and results are shown in Table 6.

Table 6: CO_2 loadings at different temperature and concentrations of mixed solvent

	Concentration of solvent (wt%)			
AMP	30	20	10	0
MEA	0	10	20	30
Temperature (℃)	**CO_2 Loading (Mole CO_2/mole amine)**			
30	0.41	0.37	0.34	0.31
35	0.37	0.33	0.31	0.28
40	0.34	0.31	0.28	0.26
45	0.31	0.28	0.26	0.24
50	0.29	0.26	0.24	0.22
55	0.27	0.25	0.22	0.21

The graph of carbon dioxide loadings versus different temperatures for different concentrations of solvent is plotted.
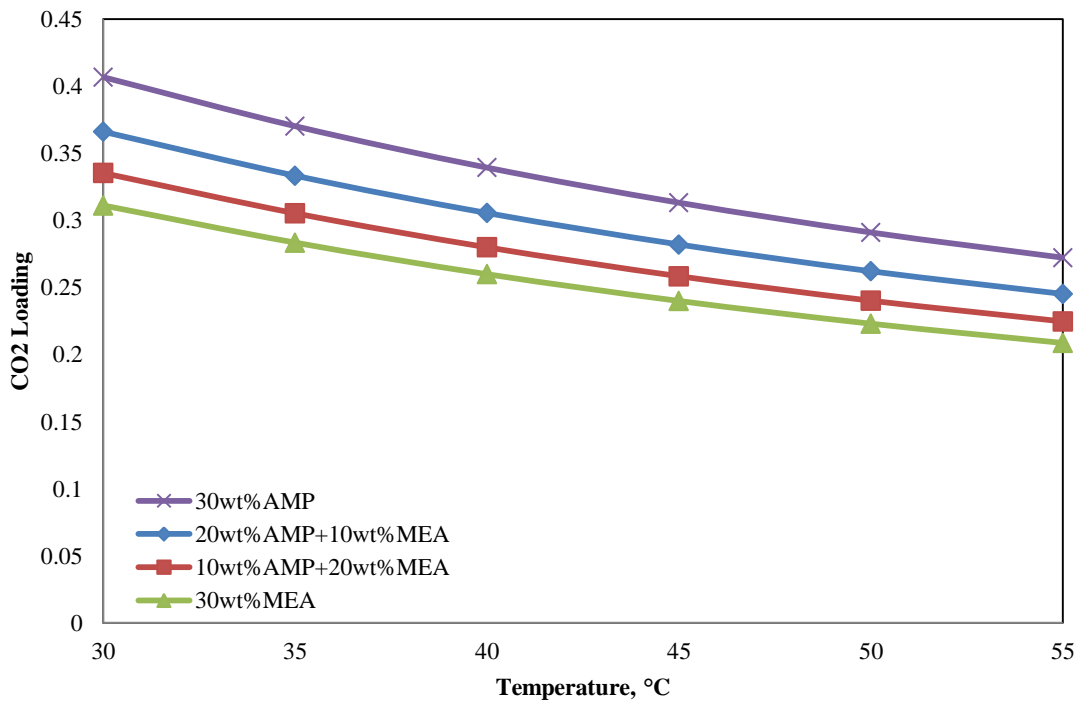

Figure 6: Graph of carbon dioxide loadings versus different temperatures for different concentration of solvent

From Figure 6, the graph shows a trend that absorption favours lower temperature. This is because the CO_2 loading decreases as temperature increases. As in the graph, for 30 wt % AMP, CO_2 loading at 30 ℃ is 0.41 whereas at 55 ℃ is 0.27 mole of CO_2/mole of AMP. For 20 wt% AMP + 10 wt% MEA, the CO_2 loading decreases gradually as the temperature increases from 30 ℃ to 55 ℃ with 0.37 to 0.24 mole CO_2/mole amine. Moreover, for 10 wt% AMP + 20 wt% MEA, it is 0.34 to 0.22 mole CO_2/mole amine and for 30 wt% MEA, it is 0.31 to 0.21 mole CO_2/ mole amine when temperature increases from 30 ℃ to 55 ℃. Hence, it is shown that lower temperature, CO_2 absorption will be highest and more CO_2 can be removed from the gas stream at lower temperature.

4.2.2 Effect of Different Pressure on the CO_2 Loadings

Then, simulations have been repeated with temperature kept constant at 30 ℃ but at different pressure of the system ranging from 10 to 70 bar. The flow rate of each mixed solvent concentration inserted into the HYSYS software is shown in Table 7.

Table 7: Flow rate of AMP and MEA at different concentration of solvents

	Concentration of solvent wt%			
AMP	30	20	10	0
MEA	0	10	20	30
	Amine in Solvent (kmol/h)			
AMP	476.90	314.10	161.80	0
MEA	0	229.19	472.23	714.70
Total	476.90	543.29	634.03	714.70
Total Solvent flow rate	5983	6109	6238	6369

Then, simulation was run for each concentration of solvents at different pressures and amount of CO_2 absorbed from the gas stream into the solvent are obtained and tabulated in Table 8.

Table 8: Amount of CO_2 absorbed at different pressures

Concentration of solvent (wt%)			
AMP	30	20	10	0
MEA	0	10	20	30
Pressure (bar)	CO$_2$ Removed (kmol/h)		
10	30.49	31.90	33.36	34.87
20	58.95	61.76	64.64	67.63
30	87.49	91.62	95.94	100.39
40	116.05	121.57	125.76	131.58
50	144.70	149.30	156.28	163.51
60	170.29	178.32	186.63	195.26
70	197.88	207.19	216.84	226.84

The performance of carbon dioxide removal is evaluated by calculating the CO_2 loadings using Equation (7) and results are shown in Table 9.

Table 9: CO_2 loadings at different pressures

Concentration of solvent (wt%)			
AMP	30	20	10	0
MEA	0	10	20	30
Pressure bar	CO$_2$ Loading mole CO$_2$/mole amine		
10	0.06	0.06	0.05	0.05
20	0.12	0.11	0.10	0.09
30	0.18	0.17	0.15	0.14
40	0.24	0.22	0.20	0.18
50	0.30	0.27	0.25	0.23
60	0.36	0.33	0.29	0.27
70	0.41	0.38	0.34	0.32

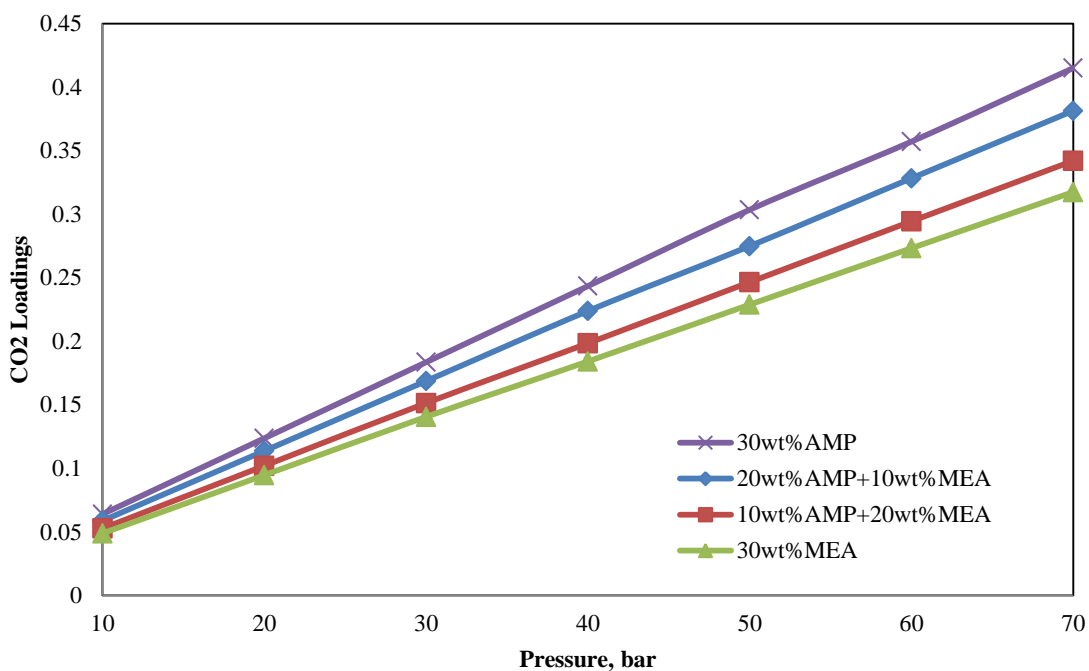The graph of CO_2 loadings versus different pressures for different concentration of solvent is plotted.

Figure 7: Graph of CO_2 loadings versus different pressures for different concentration of solvent

Figure 7 shows that absorption of carbon dioxide by amine solvent is proportional to the pressure. So, higher the pressure, more carbon dioxide will be removed. For 30 wt% AMP, CO_2 loading is 0.06 mole CO_2/ mole amine at 10 bar and 0.41 mole CO_2/ mole amine at 70 bar; for 20 wt% AMP with 10 wt% MEA, CO_2 loading is 0.06 mole CO_2/ mole amine at 10 bar and 0.38 mole CO_2/ mole amine at 70 bar; for 10 wt% AMP with 20 wt% MEA, CO_2 loading is 0.05 mole CO_2/ mole amine at 10 bar and 0.34 mole CO_2/ mole amine at 70 bar; whereas for 30 wt% MEA, CO_2 loading is 0.05 mole CO_2/ mole amine at 10 bar and 0.32 mole CO_2/ mole amine at 70 bar. This shows that at 70 bar which is the highest pressure tested, the carbon dioxide absorption into the solvent is higher. Hence, carbon dioxide removal through absorption has better performance at higher pressure.

4.2.3 Effect of Different Concentrations of AMP and MEA Solvent

In this section, the effects of different concentration of AMP and MEA in the solvent on the performance of carbon dioxide removal are tested. The simulation was run for a total 30 wt% of amine with 10 wt% increment/decrement of each solvent, which are 30 wt% AMP with absence of MEA, 20 wt% of AMP with 10 wt% MEA, 10 wt% AMP with 20 wt% of MEA and followed by 30 wt% MEA with absence of AMP. The temperature profiles of absorber for different concentration of solvent are shown in Table 10.

Table 10: Temperature profile of different concentration of solvent for each stages

Stages	Temperature for different concentration of solvent			
	30wt%AMP	20wt%AMP+ 10wt%MEA	10wt%AMP+ 20wt%MEA	30wt%MEA
1	32.07	32.18	32.29	32.40
2	33.21	33.32	33.43	33.54
3	33.70	33.79	33.89	33.98
4	33.91	33.99	34.07	34.15
5	34.00	34.07	34.15	34.22
6	34.04	34.11	34.18	34.25
7	34.03	34.11	34.19	34.26
8	34.05	34.12	34.20	34.25
9	34.06	34.13	34.20	34.26
10	34.07	34.13	34.20	34.26
11	34.08	34.13	34.20	34.26
12	34.07	34.13	34.20	34.26
13	34.07	34.13	34.20	34.26
14	34.07	34.13	34.19	34.26
15	34.07	34.13	34.19	34.26
16	34.07	34.13	34.19	34.25
17	34.07	34.13	34.20	34.26
18	34.06	34.13	34.19	34.25
19	34.06	34.13	34.19	34.25
20	34.06	34.13	34.19	34.26
21	34.06	34.13	34.19	34.26
22	34.06	34.13	34.20	34.26
23	34.06	34.13	34.20	34.26
24	34.06	34.13	34.19	34.26
25	34.06	34.13	34.19	34.26

26	34.06	34.13	34.19	34.26
27	34.06	34.13	34.19	34.26
28	34.06	34.13	34.19	34.26
29	34.05	34.13	34.19	34.26
30	34.06	34.13	34.19	34.26
31	34.06	34.12	34.19	34.26
32	34.06	34.12	34.20	34.26
33	34.06	34.12	34.19	34.26
34	34.06	34.12	34.19	34.26
35	34.06	34.12	34.19	34.25
36	34.06	34.12	34.19	34.25
37	34.06	34.12	34.19	34.25
38	34.06	34.12	34.19	34.25
39	34.06	34.12	34.19	34.25
40	34.06	34.12	34.19	34.25
41	34.06	34.12	34.19	34.25
42	34.06	34.12	34.19	34.25
43	34.06	34.12	34.19	34.24
44	34.06	34.12	34.19	34.24
45	34.06	34.12	34.19	34.25
46	34.05	34.12	34.17	34.25
47	34.05	34.12	34.19	34.25
48	34.05	34.12	34.19	34.25
49	34.05	34.12	34.18	34.25
50	34.05	34.12	34.18	34.25
51	34.05	34.12	34.18	34.25
52	34.05	34.12	34.18	34.25
53	34.05	34.12	34.15	34.25
54	34.05	34.12	34.17	34.25
55	34.05	34.11	34.18	34.25
56	34.05	34.12	34.18	34.25
57	34.05	34.12	34.18	34.25
58	34.05	34.12	34.18	34.25
59	34.05	34.12	34.18	34.25
60	34.00	34.07	34.13	34.19

The graphs of temperature profiles of absorber for different concentration of solvent are shown as below.
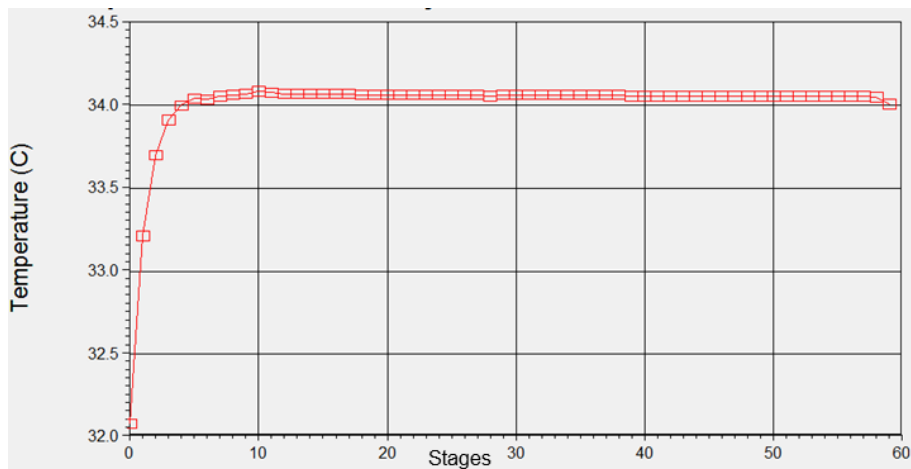

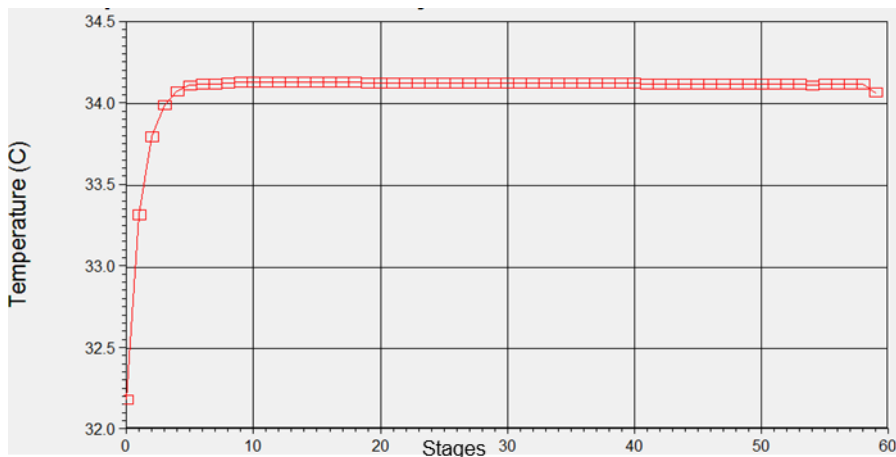Figure 8: Temperature profiles of absorber for 30 wt% AMP solvent

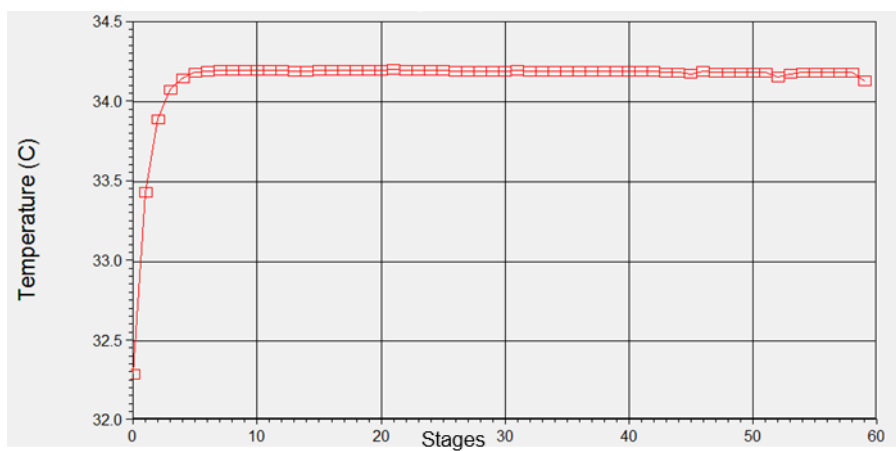Figure 9: Temperature profiles of absorber for 20 wt% AMP + 10 wt% MEA solvent

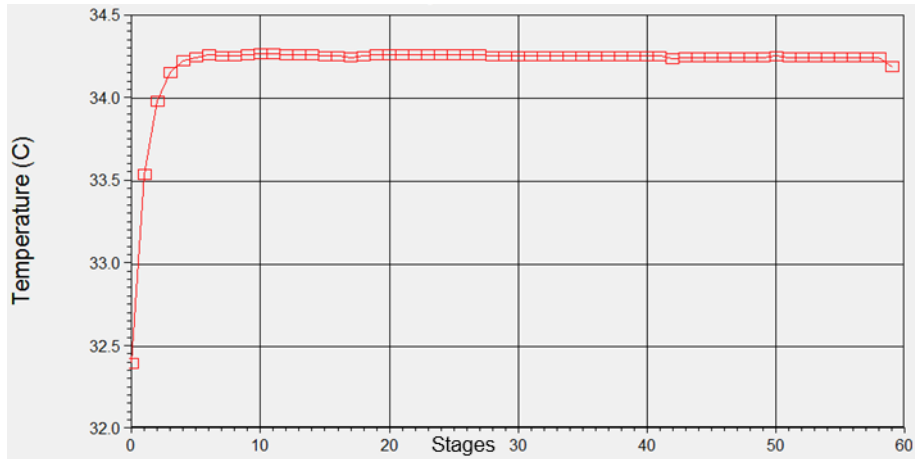Figure 10: Temperature profiles of absorber for 10 wt% AMP + 20 wt% MEA solvent

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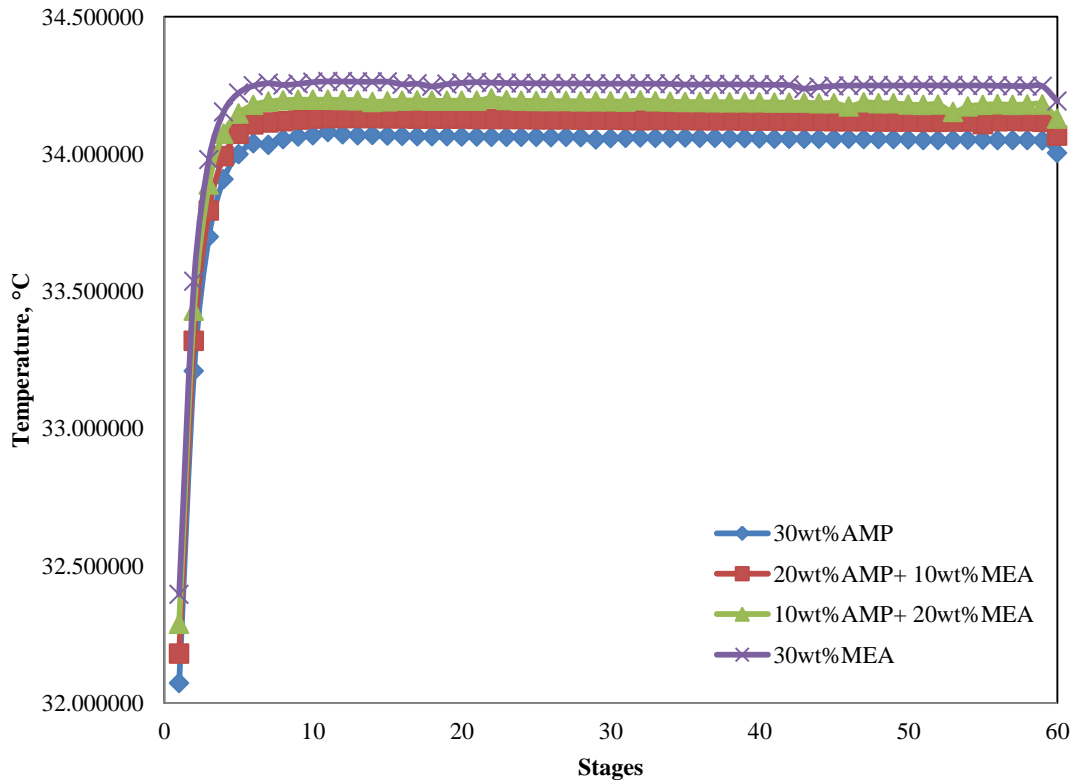Figure 11: Temperature profiles of absorber for 30 wt% MEA solvent

Figure 12: Graph of temperature versus stages for each concentration of solvent

From Figure 12, it is shown that AMP will have lower heat of absorption than MEA. This is because the temperature across the stages is lowest for 30 wt% AMP and the highest is 30 wt% MEA.

The pressure profile for each different concentration of solvent are observed (tabulated in Table 11) and a graph (Figure 14) is plotted to compare the difference. The pressure across the stages for each concentration of solvent is the same, which is as below.
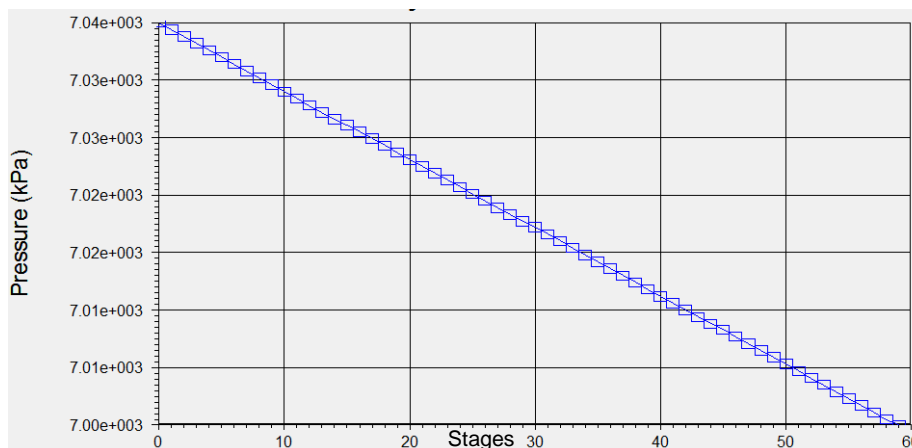

Figure 13: Pressure profile versus stages for different concentration of solvent

Table 11: Pressure profile for different concentration of solvent

Stages	Pressure for different concentration of solvent			
	30wt%AMP	20wt%AMP+ 10wt%MEA	10wt%AMP+ 20wt%MEA	30wt%MEA
1	7035	7035	7035	7035
2	7034.41	7034.41	7034.41	7034.41
3	7033.81	7033.81	7033.81	7033.81
4	7033.22	7033.22	7033.22	7033.22
5	7032.63	7032.63	7032.63	7032.63
6	7032.03	7032.03	7032.03	7032.03
7	7031.44	7031.44	7031.44	7031.44
8	7030.85	7030.85	7030.85	7030.85
9	7030.25	7030.25	7030.25	7030.25
10	7029.66	7029.66	7029.66	7029.66
11	7029.07	7029.07	7029.07	7029.07
12	7028.47	7028.47	7028.47	7028.47
13	7027.88	7027.88	7027.88	7027.88
14	7027.29	7027.29	7027.29	7027.29
15	7026.69	7026.69	7026.69	7026.69
16	7026.10	7026.10	7026.10	7026.10
17	7025.51	7025.51	7025.51	7025.51
18	7024.92	7024.92	7024.92	7024.92
19	7024.32	7024.32	7024.32	7024.32

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|			
20	7023.73	7023.73	7023.73	7023.73
21	7023.14	7023.14	7023.14	7023.14
22	7022.54	7022.54	7022.54	7022.54
23	7021.95	7021.95	7021.95	7021.95
24	7021.36	7021.36	7021.36	7021.36
25	7020.76	7020.76	7020.76	7020.76
26	7020.17	7020.17	7020.17	7020.17
27	7019.58	7019.58	7019.58	7019.58
28	7018.98	7018.98	7018.98	7018.98
29	7018.39	7018.39	7018.39	7018.39
30	7017.80	7017.80	7017.80	7017.80
31	7017.20	7017.20	7017.20	7017.20
32	7016.61	7016.61	7016.61	7016.61
33	7016.02	7016.02	7016.02	7016.02
34	7015.42	7015.42	7015.42	7015.42
35	7014.83	7014.83	7014.83	7014.83
36	7014.24	7014.24	7014.24	7014.24
37	7013.64	7013.64	7013.64	7013.64
38	7013.05	7013.05	7013.05	7013.05
39	7012.46	7012.46	7012.46	7012.46
40	7011.86	7011.86	7011.86	7011.86
41	7011.27	7011.27	7011.27	7011.27
42	7010.68	7010.68	7010.68	7010.68
43	7010.08	7010.08	7010.08	7010.08
44	7009.49	7009.49	7009.49	7009.49
45	7008.90	7008.90	7008.90	7008.90
46	7008.31	7008.31	7008.31	7008.31
47	7007.71	7007.71	7007.71	7007.71
48	7007.12	7007.12	7007.12	7007.12
49	7006.53	7006.53	7006.53	7006.53
50	7005.93	7005.93	7005.93	7005.93
51	7005.34	7005.34	7005.34	7005.34
52	7004.75	7004.75	7004.75	7004.75
53	7004.15	7004.15	7004.15	7004.15
54	7003.56	7003.56	7003.56	7003.56
55	7002.97	7002.97	7002.97	7002.97
56	7002.37	7002.37	7002.37	7002.37
57	7001.78	7001.78	7001.78	7001.78
58	7001.19	7001.19	7001.19	7001.19
59	7000.59	7000.59	7000.59	7000.59
60	7000	7000	7000	7000
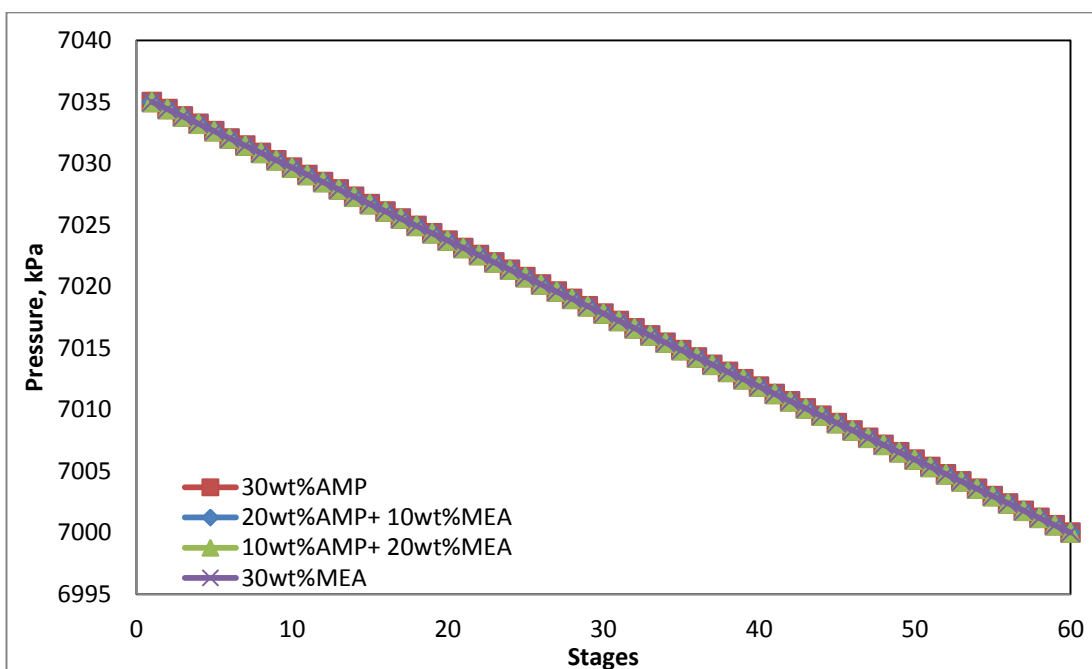
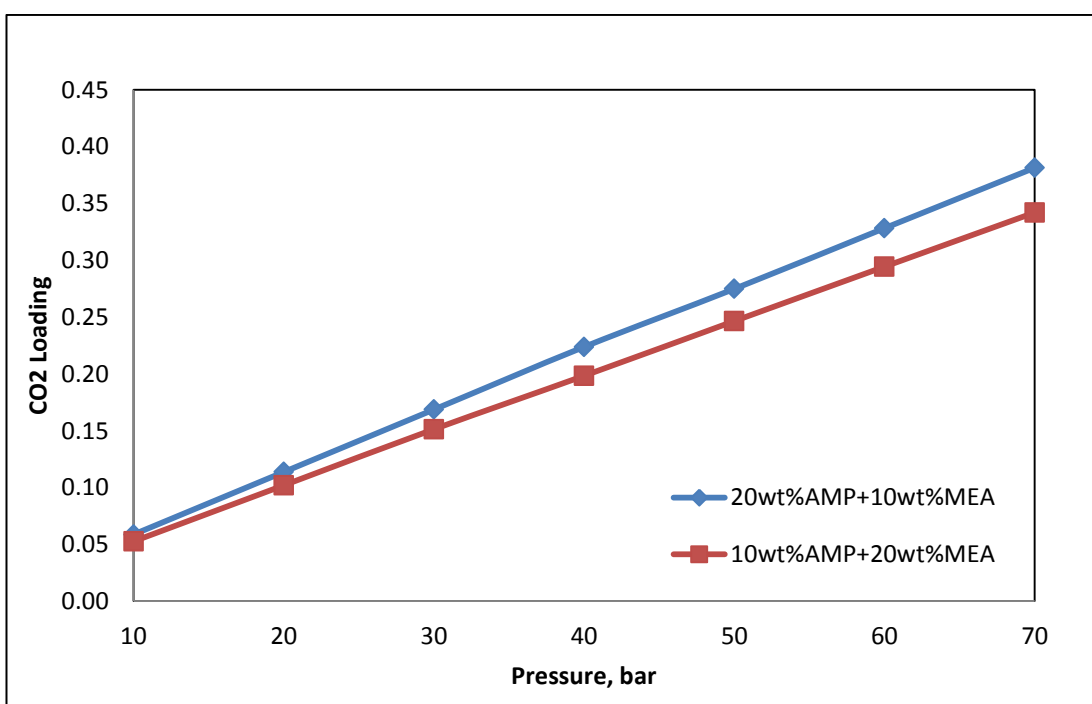Figure 14: Graph of Pressure versus stages for different concentration of solvent

Figure 15: Graph of CO_2 loadings at different pressure for different mixed solvent

From Figure 15, 20 wt% AMP + 10 wt% MEA solvent has higher CO2 loadings from 10 bar to 70 bar compared to 10 wt% AMP + 20 wt% MEA solvent. Hence, it is proven that sterically hindered amine, AMP have better performance in carbon dioxide loadings compared to conventional amine, MEA. With higher concentration

of AMP in the mixed solvent, more carbon dioxide will be absorbed into the solvent and removed from the gas stream.
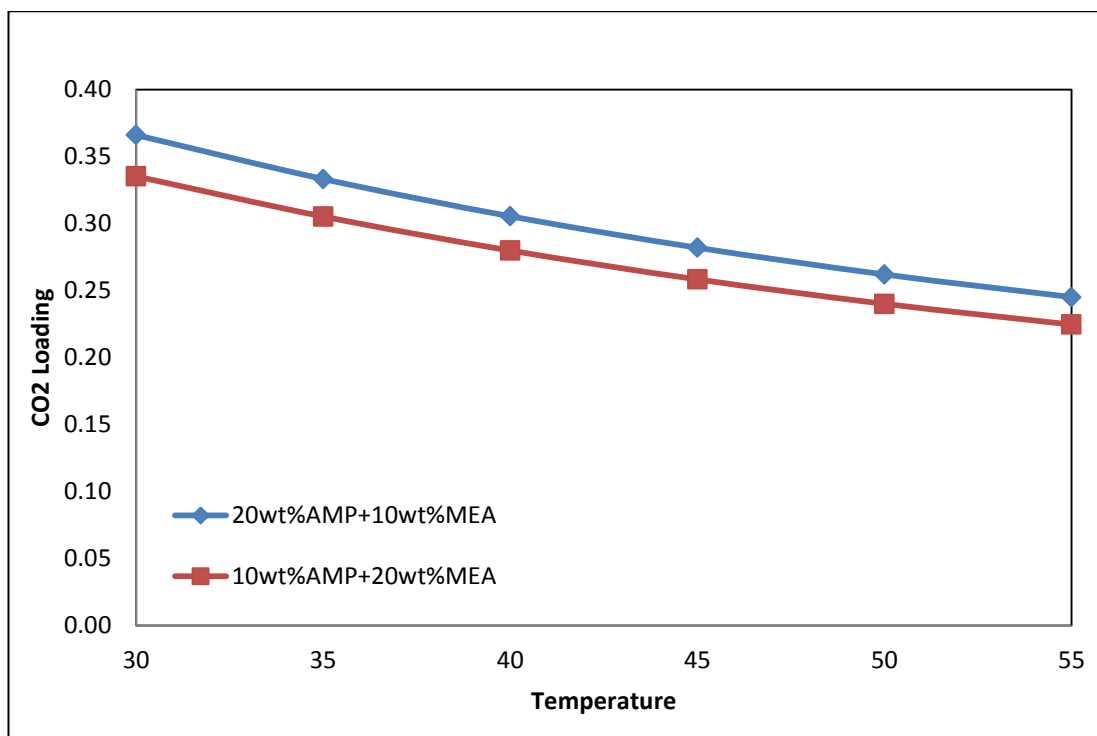

Figure 16: Graph of CO_2 loadings at different temperature for different mixed solvent

Besides, in Figure 16, it is shown that AMP has better performance than MEA regardless at any temperature. Simulation with 20 wt% AMP + 10 wt% MEA solvent exhibit higher CO_2 loading at each temperature from 30 °C to 55 °C compared to simulation with 10 wt% AMP + 20 wt% MEA solvent. Thus, it is proven that higher concentration of AMP in the mixed solvent will have higher performance of carbon dioxide removal.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

In this project, a flowsheet simulation of removal of carbon dioxide through chemical reactive absorption process with mixed (AMP+MEA) solvent was developed using Aspen HYSYS. The simulation provides the basic to study the effects of temperature, pressure and concentration of solvent on the performance of carbon dioxide removal in actual case. The simulation is converged and the conditions are tested to obtain the optimum operating condition prior applying into industrial case. The results show that chemical reactive absorption favors low temperature and high pressure. For mixed solvent of 20 wt% AMP + 10 wt% MEA, CO_2 loading is higher for temperature at 30 ℃ (0.3662 mole CO_2/mole amine) than at 55 ℃ (0.2452 mole CO_2/mole amine); and the CO_2 loading is higher for pressure at 70 bar (0.3814 mole CO_2/mole amine) compared to that at 10 bar (0.0587 mole CO_2/mole amine). Besides, it also proves that the sterically hindered amine, AMP exhibits a better performance in carbon dioxide removal compared to MEA from the conventional solvent at any temperature and pressure. From the simulation, at temperature of 30 ℃ and pressure of 68.6 bar, the CO_2 loading of 30 wt% AMP (0.4068 mole CO_2/mole amine) is higher than that in 30 wt% MEA (0.3112 mole CO_2/mole amine). Hence, sterically hindered amine, AMP is a solvent that is worth to be invested in industrial for more efficient carbon dioxide removal. Therefore, the objectives of this project are achieved.

5.2. Suggested Future Work

The future expansion which can be done is to conduct simulation of the carbon dioxide removal by using other simulation software. This can be done to validify the trend of the effects of the temperature, pressure and concentration on the carbon dioxide removal performance.

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