Kinetics Modelling of CO_2 Reactive Absorption from Natural Gas using MATLAB

by

Nurhamizah Binti Ismail

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

JANUARY 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Kinetics Modelling of CO_2 Reactive Absorption from Natural Gas using MATLAB

by

Nurhamizah Binti Ismail

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Murni Melati Ahmad)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2010

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.

_____

NURHAMIZAH BINTI ISMAIL

ABSTRACT

Natural gas is a reliable source of energy. However, raw natural gas is also composed of impurities such as hydrogen sulphide (H_2S) and carbon dioxide (CO_2). The removal of these acid gases is a significant operation in gas processing but amine solutions such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) can only treat natural gas containing less than 20% concentration of CO_2. This research project mainly focuses on the kinetics modeling of reactive absorption of CO_2 from raw natural gas, that uses aminated resin to reduce the CO_2 concentration to 20% so that the current acid gas removal system at the gas refineries can further process the gas. As a starting point, a rigorous numerical mass-transfer model was employed to study the kinetics of the aminated resin, following the work done by Rinker et al [5]. The kinetics behavior was simulated in MATLAB. With the reaction rate kinetics found, together with the equilibrium constant found using the correlations proposed in past literatures, the liquid bulk concentration for the aminated system was determined.

Keywords: Kinetics modelling, reactive absorption, CO_2 removal

ACKNOWLEDGEMENTS

First and foremost, I would like to express my gratefulness towards the Almighty God, for His love and blessing upon me throughout the execution of this Final Year Project until I manage to finish this dissertation successfully.

I owe sincere and earnest thankfulness to Dr Murni Melati Ahmad for her guidance given, constructive comments and support as my Final Year Project supervisor. Her encouragement throughout these two semesters has been very important for me to be able to work on this project. I am sure this project would have not been possible without her help.

The appreciation also goes to my parents who had never failed to support their daughter both mentally and spiritually in the time frame of this Final Year Project execution. Not being forgotten, thank you to all my beloved housemates and coursemates for the constant support given and valuable information sharing that had ease the execution of this project and dissertation writing.

Finally, I would like to thank the people whose name I did not mention but had directly or indirectly contributed towards this Final Year Project execution and dissertation writing. I am truly indebted and thankful to you all. Again, thank you very much to all.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATION AND NOMENCLATURES

a	specific area of the packed bed
AMP	2-amino-2-methyl-1-propanol
CO_2	Carbon Dioxide
DEA	Diethanolamine
EIA	Energy Information Administration
GMS	Generalized Maxwell Stefan
H_2O	Water
H_2S	Hydrogen Sulphide
IA	Immobilized amine
k_{app}	Apparent rate coefficient for the reaction between CO_2 and amine solution
k_{eff}	Effective mass transfer coefficient
k_i	Forward rate coefficient of reaction (i)
k_{-i}	Reverse rate coefficient of reaction (i)
K_i	Equilibrium constant for reaction (i)
MDEA	N-methyldiethanolamine
MEA	Monoethanolamine
NaCl	Sodium Chloride
q	Solid phase concentration
q_{eq}	Equilibrium solid phase concentration

CHAPTER 1: INTRODUCTION

1.1. Background

Natural gas is a combustible mixture of hydrocarbon gases that is colourless, shapeless and odourless in its pure form. It gives off an enormous deal of energy when combusted and is a vital component of the world's supply of energy. Unlike other fossil fuel such as coal and crude oil, natural gas emits lower level of potentially harmful byproducts into the air when burnt. It is known as one of the cleanest, safest, and most useful of all energy sources [1]. The need for energy has elevated natural gas to such a level of importance in our society and living.

Energy Information Administration (EIA) reported that energy from natural gas accounts for 23% of total energy consumed in the United State [13]. Uses of natural gas vary from commercial use to industry. Figure 1-1 shows the distribution of natural gas use per sector.

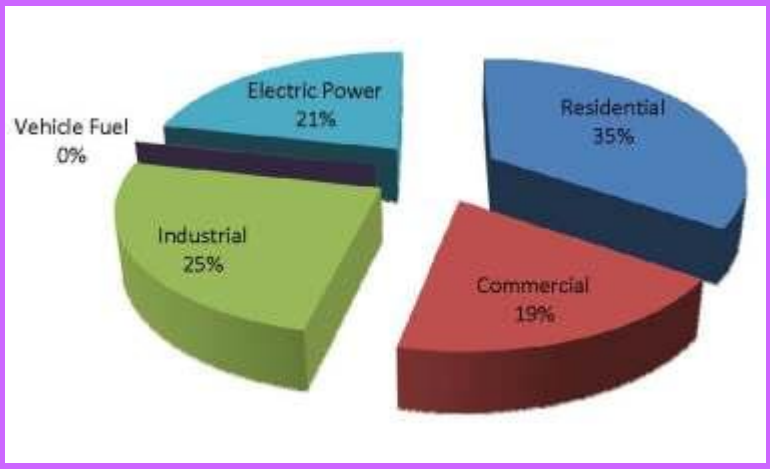

Figure 1-1: Natural Gas Use by Sector [13]

The composition of natural gas varies widely. Apart from hydrocarbons, natural gas from some well contains significant amount of CO_2. Table 1-1 shows the typical composition of natural gas before it is refined.

Table 1-1: Typical Composition of Natural Gas[1]

Component	Formula	Composition
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen Sulphide	H_2S	0-5%
Rare gases	A, He, Ne, Xe	Trace

CO_2, when react with water creates carbonic acid that is corrosive. It also reduces the energy value of gas. In concentration of more than 2% or 3%, the gas is unmarketable[2]. The removal of acid gases such as CO_2 is often referred to gas sweetening process. Removing CO_2 will increase the heating value of the natural gas and as well prevent corrosion of the pipelines and the process equipment. Crystallization of CO_2 during cryogenic process will also be avoided in the liquefaction process [11].

CO_2 can be removed by a number of ways. Four major processes available are absorption process, adsorption process, physical separation and hybrid solution [12]. CO_2 removal via absorption process can be divided into two. One is physical absorption and the other one is chemical absorption. Physical absorption process involved the use of organic solvent to physically absorb gas component. Among the famous physical absorption process is Selexol process, Rectisol process and Flour process [12].

In the industry, CO_2 is widely removed by amine treating through absorption and chemical reaction, where most of the reactions are reversible. In this case, reactive material (amine solvent) removes CO_2 at high pressure and low temperature. The secondary amine diethanolamine (DEA) and the tertiary amines N-methydiethanolamine (MDEA) are among the most commonly used alkanolamines

[5]. Primary amine monoethanolamine (MEA) are also has been used extensively because of its high reactivity and low solvent cost. However, its maximum CO_2 loading is limited to 0.5 mol of CO_2 per mole of amine.

Mixed amine solutions were introduced to increase the loading [9]. Primary and secondary amine such as MEA and DEA that have high reaction rate is combined with tertiary amine with high equilibrium capacity. Other than MDEA, sterically-hindered primary amine, 2-amino-2methyl-1-propanol (AMP) is also used in blending with other primary and secondary amine to produce better amine solutions.

In 2006, PETRONAS has presented that over 13 Tscf of hydrocarbon gas remains undeveloped in high CO_2 fields [25]. Reported that average peninsular Malaysia hydrocarbon gas fraction is 54% while the rest is CO_2. In Sarawak, average CO_2 fraction in a total of 5 fields was 72%. Thus, due to the limitations in amine solution performance, aminated resin is to be used in order to treat the high CO_2 content in raw natural gas unexplored reserves.

1.2. Problem Statement

In some reserves which have not been explored, the composition of carbon dioxide in raw natural gas is found to be high. For example, the CO_2 content in Bujang Field (Penisular Malaysia) is 66 mol% [25]. Amine solutions which are widely used for acid gases treatment in refinery could not handle the high composition of carbon dioxide in raw natural gas. Current proven technology that is commercially and economically available for efficient removal of CO_2 from natural gas to pipeline and cryogenic quality natural gas is only limited to low CO_2 concentration, which is up to 20% only. Therefore, a new system which is located at the reserves itself is proposed to be set up to reduce the concentration to meet the downstream demand that can next be treated by the existing amine system at refinery. The absorption of carbon dioxide in the new system will be done by using aminated resin. The difference between this aminated resin and the existing amine solution is, this aminated resin will be producing solid as a result of the absorption process. The aminated resin performance capability in absorbing carbon dioxide from raw natural gas as well as the best operating parameters for the reaction is to be further studied

via modelling and simulation of the relevant reactions in MATLAB. This is due to the extensive and exhaustive range of operation that is feasible for the system hence making the experimental work quite expensive and limited.

1.3. Objectives

1. To screen and identify mathematical models that represents reactive absorption kinetics of CO_2 removal from natural gas using the aminated resin for off-shore application
2. To use the developed model to estimate the kinetic rate coefficient of the aminated resin
3. To estimate the Arrhenius equation of the aminated resin
4. To estimate the liquid bulk concentration of the aminated resin system using correlation proposed in past literatures.

1.4. Scope of Study

This research project focused on modelling the kinetics behaviour of carbon dioxide reactive absorption from raw natural gas using aminated resin for the off-shore application in order to treat the natural gas at reserves having high pressure and high CO_2 concentration. The need of this aminated resin is to absorb the carbon dioxide that is found high in concentration in certain reserves that are not yet being explored to 20% that can be then treated by existing amine system available at gas refineries. This new system is to be installed at the reserves itself, where the feed gas is of high pressure and high partial pressure in CO_2. CO_2 concentration of the gas reserves were assumed to range between 30 to 70% of the feed gas concentration. The reaction between CO_2 and this aminated resin will result in solid particle formation, due to the chemistry of the aminated resin itself. Mathematical model that best represents reactive absorption of carbon dioxide will be identified through literature study. Modelling of the kinetics behaviour and simulation process will be done using MATLAB. Feasibility study for the best operating parameters for the reactive absorption process to take place will be carried out at the end of the study.

CHAPTER 2: LITERATURE REVIEW AND THEORY

A raw natural gas containing acid gas impurities such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) must be treated before it can be used. This removal of acid gas impurities is a significant operation in gas processing. The purification process is to make sure that the raw natural gas meets the quality standards specified by major pipeline transmission and distribution companies. The quality standards vary from pipeline to pipeline and are usually a function of a pipeline system's design and the markets that it serves. Among the standard specified for natural gas is to contain no more than trace amounts of H_2S and CO_2 [3].

Reaction between CO_2 and amine solution will produce zwitterions intermediate which will then be deprotonated by a base to produce carbamate ions[5]. There are two limiting cases in zwitterions mechanism which relates to the reaction order. When zwitterions formation is rate limiting, the reaction rate is first order in both the amine and CO_2 concentrations. The second limiting case is when zwitterion deprotonation is rate limiting. Overall reaction rate appears to have a fractional order between 1 and 2 in the amine concentration. In the case of monoethanolamine (MEA), the reaction rate follows the first case [10] while for diethanolamine (DEA) and 2-amino-2-methyl-1-propanol (AMP), a sterically-hindered primary amine, the second case is observed.

2.1. Amine System for CO_2 Removal

Amine gas treating process is commonly used to reduce the acid gases impurities to acceptable level. The alkanolamine process has been considered the best approach in removing H_2S and CO_2 acid gases from natural gas. It is based on the reaction of a weak base (alkanolamine) and a weak acid (H_2S and/or CO_2) to give a water-soluble amine acid gas salt [4]. Secondary amine, diethanolamine (DEA) and the tertiary amine, N-methyldiethanolamine (MDEA) are among the alkanolamines that are most commonly used. Compared to tertiary amines, secondary amines are often used to absorb CO_2 because of the faster reaction. For H_2S removal, tertiary amines are more selective. The best performance can be achieved by using blends of DEA and MDEA [5].

Rinker et al. in their work has summarized the result of past literatures done on kinetics of reaction between CO_2 and aqueous DEA. All but one reported the kinetics to be fractional orders between 1 and 2 with respect to DEA concentration [5]. However, the experiments were done under transient batch conditions and there is very limited kinetic data for temperatures other than 298 K. Rinker et al. in their work measured the rate of absorption of CO_2 into aqueous diethanolamine (DEA) solutions in a laminar liquid jet absorber under continuous, steady-state conditions, over the temperature range of 293 – 343 K and wide range of DEA concentrations.

The kinetic rate coefficients were estimated from the experimental absorption data using rigorous mass-transfer model that they developed based on penetration theory. For this, all the chemical reactions are considered to be reversible. Formation of zwitterion is represented in the following reaction [5]:

$$CO_2 + RR'NH \overset{k_1, k_{-1}, K_1}{\leftrightarrow} RR'NH^+COO^- \quad (1)$$

Neglecting the other bases and taking DEA as the only base that deprotonates the zwitterions, the deprotonation reaction is as below:

$$RR'NH^+COO^- + RR'NH \overset{k_2, k_{-2}, K_2}{\leftrightarrow} RR'NH_2^+ + RR'NHCOO^- \quad (2)$$

Sum of both reactions gives:

$$CO_2 + 2RR'NH \overset{K_3K_4}{\leftrightarrow} RR'NH_2^+ + RR'NHCOO^- \quad (3)$$

While $K_3K_4 = k_3k_4 / k_{-3}k_{-4}$

Analysis of their experimental data gives the apparent second-order rate coefficient as below:

$$\frac{1}{k_{app}} = \frac{1}{k_3} + \frac{1}{k_3(k_4/k_{-3})[RR'NH]} \quad (4)$$

The Arrhenius equation that fits the rate coefficient estimates of their work are:

$$k_3 = 1.24\ x\ 10^6 \exp\left(-\frac{1701}{T}\right) \quad (5)$$

$$\frac{k_3 k_4}{k_{-3}} = 3.18\ x\ 10^7 \exp\left(-\frac{3040}{T}\right) \quad (6)$$

The result was found to be consistent with the zwitterion mechanism. The authors in the end concluded that, for complicated kinetics such as that of CO_2 with aqueous DEA, employing such a model is the only reliable method for obtaining accurate estimates of the kinetic rate coefficients[5].

Reactive absorption is of a multicomponent nature and its modeling and design is based on a theoretical description of reaction and mass transport in multicomponent systems [6]. Kenig, Wiesner & Gorak (1997) demonstrated the use of Maxwell-Stefan equations for NO_x reactive absorption modelling. Since Maxwell-Stefan equations govern the multicomponent isothermal isobaric diffusion in an ideal gas mixture, some modifications are made to turn it into a generalized form that can be used for the description of real gases and liquids. They develop a film-model-based approach to which allow to deal with liquid-gas reactive absorption units with complex hydrodynamics.

In 1998, Pacheco and Rochelle studied the reactive absorption of CO_2 and H_2S into aqueous methyldiethanolamine (MDEA) using rate-based modelling. They develop a general framework to model the transport processes that take place during reactive absorption. RATEFRAC from Aspen Technology which uses Generalized Maxwell Stefan (GMS) approach was utilized to model the mass and heat transfer processes involved. Both rate- and equilibrium-controlled reactions are considered to occur in the liquid phase. In their work, the Maxwell-Stefan approach to mass transfer is combined it with the enhancement factor theory, which is based on pseudo-binary mass transfer. This was to model both kinetic and equilibrium-controlled reactions [7]. These two theories were found consistent for the first and second-order irreversible reactions showed by Frank in 1995 [7].

In 2001, Kenig, Schneider and Gorak concluded that reactive absorption design is often dominated by the mass transfer rate. The paper highlighted that the mass

transport can be well described based on the Maxwell-Stefan equations which were derived from the kinetic theory of gases [8]. With some modifications, the Maxwell-Stefan equations that governed the multicomponent isothermal isobaric diffusion in an ideal gas mixture can be used for real gases and liquids description [6][8]. Reaction rates can vary over a wide range, in different parts of fluid phases. Sufficient model complexity is required in order to model the process in adequate and for this work, the rate-base approach is applied to the steady state and dynamic modeling of reactive absorption[8].

Aboudheir et al. (2003) had tabulated a summary of the available kinetic data of the reaction between CO_2 and aqueous MEA in past literature [10]. The authors grouped the reaction-rate constants based on decades they were obtained. Observed that the *k* value vary at certain same temperature. For example, at temperature equal to 298 K, the *k* value varies from 3880 to 8400dm^3/mol.s. Thus, in the authors project work, a numerically solved absorption-rate/kinetic model were used to interpret the kinetics data of the reaction between carbon dioxide and high CO_2-loaded, concentrated aqueous solution of MEA obtained in a laminar-jet absorber[10].

In the literatures, the reaction between CO_2 and MEA solution have been describe by two mechanisms which are the zwitterions mechanism that has been discussed earlier and the termolecular mechanism which has been introduced by Crooks and Donnelan [15].Aboudheir et al. [10] discussed on the reactions mechanisms occurred when CO_2 absorbs into and reacts with aqueous MEA. The reactions are as below:

Ionization of water:

$$2H_2O \overset{K_1}{\leftrightarrow} OH^- + H_3O^+ \quad (1)$$

Dissociation of dissolved CO_2 through carbonic acid:

$$CO_2 + 2H_2O \overset{k_2,k_{-2},K_2}{\leftrightarrow} HCO_3^- + H_3O^+ \quad (2)$$

Dissociation of bicarbonate:

$$HCO_3^- + H_2O \overset{K_3}{\leftrightarrow} CO_3^{2-} + H_3O^+ \quad (3)$$

Zwitterion formation from MEA and CO_2 reaction:

$$CO_2 + RNH_2 \overset{k_4,k_{-4},K_4}{\leftrightarrow} RNH_2^+COO^- \quad (4)$$

Carbamate formation by deprotonation of the zwitterion:

$$RNH_2^+COO^- + RNH_2 \overset{k_5,k_{-5},K_5}{\leftrightarrow} RNH_3^+ + RNHCOO^- \quad (5)$$

$$RNH_2^+COO^- + H_2O \overset{k_6,k_{-6},K_6}{\leftrightarrow} H_3O^+ + RNHCOO^- \quad (6)$$

$$RNH_2^+COO^- + OH^- \overset{k_7,k_{-7},K_7}{\leftrightarrow} H_2O + RNHCOO^- \quad (7)$$

Carbamate reversion to bicarbonate (hydrolysis reaction):

$$RNHCOO^- + H_2O \overset{k_8,k_{-8},K_8}{\leftrightarrow} RNH_2 + HCO_3^- \quad (8)$$

Dissociation of protonated MEA:

$$RNH_3^+ + H_2O \overset{k_9,k_{-9},K_9}{\leftrightarrow} RNH_2 + H_3O^+ \quad (9)$$

Bicarbonate formation:

$$CO_2 + HO^- \overset{k_{10},k_{-10},K_{10}}{\leftrightarrow} HCO_3^- \quad (10)$$

All species represented are in aqueous solution. Additional reactions become essential due to the significant concentrations of bicarbonates and carbonates in the aqueous solutions. These two species as well contributes to the zwitterions intermediate formation. The additional reactions are [10]:

$$RNH_2^+COO^- + HCO_3^- \overset{k_{11},k_{-11},K_{11}}{\leftrightarrow} H_2CO_3 + RNHCOO^- \quad (11)$$

$$RNH_2^+COO^- + CO_3^{2-} \overset{k_{12},k_{-12},K_{12}}{\leftrightarrow} HCO_3^- + RNHCOO^- \quad (12)$$

Therefore, the general rate of reaction of CO_2 with MEA via the zwitterions mechanism [10] is described as below:

$$r_{CO_2\text{-MEA}} = \frac{[CO_2][RNH_2] - k_{-4}/k_4[RNHCOO^-](\sum k_{-b}[BH^+]/\sum k_b[B])}{\frac{1}{k_4} + (k_{-4}/k_4 \sum k_b[B])} \quad (13)$$

B designates any base species in the solution that can deprotonates the zwitterions intermediate into carbamate. The termolecular mechanism assumes that the reaction between CO_2 and MEA is of a single-step. The initial product was claimed not to be zwitterions but a loosely bound encounter complex with a mechanism as the next figure:

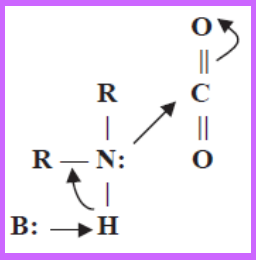

Figure 2-1: Single-step, Termolecular Reaction Mechanism for the Formation of Carbamate [15]

Bond-formation and charge-separation occur only in the second step. The forward reaction rate is as below:

$$r_{CO_2-MEA} = -k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O][RNH_2][CO_2] \quad (14)$$

Aboudheir et al. studied on the reaction between CO_2 and high CO_2 loaded, concentrated aqueous solutions of monoethanolamine (MEA) over the temperature range from 293 to 333 K. The MEA concentration ranged from 3 to 9M, and CO_2 loading from ~0.1 to 0.49 mol/mol. They obtained the experimental kinetic data in a laminar jet absorber at various contact-times between gas and liquid. Interpretation of the data was done with the aid of a numerically solved absorption rate/kinetic model.

With this kinetics model, they obtained results which are found to be in accord with the experimental behavior obtained in laminar jet absorber. In their work, they utilized both mechanisms; zwitterions and termolecular to evaluate the kinetic data to find the explanation of previous literatures' data. From the previous forward reaction equation, the apparent reaction rate expression of the termolecular mechanism was presented by:

$$k_{app} = k_{RNH_2}[RNH_2]^2 + k_{H_2O}[H_2O][RNH_2] \quad (15)$$

Values of k_{RNH_2} and k_{H_2O} were obtained by fitting the experimental k_{app} constants obtained from the absorption-rate/kinetics model [10]. From the data a linear regression analysis then was done and kinetics expressions as below are obtained:

$$k_{RNH_2}=4.61\times10^{9}\exp\left(\frac{-4412}{T}\right) \quad (42)$$

$$k_{H_2O}=4.55\times10^{6}\exp\left(\frac{-3287}{T}\right) \quad (43)$$

Based on both the precious equations, the reversible reaction rate for CO_2 absorption into MEA solutions can then be presented by:

$$r_{CO_2-MEA} = -(k_{RNH_2}[RNH_2]+k_{H_2O}[H_2O])\times\left([RNH_2][CO_2]+\frac{1}{k_{RNH_2}}[RNHCOO^-][H_3O^+]\right) \quad (44)$$

The analysis results by using zwitterions mechanism are found to be the same as those obtained by using termolecular mechanism. Fitting the k_{app} constant, only two parameters were found to fit the experimental data which are k_{RNH_2} and k_{H_2O} which means that only $[RNH_2]$ and $[H_2O]$ are the bases that completed the deprotonation of the zwitterion. The analysis proves that the new developed kinetic model parameter can accurately predict published kinetics data at low concentrations and low loadings according to termolecular reaction mechanism. Together with the aid of numerically solved absorption model, the new model has been used to accurately predict for the first time CO_2 absorption into high CO_2 loaded and highly concentrated aqueous MEA solutions.

2.2. Blends of Amine Solutions

Mandal et al. in 2001 has came out with a paper on modeling of absorption in blended amine solutions. High selectivity and low solvent cost has result in the extensive used of primary amine, monoethanolamine (MEA). However, the maximum CO_2 loading in MEA is limited by stoichiometry which is 0.5 mol of CO_2 per mole of amine when carbamate (deprotonated zwitterions intermediate) is the final product of the reaction. Tertiary amine, methydiethanolamine (MDEA) and sterically-hindered primary amine, 2-amino-2-methyl-1-propanaol (AMP) was blended with MEA to increase the loading capacity [9]. This mixed amine system combines the higher equilibrium loading capacity of the tertiary amine and the higher reaction of the primary or the secondary amine.

CO_2 loading in MDEA and AMP approaches a value of 1.0 mol of CO_2 per mole of amine. The reaction rate constant for CO_2-AMP is much higher than that of CO_2-MDEA. AMP does not form stable carbamate. Bicarbonate and carbonate ions may be present in the solution in larger amounts than carbamate ions. Hence, regeneration energy costs when an aqueous solution of AMP is used to absorb CO_2 may be lower as in the case of using MDEA. Therefore the blends of AMP+MEA+H_2O appears to be an attractive new blended amine solvent other than MDEA+MEA+H_2O for gas treating process.

Rigorous mass transfer model is best for the interpretation model of mixed amine data since simplistic approximation are likely to fail [9]. So far, model developed by Hagewieshce et al. is one of the most comprehensive rigorous models reported to represent CO_2 mass transfer in mixed amine solvents. Extensive set of reversible reactions was incorporated in the model. The coupling between the chemical equilibrium, mass transfer, and chemical kinetics are also taken into account.

In their work, mathematical models following the work of Hagewieshce [14] are presented to describe the absorption of CO_2 in (MDEA+MEA+H_2O) and (AMP+MEA+H_2O). The diffusion reaction processes are modelled according to Higbie's penetration theory with the assumption that all reactions are reversible. The formation of carbamate ions was neglected due to low carbamate stability constant of AMP. Addition of small amount of MEA to an aqueous solution MDEA and AMP enhances the enhancement factor and rate of absorption for both solvents. The enhancement is found higher in (AMP+MEA+H_2O) compared to in (MDEA+MEA+H_2O). The results were found to be in excellent agreement with the experimental results done earlier.

2.3. Limitations of Amines Solutions

Through absorption process, amine solution enters the top of an absorption tower while the gas stream with carbon dioxide enters from the bottom. In counter-current contact with the gaseous stream, the amine solution chemically absorbs the carbon dioxide. Desorption of the absorbed carbon dioxide proceeds through thermal regeneration process. During this regeneration process, carbon dioxide and water

evolve from the amine solution. The water vapor is being condensed in a heat exchanger and be separated. The regenerated amine solution is then sent back to the absorption tower for the next carbon dioxide absorption cycle [16][17].

Utilization of amines in aqueous phase to reduce carbon dioxide via absorption has certain limitations. During the desorption process, when amine solution is heated, oxygen present in the gas stream oxidizes the amine [16]. Degradation of the amine through oxidation results in amine solution to have limited life. This is because the oxidation is believed to reduce the amount of amine primary and secondary functional group that are available for carbon dioxide absorption. The amine solution useful life is then limited to only about six months of continuous use [17].

Adjusting the desorption process to take place at ambient temperatures may extend the useful life of the amine solution, but the performance will be limited by low desorption rate [16][17]. A solution of it is, amine sorbents utilized are often regenerated at approximately ambient temperatures for a fixed desorption time, due to energy requirement and oxidation related degradation. Incomplete desorption of carbon dioxide, which is due to insufficient time, will consequently result in a remaining portion of carbon dioxide in the sorbent[16]. This thereby, reduces the capacity of the sorbent to further absorb additional carbon dioxide. Thus, throughout the absorption-desorption cyclical process, a decreasing portion of the carbon dioxide sorbent is used[17].

The advantage of using blends of primary or secondary amines with tertiary amines is the combination of ‘physical’ solvent characteristic of the tertiary amines and the high absorption rate of primary and secondary amines [18]. However, the acceleration of CO_2 absorption via rapid carbamates formation by primary and secondary amines is only required within certain section of the absorption column, and this may give rise to well-documented side effects in other parts of the absorption column, such as increased corrosion or higher energy requirements for regeneration [19].

2.4. Supported Amine-Polyol Sorbent

Birbara et al. presented an invention relates to a supported amine-polyol sorbent [16]. The paper focused on methods to prepare the supported amine-polyol sorbent together with the test for absorption and desorption of carbon dioxide. The sorbent comprised of amine which absorbs and desorbs carbon dioxide from the gaseous stream, a polyol which increases the desorption rate and a support to provide structural integrity to the amine and polyol. The relatively low viscosity of polyol helps to lowers the high viscosity of the pure amine and enables faster diffusion of carbon dioxide and waters to the amine. Alcohol based solvent is used to wets the support and then dissolves the amine and polyol. The mixture is then dried to remove the solvent [16].

The authors proved that their invented sorbent has greater carbon dioxide cyclic capacity at ambient temperatures [16]. During desorption, their supported amine-polyol sorbent desorbs a greater amount of carbon dioxide compared to amine solvent, where the rate of desorption is higher. The same goes to the absorption rate. As compared to amine solution, this supported amine-polyol sorbent breakthrough at later time. Thus, improvement of the desorption kinetics by the addition of polyol compound improves the carbon dioxide cyclic capacity of the sorbent.

In 1996, Birbara et al. [17] presented additional invention to their past invention of amine-polyol sorbent in 1992 [16]. The authors proposed a system that utilized two or more sorbent beds operating cyclically. The first bed is in the absorption cycle while the second bed is in the desorption cycle [17]. Exothermic heat from the absorption will be utilized in the desorption process. This absorption and desorption cycling of the bed permits continuous absorption of carbon dioxide and water vapor [17].

2.5. Immobilized Activators

The use of immobilized primary and secondary amines group on solid supports has been proposed by Schubert et al. in 2001 [18]. With this, the localization of these activating additives can be limited to those parts of the absorption process where they are beneficial and exclude them from other section which then will avoid the corrosion problem or high demand in regeneration process. The solid support structure in addition can simultaneously serve as packing material in absorption column. It can also enhance the mass transfer kinetics at the gas liquid interface if were used in slurry or fluidized bed reactors.

In 1983, a so called 'shuttle' mechanism is presented [20], which is the enhancement of gas absorption processes with solid particles dispersed in reactor. The authors suggested that the particles adsorb the dissolved gas in the liquid film at the gas-liquid interface. The gas is then transported to the bulk of the liquid. Saha et al. in 1992 [21] also demonstrated an experimental study on the effect of additional fine active carbon particle into aqueous MEA, DEA and AMP solutions. The CO_2 absorption rate was found to increase significantly.

In contrast to the 'shuttle' mechanism Schubert et al. exploited a reaction mechanism for CO_2 absorption on immobilized activator in their work. The formation of carbamate thus, takes place as a parallel reaction. This step is classified as a kind of chemical adsorption process, where the CO_2 react with the immobilized and largely stationary primary and secondary amines [22]. The adsorption sites are continuously regenerated 'in-situ' by the reaction between aqueous MDEA that flows over the solid surface and the adsorbed carbamate. Bicarbonate is released into the solution in the process. Figure 2-3 shows the reaction mechanism for immobilized activators [19].

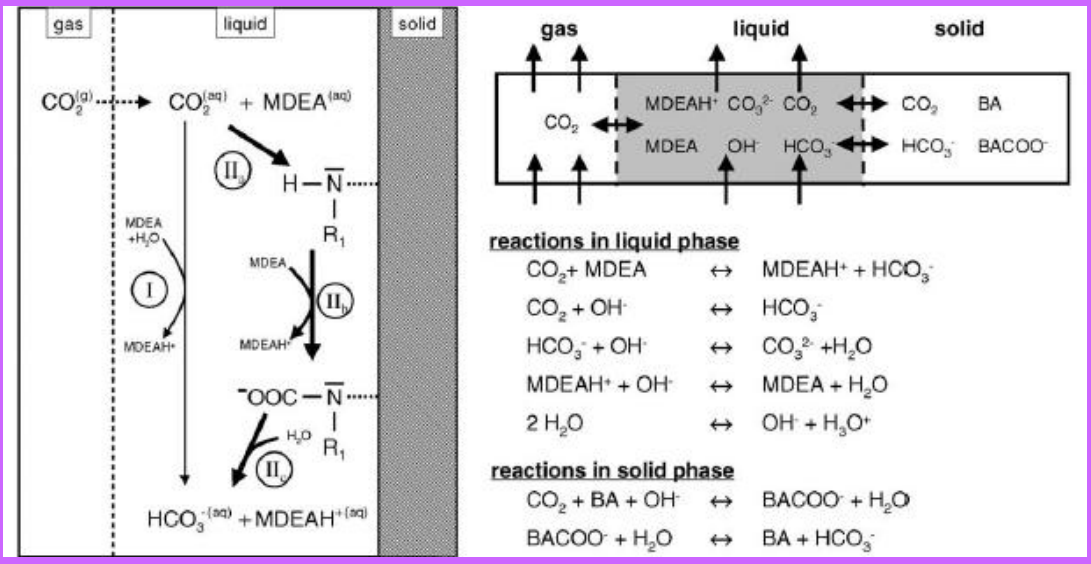

Figure 2-2: Schematic Reaction Mechanism for Immobilized Activators [19]

With assumption that hydrodynamics of gas and liquid flows can be described by convective and axial dispersion transport mechanisms and the change of the axial flow is negligible, the three-phase fluidized bed is described by a set of differential equations for each phase [19].

The solid is retained within the column and only axial backmixing is assumed for the solid. The behavior of the three phases is linked by gas-liquid and liquid-solid mass transfer, modeled using linear driving forces where the equilibrium between gas and liquid are described by Henry's law. The volumetric reaction rates in the liquid phase are calculated by method proposed by Rinker et al. [23]. Bronsted relation was used to estimate the second order rate coefficient of the carbamate formation for the reaction between carbon dioxide and the immobilized benzylamine. Parameters used in the model were estimated by using empirical correlations taken from the literature. Their simulation result clearly illustrate that use of immobilized activator enhances the CO_2 absorption process. The increase in bicarbonate production improves solvent loading by the virtue of superior reactive mass transfer characteristic.

The author also has conducted experimental studies to see the positive effect of the immobilized activator. An adsorber resin functionalized with benzyl amine (BA) groups (Lewatit VP OC 1065, Bayer AG) was chosen as the immobilized activator

[23]. 2 *l*/min gas with 50vol% of CO_2 was feed continuously into a reactor of 0.15m inner diameter with four blade impeller arranged symmetrically on the reactor wall through a tube with 0.004m internal diameter with opening of 0.025 m under the impeller. The liquid level in the reactor was adjusted to 0.15 m and the reactor contents are maintained at a 25^{o}C.

Observed that, with the use of aqueous suspension of the activator, the absorption capacity increase, the extent to which depends on the amount of the solid being introduced. However, the increase is much less than that found with equivalent amounts of soluble primary or secondary amines. Absorption of CO_2 in MDEA follows a rapid breakthrough up to about 50% of the inlet concentration but after 20-25 min, the absorption capacity exhausted and the concentration rises steeply towards inlet value. In DEA, similar behavior is observed but the absorption rate is higher compared to MDEA.

The authors also conducted experiment to compare the result of using of DEA additive and immobilized activators into the MDEA solution. Adding just 0.05mol/*l* DEA to a 0.2 molar MDEA solution yields similar absorption rates in pure 0.2molar DEA solution. This fact is explained by the mass transfer accelerating and influence of primary and secondary amines in the mechanism. Replacing the DEA with 400ml Lewatit, containing the equivalent quantity of immobilized amine groups, similar enhancement is observed.

Subsequent experimental studies were carried out in continuous absorption apparatus. This was to provide initial evaluation of the technical potential of the concept [19]. Further study on the regeneration process demonstrated that CO_2 loaded immobilized activator can be regenerated with both NaOH (0.5 M) and MDEA (0.5M) solutions. The breakthrough curves are identical to that of fresh material [19].

For the experiments conducted in three phase fluidized bed absorber, only 8% of the feed CO_2 absorbed in water alone. With simple MDEA solution, the CO_2 concentration in the exit gas is initially only 8% of the inlet value and the level subsequently drifts up to a steady-state value of 74%. However, a much higher

residual CO_2 concentration in gas phase exhibited when 2.5l of Lewatit immobilized amine was introduced in the reactor.

Presence of solid particle deposit were found to cause deterioration in uniformity of phase distribution which induced the shift in the flow pattern at the bottom of the column is a likely explanation [19]. In the later stages of the experiment, interestingly, higher absorption rates were observed in comparison to the control case without activator, prior to steady-state value of 73% being finally attained [19].

The authors in 2005 has conducted additional experiments with gas in a fixed-column, in a gas-liquid suspension double-stirred cell reactor and with liquid medium in a fixed-bed column to quantify the various mass transfer and reaction steps occurring in the three-phase system and to identify the rate limiting steps [23]. This is to present the kinetics measurement for the absorption of dissolved CO_2 on immobilized amine (IA) and for the desorption of CO_2-loaded IA with MDEA with the liquid medium fixed-bed column.

The authors suggested on two possible mechanisms for the three-phase system based on the measured kinetics and the mechanisms are compared with one another. Simple linear-driving-force mathematical model has been developed for the simulation of the experiments and found to give an accurate description of the CO_2 breakthrough profiles at the reactor exits [23]. There is no direct reaction between tertiary alkanolamines and CO_2. Tertiary amine acts as a basic catalyst for the reaction between CO_2 and water and Donaldson and Nguyen [26] has proposed the reaction to be as:

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3^- \quad (1)$$

Based on mechanisms, two possible mechanisms are suggested for the novel three-phase CO_2 absorption system with primary and secondary Immbolized Amine and MDEA. Figure 2-3 and 2-4 shows the mechanisms.

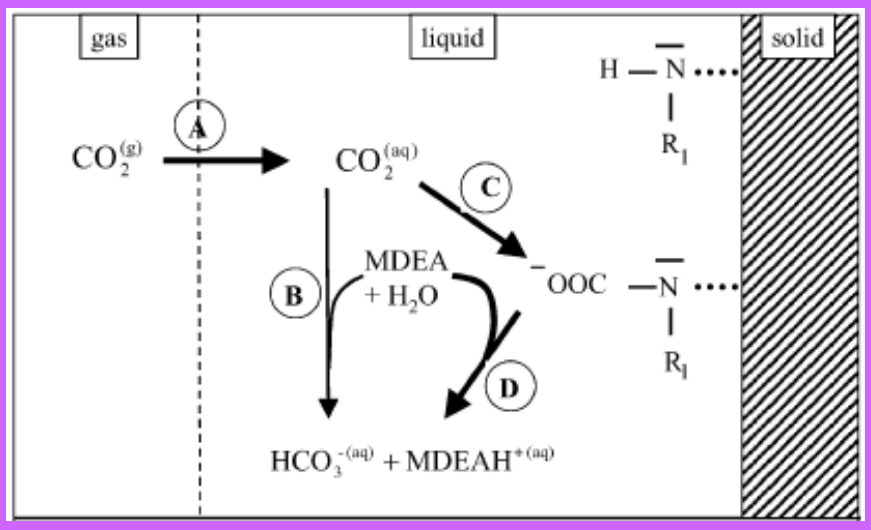

Figure 2-3 : Gas-liquid-solid-liquid Mechanism [23]

Figure 2-3 shows that CO_2 from the gas phase dissolves in the liquid phase and form carbamates in reaction with the immobilized amine.

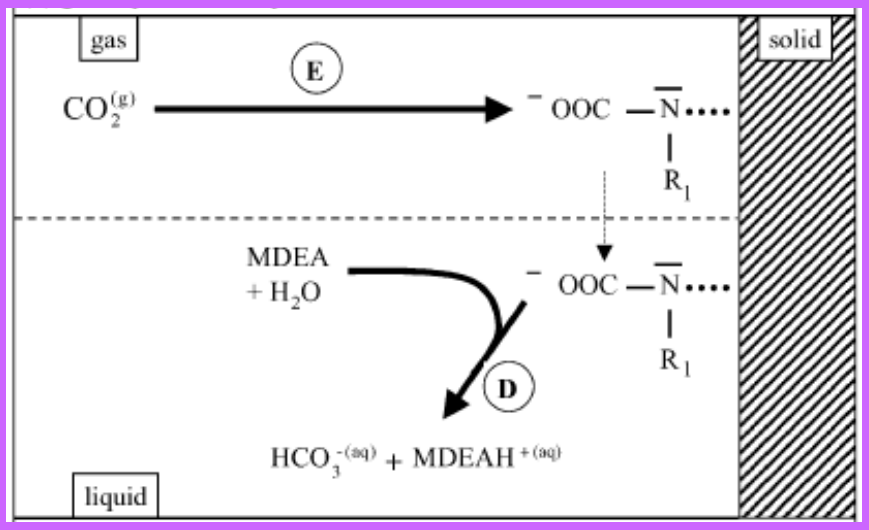

Figure 2-4 : Gas-solid-liquid Mechanism [23]

Figure 2-4 shows the gas first directly contact the solid phase. The CO_2 adsorbs on the surface and form carbamates. Liquid phase then replace the gas phase and desorption takes place as the first mechanism.

Four individual steps in the mechanisms are described in their work. They are the gas-liquid mass transfer, the gas-solid ‘adsorption’, the liquid-solid ‘adsorption’ and

the solid-liquid ‘desorption’. In identifying the rate-limiting step in the three-phase system, the kinetics of these four steps had been measured separately [23].

Assumptions made for the main model used are as follows: an isothermal, isobaric operation, ‘adsorption’ equilibrium described by a single-site Langmuir type model, adsorption kinetics described by the linear-driving force model, plug flow with axially dispersion within the adsorbent fixed-bed [23].The linear-driving-force model, used in their research can be written as:

$$\frac{\partial q}{\partial t} = k_{eff}\, a(q_{eq} - q) \qquad (2)$$

where k_{eff} is the effective mass transfer coefficient, a is the specific area of the packed bed, q_{eq} is equilibrium solid phase concentration and q is the solid phase concentration.

A fixed bed reactor with diameter of 20mm and height of 110mm was used to measure the kinetic of CO_2 adsorption (dissolved in water) with the immobilized amine and the desorption of CO_2-loaded immobilized amine with an aqueous MDEA solution. The reactor was packed with 34.5m*l* Lewatit. Input and output concentration-time profiles with tracer solution (0.1M NaCl) were measured and simulated first. Based on the simulation, the axial dispersion coefficient D_{ax} was determined as 7.858 x 10^{-7} m^2/s at 15^{o}C and the bed porosity $\varepsilon_{b,}$ as 0.6144 [23].

For reaction between CO_2 and immobilized amine, the authors used the isotherm adsorption model to simulate the isotherm data of this reaction. It was found that the model fit the experimental data very good. CO_2 loading on immobilized amine for experiment with various CO_2-concentration are calculated from the input and adsorption concentration-time profile.

The adsorption rate data were fitted using the single-site Langmuir model and the adsorption parameters determined are given in the Table 2-1.

Table 2-1: Calculated Adsorption Parameters [23]

Temperature (K)	q_{max} (mol/kg)	k_L (m^3/mol)	$k_{eff}a(s^{-1})$	k_{eff}(m/s)
288	1.969	0.0721	4.9×10^{-4}	1.21×10^{-7}
298	1.970	0.0632	6.2×10^{-4}	1.54×10^{-7}

The model accurately describes the adsorption at various CO_2 concentrations, flow rates and temperatures. The CO_2 concentration has significant influence on the adsorption rate. The mass transfer kinetics of adsorption increases with the rising temperature. Flow rate only exerts little influence. Both however have positive influence on the process. The effective mass transfer kinetics at 25°C is larger than that of 15°C.

The model is also proved sensitive to the effective mass transfer rate of desorption. All of the mass transfer coefficients for the above mentioned four steps of the gas-liquid-solid system are summarized in Table 2-6. The liquid-solid adsorption and solid-liquid desorption steps are rate limiting steps which will retard the overall mass transfer. The data also shows that the gas-solid adsorption step is the fastest steps of the system. Considering this, the second mechanism which is the gas-solid-liquid mechanism would be faster than the first mechanism. The authors proposed to suppress the first mechanism and encourage the second one in the absorber [23].

Table 2-2: Comparison of Mass Transfer Kinetics for Different Steps at 298K [23]

	Mass transfer process	$k_{eff}(10^{-8}$m/s)	$k_{eff}a(10^{-4}s^{-1})$	Assessment
Gas-Liquid	Absorption	3600	1458	Slow
Gas-Solid	Adsorption	Instantaneous	Instantaneous	Instantaneous
Liquid-Solid	Adsorption	15.4	6.2	Rate-limiting
Solid-Liquid	Desorption/regeneration	5.6	2.3	Rate-limiting

As the rate-limiting steps, the liquid-solid adsorption and solid-liquid desorption steps both include two sub-steps which could contribute to the mass transfer residence. First the formation or hydrolysis of carbamate and second is mass transfer of CO_2 and HCO_3^- through the liquid film around particle surface. The kinetics can

be assumed to be equal to that of CO_2 in MDEA solution (k=5.656 x 10^{-5} m/s, 313K) [23].

A periodic operation of the fixed-bed with alternating liquid and gas cycle is being investigated as a consequence of mass transfer residence in the rate limiting steps and the limitation on mass transfer imposed by the presence of a liquid film on the IA surface. The solid phase is contacted alternately with gas and liquid in the periodic fixed-bed operation. CO_2 would thus be first adsorbed on the solid during the gas-solid contact and then regenerated 'in-situ' again during the subsequent liquid-solid contact interval. This 'micro-cycle' would be recycled in the fixed-bed and CO_2 from sour gas is separated continuously [23].

CHAPTER 3: METHODOLOGY/PROJECT WORK

This project work started with literature research. Literature research was made by using the keywords of kinetics modelling, reactive absorption, amine treating, CO_2 absorption and CO_2 removal. Focus was given to those literatures that present the kinetics modelling of the reactive absorption process. Various types of model presented in past literatures are studied to see whether the model can be employ for the reactive absorption process in the aminated resin. Reactions that produced solid are of the main concern, since the aminated resin is expected to produce solids in the end of the absorption process.

Each literature found was studied and the mathematical model and the model parameters used were taken into note. Suitable mathematical model identified is used in this research project. The reaction kinetics equation between CO_2 and the aminated resin was developed based on the literatures and other references. As a starting point, the reaction mechanisms proposed by Rinker et al. [5] is adapted to represent the CO_2 absorption reaction with the aminated resin. The mechanism is represented as per discussed in section 3.3.

The next approach was to estimate the Arrhenius equation that best represent the reaction between CO_2 and the aminated resin. This was done following Rinker et al. [5] approach as well. All the estimation works is done by MATLAB modelling and simulation. Using the correlation proposed in past literatures, the liquid bulk concentration of all the chemical species at certain temperature was estimated. These liquid bulk concentrations are essential in order to study the kinetic behavior of the aminated resin. The estimated liquid bulk concentrations are obtained by solving related equations using MATLAB.

The model used to simulate the kinetic behavior of the aminated resin is to be validated to see whether it presents the system behaviour well or not and whether the deviation is within the tolerance. If the model does, the best operating condition for the aminated resin will be identified, again using MATLAB. However, if the results fail, other model will then be adopted and validated. The process continues until the best model is found.

3.1. Process Flow of Final Year Project

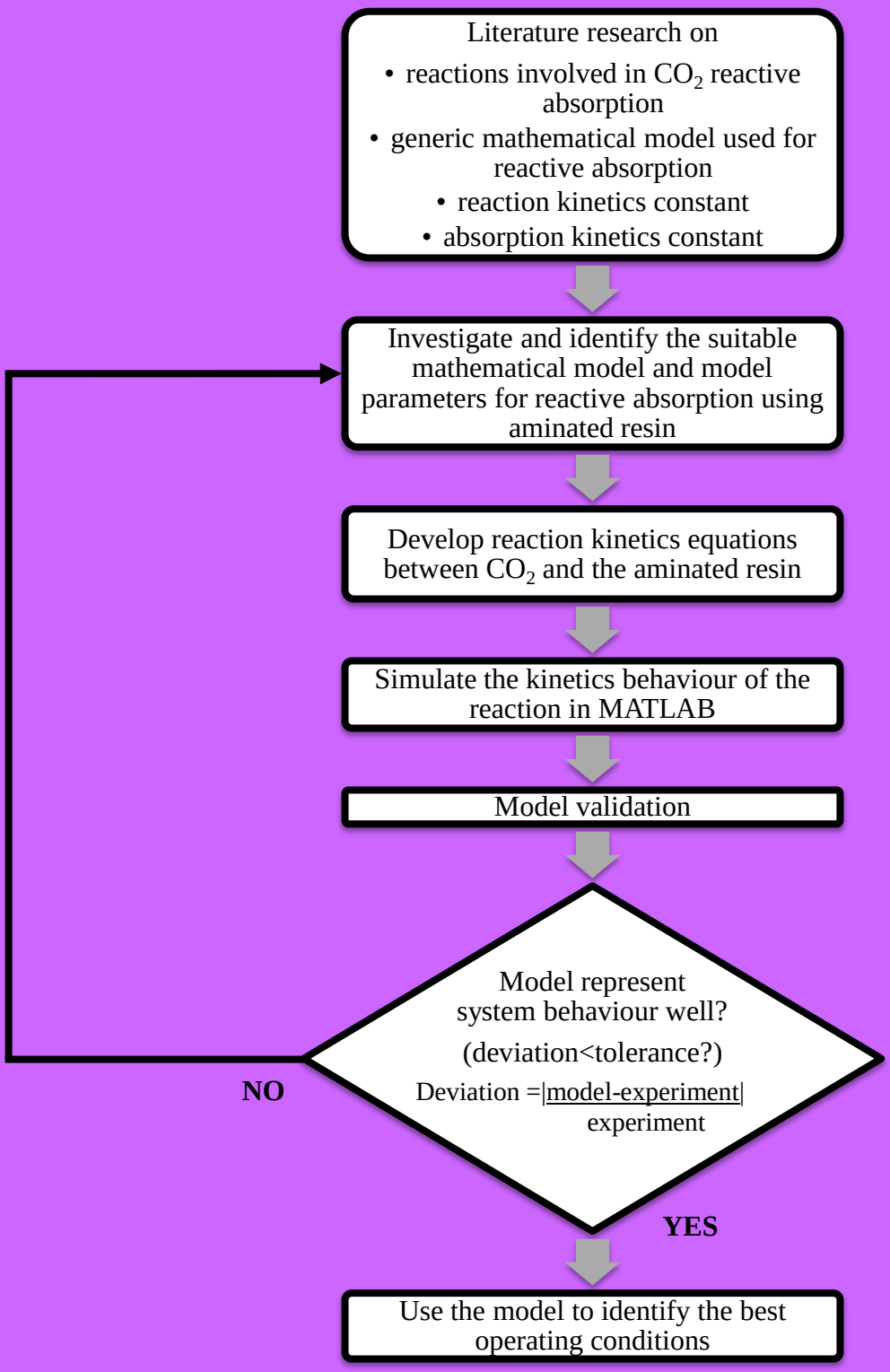

Figure 3-1: Project Process Flow

3.2. Milestone

For last semester, we had focus more on the literature research and learn to use MATLAB. Literature research is done to collect as much data and information as possible on CO_2 reactive absorption, especially on the amine system treatment. The reaction process, kinetics involved, mathematical models used in past literature is studied. Reaction kinetics equation is to be developed based on the suitable model proposed in past literature. For our project work, the model proposed by Rinker et al.[5] was adapted.

In this semester, more literature research is done on the kinetics correlations used in past literature for reactive absorption. The reaction mechanism for this project work was developed by adapting the mechanism proposed by Rinker et al.[5] for the reaction between DEA. The Arrhenius equations that relates the reaction between CO_2 and the aminated resin was also developed using the approached proposed by them [5]. The kinetics found is used to find the equilibrium constants which then were used to estimate the liquid bulk concentration of the chemical species involved in the reactive absorption. Correlations for equilibrium constant proposed by past authors are being used to support the calculations which were done in MATLAB.

In the future, the concentration profiles of each species will be estimated following Rinker et al.[5] as well. The liquid bulk concentration obtained is used to specify the initial condition and boundary condition of each chemical species. The result obtained from the simulation of the developed kinetic model will then be compared to the experimental result to validate the model. The best operating parameters will then be investigated should the model developed is valid to be used.

3.3. Reaction mechanism

Approach used is adapted from the approach proposed by Rinker et al. [5]. The aminated resin is assumed to be a secondary alkanolamine that have been functionalized to an unknown resin, R_sRNH where R_s denotes the resin group. Adapting Rinker et al. model for absorption of CO_2 into aqueous DEA, a rigorous numerical mass transfer model based on penetration theory in which all chemical reactions are considered to be reversible was developed in estimating the kinetic rate coefficients.

3.3.1. Adaptation of kinetics modelling approach proposed by Rinker et al. [5]

Same mechanism scheme is followed accept it is assumed that the aminated resin acts as the DEA solvent with 10% increment in apparent rate coefficient, k_{app} for the reaction between CO_2 and the aminated resin compared to that with DEA.

Scheme 1:

$$CO_2 + H_2O \overset{K_1,k_1}{\longleftrightarrow} H_2CO_3 \quad (1)$$

$$CO_2 + OH^- \overset{K_2,k_2}{\longleftrightarrow} HCO_3^- \quad (2)$$

$$CO_2 + R_sRNH \overset{K_3,k_3,k_{-3}}{\longleftrightarrow} R_sRNH^+COO^- \quad (3)$$

$$R_sRNH^+COO^- + R_sRNH \overset{K_4,k_4,k_{-4}}{\longleftrightarrow} R_sRNH_2^+ + R_sRNCOO^- \quad (4)$$

$$R_sRNH^+COO^- + H_2O \overset{K_5,k_5,k_{-5}}{\longleftrightarrow} H_3O^+ + R_sRNCOO^- \quad (5)$$

$$R_sRNH^+COO^- + OH^- \overset{K_6,k_6,k_{-6}}{\longleftrightarrow} H_2O + R_sRNCOO^- \quad (6)$$

$$R_sRNH^+COO^- + HCO_3^- \overset{K_7,k_7,k_{-7}}{\longleftrightarrow} H_2CO_3 + R_sRNCOO^- \quad (7)$$

$$R_sRNH^+COO^- + CO_3^{2-} \overset{K_8,k_8,k_{-8}}{\longleftrightarrow} HCO_3^- + R_sRNCOO^- \quad (8)$$

$$R_sRNCOO^- + H_2O \overset{K_9,k_9}{\longleftrightarrow} R_sRNH + HCO_3^- \quad (9)$$

$$R_sRNH_2^+ + OH^- \overset{K_{10}}{\leftrightarrow} R_sRNH + H_2O \quad (10)$$

$$HCO_3^- + OH^- \overset{K_{11}}{\leftrightarrow} CO_3^{2-} + H_2O \quad (11)$$

$$HCO_3^- + H_3O^+ \overset{K_{12}}{\leftrightarrow} H_2CO_3 + H_2O \quad (12)$$

$$2H_2O \overset{K_{13}}{\leftrightarrow} OH^- + H_3O^+ \quad (13)$$

Reaction (3) represents the formation of zwitterion while reactions (4) – (8) are the zwittterion deprotonation reactions. For this aminated resin, we have R_s-R=Resin-CH_2OH. K_i,k_i and k_{-i} are the equilibrium constant, the forward rate coefficient and the reverse rate coefficient for reaction (i), respectively. Reaction (1) – (9) are considered to be reversible with finite reaction rates whereas reactions (10) – (13) are considered to be reversible and instantaneous with respect to mass transfer and at equilibrium, since they involve only proton transfer. For convenience the chemical species are renamed as follows:

$u_1=[CO_2]$

$u_2=[R_sRNH]$

$u_3=[R_sRNH_2^+]$

$u_4=[HCO_3^-]$

$u_5=[OH^-]$

$u_6=[CO_3^{2-}]$

$u_7=[H_3O^+]$

$u_8=[R_sRNCOO^-]$

$u_9=[H_2CO_3]$

$u_{10}=[H_2O]$

The liquid bulk concentration of all chemical species can be estimated from the initial concentrations of the aminated resin, $[R_sRNH]_{initial}$,the initial CO_2 loading of the solution L_a and the assumption that all reactions are at equilibrium. We have the following equiations for the liquid bulk concentration u_1^o,...,u_9^o:

Overall R_sRNH balance:

$$u_2^o + u_3^o + u_8^o = [R_sRNH]_{initial} \quad (14)$$

Overall carbon (from CO_2) balance:

$$u_1^o + u_4^o + u_6^o + u_8^o + u_9^o = L_1[R_sRNH]_{initial} \quad (15)$$

Electroneutrality balance:

$$u_3^o + u_7^o - u_4^o - u_6^o - 2u_6^o - u_8^o = 0 \quad (16)$$

All reactions at equilibrium (only independent equilibrium constants):

$$K_2 = \frac{u_4^o}{u_1^o u_5^o} \quad (17)$$

$$K_3K_4K_{10}K_{13} = \frac{u_7^o u_8^o}{u_1^o u_2^o} \quad (18)$$

$$K_{10} = \frac{u_2^o}{u_3^o u_5^o} \quad (19)$$

$$K_{11} = \frac{u_6^o}{u_4^o u_5^o} \quad (20)$$

$$K_{12} = \frac{u_9^o}{u_4^o u_7^o} \quad (21)$$

$$K_{13} = u_5^o u_7^o \quad (22)$$

In 1996, Rinker et al. [5] used Higbie's penetration model was to describe the absorption of CO_2 into aqueous solutions of primary and secondary alkanolamine in a laminar-liquid jet absorber. We assumed that our aminated resin to acts similar with DEA, the secondary alkanolamine when it comes in contact with CO_2. All reactions were treated as reversible reactions. Reaction (1) – (9) have finite reaction rates which are given by the following reaction rate expressions. R_i is the reaction rate expression for reaction (i):

$$R_1 = -k_1 u_1 + \frac{k_1}{K_1} u_9 \quad (23)$$

$$R_2 = -k_2 u_1 u_5 + \frac{k_2}{K_2} u_4 \quad (24)$$

Assuming pseudo-steady state with respect to the concentration of zwitterions intermediates ($R_s RNH^+COO^-$) the equation below is derived.

$$R_{3,\ldots,8} = \frac{-k_3[u_1 u_2 - (\frac{A}{B})u_8]}{1 + \frac{1}{B}} \quad (25)$$

where

$$A = \left(\frac{k_4}{k_{-3}}\right)\frac{u_3}{K_3 K_4} + \left(\frac{k_5}{k_{-3}}\right)\frac{u_7}{K_3 K_5} + \left(\frac{k_6}{k_{-3}}\right)\frac{u_{10}}{K_3 K_6} + \left(\frac{k_7}{k_{-3}}\right)\frac{u_9}{K_3 K_7} + \left(\frac{k_8}{k_{-3}}\right)\frac{u_4}{K_3 K_8} \quad (26)$$

and

$$B = \left(\frac{k_4}{k_{-3}}\right)u_2 + \left(\frac{k_5}{k_{-3}}\right)u_{10} + \left(\frac{k_6}{k_{-3}}\right)u_5 + \left(\frac{k_7}{k_{-3}}\right)u_4 + \left(\frac{k_8}{k_{-3}}\right)u_6 \quad (27)$$

$$R_9 = -k_9 u_8 + \frac{k_9}{K_9} u_2 u_4 \quad (28)$$

The aminated resin to be used will be in the form of unloaded aqueous resinated secondary alkanolamines solution. Thus, the works done by Rinker et al. are followed with some reasonable modification.

The carbamate to bicarbonate reversion reaction is found to be very slow in Rinker's work [5], thus we assume the contribution of reaction (9) to the rate of absorption is negligible. The gas-liquid contact times found in the experiment was very short, the concentration of bicarbonate and carbonate in aqueous solution are very small and contribution to deprotonation of the zwitterions is negligible. Thus, reaction (7) and (8) are eliminated.

Concentration of hydroxide is very small and changes significantly as CO_2 is absorbed, reaction (6) is neglected. This is due to the difficulties to quantify the contribution of hydroxide to the deprotonation of the of the zwitterion[5]. In

Rinker's work, they also found that the effect of water as the deprotonating base was so small compared to DEA. Thus we neglect water as a deprotonating base in the interpretation of our data and we eliminate reaction (5).

Hence, we have neglected reactions (5)-(9) in our project work. Therefore, equation 25-27 can then be reduced to the following rate expression for the consumption of CO_2 according to the zwitterion mechanism, with our aminated resin being the only base that deprotonates the zwitterions:

$$R_{3,4} = \frac{-k_3}{1+\frac{1}{(k_4/k_{-3})u_2}}\left(u_1 u_2 - \frac{1}{K_4/K_3}\frac{u_3 u_8}{u_2}\right) \quad (29)$$

Note that K_4/K_3 is the equilibrium constant of the overall reaction between CO_2 and the solvent which is the sum of reaction (3) and (4):

$$CO_2 + 2R_sRNH \overset{K_3,K_4}{\longleftrightarrow} R_sRNH_2^+ + R_sRNCOO^- \quad (30)$$

and $K_4/K_3 = k_3k_4/k_{-3}k_{-4}$

From the analysis of their experimental data Rinker et al. has come out with an apparent second-order rate coefficient which is defined as equation below:

$$k_{app} = \frac{-k_3}{1+\frac{1}{(k_4/k_{-3})u_2}} \quad (31)$$

Equation 31 is then rearranged to:

$$\frac{1}{k_{app}} = \frac{1}{k_3} + \frac{1}{k_3(k_4/k_{-3})u_2} \quad (32)$$

Hence, this is the equation that is used to generate k_3 and $k_3(k_4/k_{-3})$ after adaptation of Rinker's approach and equation on the prediction of k_{app}.

3.3.2. The generated apparent rate coefficient, k_{app}

The range of k_{app} obtained by Rinker et al. in their experiment at 298K is between 300-1800 m^3/kmol.s for DEA concentration between 0.1-3.0 kmol/m^3[5]. We assume the performance of this aminated resin will be 10% higher for the same solution concentration. This assumption was made since there is still no available experimental data for the aminated resin. Thus, our estimated k_{app} value would be:

Table 3-1: Assumption of $\boldsymbol{k_{app}}$ for project work at 298K.

$[R_sRNH]$ kmol/m^3	0.1	1.0	2.0	3.0
k_{app} m^3/kmol.s	330	990	1430	1980

3.3.3. Estimation of k_3 and k_3 (k_4/k_{-3})

Equation (32) will be used to estimate the value of k_3 and k_3 (k_4/k_{-3}). The steps involved are:

Step 1: Plot generated k_{app} for aminated resin at 298K

Step 2: Replot the reciprocal of k_{app} at 298K with respect to the reciprocal of solvent concentration to fit equation (32)

Step 3: Estimate the reciprocal value of k_3 and k_3 (k_4/k_{-3}) at 298K from the generated graph

Step 4: Calculate for k_3 and k_3 (k_4/k_{-3}) at 298K

Step 5: Estimating k_3 and k_3 (k_4/k_{-3}) at other temperatures following the same trend as in Rinker's work

Step 6: Fit k_3 and k_3 (k_4/k_{-3}) into Arrhenius equation

3.3.4. Liquid Bulk Concentration of All Chemical Species

Following work done by Rinker et al. [5] the liquid bulk concentration for all chemical species is estimated in MATLAB using nine equations, which are equation (14) to (22). It is assumed that the initial concentration of the aminated resin to be 1 kmol/m^3 with initial CO_2 loading in the aminated resin, L_1 equal to zero. The forward rate coefficients of reactions (1) and (2) (k_1 and k_2) were estimated from the correlation reported by Pinsent et al. (1956) [30]. In 2003, Mandal et al. recited the correlations proposed by Oloffson and Hepler (1975) for K_{13} [31]. The authors also recited the correlation for K_{11}, which was proposed by Danckwerts and Sharma in 1966. Correlation for K_{10} which was proposed by Barth et al. (1981) was also recited in their work [31]. Adopting the equilibrium constant correlations proposed in previous work, the equilibrium constant for each reaction involved in the liquid bulk concentration calculation was estimated. The summary of the correlation used is as per Table 3-2.

Table 3-2: Correlation Used for Equilibrium Constant Estimation

K(i)	Correlation	Reference
K2	Log(K2)= 13.635 – (2895/T)	[30]
K10	Log(1/K10) = -4.0302 – (1830.15/T) + 0.0043*T	[31]
K11	Log(K11) = 6.498 – 0.0238*T – (2902.4/T)	[31]
K13	Log(1/K13) = 8909.483 – (142613.6/T) – 4229.195*log10(T) + 9.7384*T – 0	[31]

CHAPTER 4: RESULT AND DISCUSSION

4.1. Adaptation of Rinker et al. [5] proposed model to generate Arrhenius Equation

4.1.1. Step 1: Increase k_{app} reported by Rinker et al.[5] by 10%

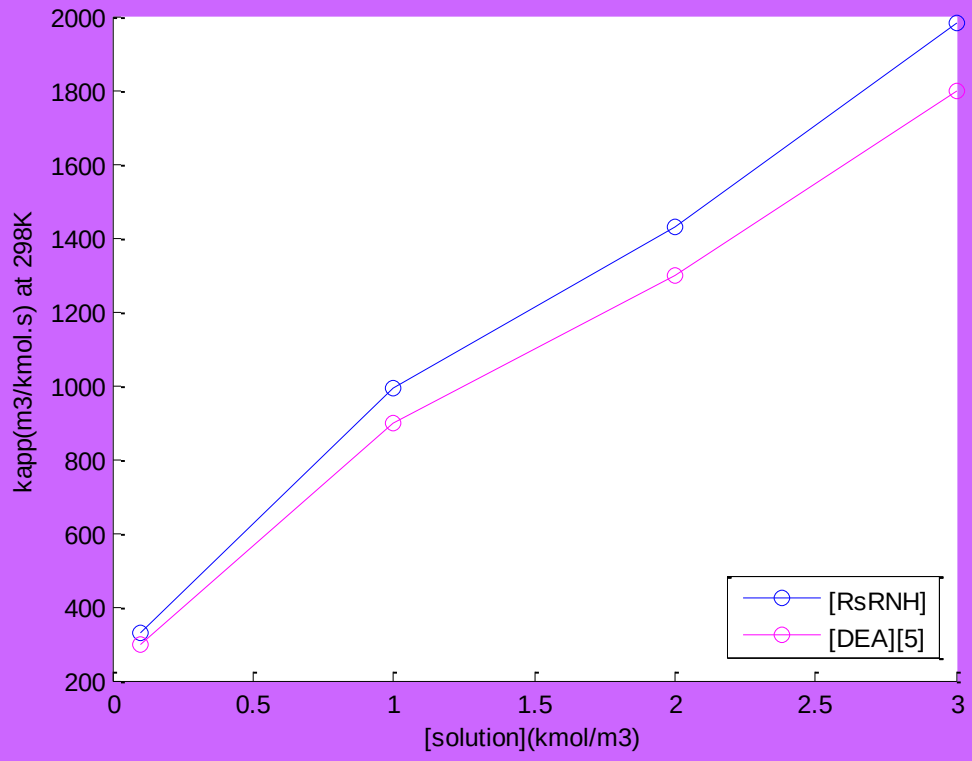

Figure 4-1 : Assumed k_{app} for aminated resin at 298 K

Figure 4-1 showed the comparison of the aminated resin apparent second-order rate coefficient, k_{app} which the value is assumed to be 10% higher than that of DEA in Rinker's et al. work [5].

4.1.2. Step 2: Fitting the reciprocal of generated k_{app} with respect to the reciprocal of increasing solution concentration into equation (32)

The value of slope and intercept is to be obtained from the graph and then used to calculate k_3 and $k_3(k_4/k_{-3})$.

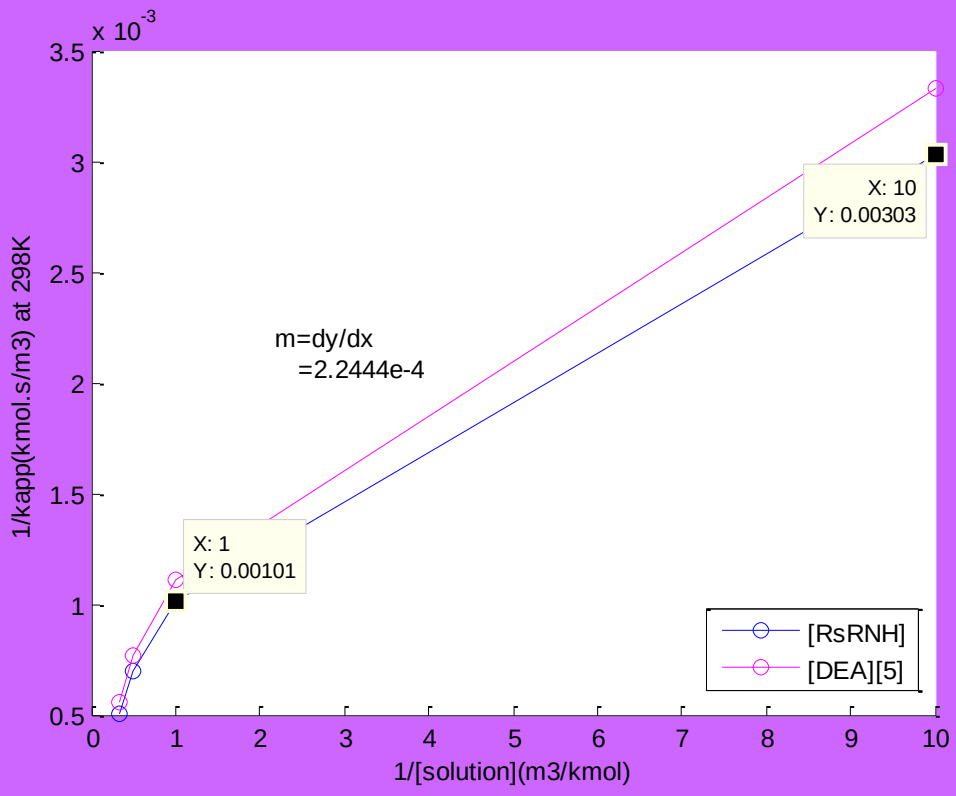

Figure 4-2: Fitting k_{app} into equation (32)

From equation (32) the value of k_3 and $k_3(k_4/k_{-3})$ can be found by plotting $1/k_{app}$ versus 1/[solution].

$$\frac{1}{k_{app}} = \frac{1}{k_3} + \frac{1}{k_3(k_4/k_{-3})u_2} \leftrightarrow y = c + mx$$

Note that $\frac{1}{k_3} = c$ while $\frac{1}{k_3(k_4/k_{-3})} = m$.

Estimating the value of k_3 at 298K:

From Table 2[5], the k_3 at 298K is 4089 m^3/kmol.s, which means:

$$\frac{1}{k_3} = c = 2.446 \times 10^{-4} kmol.s/m^3$$

Note that the above value is the $\frac{1}{k_{app}}$ value at very high concentration of DEA. The aminated resin should react better than the DEA since it has been resinated. Since we assume it will behave 10% better, thus the $\frac{1}{k_{app}}$ value at very high concentration of aminated resin will be 1/1.1 times that of DEA at the same temperature.

The estimated value is:

$$\frac{1}{k_{app}} = \frac{1}{k_3} = c = 2.224\ x\ 10^{-4} kmol.s/m^3$$

Thus,

$$k_3 = 4496\ m^3/kmol.s$$

Estimating the value of $k_3\ (k_4/k_{-3})$ at 298 K:

From Figure 4-2:

$$\frac{1}{k_3\ (k_4/k_{-3})} = 2.244\ \times\ 10^{-4} kmol^2.s/m^6$$

Therefore:

$$k_3\ (k_4/k_{-3}) = 4456\ m^6/kmol^2.s$$

4.1.3. Estimating k_3 and $k_3(k_4/k_{-3})$ value at other temperatures

Based on the approach proposed by Rinker et al. [5] who confirmed their finding with Little et al.[27] and Versteeg & Oyevaar[28] a linear relationship between k_3 and $k_3(k_4/k_{-3})$ with respect to 1000/T was proposed.

Estimating k_3 value at other temperatures:

Plotting experimental result done by Rinker et al. for comparison:

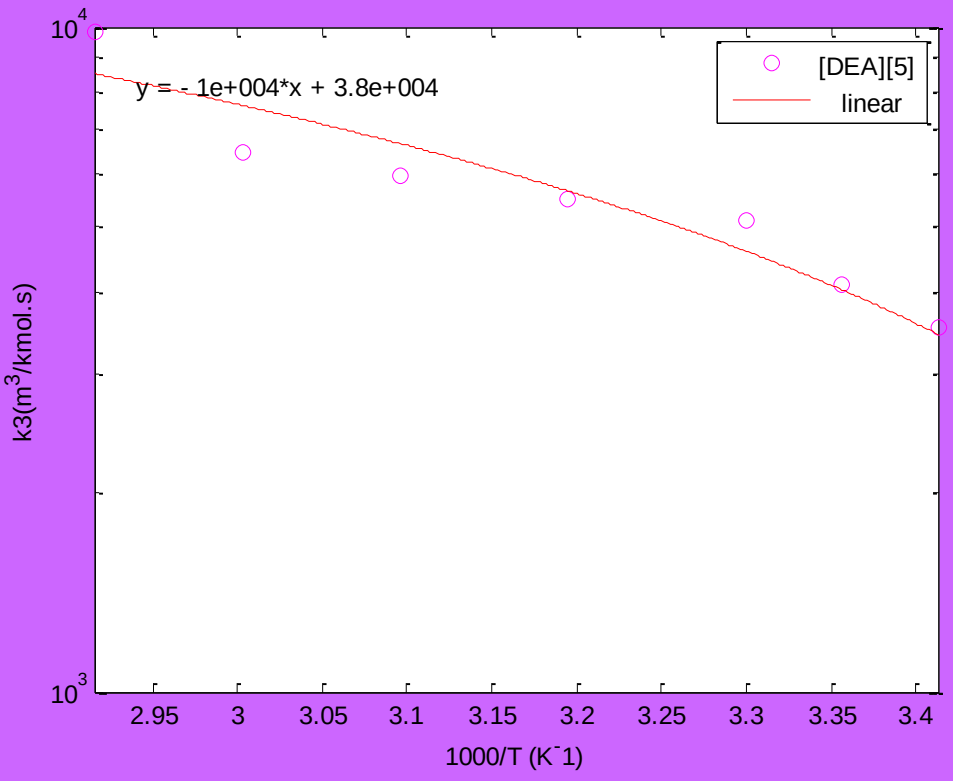

Figure 4-3: Temperature Dependence of k_3 [5]

Using the linear relationship given by:

$$y = -1e^4x + 3.8e^4 \quad (33)$$

in Figure 4-3, and assuming the aminated resin to exhibit the same trend, we obtain Figure 4-4.

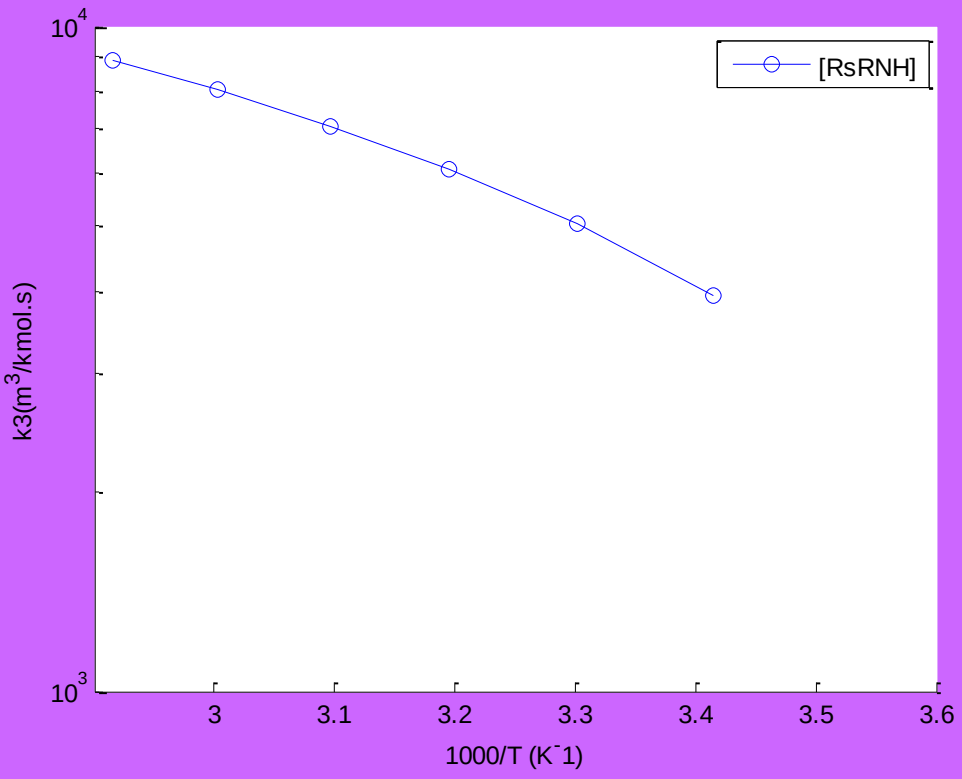

Figure 4-4: Temperature Dependence of k_3 for aminated resin

Estimating $k_3\,(k_4/k_{-3})$ value at other temperatures:

Plotting experimental result done by Rinker et al. [5] for comparison:

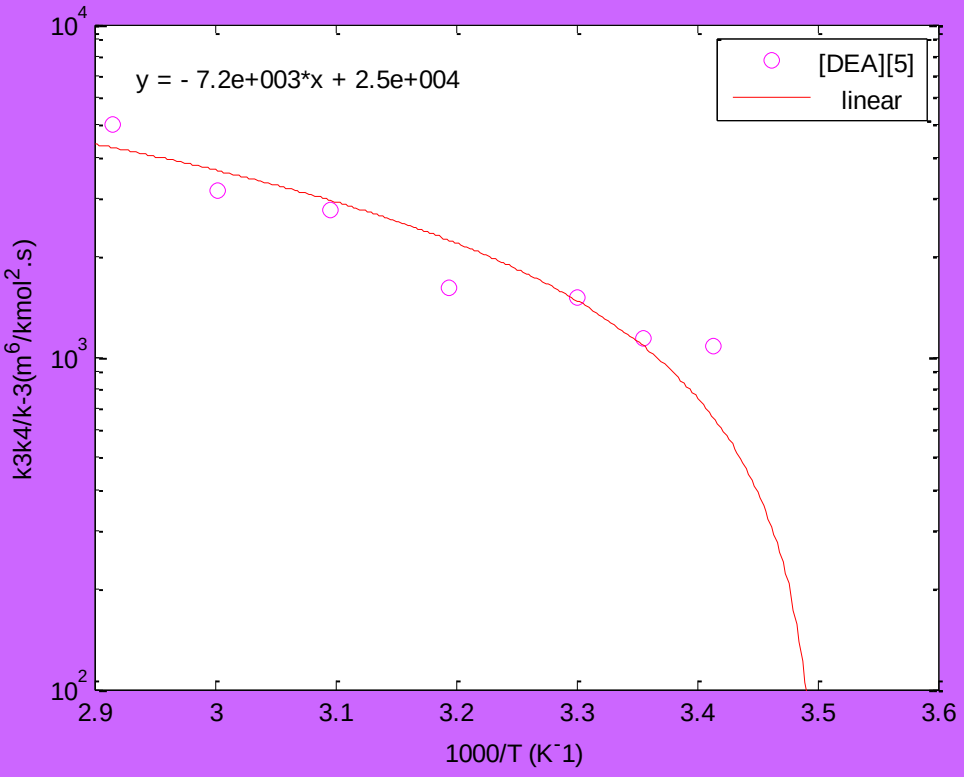

Figure 4-5: Temperature Dependence of $k_3\,(\boldsymbol{k_4/k_{-3}})$[5]

Using the linear relationship given by:

$$y = -7.2e^3x + 2.5e^4 \qquad (34)$$

in Figure 4-5, and assuming the aminated resin to exhibit the same trend, we obtain Figure 4-6.

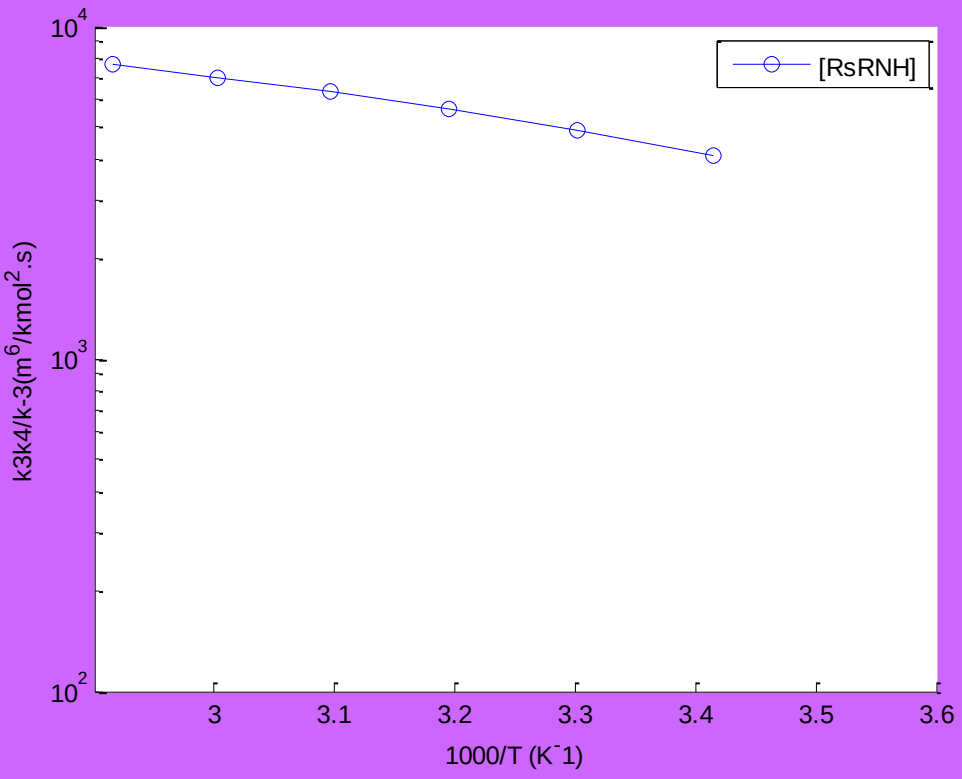

Figure 4-6: Temperature Dependence of $k_3\,(\boldsymbol{k_4/k_{-3}})$ for aminated resin

4.1.4. Step 4: Fitting estimated k_3 and k_3 (k_4/k_{-3}) value into Arrhenius equation

To obtain the Arrhenius equation that fits both k_3 and k_3 (k_4/k_{-3}) for our aminated resin, data in Table 4-1 is again plotted and simulated in MATLAB.

Table 4-1: Aminated resin data from MATLAB Simulation

T (K)	k_3 (m^3/kmol.s)	k_3k_4/k_{-3} (m^6/$kmol^2$.s)
293	3923.4	4083.7
303	5049.7	4894.7
313	6104.2	5653.9
323	7093.3	6366.1
333	8023	7035.5
343	8898.5	7665.8

Arrhenius equation is given by:

$$k = Ae^{-E/RT}$$

Take logs on both sides of the equation gives:

$$lnk = lnA - E/RT$$

Plotting lnk versus $1/T$ and adding linear fitting line gives:

For k_3:

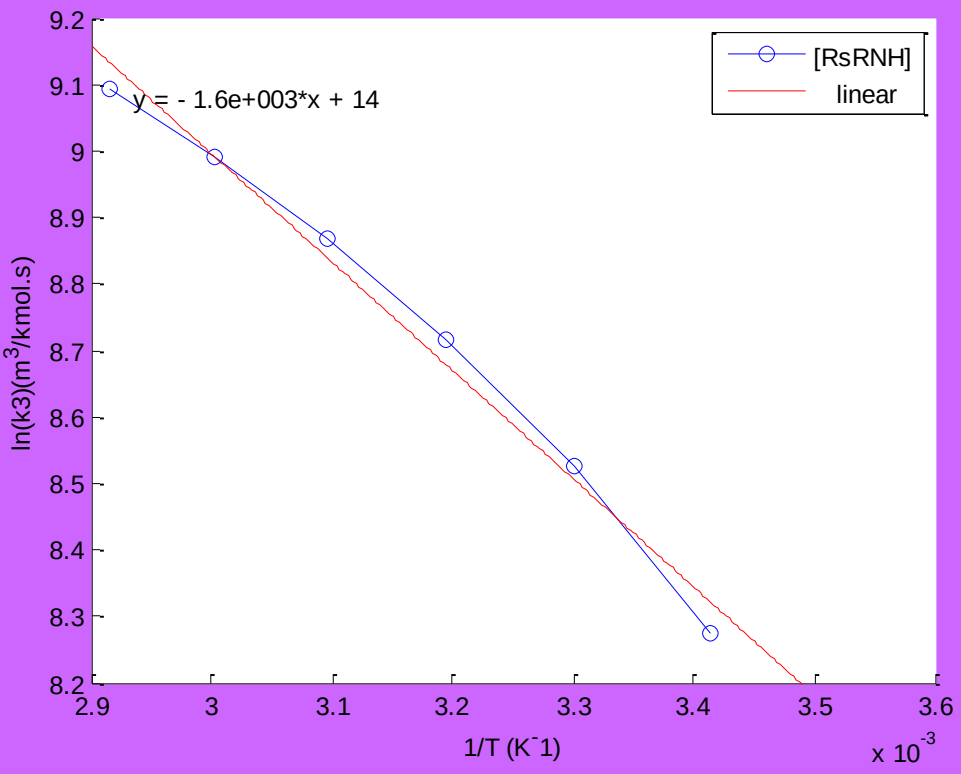

Figure 4-7: $\boldsymbol{lnk}$ versus $\boldsymbol{1/T}$

From the graph, note that the slope represent $-E/R$ and the intercept represent lnA.

Thus calculating for A:

$lnA = 14 \rightarrow A = 1.203 \times 10^6$

Thus,

$$k_3 = 1.203 \times 10^6 e^{(-\frac{1600}{T})} \quad \textbf{(35)}$$

For $k_3(k_4/k_{-3})$:

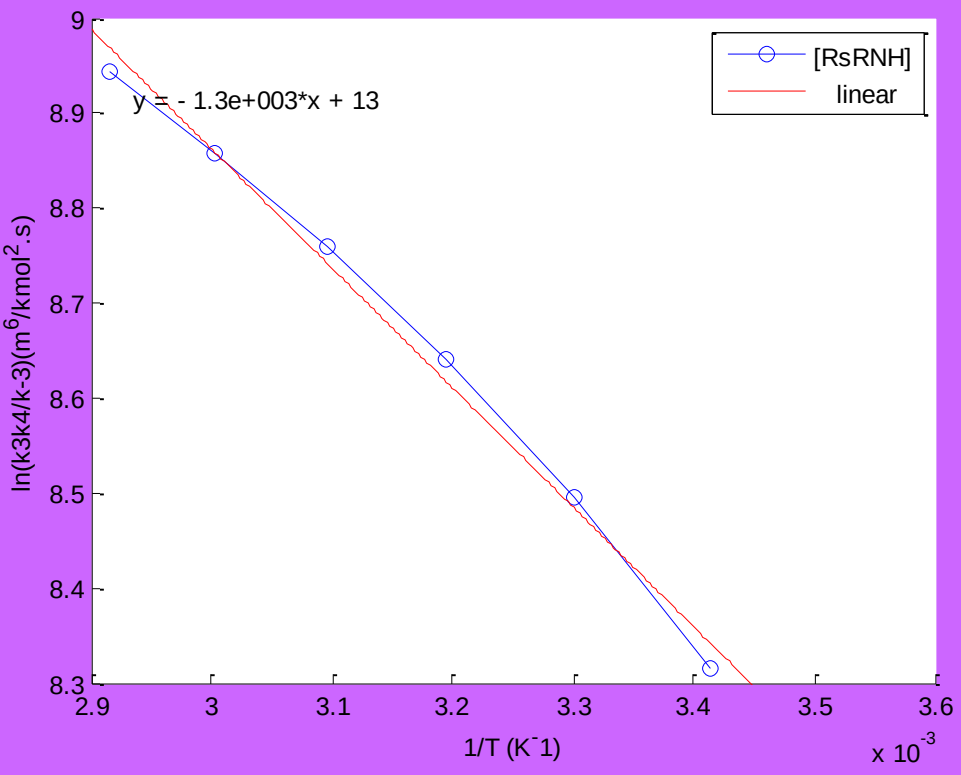

Figure 4-8: $\boldsymbol{lnk}$ versus $\boldsymbol{1/T}$

$lnA = 13 \rightarrow A = 4.424 \times 10^5$

$$k_3\,(k_4/k_{-3}) = 4.424 \times 10^5 e^{(-\frac{1300}{T})} \quad \textbf{(36)}$$

4.2. Estimating liquid bulk concentration for all chemical species

In estimating the liquid bulk concentration, equations (14) to (22) are make used with the initial assumption of initial aminated resin concentration to be 1 kmol/m^3 with zero initial CO_2 loading, L_1 in the solution. The equilibrium constant for each reaction are calculated using the correlations given in Table 3-2. MATLAB program used to simulate the result is as per attached in appendix 10.

4.2.1. Equilibrium constant for reaction (i)

Using the correlation listed in Table 3-2, the equilibrium constant calculated are given in Table 4-2.

Table 4-2: Equilibrium Constant Estimation

T(K)	298	303	318
K_2	0	0	0
$K_3K_4K_{10}K_{13}$	0	0	0
K_{10}	7.7668e+008	5.8533e+008	2.6181e+008
K_{11}	4.6345e-011	5.1018e-011	6.3468e-011
K_{12}	4.6345e-011	5.1018e-011	6.3468e-011
K_{13}	0	0	0

When the temperature increases, the equilibrium constant for reaction (10) is found to decrease while the equilibrium constant for reaction (11) and (12) seems to increase with temperature. Note that the calculation for K_2 and $K_3K_4K_{10}K_{13}$ is related to K_{13}. Thus, when K_{13} is zero, the K_2 and $K_3K_4K_{10}K_{13}$ will also be zero.

4.2.2. Liquid bulk concentration for all chemical species

Having the equilibrium constant and with the assumed initial concentration of aminated resin of 1 kmol/m^3, the result in Table 4-3 is obtained for the liquid bulk concentration for each chemical species. Note that the initial CO_2 loading in the solution, L_1 is zero.

Table 4-3: Liquid Bulk Concentration (kmol/m^3)

T(K)	298	303	318	Rinker et al. [5]
$[CO_2°]$	0	0	0	0
$[R_sRNH°]$	0.99996412	0.99995867	0.99993820	0.93496530
$[R_sRNH_2^+°]$	0.3588e-4	0.4133e-4	0.6180e-4	0.3470e-4
$[HCO_3^-°]$	0	0	0	0
$[OH^-°]$	0.3588e-4	0.4133e-4	0.6180e-4	0.3470e-4
$[CO_3^{2-}°]$	0	0	0	0
$[H_3O^+°]$	0	0	0	0
$[R_sRNCOO^-°]$	0	0	0	0
$[H_2CO_3°]$	0	0	0	0

Note that when the initial CO_2 loading in the solution equal to zero, all the chemical species involved in equation (15) have zero liquid bulk concentration. The initial bulk concentration of aminated resin decreases with increasing temperature. The accuracy of developed model used to was validated by recalculating liquid bulk concentration in Rinker et al. [5] work. The values obtained are as in Table 4-3. Figure 1 [5] confirmed the values that we obtained with this model are accurate.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1. Conclusions

Assuming the aminated resin to be a secondary alkanolamines that has been functionalized with an uknown resin, the kinetics of the reactive absorption between CO_2 and aminated resin can be described by the zwitterrion mechanism. Following the work done by Rinker et al. [5], the rigorous numerical mass-transfer model was used to estimate the reaction rate kinetics of the aminated resin with all reactions are considered to be reversible. The correlations proposed in past literatures are modeled into the MATLAB to fine the liquid bulk concentration of the aminated resin. The result obtained from the mathematical model developed in MATLAB seems promising and the model is proven feasible to be use to find the kinetics of CO_2 reactive absorption in aminated resin system.

5.2. Recommendations

Further study must be done on the nature of the aminated resin so that the exact composition and properties of it can be obtained. In future, the relationship between CO_2 concentration with respect to time, temperature, pressure and the aminated resin concentration itself should be modelled and simulated. Feasibilty of using the aminated resin must be investigated by simulating the kinetics behavior in MATLAB. Comparison of the simulation result and the experimental result should be done and if the deviation is high, other model should be employed. In the end, the best operating parameters for the aminated resin need to be identified.

REFERENCES

[1] http://www.naturalgas.org/overview/background.asp

[2] http://www.newpointgas.com/amine_treating.php

[3] Anonymous. (2006). Natural gas processing: The crucial link between natural gas production and its transportation to market. *Energy Information Administration. Office of Oil and Gas*.

[4] Haws, R. (2001). Contaminants in amine gas treating.

[5] Rinker, E.B., Ashour, S.S., & Sandall, O.C. (1996). Kinetics modelling of carbon dioxide absorption into aqueous solution of diethanolamine. *Industrial and Engineering Chemistry Research*, 35, 1107-1114.

[6] Kenig, E.Y., Wiesner, U., & Gorak, A. (1997). Modelling of reactive absorption using the Maxwell-Stefan equations. *Industrial and Engineering Chemistry Research*, 36, 4325-4334.

[7] Pacheco, M.A, & Rochelle, G.T (1998). Rate-based modelling of reactive absorption of CO_2 and H_2S into aqueous methyldiethanolamine. *Industrial and Engineering Chemistry Research*, 38, 4107-4117.

[8] Kenig, E. Y., Schneider, R., & Gorak, A. (2001), Reactive absorption: Optimal process design via optimal modelling. *Chemical Engineering Science*, 56, 343-350.

[9] Mandal, B. P., Guga, M., Biswas, A. K., & Bandyopadhyay, S. S. (2001). Removal of carbon dioxide by absorption in mixed amines: Modelling of absorption in aqueous MDEA/MEA and AMP/MEA solutions. *Chemical Engineering Science*, 56, 6217-6224.

[10] Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., & Idem, R. (2003). Kinetics of the reactive absorption of carbon dioxide in high CO_2-loaded, concentrated aqueous monoethanolamine solutions. *Chemical Engineering Science*, 58, 5195-5210.

[11] Ebenezer, S. A. (2005). Removal of carbon dioxide from Natural gas for LNG production. Institute of Petroleum Technology, Norwegian University of Science and Technology.

[12] Maddox, R. N. (1982) Gas Conditioning and Processing – Advanced Techniques and Applications, Ed.: *Campbell Petroleum Series, Norman, Okla*. p.370

[13] http://www.naturalgas.org/overview/uses.asp

[14] Hagewiesche, D.P., Ashour, S.S., Al-Ghawas, H. A., & Sandall, O.C. (1995). Absorption of carbon dioxide into aqueous blends of monoethanolamine and N-methyldieathanolamine. *Chemical Engineering Science*, 50, 1071-1079.

[15] Crooks, J. E., Donnellan, J.P. (1989). Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. *Journal of Chemical Society of PerkinnTransaction II,* 331-333.

[16] Birbara, P.J., Locks, W., Nalette, T.A., Tolland, all of Conn. (1992). Regenerable Supported Amine-Polyol Sorbent. U.S Patent. Patent Number: 5376614.

[17] Birbara, P.J., Locks, W., Filburn, T.P., Granby., Nalette, T.A., Tolland, all of Conn. (1996). Regenerable Solid Amine Sorbent. U.S Patent. Patent Number: 5876488.

[18] Kohl, A.L., & Nielsan, R. B. (1997). *Gas purification*. Houston: gulf Publishing Company.

[19] Schubert, S., Grunewald, M., Agar, D.W. (2001). Enhancement of carbon dioxide absorption into aqueous methyldiethanolamine using immobilized activators. *Chemical Engineering Science*, 56, 6211-6216.

[20] Alper, E., & Deckwer, W.D., (1983). Some aspects of gas absorption mechanism in slurry reactors. *NATO ASI series E*, No, 73, Vol. 2 (pp. 199-224). The Hague: Martinus Nijhoff.

[21] Saha, A.K., Bandyopadhyay, S. S., & Biswas, A.K. (1992). Absorption of carbon dioxide in alkanolamines in the present of fine activated carbon particles. *Canadian Journal of Chemical Engineering*, 70(2), 193-196.

[22] Diaf, A., Enick, R. M., & Beckmann, E.J., (1993). Molecular redesign of expanded polystyrene to allow use of carbon dioxide as a foaming agent. I. Reversible binding of CO_2. *Journal of Applied Polymer Science*, 50, 835-844.

[23] Rinker, E. B., Ashour, S. S., & Sandall, O. C. (1995). Kinetics and modelling of carbon dioxide absorption into aqueous solutions of N-methyldiethanolamine. *Chemical Engineering Science*, 50(5), 755–768.

[24] Zhang, X.,Schubert, S., Grunewald, M., & Agar, D.W. (2003). Studies on the kinetics of carbon dioxide absorption with immobilized amines (IA). *Chemical Engineering Science*, 107, 97-102.

[25] Technical Challenges and Solution on Natural Gas Development in Malaysia (2006). Presented by Dr. Nasir Haji Darman/Abd Rahman B Harun.

[26] T.L. Donaldson, Y.N. Nguyen, Carbon dioxide reaction kinetics and transport in aqueous amine membranes, Ind. Eng. Chem. Fundam. 19 (1980) 260-266.

[27] Little, R.J.;Versteeg, G.F.;van Swaaij, W.P.M. Kinetics of CO_2 with primary and secondary amines in aqueous solution-II. Influence of temperature on zwitterions formation and deprotonation rates. *Chem. Eng. Sci*. 1992, 47, 2037-2045.

[28] Versteeg, G. F.; Oveyar, M. H. The reaction between CO_2 and diethanolamine at 298K. *Chem. Eng. Sci.* 1989, 44, 1264-1268.

[29] Yoon, J. H.; Baek, J. I., Yamamoto, Y., Komai, T., Taro, K. Kinetics of removal of carbon dioxide by aqueous 2-amino-2-methyl-1,3-propanediol. *Chem. Eng. Sci.* 2003, 58, 5229-5237.

[30] Lin, C.Y., Soriano, A.N., Li, M. H. Kinetics study of carbon dioxide absorption into aqueous solutions containing *N*-methyldiethanolamine + diethanolamine. *Journal of the Taiwan Institute of Chemical Engineers.* 2009, 40, 403-412.

[31] Mandal, B.P., Boswas, A.K. Bandyipadhyay, S.S. Absorption of carbon dioxide into aqueous blends of 2-amino-2methyl-1-propanol and diethanolamine. *Chem. Eng. Sci.* 2003. 58, 4137-4144.

APPENDICES

Appendix 1: Gantt chart and Milestone for the First Semester

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic								Mid-Semester break							
2	Preliminary Research Work • Natural Gas composition • CO_2 treating process • Solutions used in CO_2 removal • CO_2 content in unexplored reserves															
3	Submission of Preliminary Report					x										
4	Literature Research on • Mechanism involved in CO_2 Absorption • Generic Mathematical Model used for reactive absorption • Reaction kinetics constant • Absorption kinetics constant															
4	Seminar 1 (optional)															

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
5	Find literatures that studied on reactive absorption of similar reactions.							■		■						
6	Submission of Progress Report									x						
7	Seminar 2 (compulsory)										■	■	■	■		
8	Screen and identify suitable reaction kinetics equations for Project Work										■	■	■	■		
9	Learn to use MATLAB									■	■	■	■	■		
10	Submission of Interim Report Final Draft														x	
11	Oral Presentation															x

x Milestone

■ Process

Appendix 2: Gantt chart and Milestone for the Second Semester

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Screen and identify suitable reaction kinetics equations for Project Work															
2	Develop basic equation for the reaction between CO_2 and the aminated resin															
3	Investigate and identify the suitable mathematical model and model parameters for reactive absorption from past literatures															
4	Submission of Progress Report 1					x										
5	Develop reaction equations to represent the reaction between CO_2 and the aminated resin															
6	Screen and identify mathematical models that represent reactive absorption kinetics															
7	Model and simulate the Arrhenius equation in MATLAB using approach proposed in past literature															
8	Submission of Progress Report 2									x						

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
9	Seminar															
10	Project work continue															
11	Start designing Poster															
12	Poster Exhibition												x			
13	Develop MATLAB programme to estimate the liquid bulk concentration for all chemical species															
13	Submission of Dissertation (soft bound)													x		
14	Oral Presentation														x	
15	Submission of Project Dissertation (Hard Bound)															X

x Milestone

Process

Appendix 3: Mathematical programme used for Figure 4.1

```
close all;
clear all;
clc;
x=[0.1 1.0 2.0 3.0];
yDEA=[300 900 1300 1800];
y=[1.1]*[yDEA];
%[330 990 1430 1980];

figure (1)
hold on;
plot(x,y,'bo-',x,yDEA,'mo-')
xlabel('[solution](kmol/m3)')
ylabel('kapp(m3/kmol.s) at 298K')
legend('[RsRNH]','[DEA][5]')
```

Appendix 4: Mathematical programme used for Figure 4.2

```
close all;
clear all;
clc;
x=[0.1 1.0 2.0 3.0];
yDEA=[300 900 1300 1800];
y=[1.1]*[yDEA];
x1=[1/x(1) 1/x(2) 1/x(3) 1/x(4)];
y0=[1/yDEA(1) 1/yDEA(2) 1/yDEA(3) 1/yDEA(4)];
y1=[1/y(1) 1/y(2) 1/y(3) 1/y(4)];

figure (2)
hold on;
plot(x1,y1,'bo-',x1,y0,'mo-')
xlabel('1/[solution](m3/kmol)')
ylabel('1/kapp(kmol.s/m3) at 298K')
legend('[RsRNH]','[DEA][5]')
```

Appendix 5: Mathematical programme used for Figure 4.3 and 4.5

```
close all;
clear all;
clc;
T=[293 298 303 313 323 333 343];
x=[1000/T(1) 1000/T(2) 1000/T(3) 1000/T(4) 1000/T(5) 1000/T(6)
1000/T(7)];
k3=[3530 4089 5121 5516 5983 6485 9830];
%k4=k3k4/k-3
k4=[1079 1135 1511 1617 2782 3160 5015];
figure(3);
plot(x,k3,'mo');
xlabel('1000/T (K^-1)')
ylabel('k3(m^3/kmol.s)')
legend('[DEA][5]')
figure(4);
plot(x,k4,'mo');
xlabel('1000/T (K^-1)')
ylabel('k3k4/k-3(m^6/kmol^2.s)')
legend('[DEA][5]')
```

Appendix 6: Mathematical programme used for Figure 4.4

```
close all;
clear all;
clc;
%y=mx+c
%c=y-mx
m3=-1e4;
T=298;
x=1000/T;
k3=4496;

c3=k3-m3*x;
k3=m3*x+c3;
a=1;
for T=293:10:343
    x=1000/T;
    k3=m3*x+c3;
    matrix_x(a)=x;
    matrix_y(a)=k3;
    a=a+1;
end
    figure(1)
    hold on;
    plot(matrix_x,matrix_y,'bo-');
    xlabel('1000/T (K^-1)')
    ylabel('k3(m^3/kmol.s)')
    legend('[RsRNH]')
```

Appendix 7: Mathematical programme used for Figure 4.6

```
close all;
clear all;
clc;
%y=mx+c
%c=y-mx
m4=-7.2e3;
T=298;
x=1000/T;
%k4=k3k4/k-3
k4=4496;

c4=k4-m4*x;
k4=m4*x+c4;
a=1;
for T=293:10:343
    x=1000/T;
    k4=m4*x+c4;
    matrix_x(a)=x;
    matrix_y(a)=k4;
    a=a+1;
end
    figure(1)
    hold on;
    plot(matrix_x,matrix_y,'bo-');
    xlabel('1000/T (K^-1)')
    ylabel('k3k4/k-3(m^6/kmol^2.s)')
    legend('[RsRNH]')
```

Appendix 8: Mathematical programme used for Figure 4.7

```
close all;
clear all;
clc;
%y=mx+c
%c=y-mx
m3=-1e4;
T=298;
x=1000/T;
k3=4496;

c3=k3-m3*x;
k3=m3*x+c3;
a=1;
for T=293:10:343
    x=1000/T;
    t=1/T;
    k3=m3*x+c3;
    lnk3=log(k3);
    matrix_x(a)=x;
    matrix_y(a)=k3;
    matrix_t(a)=t;
    matrix_lnk3(a)=lnk3;
    a=a+1;
end
    figure(1)
    hold on;
    plot(matrix_t,matrix_lnk3,'bo-');
    xlabel('1/T (K^-1)')
    ylabel('ln(k3)(m^3/kmol.s)')
    legend('[RsRNH]')
```

Appendix 9: Mathematical programme used for Figure 4.8

```
close all;
clear all;
clc;
%y=mx+c
%c=y-mx
m4=-7.2e3;
T=298;
x=1000/T;
%k4=k3k4/k-3
k4=4496;

c4=k4-m4*x;
k4=m4*x+c4;
a=1;
for T=293:10:343
    x=1000/T;
    t=1/T;
    k4=m4*x+c4;
    lnk4=log(k4);
    matrix_x(a)=x;
    matrix_y(a)=k4;
    matrix_t(a)=t;
    matrix_lnk4(a)=lnk4;
    a=a+1;
end
    figure(1)
    hold on;
    plot(matrix_t,matrix_lnk4,'bo-');
    xlabel('1/T (K^-1)')
    ylabel('ln(k3k4/k-3)(m^6/kmol^2.s)')
    legend('[RsRNH]')
```

Appendix 10: Equilibrium constant and liquid bulk concentration at 298K

```
function LiqBulkConc2

%Assume initial concentration of RsRNH = 1 kmol/m^3 with initial CO2
%loading in solution L1=0

%eq1= u2o + u3o + u8o = RsRNHint = 1;
%eq2= u1o + u4o + u6o + u8o + u9o = L1*RsRNHint;
%eq3= u3o + u7o - u4o - u5o - 2*u6o -u8o = 0;

T=input('Enter T value: ');

k1=0.026 %s-1,at 25oC(very slow).May usually be neglected as
suggested by Blauwhoff et.al(1984)

%log10K2 = 13.635 - (2895/T)--> (Pinsent et al.,1956)
log10K2= 13.635 - (2895/T);
k2=10^(log10K2)

%log10(1/K6) = -4.0302 - (1830.15/T) + 0.0043*T --> Barth (1981)
log101ovrK10 = -4.0302 - (1830.15/T) + 0.0043*T;
K10=1/(10^(log101ovrK10))

%log10K11 = 6.498 - 0.0238*T - (2902.4/T)-->Danckwerts & Sharma
(1966)
log10K11 = 6.498 - 0.0238*T - (2902.4/T);
K11=10^(log10K11)

%log10(1/K13) = 8909.483 - (142613.6/T) - 4229.195*log10(T) +
9.7384*T - 0
%--> Oloffson & Hepler (1975)
log101ovrK13 = 8909.483 - (142613.6/T) - 4229.195*log10(T) +
9.7384*T - 0;
K13=1/(10^(log101ovrK13))

%calculation for K2----
log10K2ovrK13 = 179.648 + (0.019244*T) - 67.341*log10(T) +
7495.441/T ;
```

```
K2ovrK13=10^(log10K2ovrK13)
K2=K2ovrK13*K13

%calculation for K1----
log10K4ovrK13 = (-7261.78/T) -22.4773*log(T) + 142.58612;
K4ovrK13=10^(log10K4ovrK13)
K1=K2*K4ovrK13

%calculation for K3K4---
k3=1.203E6*exp(-1600/T);
%neglect k4r
%K3K4=k3k4k3r
k3k4k3r=4.424E5*exp(-1300/T);
K3K4=4.424E5*exp(-1300/T)

%calculatoion for K3K4K10K13
K3K4K10K13=K3K4*K10*K13

%no correlation found to fit K12, thus:
K12=K11 %assumed rate of these two is same
%-----------------------------------------------------------------------
T
K2
K3K4K10K13
K10
K11
K12
K13
%-----------------------------------------------------------------------
```

```
S = solve ('u2o + u3o + u8o - 1 = 0 ','u1o + u4o + u6o + u8o + u9o =
0','u3o + u7o - u4o - u5o - (2*u6o) -u8o = 0','u4o - (0*(u1o*u5o)) =
0','(u7o*u8o) - (0*(u1o*u2o)) = 0','u2o- (7.7668e+008*(u3o*u5o)) =
0','u6o - (4.6345e-011*(u4o*u5o)) = 0','u9o - (4.6345e-
011*(u4o*u7o)) = 0','(u5o*u7o) = 0')
%S = solve('RsRNH=1','u2o + u3o + u8o - RsRNH = 0 ','L1=0','u1o +
u4o + u6o + u8o + u9o - (L1*RsRNH) = 0','u3o + u7o - u4o - u5o -
(2*u6o) -u8o = 0','T=298','(8909.483*T) - (142613.6) -
(4229.195*T*log10(T)) + (9.7384*T*T) - 0
=(log101ovrK13*T)','(K13*(10^(log101ovrK13)))=1','(179.648*T) +
(0.019244*T*T) - (67.341*T*log10(T)) +
7495.441=(log10K2ovrK13*T)','K2ovrK13=(10^(log10K2ovrK13))','K2=(K2o
vrK13*K13)','u4o - (K2*(u1o*u5o)) = 0','(-4.0302*T) - (1830.15) +
(0.0043*T*T)=(log101ovrK10*T)','K10*(10^(log101ovrK10))=1','K3K4=(4.
424E5*exp(-1300/T))','K3K4K10K13=(K3K4*K10*K13)','(6.498*T) -
(0.0238*T*T) -
(2902.4)=(log10K11*T)','K11=(10^(log10K11))','K12=K11','(u7o*u8o) -
(K3K4K10K13*(u1o*u2o)) = 0','u2o- (K10*(u3o*u5o)) = 0','u6o -
(K11*(u4o*u5o)) = 0','u9o - (K12*(u4o*u7o)) = 0','(u5o*u7o)- K13 =
0')
u1o=S.u1o;
u2o=S.u2o;
u3o=S.u3o;
u4o=S.u4o;
u5o=S.u5o;
u6o=S.u6o;
u7o=S.u7o;
u8o=S.u8o;
u9o=S.u9o;

u1o=S.u1o(2)
u2o=S.u2o(2)
u3o=S.u3o(2)
u4o=S.u4o(2)
u5o=S.u5o(2)
u6o=S.u6o(2)
u7o=S.u7o(2)
u8o=S.u8o(2)
u9o=S.u9o(2)
```