KINETIC STUDY OF THE CATALYTIC DESORPTION OF CARBON DIOXIDE (CO₂) FROM CO₂-LOADED MONOETHANOLAMINE (MEA) AND BLENDED MONOETHANOLAMINE-METHYLDIETHANOLAMINE (MEA-MDEA) DURING POST-COMBUSTION CO₂ CAPTURE FROM INDUSTRIAL FLUE GASES

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In Partial Fulfillment of the Requirements
For the Degree of

Master of Applied Science

in
Process Systems Engineering
University of Regina

By
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Regina, Saskatchewan
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Ananda Udochi Akachuku, candidate for the degree of Master of Applied Science, has presented a thesis titled, *Kinetic Study of the Catalytic Desorption of Carbon Dioxide (CO2) from CO2-Loaded Monoethanolamine (MEA) and Blended Monoethanolamine-Methyldiethanolamine (MEA-MDEA) during Post Combustion CO2 Capture from Industrial Flue Gases*, in an oral examination held on October 31, 2016. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

The objective of this research was to elucidate the kinetics of the catalyst-aided desorption of CO$_2$ from CO$_2$-loaded aqueous solutions of single monoethanolamine (MEA), and monoethanolamine blended with methyldiethanolamine (MEA-MDEA) during the post-combustion capture of CO$_2$ from industrial flue gases. The experiments were performed over γ-Al$_2$O$_3$ and HZSM-5 catalysts in a complete absorber – desorber CO$_2$ capture pilot plant unit with the absorber and desorber columns having an internal diameter of 2-inches (0.051 m) and a total height of 3.5 ft (1.067 m). The experimental kinetic data for CO$_2$ desorption were obtained in the catalytic packed bed tubular desorber at three temperatures (348, 358, and 358 K), using MEA and MEA-MDEA concentrations respectively of 5M and 5.2M (molar ratio and total molarity of 7M) and CO$_2$ loading ranging from ~ 0.331-0.5 mol CO$_2$/mol amine for different ratios of weight of catalyst/flow rate of amine (W/F$_{Am}$). The kinetic performance was evaluated in terms of conversion (i.e. %CO$_2$ desorbed), activation energy, frequency factor and rate constants. A comprehensive first order power law rate model and Langmuir-Hinshelwood-Hougen-Watson (LHHW), mechanistic models for the heterogeneous reactions, were developed. The results showed that HZSM-5 catalyst with higher Brønsted/Lewis acid site ratio exhibited dual site adsorption mechanism and provided faster kinetics and higher conversions with lower activation energy in comparison with γ-Al$_2$O$_3$ for both solvents. Also, a statistical analysis using four catalysts, namely, HZSM-5, γ-Al$_2$O$_3$, silica-alumina and HY (of widely varying characteristics in terms of BET surface area, pore size and distribution, pore volume, total acid sites, acid site strength and Brønsted/Lewis acid site ratio), as well as an inert parking scenario to determine the contributions of each characteristic to catalyst performance in CO$_2$ desorption from CO$_2$-loaded aqueous amines. The results showed that catalyst
performance on CO$_2$ desorption from CO$_2$-rich MEA solution depended strongly on both the combined high acid strength with high B/L ratio as well as the high ratio of pore size to pore volume.
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## TABLE OF CONTENT

**ABSTRACT** ................................................................................................................................................. i  

**ACKNOWLEDGEMENTS** ................................................................................................................................. iii  

**TABLE OF CONTENT** ......................................................................................................................................... iv  

**LIST OF TABLES** ............................................................................................................................................... viii  

**LIST OF FIGURES** ............................................................................................................................................... x  

**NOMENCLATURE** ............................................................................................................................................... xii  

**CHAPTER 1: INTRODUCTION AND BACKGROUND** ......................................................................................... 1  

1.1 The Need for Capture CO₂ ................................................................................................................................. 1  

1.2 CO₂ Capture Technologies ...................................................................................................................................... 2  

1.2.1 Post-combustion CO₂ capture .......................................................................................................................... 2  

1.2.2 Pre-Combustion CO₂ capture .......................................................................................................................... 7  

1.2.3 Oxy-fuel Combustion ........................................................................................................................................ 7  

1.3 Amine Solvents used in CO₂ Capture and Regeneration ................................................................................... 10  

1.3.1 Solvent Chemistry: CO₂ Amine Interaction ..................................................................................................... 11  

1.4 Importance of Kinetic Data in Design and Simulation of CO₂ Capture Unit ................................................. 17  

1.5 Fundamental Processes in Amine-based CO₂ Capture: CO₂ Absorption and CO₂ Desorption. ......................... 18  

1.5.1 Issues associated with absorption .................................................................................................................. 18  

1.5.2 Issues Associated with Desorption ................................................................................................................ 19  

1.5.3 Catalytic CO₂ desorption mechanism ........................................................................................................... 20  

1.6 Thesis objectives and outline ............................................................................................................................. 22  

1.6.1 Research Objective .......................................................................................................................................... 23  

1.6.2 Scope of Thesis .............................................................................................................................................. 25  

1.6.3 Organization of Thesis ................................................................................................................................... 25  

**CHAPTER 2: LITERATURE REVIEW** ................................................................................................................. 27  

2.1 Kinetics Data for CO₂ Absorption and Desorption in aqueous MEA system .............................................. 29  

2.2 Kinetics Data for CO₂ Absorption and Desorption in aqueous MEA-MDEA System .................................. 31  

2.3 Vapor Liquid Equilibrium (VLE) ..................................................................................................................... 34  

2.4 Major and Important ions present in Single and Blended Amine-CO₂-H₂O System ...................................... 35
Appendix E: Regression Analysis: Conversion versus BET, Ratio, Total acid s, Acid strength, B/L

173
LIST OF TABLES

Table 1.2-1: Advantages and disadvantages associated with existing CO₂ capture technologies

Table 2.2-1: Summary of result of reported on desorption kinetics of CO₂ MEA-MDEA system

Table 3.4-1: Packing parameter and operating conditions

Table 3.4-2: Operating conditions for solubility tests

Table 4.2-1(a): Rate models based on LHHW mechanism for MEA+ + CO₂ +H₂

Table 4.2-2(b): Rate models based on LHHW mechanism for MEA+MDEA + CO₂ +H₂O

Table 5.1-1: Structural properties of catalyst

Table 5.2-1: Heat transport effect for CO₂ + MEA system

Table 5.2-2: Heat transport effect for CO₂ + MEA+MDEA system

Table 5.2-3: Mass transfer limitations for CO₂+MEA+H₂O system

Table 5.2-4: Plug flow conditions

Table 5.3-1: Percentage contribution of MEACOO⁻ and HCO₃⁻ to the total concentration of desorbed CO₂ for MEA system

Table 5.3-2: Percentage conversion of MEACOO⁻ and HCO₃⁻ to CO₂ for MEA System

Table 5.3-3: Percentage contribution of MEACOO⁻ and HCO₃⁻ to the total concentration of desorbed CO₂ for MEA-MDEA system

Table 5.3-4: Percentage conversion of MEACOO⁻ and HCO₃⁻ to CO₂ for MEA-MDEA System

Table 5.3-5: Parameter estimation for CO₂+ MEA+ H₂O system for γ-Al₂O₃ and HZSM-5
Table 5.3-6 Parameter estimation for CO₂+ MEA+ MDEA+ H₂O system for γ-Al₂O₃ and HZSM-5 ................................................................. 107
Table 5.3-7 Thermodynamic scrutiny for CO₂+MEA+H₂O system............... 114
Table 5.4-1: Si/Al ratio, ratio (Pore size/pore volume), total acid site, acid strength, B/L ratio and conversion for 5M MEA at 368K. ......................................................... 117
LIST OF FIGURES

Figure 1.2-1: Temperature data from four International science institutions\textsuperscript{3} pressure of CO\textsubscript{2}. This makes the chemical process a more viable and effective option for the case of power plant flue gases which exist at atmospheric pressure and low CO\textsubscript{2} partial pressure. .......................................................................................................................... 4

Figure 1.2-2: Block diagram showing CO\textsubscript{2} capture technologies\textsuperscript{6} ........................................... 6

Figure 1.3-1: Molecular Structure of commonly used amines............................................. 13

Figure 1.5-1: Non catalytic Pathway for CO\textsubscript{2} Desorption\textsuperscript{46}................................. 21

Figure 2.1.5-2: Lewis acidity and basicity ................................................................. 39
   Figure 2.1.5-2: Brønsted Acidity of HZSM-5......................................................... 42

Figure 3.4-1: Packing materials and arrangement .............................................. 48

Figure 3.4-2: Schematic of the experimental Setup............................................. 52

Figure 3.4-3: Experimental setup for CO\textsubscript{2} solubility (CO\textsubscript{2}+MEA+MDEA+H\textsubscript{2}O system .............................................................................................................................. 55

Figure 3.4-4 VLE model at 358K for MEA-MDEA-CO\textsubscript{2} absorption- desorption ..... 57

Figure 5.1-1: BET surface area and pore size distribution .......................................... 78

Figure 5.1-2: TPD pattern of $\gamma$-Al\textsubscript{2}O\textsubscript{3} and HZSM-5 catalyst.......................... 81

Figure 5.1-3: XRD pattern of $\gamma$-Al\textsubscript{2}O\textsubscript{3} and HZSM-5 catalyst...................... 81

Figure 5.3-1: Variation of catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant MEA flow rate 60 ml/min ................................................................. 91

Figure 5.3-2: Variation of catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant MEA-MDEA flow rate 60 ml/min ......................................................... 92

Figure 5.3-3: Comparison of MEA and MEA-MDEA system $\gamma$-Al\textsubscript{2}O\textsubscript{3}. Catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant amine flow rate (60 ml/min)................................................................................................................... 93
Figure 5.3-4: Comparison of MEA and MEA-MDEA system HZSM-5 Catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant amine flow rate (60 ml/min) ........................................................................................................ 94

Figure 5.3-5: Effect of MEA flow rate (50, 60, 70,80ml/min) on Conversion, X at different catalyst weight (0-300g) at 358 ........................................................................................................ 97

Figure 5.3-6: Arrhenius plot (CO2+MEA+MDEA system) ............................................ 103

Figure 5.3-7: Arrhenius plot (MEA-MDEA system) ..................................................... 104

Figure 5.3-8: Parity chart for all developed models (MEA and MEA-MDEA system) .................................................................................................................................................. 109

Figure 5.3-9: Parity chart for all developed models involving bicarbonate ion (MEA system) ........................................................................................................................................ 110

Figure 5.3-10: Parity chart for all developed models involving bicarbonate ion MEA and (MEA-MDEA system) .................................................................................................................. 111

Figure 5.4-1: Conversion for different acid catalyst ..................................................... 116

Figure 5.4-2: Matrix Scatter plot of all variables .......................................................... 119
NOMENCLATURE

**Notation**

[A] Concentration of species, mol/dm$^3$

$AAD$ average absolute deviation

$C_{wp,ipd}$ Weisz–Prater criterion for internal pore diffusion

d internal diameter of reactor, m

d$p$ diameter of particle, mm

$D$ diffusivity coefficient, m$^2$ s$^{-1}$

$E_a$, activation energy, J mol$^{-1}$

$F_{Amine}$ Molar flow rate of species mol min$^{-1}$

$kc$ mass transfer coefficient, m$^2$ s$^{-1}$

$k_0$ pre-exponential or collision factor

$K_i$ adsorption constant for the species ($i = 1, 2, 3, 4$)

$L$ length of catalyst bed, m

$P$ pressure, atm

$r$ radius of the catalyst bed, m

$r_i$ rate of reaction based on a particular species, mol gcat$^{-1}$ min$^{-1}$ ($i = A,B,C,\ldots$)

$R$ universal gas constant, kJ kmol$^{-1}$ K$^{-1}$

$R_c$ radius of catalyst particle, m

$T$ temperature, K

$W$ weight of catalyst, g

$(W/F_{Amine})$ Contact time, min

$X_i$ conversion of component $i$
Greek Letters

$\Delta H$  Enthalpy of reaction, KJ kmol$^{-1}$

$\Delta S$  Entropy of reaction, KJ kmol$^{-1}$

$\Delta G$  Gibbs free energy of reaction, KJ kmol$^{-1}$

$\varepsilon$  Porosity

$\lambda$  Thermal conductivity KJ m$^{-1}$s$^{-1}$K$^{-1}$

$\mu$  Viscosity

$\rho_b, \rho_c$  Density, kg m$^{-3}$

$\tau$  Toutorsity factor

Superscripts

$n$, reaction order with respect to CO$_2$

Inlet entering the reactor

Outlet exiting the reactor

Superscripts

$b$  Bulk

c  Catalyst

$p$  Pellet or particle

$eff$  Effective

ipd  Internal pore diffusion

obs  Observed

C  Carbamate

H  Protonated MEA

A  Free MEA, MDEA
CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 The Need for Capture CO₂

Carbon dioxide (CO₂), as well as other greenhouse gases (water vapour, methane, and nitrous oxide), are naturally present in the atmosphere. These gases are less harmful to the environment in their natural quantities. However, the continuous increase in the rate of CO₂ production resulting from human activities such as fossil fuel combustion and other industrial activities and its emission into the atmosphere has increased the importance placed on CO₂ mitigation processes in light of fear of climate change, as recent studies¹ show its significant contribution to the constant rise in global temperature (Figure 1.2-1).

Recently, Canada amongst other nations reached a landmark agreement to combat climate change at the 21st Conferences of Parties, COP 21, Paris Summit (2016), which aims at keeping the global temperature rise below 2°C, which is directly above the pre-industrial level. This agreement involves development and modification of Carbon Capture Storage (CCS) technologies. According to the International Energy Agency (IEA), Carbon Capture Storage is the only technology available to reduce the GHG emission resulting from industrial scale combustion of fossil fuels². This technology accounts for about 20 percent of global GHG emission reduction needed by 2050 as per the COP 21 agreement. The ultimate goal of CCS is to store the captured CO₂. However, the captured CO₂ can be used in several industrial processes such as enhanced oil recovery (EOR), where it is injected into an oil reservoir and drives out the oil via the production well. It can also used in the food industry in the manufacture carbonated drinks.
1.2 CO₂ Capture Technologies

Several CCS technologies have been developed for capturing CO₂ from carbon-based energy systems. Among these developed technologies, economic factors play a key role in process selection. Some of the developed technologies include post-combustion capture, pre-combustion capture, and oxyfuel combustion systems (Figure 1.2-2).

1.2.1 Post-combustion CO₂ capture

This is the most common technology used for CO₂ capture. It involves the capture of CO₂ downstream of a combustion system. Fossil fuels are combusted in air to generate flue gas streams with a CO₂ concentration of 10-15 v/v% and 5-8 v/v%² for coal, and natural gas-fired plants, respectively. A variety of techniques can be used to capture CO₂ via post-combustion methods. Such techniques include absorption, adsorption, membrane separation, and cryogenic separation. Among these techniques, solvent absorption is considered to be the most viable option.

1.2.1.1 Absorption Process

Absorption process involves the counter current flow of CO₂ using an absorption unit. The flue gas is introduced at the bottom of the absorber, and the liquid absorbent is introduced at the top, allowing for the counter current flow. CO₂ absorption process can further be divided into physical and chemical process. The physical process involves the dissolution of CO₂ in the physical solvent without any chemical interaction, whereas the chemical absorption process involves the use of chemical reactive solvent to absorb CO₂ from the flue gas stream. However, the physical method is only favorably at high total pressure and high CO₂ partial pressure.
as the capacity of absorption and driving force depends strongly on both the total pressure and partial pressure.

1.2.1.2 Adsorption process

Adsorption involves the use of solid materials such as zeolites and activated carbon to adsorb CO₂ from flue gas streams. The flue gas is passed through the bed containing the adsorbent. The two types of adsorption processes commonly used are the pressure swing adsorption (PSA) and temperature swing adsorption (TSA). Here the gas flows through the adsorbent bed at high pressure until equilibrium is achieved. Regeneration of bed occurs by lowering the pressure in PSA and increasing the temperature of the bed in the case of TSA. The major disadvantage of the adsorption technique is the low availability of CO₂ selective- and high capacity-adsorbents.

1.2.1.3 Cryogenics

Cryogenic separation process separates the CO₂ content present in the combustion flue gas stream by liquefying the flue gas via cooling and condensation. The liquefied CO₂ is then separated from the gas phase. This method has been used for purification of gases having high CO₂ concentration. The major advantage of this process is that it produces CO₂ in the liquefied form which allows for easier transportation. However, cryogenic methods are quite expensive because of the cost and energy associated with the compression and cooling of CO₂ gas.
Figure 1.2-1: Temperature data from four International Science institutions' pressure of CO₂. This makes the chemical process a more viable and effective option for the case of power plant flue gases which exist at atmospheric pressure and low CO₂ partial pressure.
Membrane process involves the use of semi-permeable barrier which allows the passage of selected components. The driving force is based on the diffusion rate of individual gas components from one side of the membrane barrier to the other side. This driving force can either be concentration or pressure driven and can occur between two gas phases, two liquid phases or between a gas and liquid phase.

There are two types of membrane separation systems; pressure membrane and gas absorption membrane. In the gas absorption separation technique, the driving force is concentration driven such that one component in the gas stream passes through faster than the other components by diffusing through the membrane. This method is usually used for CO$_2$ separation. The microporous membrane is in direct contact with the liquid absorbent. The CO$_2$ gas must first dissolve and penetrate the pores of the membrane before being absorbed into the liquid absorbent. This controls the movement of each molecule between the miscible phases$^3$. Pressure membrane involves processes such as ultrafiltration, microfiltration, and reverse osmosis. It involves the separation of very small components that are suspended in liquids. The process occurs at high pressure, deriving its driving force from the differential pressure. A good example is the separation of salt from low molecular solutes at high pressure using membranes with NMWLs.$^4$
Figure 1.2-2: Block diagram showing CO₂ capture technologies

---

**Post-Combustion**

- **Boiler**
  - Fuel
  - Air

- **Flue gas**
  - N₂ (70%)
  - CO₂ (3-15%)

- **CO₂ Capture**

- **Nitrogen**

**Pre-Combustion**

- **Air Separation Unit**
  - Oxygen

- **Gasifier/Shift**
  - Fuel

- **Syn gas**
  - H₂ (40%)
  - CO₂

- **CO₂ Capture**

- **Combustion Turbine**
  - H₂
  - Air
  - Heat

**Oxy-Combustion**

- **Air Separation Unit**
  - Oxygen

- **Steam Turbines**

- **Boiler**
  - Fuel

- **Recycle Flue Gas**

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6
1.2.2 Pre-Combustion CO$_2$ Capture

Pre-combustion CO$_2$ capture involves the conversion of carbon containing fuels into syngas (hydrogen, H$_2$ and carbon monoxide, CO) through steam reforming, gasification or partial oxidation. Carbon monoxide is further converted into CO$_2$ via the water gas shift reaction. This process generates a high concentration of CO$_2$ (25-40%) and is conducted at pressures of 2.5-5 Mpa, resulting in high total pressure and CO$_2$ partial pressure which favors the separation of CO$_2$ from H$_2$ gas through scrubbing using physical solvents$^2$. H$_2$ can further be used as a feedstock or combusted in a turbine to produce electricity. The name pre-combustion is as a result of the separation of CO$_2$ before H$_2$ utilization.

1.2.3 Oxy-fuel Combustion

Oxy-fuel combustion technique is an alternative method for CO$_2$ capture. This technique separates CO$_2$ from the flue gas in the absence of nitrogen. The flue gas is burned with approximately 95% pure oxygen mixed with recycled flue gas. In the most recent development, the pure oxygen is supplied by a cryogenic air separator unit (ASU)$^6$ and is further mixed with recycled flue gas before combustion. This is done to allow the material to withstand the high temperature generated during coal combustion in oxygen. The main advantage associated with oxy-fuel combustion is the predominate production of CO$_2$ and water. Water can further be removed by condensation and CO$_2$ can be further purified to remove O$_2$ and other diluents such as SO$_2$ and NOx.
Nevertheless, the selection of a suitable CO₂ capture method depends on several factors such as the initial condition of the flue gas stream, the desired treated gas purity, end use of purified gas and concentration of CO₂ in the gas stream. Each method has its advantages and limitation as presented in Table 1.2-1. Despite the drawback associated with the high heat required for solvent regeneration, CO₂ capture by amine solvent absorption remains the best technique applied in CCS due to its ability to be retrofitted into an existing power plant.
Table 1.2-1: Advantages and disadvantages associated with existing CO₂ capture technologies

<table>
<thead>
<tr>
<th>CO₂ Capture Techniques</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Post combustion</td>
<td>• Can be easily retrofitted to existing power plant</td>
<td>• Flue gas contains low CO₂ partial pressure</td>
</tr>
<tr>
<td></td>
<td>• Handles large amount of exhaust stream</td>
<td>• High capture level requires high circulation volume</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Pressure of captured CO₂ gas is lower than the required pressure needed for sequestration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High cost associated with amine regeneration</td>
</tr>
<tr>
<td>Pre- combustion</td>
<td>• High CO₂ partial pressure</td>
<td>• Cannot be easily retrofitted into an existing power plant</td>
</tr>
<tr>
<td></td>
<td>• High driving force need for separation</td>
<td>• High cost of equipment</td>
</tr>
<tr>
<td></td>
<td>• Several technologies are available for separation</td>
<td>• Requires an extensive support system</td>
</tr>
<tr>
<td></td>
<td>• Reduction in the CO₂ compression cost</td>
<td></td>
</tr>
<tr>
<td>Oxy-fuel Combustion</td>
<td>• High CO₂ concentration</td>
<td>• Requires large amount of cryogenic O₂ production</td>
</tr>
<tr>
<td></td>
<td>• Options to retrofit into an existing power plant</td>
<td>• recirculation of cooled CO₂ is required to contain temperature tolerance of combustor materials</td>
</tr>
</tbody>
</table>
1.3 Amine Solvents used in CO₂ Capture and Regeneration

Amine based CO₂ scrubbing is well known and has been used in the separation of CO₂ from natural gas and hydrogen power plant since 1930⁷. The most common primary, secondary and tertiary amines used in CO₂ capture and regenerations are monoethanolamine (MEA), Dieethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA)⁸⁻¹⁰. A number of experiments and flowsheet models have been carried out to investigate the properties of these amines⁸⁻¹⁰⁻¹⁵. As shown in Figure 1.2-3, amines solvents are grouped into primary, secondary and tertiary amines. This is based on the number of hydrogen atoms directly bonded to the nitrogen atom, with the primary amine having two hydrogen atoms bonded to the nitrogen atom; secondary and tertiary amines have one and zero hydrogen atom bonded to the nitrogen atoms, respectively. Primary and secondary amines such as MEA and DEA react at a fast rate to form carbamate and protonated amine. This process, however, is associated with high heat of CO₂ absorption which reflects in a high solvent regeneration cost. Another major disadvantage of these amines is their limited CO₂ absorption capacity of 0.5 mol of absorbed CO₂ per mole of amine. Tertiary amines such as MDEA do not react directly with CO₂. They rather act as a base, to catalyze the hydrolysis of CO₂ to form bicarbonates and protonated amines. The lower heat of formation and easier deprotonation of protonated MDEA associated with this reaction lowers the solvent regeneration cost, making it a desirable solvent. MDEA also has a higher absorption capacity of 1 mol of CO₂ per mole of amine. Sterically hindered amines, such as AMP also react with CO₂ to form an unstable carbamate ion which further hydrolysis to form a bicarbonate and free AMP. This free AMP can then react with CO₂, thus increasing its absorption capacity to 1
mol of CO$_2$ per mole of amine$^8,9$. In addition, AMP performance increases at higher CO$_2$ partial pressure (8-15%)$^{12}$.

Blended amines were introduced by Charkravarty et al.$^{16}$ in 1985. These researchers suggested the mixing of primary or secondary amines with tertiary amines with the aim of taking full advantage of the desirable properties of each amine. By mixing these amines, the fast rate of absorption observed in primary and secondary amines and the high CO$_2$ absorption capacity and low regeneration energy associated with tertiary amines are fully utilized. Also, a reduction in solvent circulation rate and lower heat duty is achieved. The benefits of using blended amines have been proven and have been documented in the literature$^{11,13,17-22}$, with the most recent being the mixture of the newly synthesized tertiary amine, 4-(diethylamino)-2-butanol (DEAB) with baseline solvent MEA$^{23,24}$. The MEA-DEAB blend further proofed the benefits of using blended solvents in CO$_2$ capture.

1.3.1 Solvent Chemistry: CO$_2$ Amine Interaction

As mentioned earlier, amines have been widely used in gas treating processes for removal of acid gases such as CO$_2$. These primary, secondary and tertiary solvents are characterized by the presence of the hydroxyl ion (OH) and the amino group ($\text{NH}_x$). The hydroxyl ion helps to increase the water solubility of the amine while reducing their vapor pressure. On the other hand, the amine group enables the solvent to react with the acid gas, resulting in the CO$_2$ absorption or desorption features of the amines$^{10}$. CO$_2$ capture process with the use of amine solvents relies mainly on bond generation by the reaction of weak amines with the weak CO$_2$ acid gas to produce water.
soluble salt (carbamate) or polyatomic anion (bicarbonate), while the regeneration process relies on the bond cleavage obtained at a higher temperature.

The reaction kinetics and mechanism of CO₂-amine based reactions have been summarized and reviewed by numerous researchers in the literature²⁵-³⁰. The absorption reaction between CO₂ and primary or secondary amine was introduced Caplow et al.³¹ in 1968, and was later reintroduced by Danckwerts et al.³² in 1970. These researchers described the reaction as a zwitterion mechanism, which is a two-step reaction comprising of the reaction of aqueous CO₂ with primary/secondary amine to form zwitterion which further reacts with any base in the system to produce the carbamate. Later, the termolecular mechanism was introduced by Crooks and Donellan et al.²⁵ in 1989. Most of the published kinetic data for MEA, DEA and PZ have been analyzed using both mechanisms. The base-catalyzed reaction was later introduced by Donaldson and Nguyen³³ and has been used to explain the kinetic results for tertiary amines.
Figure 1.3-1: Molecular structure of commonly used amines

Monoethanolamine (MEA)

Diethanolamine (DEA)

2-amino-2-methyl-1-propanol (AMP)

Methyldiethanolamine (MDEA)
1.3.1.1 Primary Amine Chemistry

As mentioned, primary amine such as (MEA) reacts rapidly with CO$_2$ to form carbamates. This reaction is reversible with the forward reaction favored at lowered temperature. The reaction is shown in the simplified form by:

$$2RNH_2 + 2CO_2 \leftrightarrow RNH-COO^-_{carbamate} + RNH_2^+$$  \hspace{1cm} (1.1)

The two-step zwitterion mechanisms are as follows:

Step 1:

$$RNH_2 + CO_2(aq) \leftrightarrow RNH_2^+COO^-$$  \hspace{1cm} (1.2)

Step 2:

$$RNH_2^+COO^- + B \leftrightarrow RNHCOO^- + B^+$$  \hspace{1cm} (1.3)

The $B^+$ is considered to be any base in the system, and, as described by Blauwhoff et al.$^{34}$, contributes to the deprotonation of the zwitterion ion as shown in the equations below:

$$RNH_2^+COO^- + H_2O \leftrightarrow RNHCOO^- + H_3O^+$$  \hspace{1cm} (1.4)

$$RNH_2^+COO^- + OH^- \leftrightarrow RNHCOO^- + H_2O$$  \hspace{1cm} (1.5)

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + RNH_2^+$$  \hspace{1cm} (1.6)

This clearly shows that the CO$_2$ loading capacity of regular primary and secondary amines are limited to 0.5 mol of CO$_2$ per mol of amine. This is as a result of the low rate hydrolysis of CO$_2$ to form bicarbonate and the very highly stable carbamate ion formed$^{32}$. Danckwerts et al.$^{32}$ further developed the reaction rate based on the provided mechanism, as given below:
\[ r = \frac{k_2[CO_2][RNH_2]}{1 + \frac{K_{-1}}{\Sigma k_B[RNH_2]}} \]  

(1.7)

The term \(1 + \frac{K_{-1}}{\Sigma k_B[RNH_2]}\) represents deprotonation by a base in the solution. In the case of high amine concentration, the term \(\frac{K_{-1}}{\Sigma k_B[RNH_2]}\) << 1 (i.e., Zwitterion deprotonation is faster than its formation), the equation takes the form of a second order kinetics and reduces to:

\[ r_{CO_2} = k_2[CO_2][RNH_2] \]  

(1.8)

Experiments conducted using a single amine showed insignificant change in amine concentrations during the reaction. Therefore, equation 1.8 can further be reduced to:

\[ r_{CO_2} = k_{app}[CO_2] \]  

(1.9)

Where \(k_{app} = k_2[RNH_2] \)  

(1.10)

Equation 1.7 is applicable to both absorption and desorption, with the desorption reaction occurring at high temperatures in the reverse reaction. More detailed reaction mechanism and pathway for amine-CO\(_2\)-regeneration process are discussed in chapter 4.

1.3.1.2 Tertiary Amine Chemistry

Tertiary amines do not react directly with \(CO_2\) to form carbamate ion. This is due to the nonexistence of hydrogen atom to be displaced by \(CO_2\). The reaction is therefore described as a base catalyzed reaction and is represented as follows:

\[ R_3R_2R_3N + H_2O + CO_2 \leftrightarrow R_3R_2R_3N^+H + HCO_3^- \]  

(1.11)
The tertiary amine facilitates the reaction of CO$_2$ with H$_2$O to form bicarbonates. This reaction is desirable because of the low heat of reaction associated with the process. Hence tertiary amines like MDEA are usually blended with primary amines like MEA to reduce the cost of regeneration$^{29}$.

In the case of an aqueous solution, the following reactions may occur:

\[ \text{RNH}_2/\text{R}_1\text{R}_2\text{R}_3\text{N} + \text{H}_2\text{O} \leftrightarrow \text{RNH}_2^+ /\text{R}_1\text{R}_2\text{R}_3\text{N}^+\text{H} + \text{OH}^- \]  \hspace{1cm} 1.12

\[ \text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^- \]  \hspace{1cm} 1.13

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]  \hspace{1cm} 1.14

The overall rate of reaction of the tertiary amine can be written as follows:

\[ r_{overall} = (k_{\text{RN}}[\text{RN}] + k_{\text{OH}^-}[\text{OH}^-] + k_{\text{H}_2\text{O}}[\text{CO}_2]) \]  \hspace{1cm} 1.15

1.3.1.3 Blended Amine Chemistry

The presence of one or more amine mixtures (e.g. MEA+MDEA, DEA+MDEA, AMP+MDEA) allows the zwitterion formed by carbamate-forming amines such as MEA and DEA to be deprotonated by the tertiary amine such as (MDEA) present in the system. The MEA+ MDEA + CO$_2$ + H$_2$O system reaction is given as:

\[ \text{RNH}_2^+\text{COO}^- + \text{RNH}_2/\text{R}_1\text{R}_2\text{R}_3\text{N} \leftrightarrow \text{RN}\text{HCOO}^- + \text{RNH}_2^+/\text{R}_1\text{R}_2\text{R}_3\text{N}^+\text{H} \]  \hspace{1cm} 1.16

The kinetic data for blended amines are treated in the same manner as single amines$^{35,36}$. The rate equation (1.7) is also used to express the overall reaction for blended amine. The only difference is the addition of the tertiary amine to the number of bases available to deprotonate the Zwitterion.
1.4 Importance of Kinetic Data in Design and Simulation of CO\(_2\) Capture Unit

CO\(_2\) capture using amine solvents has been studied and commercially applied for more than half a century. However, it is only of recent that extensive progress has been made in developing fundamental understanding of the entire CO\(_2\)-amine absorption-desorption reactions. Recent computer technologies allow the use of mass transfer rate-based models to design and simulate CO\(_2\) capture systems. An important advantage of these models is their usefulness in mixed solvent development, advancement and commercialization.

A robust and comprehensive model requires several calculations comprising of material and energy balances around each unit and along every stage of packing in the absorber-desorber unit. This further involves the determination of the driving forces, heat and mass transfer coefficients, mass transfer and chemical reaction interactions and interfacial areas. Hence, a rate-based model comprises of the hydrodynamic model, vapor-liquid equilibrium model, reaction kinetic model and a mass transfer model that shows the effect of reaction kinetics. Therefore, in order to commercially implement a CO\(_2\) capture unit into an existing power plant, an effective (absorber-desorber) design of the absorption-desorption CO\(_2\) capture unit which takes into account the fundamental mechanism of the kinetic phenomena underlying the CO\(_2\) capture and regeneration processes is required.
1.5 Fundamental Processes in Amine-based CO\textsubscript{2} Capture: CO\textsubscript{2} Absorption and CO\textsubscript{2} Desorption.

A typical amine based CO\textsubscript{2} capture and regeneration process involves the full cycle absorption-desorption of CO\textsubscript{2} using amine solvents. The flue gas stream containing CO\textsubscript{2} is introduced into a parked bed absorber column where it flows counter currently as it comes in contact with the lean amine, allowing for efficient absorption. After absorption, the loaded (rich) amine solvent then flows through the rich- lean heat exchanger before being introduced into the desorber column for thermal regeneration. In the desorber column, heat is supplied to strip out the captured CO\textsubscript{2}. This free (lean) amine solvent then enters the absorber column. The minimum energy that is theoretically needed for the recovery and compression of CO\textsubscript{2} from flue gas steam to 150bar is 0.396GJ/tonne CO\textsubscript{2}. However, in practical operation the achievable minimum energy has been estimated to be 0.72Gj/tonne\textsuperscript{37}. Absorption Operation and efficiency as well as reduction in thermal regeneration energy is needed to achieve a 90% efficiency with less than 35% increase in the post-combustion process\textsuperscript{38}

1.5.1 Issues associated with absorption

CO\textsubscript{2} absorption process depends on many solvent (amine) related factors. Such factors include the absorption capacity (equilibrium loading), absorption rate kinetics and heat of absorption. These factors are very important in choosing solvent types. Primary amines are known to have low absorption capacity and high heat of absorption, amine degradation and equipment corrosion rates. These drawbacks can be greatly reduced by solvent optimization and process configuration\textsuperscript{37}. Chakravarty et al\textsuperscript{16} suggested blending primary/secondary amine with tertiary amine solvent to tackle the low CO\textsubscript{2} capacity and improve the overall absorption process. The benefits of blending
amine solvents have been proven by several authors. Other methods include the use of alternative solvents such as amino acid\textsuperscript{39} and sodium carbonate\textsuperscript{40}

1.5.2 Issues Associated with Desorption

Certain factors like the desorption kinetics, cyclic capacity and heat duty are required to determine the overall desorption process. The heat associated with solvent regeneration remains one of the toughest challenges faced in post combustion. Also with major focus on absorption, desorption kinetic data which are also important for process design of and optimization are lacking in literature.

1.5.2.1 Heat Duty for Solvent Regeneration

The reboiler heat duty needed for solvent regeneration consist of 3 terms: (i) Sensible heat (ii) heat of Vaporization and (c) heat of absorption\textsuperscript{41}. It has been reported that about 50-60\% of the overall reboiler heat duty is associated with the heat of absorption\textsuperscript{42}, which is a factor of temperature, amine type and concentration. The up-to-date strategies still applied to minimize heat duty includes solvent optimization, and process design for higher heat and mass transfer\textsuperscript{43} yet the minimum theoretical energy is still far from reach. This has prompted researchers to introduce novel methods that can be used to tackle this problem.

1.5.2.2 CO\textsubscript{2} Desorption Rate

The desorption rate is an essential parameter needed process design. It takes into account all reacting species in the system; accounting for their reaction mechanism and activation energy. A faster desorption rate allows for smaller vessel as well as reduced heat duty. Desorption rate is greatly enhanced with blended solvents. This is because majority of the reactions (i.e carbamate and bicarbonate breakdown) depends
on the availability of free protons which are bonded to the amines. The protonated tertiary amine (MDEAH\textsuperscript{+}) found in blended solvents are less basic than protonated primary amine (MEAH\textsuperscript{+}) allowing for easier deprotonation. These free protons then react carbamate and bicarbonate ions, thus increasing the desorption rate. The addition of solid acid catalyst as recommended by Idem et al.\textsuperscript{44} has been seen to increase the desorption rate of CO\textsubscript{2}. Other approaches include the use of enzyme such as carbonic anhydrase\textsuperscript{45,46} and solvent optimization which involves the use of amino acid salt, phase change solvent, chilled ammonia and ionic liquids\textsuperscript{47}.

1.5.3 Catalytic CO\textsubscript{2} desorption mechanism

In the absence of solid acid catalyst, the rich solvent containing carbamate and bicarbonate are heated up via low pressure steam. This heat weakens the hydrogen bond of the hydronium ion which then attacks the nitrogen in carbamate ion, weakening the N-C bond. The N-C bond then breaks forming free CO\textsubscript{2} and amine as shown in figure 1.5-1. The addition of catalyst introduces a different pathway with lower activation energy.

1.5.3.1 Brønsted acid catalyst

The presence of both Brønsted acidity increases the desorption of CO\textsubscript{2} by donating proton directly to the carbamate ion. This proton donation converts the carbamate ion to a carbamic acid (MEACOOH). This is then followed by chemisorption on the Al site which results in the weakening of the N-C bond. According to Idem et al.\textsuperscript{44}, HZSM-5 serves as a good Brønsted catalyst which has the ability to also transfer its available proton to bicarbonate ions, thus increasing the amount of desorbed CO\textsubscript{2}.
Figure 1.5-1: Non catalytic Pathway for CO$_2$ Desorption$^{44}$
1.5.3.2 Lewis acid catalyst.

Lewis acid catalyst aids in the desorption rate by accelerating the deprotonation of protonated amines. For instance, the metal cation and oxide anion that are found on the surface of Lewis acid $\gamma-Al_2O_3$ enables it to act as an acid and base, respectively. In the basic region, the lone pair electron density found in the N atom of the carbamate is attacked by the cation ion: $Al^{3+}$ (Lewis acid). This weakens the N-C bond, resulting in the dissociative chemisorption of the carbamate ion. On the other hand, the oxide anion-$AlO_2^-$ attacks the $H^+$ found in $MEAH^+$.

1.6 Thesis objectives and outline

The overall objective of this research is to study and develop reaction kinetic models that adequately describe the catalytic desorption of CO$_2$ from CO$_2$-loaded primary amine (MEA) and CO$_2$-loaded primary-tertiary amine blend (MEA-MDEA). In order to achieve this, fundamental knowledge of the solvent chemistry as well as the reaction mechanism between CO$_2$-amine-H$_2$O system and solid acid catalyst are required. The reason for choosing the solvent and catalyst types are as follows:

Monoethanolamine (MEA): MEA has been studied extensively as a solvent for CO$_2$ capture and regeneration and therefore has a lot of experimental data available in the literature for comparison. It was therefore wise to use MEA in the absence of solid acid catalyst as the base case solvent and then compare it catalytic results.

Monoethanolamine and Methyl diethanolamine (MEA/MDEA) is one of the most studied tertiary amine in CO$_2$ capture with low solvent regeneration energy. Since the major drawback associated with CO$_2$ regeneration is the large heat duty required for
CO₂ desorption. It was decided to blend MEA-MDEA to reduce the regeneration energy and also compare it with the base case scenario of MEA in the absence and presence of catalyst.

**Catalyst (γ − Al₂O₃ and HZSM 5):** The addition of catalyst to the CO₂-amine-H₂O system was chosen in order to investigate the contribution of the solid acid catalyst in the CO₂ desorption system. γ − Al₂O₃ and HZSM − 5 catalysts were chosen particularly because of their electron acceptor and proton donation ability, respectively. These acidic properties are precisely desirable in CO₂ desorption because of their potential ability to reduce the heat needed to deprotonate and breakdown carbamate respectively.

1.6.1 Research Objective

The main research objectives of this thesis were achieved in various phases as described below:

**Phase 1: Catalyst Characterization**

The main objective of this phase was to study and obtain the physiochemical properties of each catalyst (γ − Al₂O₃, HZSM 5, SiO-Al₂O₃ and HY). In order to achieve this objective, all catalysts were characterized using various experimental technique such as X-ray diffraction, BET surface area, temperature programmed desorption (TPD) and Fourier Transformer Infrared Spectroscopy (FTIR).

**Phase 2: Catalyst performance and evaluation**

The following objectives were obtained in phase 2:
1. Obtain intrinsic experimental kinetic data for the desorption of CO$_2$ from CO$_2$-loaded aqueous solutions of MEA and blended MEA-MDEA: This is the first objective of this thesis, and it is extremely important as intrinsic kinetic experimental data are only obtained in the absence of heat and mass transfer limitations. With this, reaction rate models are developed with the application of the right rate determining (RDS) step without fear of diffusion or heat limitation.

2. Obtain power law model: The power law model adequately shows the relationship between the reaction rate and reactant concentration in a lump sum. This model provides the overall order of reaction as well as the rate constant. It is therefore important that parameters associated with this model be obtained in order to effectively develop and compare the kinetic parameters of the comprehensive mechanistic reaction model with the power law model.

3. Develop comprehensive catalytic reaction/kinetic mechanistic model for the desorption of CO$_2$ from CO$_2$-loaded MEA and MEA-MDEA: The development of this model takes into account the effect of heat and mass transfer as well as the reaction kinetics of all possible reactions. For each catalyst and solvent, it is important to investigate and understand which properties and solvent chemistry significantly affects the system performance. This is an important aspect of this work and its correct development can aid in selection, optimization and development of solid acid catalyst.
1.6.2 Scope of Thesis

The kinetic study of the catalytic desorption focuses mainly on the performance of two types of solid acid catalysts (γ-Al₂O₃ and HZSM 5) using MEA and MEA-MDEA solvents. Silica-alumina, SiO-Al₂O₃ and HY catalyst were also studied but not as in depth as the first two acid catalysts. The addition of SiO-Al₂O₃ and HY was done mainly to carry out statistical analysis in order to determine which catalyst property aids most in the desorption of CO₂ from CO₂-rich MEA and MEA-MDEA solutions.

MEA and MEA-MDEA solvents were comprehensively studied in a catalytic packed bed reactor. The reaction kinetics were interpreted in terms of reaction rate constant, frequency factor and activation energy using both power law and mechanistic models. The contributions of the characteristics of solid acid catalysts on the frequency factor and activation energy of this reaction were also evaluated using four solid acid catalysts, namely, HZSM-5, γ-Al₂O₃, HY, and silica-alumina, and inert packing with varying characteristics. These results are presented and discussed in this thesis.

1.6.3 Organization of Thesis

This thesis is written in a standard thesis format and is outlined as follows:

Chapter 1: An overall introduction into the CO₂ Capture technology and importance of research work are discussed.

Chapter 2: A comprehensive review of literature reports on kinetics of CO₂ absorption and desorption in aqueous MEA and MEA-MDEA blends are covered. Also the importance of vapour liquid equilibrium (VLE) data and catalyst selection are discussed.
Chapter 3: Experimental setup and apparatus

Chapter 4: Mathematical modelling; Reaction kinetic theory and comprehensive mechanistic model development are presented.

Chapter 5: Result and discussion of the conducted experiments

Chapter 6: Major conclusions and recommendations for future work
MEA is considered to be the benchmark solvent used in the conventional CO\textsubscript{2} amine-based post combustion process due to its price affordability and fast reaction kinetics. However, the increase in cost of electricity and decrease in power plant efficiency which are estimated to be 80 and 30\%, respectively\textsuperscript{49} related with the use of MEA as a capture solvent makes MEA unattractive. In addition, the heat input needed to regenerate loaded CO\textsubscript{2}-MEA solution is usually supplied at about 120\degree C\textsuperscript{50}. This high parasitic heat requirement further results in MEA degradation and possible material corrosion. This has prompted researchers to look for ways to reduce the high heat of regeneration associated with CO\textsubscript{2} capture process. Several researchers have proposed ways to reduce this high energy consumption associated with CCS\textsuperscript{50-60}. Rochelle et al.\textsuperscript{7} and Davidson et al.\textsuperscript{37,51} suggested that solvent optimization and process configuration could significantly reduce the required energy. Various researchers have also reported on solvent optimization as a major energy reduction technique\textsuperscript{54,61-63} which are consistent with works of Rochelle et al.\textsuperscript{7}. In the case of process optimization, factors such as column height and diameter as well as the parking size relative to column diameter plays an important role in energy reduction. However, major inventors focus solely on this factors without clearly identifying the effective column diameter which is necessary to improve the absorber-desorber efficiency thus reducing heat duty\textsuperscript{47}. Charkravarty et al.\textsuperscript{16} introduced the blending of primary and secondary amines with tertiary amines to utilize the lower energy requirements of the tertiary amine. An example of such a blend is the MEA-MDEA mixture. Over the years, several novel amine-based solvents and blends have been developed and reported to reduce the heat duty\textsuperscript{37,54,62,64}. The addition of organic acid to CO\textsubscript{2} loaded amine has also been reported to increase reaction kinetics and lower regeneration energy\textsuperscript{65,66}. The overview of these
technologies can be seen in the work recently published by Li et al.\textsuperscript{67}. Nevertheless, the theoretical heat duty limit of 0.4356MJ/Kg CO\textsubscript{2}\textsuperscript{37} is far from being reached and requires more work in order to obtain a reasonable energy input.

Recently, Idem et al.\textsuperscript{44} introduced the addition of solid alkaline catalyst to the absorber and solid acid catalyst to the desorber. This approach has been seen to achieve a significant reduction in heat duty by directly removing the heat of vaporization of water by operating at a temperature lower than the boiling point of water\textsuperscript{68}. Several authors have confirmed this to be true\textsuperscript{68,69} by performing similar experiments using the same solid acid catalyst recommended by Idem et al.\textsuperscript{44}. Another approach is the use of enzyme such as carbonic anhydrase\textsuperscript{45,46}. This enzyme aids in the rapid hydrolysis of CO\textsubscript{2} to form bicarbonate and hydrogen ion. However, further works done by Savile and Laldone et al.\textsuperscript{70} showed that the available carbonic anhydrase are not suitable to withstand the tough environment of the post combustion process. They suggested approaches that could be used to increase the enzyme tolerance, a few of which are the use carbonic anhydrase originating from thermophilic organisms and the production of thermos-tolerant enzymes via application of protein engineering\textsuperscript{70}. Another consideration could be in the direction of solvent optimization which involves the use of amino acid salt, phase change solvent, chilled ammonia and ionic liquids\textsuperscript{47}.

The application of catalyst to amine-based CO\textsubscript{2} capture unit accelerates the absorption and desorption CO\textsubscript{2} process and seems to be the current approach used to tackle high heat duty. The catalyst is aimed at accelerating the reaction by proving alternative pathway with lower kinetic energy as well as reducing the activation energy. This method is expected to grow rapidly in coming years and implemented at the pilot plant scale where they can be extensively studied with the final goal aimed at industrial scale operation. This would drastically reduce the heat duty and plant vessel\textsuperscript{47}.
Nevertheless, in order to commercially implement these technologies into an existing power plant, an understanding of the fundamental kinetic phenomena of the acid gas reactions with single and mixed amines are essential for effective design of the absorber-desorber units.

2.1 Kinetics Data for CO₂ Absorption and Desorption in aqueous MEA system

The kinetics of monoethanolamine (MEA) has been extensively studied and commercially applied in the separation of CO₂ from natural gas. It is important to note that the full scale cycle of the absorption-desorption unit is needed for appropriative design and implementation of the CO₂ capture unit into an existing power plant yet major focus has been on the kinetics of CO₂ absorption from gas streams using MEA and is summarized in the literature overview done by Aboudheir et al. with very little reports on the desorption kinetics of CO₂ from loaded amine (MEA) and blended (MEA-MDEA). The accurately known interfacial area and high physical absorption rate of the laminar jet apparatus and wetted wall column make the aforementioned equipment attractive for obtaining experimental kinetic data in a batch system.

One of the very first investigation carried out on a batch system with focus on reaction kinetic of CO₂ desorption from MEA was done by Jamal et al. The desorption experiments were obtained from a hemispherical apparatus at 333-383K and total system pressure of 110 to 205 Kpa for CO₂ loading ranging from 0.02-0.7 mol CO₂/mol amine. They developed a rigorous mathematical model which was used to obtain desorption kinetic parameters. Their results showed that desorption experiments could be accurately used to determine both forward and backward rate constants. Later on, Ross et al. reported on the absorption/desorption of MEA and piperazine (PZ) using a wetted wall column at 7, 9 and 11M at the system temperatures
of 40 and 60°C. They reported on the liquid film mass transfer coefficient, $k_g'$. It was found that $k_g'$ which is a function of reaction kinetics and diffusion of reactants and products, does not significantly depend on temperature and amine concentration within the temperature range of 40 to 60°C. Tunnat et al.\textsuperscript{75} investigated the desorption kinetics of CO$_2$ from water and aqueous amine solvent. The experimental desorption data for loaded 1M MEA solution were obtained from a wetted wall reactor operated at a total system pressure and temperature of 1 atm and 60°C, respectively. The kinetics measurements were reported in terms of reaction rate constant. The results obtained were in close agreement to values in the literature. They concluded that their work though accurate cannot be directly transferred into a technical desorber which operates at higher pressures and temperatures due to the significant differences in fluid dynamics of desorption at these conditions.

Laboratory scale packed bed heterogeneous system has also been used to obtain intrinsic experimental kinetic data that can be used to effectively design and simulate an industrial scale unit. However, only a few studies have been carried out using the heterogeneous packed bed column in CO$_2$ desorption. Weiland et al.\textsuperscript{76} reported on the desorption of CO$_2$ from MEA in a packed column. These researchers focused solely on the mass transfer performance and its variation with process parameters. Escobillana et al.\textsuperscript{77} investigated the behavior of absorption/stripping column on the CO$_2$-MEA system using a packed bed reactor. The experiments were performed at an MEA concentration and temperature ranges of 2.331-2.720 mol/dm$^3$ and 362.15-368.15 K, respectively. The researchers developed a model which could predict experimental result with a 3% deviation. Recently, Majeed et al.\textsuperscript{78} investigated the desorption of CO$_2$ from a rotating packed bed reactor with focus on the effect of lean amine temperature and peripheral rotor gravity on the overall desorption process. They
concluded that the use of a rotating packed bed reduces reactor size and space alongside improving operating condition. However, nothing was mentioned on the desorption kinetics. Only the work earlier reported by James et al. focused on the reaction kinetics of CO$_2$ desorption from loaded MEA system. Using a 53 cm, BX gauze packed bed reactor and a 20 wt% MEA concentration, these workers analysed the desorption rate at a CO$_2$ saturated absorbent flow of 10.7lb/hr and obtained a value of 0.56 kg-mol/s $\times 10^6$ at 362 K. These investigations were however limited by (low) temperature range and MEA concentration (< 5mol/dm$^3$). Most importantly, an in depth analysis on the necessary kinetics parameters needed for a reactor design were neglected.

2.2 Kinetics Data for CO$_2$ Absorption and Desorption in aqueous MEA-MDEA System

Blended amines as introduced by Charkavarty et al. and Weiland et al. are very useful in the kinetics of CO$_2$ absorption and desorption reactions. Various reports on the kinetics of CO$_2$ absorption into mixed MEA-MDEA solvent has been reported in the literature and can be found in the works of several researchers. Critchield and Rochelle et al. used a stirred tank reactor to measure the absorption rate of CO$_2$ into MEA+MDEA+H$_2$O mixture and predicted the enhancement factors of the reaction. Versteeg et al. also investigated the parallel reversible reactions of CO$_2$ absorption into blended amine. Using the film and penetration theory, they modeled the CO$_2$ absorption process. Sandall et al. later developed a mathematical model which was used to predict the gas absorption rate and enhancement factors. A more detailed review on MEA-MDEA kinetics can be seen in the works of Cheng et al., Ramachandran et al. and Idem et al.
As earlier mentioned, works on the desorption kinetics from blended amines are lacking with very little available in literature. Table 2.2 summaries previous works done on CO$_2$ absorption/desorption kinetics. The first report on CO$_2$ desorption kinetics was done by Glasscock et al$^{35}$. In this work, he investigated both the absorption and desorption reactions of MEA/MDEA and DEA/MDEA blends at temperature ranging from 288 to 313K. Using a generalized framework for the kinetics and reaction equilibria non-ideal system, the researchers observed that the forward rate constants increase with ionic strength. they also observed that MDEA only promotes the reaction rate of DEA with CO$_2$ and has no effect on reaction rate of MEA. They explained their findings in terms of the zwitterion mechanism for amine carbamate formation. Later on, Hawgewiesche et al$^{81}$ reported on kinetics of CO$_2$ desorption from MEA+MDEA system. Their work was similar to that of Glasscock et al$^{35}$ and took into account the rigorous diffusion reaction and equilibrium models. However, not much kinetic parameters could be analyzed due temperature (313 K) and amine concentration (2.6-3 M) limitations. A more detailed study was reported by Jamal et al$^{72}$. Their work investigated the reaction rates of various single and blended amines in concentration range of 2 to 35 wt%. Using a humidified N$_2$ gas stripping medium, the desorption experiments were carried out at 333 to 383 K with CO$_2$ ranging from 0.02 to 0.7 mole of CO$_2$ per mole of amine. Their results were further developed rigorous mathematical models which were used to predict the reaction rates.
Table 2.2-1: Summary of result of reported on absorption-desorption kinetics of CO₂ MEA-MDEA system

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Temperature (K)</th>
<th>Amine concentration (Kmol/m³)</th>
<th>Rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred cell reactor</td>
<td>288-313</td>
<td>0.0-3.0</td>
<td>396 (Kmol⁶/kmol²s)</td>
<td>35</td>
</tr>
<tr>
<td>Stirred cell reactor</td>
<td>298</td>
<td>0.323</td>
<td>K_{app}= 1298-1240 (s⁻¹)</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(pseudo 1st order rate constant)</td>
<td></td>
</tr>
<tr>
<td>Hemispherical contactor</td>
<td>304</td>
<td>0-5.6</td>
<td>Pseudo 1st order rate constant</td>
<td>72</td>
</tr>
</tbody>
</table>
2.3 Vapor Liquid Equilibrium (VLE)

Vapor liquid equilibrium for aqueous CO₂-amine systems are important for the development of reaction rate kinetics models, which are in turn required for design and process simulations of CO₂ capture plants. Several researchers have proposed methods for determining VLE of various amine system. Kent and Eisenberg proposed a technique to determine the correlation of the vapor–liquid equilibria of hydrogen sulphide and CO₂ in aqueous MEA and DEA solutions. Their proposed equilibrium constant was a function of only temperature and the equilibrium constant could be used to represent the vapor liquid equilibria. Austgen et al. later proposed a thermodynamic model that could predict the solubility of MEA, DEA, MEA-MDEA and DEA-MDEA blends using the electrolyte-nonrandom two liquid (NRTL) equation. Nonetheless, several researchers that the CO₂ equilibrium solubility of acid gases in aqueous amine can only be adequately predicted when taken into consideration not only the effect of temperature but of other parameters such as CO₂ loading, free amine concentration and physically dissolved CO₂. Li and Hu et al. developed predictive models that took into account the various parameters. It could be seen from their work that the predicted equilibrium solubility was in close agreement with the experimental results.

Before VLE models and chemical equilibrium were developed, reaction schemes were studied extensively. The introduction of the acid gas (CO₂) into the aqueous amine solution results in several complex and rapid reactions. A complicated solution containing many cations, anions and free molecules are obtained at vapor-liquid equilibrium (VLE) and chemical equilibrium. The VLE of MEA-CO₂-H₂O and MEA-MDEA-CO₂-H₂O are complex since the liquid phases of such solutions are in the ionic phase. Several works in literature have reported on the VLE of MEA at various
temperatures\textsuperscript{85,88-90}. The electrolyte NRTL model was used in the works of Anusha et al\textsuperscript{6}. In his works, he compared VLE results obtained from ASPEN with the experimental VLE results of Jou et al.\textsuperscript{91}. Very little discrepancies were seen particularly at high loadings. In order to get a more accurate result, the temperature interaction parameters were modified as described by Ferguia et al.\textsuperscript{92}. VLE data of various concentrations and temperatures for MEA-MDEA-CO\textsubscript{2}-H\textsubscript{2}O system are available in literature\textsuperscript{93-95}. However, for the purpose of this study and in order to estimate the equilibrium solubility of CO\textsubscript{2}, VLE experiments were carried out at 313K and 358K with MEA-MDEA concentration of 2/5M. Details on the experimental setup and procedure can be found in chapter 3.

2.4 Major and Important ions present in Single and Blended Amine-CO\textsubscript{2}-H\textsubscript{2}O System

During absorption and desorption reactions, a fraction of the amine will convert to protonated amine (\(RNH_2^+\)) and the remaining fraction will be converted to carbamate ion. CO\textsubscript{2} will either react with MEA to produce carbamate ion or undergo hydrolysis reaction in the presence of MDEA. Carbamate ion comes only from reaction of CO\textsubscript{2} with primary or secondary amines, with little quantities of bicarbonate and carbonates ions which are only present at higher loadings. These ions can be grouped into three categories bicarbonate/carbonate (\(HCO_3^-/CO_3^{2-}\)), carbamate (\(RNHCOO^-\)) and protonated/free amine (\(RNH_2^+/RNH_2\)). The exact concentration of these ions are difficult to obtain independently as the reactions occurs simultaneously. There are fast proton exchange reactions between the ions \(HCO_3^-/CO_3^{2-}\) and \(RNH_2^+/RNH_2\). This
makes it very difficult to obtain the actual mole fractions of these ions using common analytical techniques such as titration, high performance liquid chromatography (HPLC) and Gas chromatography (GC). More accurate results can be achieved with NMR analysis technique, and also, from simulated ion speciation plot generated from ASPEN e-NRTL system model.

2.5 Catalyst Selection and Contribution in CO₂ Desorption

The addition of catalyst to any system provides alternative reaction pathway which lowers the minimum kinetic energy, alongside increasing the fraction of reactant molecules able to react at the lower activation energy. Also, the direct availability of proton increases the frequency of collision between the proton deficient atom and the proton ion leading to a change in the reaction mechanism resulting in a faster CO₂ desorption rate. Kinetically controlled finite reactions are considered as fast reactions, the rate of which are influenced by the addition of a catalyst. These reactions can be used in the development of both the power law rate and mechanistic model (chapter 4).

A breakdown of the zwitterion reaction mechanism given in Equation 1.1 is needed to explain the role of the catalyst. This reaction consists of the formation of a zwitterion complex followed by the deprotonation of the zwitterion by a base. This same route is followed during solvent regeneration and is also characterized as a two-step mechanism involving carbamate breakdown and MEAH⁺ deprotonation as shown:

\[ MEAH^+ \text{ deprotonation:} \]

\[ MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+ \quad \Delta G \sim 78.2 \text{kJ/mol (90°C)} \quad 2.1 \]

The high alkalinity of MEA makes it difficult for \( MEAH^+ \) to release its proton to \( H_2O \) thus resulting in the high heat of regeneration associated with loaded CO₂-MEA
solution. This energy requirement is reported to be 78.2 kJ/mol at (90°C)\(^6\). Conversely, the presence of a stronger base—\(HCO_3^-\) reduces the energy requirement to a value of 21.9 kJ/mol\(^6\).

Carbamate breakdown:

\[
RNH − COO^- + H_3O^+ ↔ Zwitterion ↔ MEA + CO_2 \quad ΔG ~15.47\text{kJ/mol}\(^6\) \quad 2.2
\]

Carbamate breakdown, though complex, requires less energy. It, however, requires large amount of free protons and depends greatly on reaction 1, as most of the protons are attached to MEAH\(^+\).

2.5.1 \(γ-Al_2O_3\) Structure and Catalytic Properties

\(γ\) − Alumina catalyst has been commercially applied in many refining and petro-chemistry industries due to its surface properties\(^9\). The exact crystallographic structure of \(γ − Al_2O_3\) is still thoroughly discussed. A detailed review on the structure of this catalyst can be found in the works of Wolverton\(^9\) and Gutierrez et al.\(^9\). The partially uncoordinated metal cation and oxide anion that appear at the surface of \(γ-Al_2O_3\) catalyst enables it to act as an acid and base, respectively\(^4\). In the basic region, the lone pair electron density found in the N atom of the carbamate is attacked by the cus cation ion-Al\(^3^+\) (Lewis acid). This weakens the N-C bond, resulting in the dissociative chemisorption of the carbamate ion. On the other hand, the oxide anion-\(AlO_2^-\) attacks the \(H^+\) found in MEAH\(^+\). This reaction can be considered as a dissolution reaction which etches the solid acid catalyst in the absence of silica\(^9\). The addition of silica to the alumina surface reduces the rate of dissolution to a large extent\(^9\). The \(γ-Al_2O_3\) used in this work contains an acceptable Si/Al ratio that prevents the etching
process. It has also been reported\textsuperscript{100} that at temperatures \( < 423 \text{K} \), the reaction between CO\(_2\) and \( OH^- \) groups in \( \gamma\text{-Al}_2\text{O}_3 \) results in the formation of \( HCO_3^- \). This is an important feature that tends to be significant at lean CO\(_2\) loading region. A typical Lewis acidity and basicity of \( \gamma\text{-Al}_2\text{O}_3 \) is shown in Figure 2.1.5-1.
Figure 2.1.5-1: Lewis acidity and basicity
2.5.2 HZSM-5 catalyst contribution

Zeolite catalysts are known for their unique pore size which makes them suitable as shape selective catalyst. They have high surface area and are crystalline in nature\textsuperscript{102,103}. They are aluminosilicates compounds composed of AlO\textsubscript{4} and SiO\textsubscript{4} which are linked by oxygen atoms forming a three-dimensional network. A complete ZSM 5 zeolite unit contains 5 silica-alumina tetrahedra linked into a pentagon. The acidic properties of ZSM-5 are determined by their composition. For instance, the ion exchange capacity and catalytic activity of the zeolite vary greatly with the Al content\textsuperscript{104}. Conversely, the hydrophobic nature of ZSM 5 depends on the silica to alumina (Si/Al) ratio and a high ratio content stabilizes the zeolite during hydrothermal treatment\textsuperscript{105}. Other properties such as X-ray diffraction, pore size and pore volume are independent of the composition of the acid\textsuperscript{106}.

In ZSM 5 catalyst, the acid sites lie on inter crystalline surface\textsuperscript{107} and their catalytic activities are attributed to the strong acid sites\textsuperscript{108}. The acid sites in ZSM-5 lie on inter crystalline surface on the zeolite\textsuperscript{107}. ZSM-5 exchanges its ion in an ion-exchange reaction with several cations to increase its selectivity and activity. The most common ion exchange is with protons, H\textsuperscript{+} to form superior acidic catalyst HZSM-5. The aluminum content also acts as Lewis acid sites and accept electron pairs, while the protons act as a Brønsted acid site. Thus, increasing the Al/Si ratio also increases the number of acid sites if all the exchanged cations are occupied by protons. The presence of both Brønsted and Lewis acid site in HZSM-5 increases its role in the desorption of CO\textsubscript{2}. A typical Brønsted acidity reaction is shown if Figure 2.5.1-2. The Brønsted acid site donates proton to the carbamate ion. This proton donation converts the carbamate ion to a carbamic acid (MEACOOH). This is then followed by a chemisorption on the Al site which results in the weakening of the N-C bond. According to Idem et al\textsuperscript{44} the
HZSM-5 catalyst also transfers its available proton to bicarbonate ions, thus increasing the amount of desorbed CO$_2$. The Lewis acid site attacks the free lone pair of electron density found in the N atom of the carbamate ion. It is important to mention that the negative aluminosilicate ion sites present on the surface of the catalyst inhibits the $OH^-$ group from approaching the interface, thus eliminating any possible competition between carbamate ion and hydroxyl group$^{109}$. 
Figure 2.1.5-2: Brønsted Acidity of HZSM-5
As mentioned earlier, Idem et al.\textsuperscript{44} and Shi et al.\textsuperscript{44,68}, introduced the addition of a solid acid catalyst in the desorber unit of the CO\textsubscript{2} capture system to reduce the energy penalty by directly lowering the amount of heat input needed to regenerate the CO\textsubscript{2}-loaded or CO\textsubscript{2}-rich amine solvent. A Lewis solid acid catalyst: $\gamma-Al_2O_3$, and a Brønsted solid acid catalyst: HZSM-5 were selected because of their ability to accept electron and donate proton respectively, thereby offering the potential of reducing the energy required for MEAH\textsuperscript{+} deprotonation and carbamate breakdown. Using a batch reactor, they investigated the contribution of both catalysts in the desorption of CO\textsubscript{2} from CO\textsubscript{2}-loaded MEA. The experiments were carried out at a temperature range of 50-92°C for 300 ml of 5-7M rich MEA at different rich loadings and catalyst weights. Their results were reported in terms of CO\textsubscript{2} desorption rate. It was concluded that the addition of these solid acid catalysts increases the CO\textsubscript{2} desorption rate. This can be attributed to the alternative catalytic pathway with lower activation energy provided for desorption which resulted in lower heat duty. Similar results were reported by Shi et al\textsuperscript{68} and Liang et al.\textsuperscript{68,69}. The current study is a first of its kind of a gas-liquid-solid reactor (GLS) system that incorporates the addition of a solid acid catalyst into a heterogeneous packed bed reactor, thus introducing an additional phase (i.e. solid phase) in the reactor. This greatly differs from the conventional gas-liquid (GL) system. The addition of catalyst is aimed at increasing the reaction kinetics thereby allowing for smaller reactor vessels as well as reducing the energy requirement for solvent regeneration.
CHAPTER 3: EXPERIMENTAL SECTION

3.1 Overview

In the study of CO$_2$-amine absorption/desorption system, kinetic data are typically obtained by performing experiments using special types of batch reactors such as laminar jet and wetted wall columns. The accurately known interfacial area and high physical absorption rate of these reactors makes them attractive for obtaining experimental kinetic data in a batch system. Laboratory scale packed bed heterogeneous reactors have also been used to obtain intrinsic experimental kinetic data that can be used to effectively design and simulate an industrial scale unit. In this chapter, a new reactor which incorporates the addition of a solid acid catalyst into a heterogeneous packed bed reactor is described. This additional phase (i.e. solid phase) adds an additional reaction (catalytic reaction) which increases the reaction kinetics thereby allowing for smaller reactor units as well as reducing the energy requirement for solvent regeneration.

3.2 Materials and Methods

3.2.1 Chemicals

MEA, MDEA and 1.0 M hydrochloric acid (HCL) were obtained from Sigma Aldrich with a purity of $\geq$ 98%. Ultra-high purity (99.9%) of pure CO$_2$ and N$_2$, and 15% CO$_2$ gas cylinders were supplied from Praxair Inc, Canada. $\gamma$-$Al_2O_3$ catalyst was purchased from Zeochem, USA. HZSM-5 zeolite catalyst was purchased from Zibo Yinghe Chemical Co., Ltd, Zibo City, China. All supplied chemicals were used without further purification.
3.3 Catalyst Characterization

All catalyst characterization studies were carried out at the Biomedical and Chemical Laboratory in University of Saskatchewan, Saskatoon, Canada.

3.3.1 The Brunauer-Emmett-Teller (BET) Surface Area, Pore Volume, and Average Pore Size Measurements

The (BET) surface area, pore volume, and average pore size measurements were obtained using an adsorption Micromeritics ASAP 2020 instrument. Prior to the analysis, the sample was degassed at 200°C under isothermal condition for 3 hours. Adsorption and desorption isotherms were obtained and used in the evaluation of these results. These values are distinctive for each catalyst type and are reproducible.

3.3.2 Fourier Transformed Infrared Spectroscopy (FTIR)

The IR measurements were used to quantify the amounts and ratio of Brønsted to Lewis acid sites. The IR measurements were recorded on a Bruker Vertex 70 Model. The Resolution, sample scan time and background scan time were set to 4, 16 and 16, respectively. The scan ranged from 4000 to 400 cm⁻¹, with the aperture set to 6 mm and scan velocity to 10 kHz. About 0.1 g of each sample were taken and treated with approximately 25 uL of pyridine and left overnight for adsorption to occur. The excess pyridine was removed by heating the sample to about 115°C. Lastly, the samples were examined under FTIR.

3.3.3 Powder X-ray Diffraction

XRD was used to evaluate the crystallinity and crystallite size of each catalyst. The XRD patterns were recorded on a Bruker D8 Advance Series II from Detector type using a LynxEye detector. The generator voltage and current were set to 40 kV and 40
mA, respectively. With a total number of 1707 steps, the intensity data were obtained over a 2θ scan range of 10-90° with a step size of 0.047°, using a counting time of 1s. The crystalline phases were identified based on the reference data from International Center for Diffraction Data (ICDD).

3.3.4 Temperature Program Desorption (TPD)

The TPD experiment was used to measure the total acid sites as well as the acid strength distribution for each sample. The TPD of each catalyst were measured using an Autosorb iQ from Quantachrome model with a TCD Detector type. The sample was initially exposed to helium while the furnace temperature was gradually increased to 250°C at 20°C/min ramping. After 20 min, the temperature was reduced to 50°C and 3% of ammonia in helium gas flowed for 60 min. The gas was then changed to helium, and kept at an isothermal condition at 70°C for 30 min.

3.3.5 Sample Analysis

Aqueous solution of MEA and MEA-MDEA were prepared by mixing concentrated MEA and MDEA with distilled water to the preferred concentrations, which were further verified by titration technique using a standard known volume of 1.0 kmol/m³ of hydrochloric acid (HCl), with methyl orange as indicator. Using the standard method presented by the Association of Official Analytical Chemists (AOAC), the Chittick apparatus was used to calculate the CO₂ loading of the amine solution whereas the concentration of CO₂ in the gas phase was measured along the length of the column using IR gas analyzer.
3.4 Experimental Apparatus and Procedure

The experiments were performed in complete absorber – desorber CO₂ capture pilot plant unit. Both the absorber and desorber columns in the unit were of 2-inch internal diameter and 3.5 ft total height. The packing materials and operating parameters used for this experimental set are shown in figure and table 3.5-1. Experimental kinetic data for CO₂ desorption were obtained in a catalytic packed bed tubular reactor (i.e. desorber) at three temperatures (348K, 358K, and 368K), with 5M MEA concentrations and CO₂ loading ranging from ~ 0.41-0.5 mol CO₂/mol amine, for different ratios of catalyst weight/amine flow rate (W/Fₐ). Thermocouples and concentration measurements were located along the length of the absorber and desorber column and were used to obtain gas phase CO₂ concentration and temperature profiles. Solvent losses were prevented by positioning a condenser at the top of the absorber and desorber columns. Several other auxiliary types of equipment were used in this study, namely, CO₂ cylinder, gas flow meter, feed tank, and liquid flow pump.
Figure 3.4-1: Packing materials and arrangement
Table 3.4-1 Packing parameter and operating conditions

<table>
<thead>
<tr>
<th>Desorber Characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column internal diameter (m)</td>
<td>1.067</td>
</tr>
<tr>
<td>Main Packing height(m)</td>
<td>0.051</td>
</tr>
<tr>
<td>Packing type</td>
<td>Structured Sulzer, Inert beads</td>
</tr>
<tr>
<td>Catalyst</td>
<td>$\gamma-Al_2O_3$ and HZSM-5 (0-300g)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas Composition</td>
<td>15% CO₂, 85% N₂</td>
</tr>
<tr>
<td>Inlet gas flowrate</td>
<td>15 SLPM</td>
</tr>
<tr>
<td>Amine circulation rate (mol/min)</td>
<td>60</td>
</tr>
<tr>
<td>MEA concentration (mol/dm³)</td>
<td>5</td>
</tr>
<tr>
<td>MDEA concentration (mol/ dm³)</td>
<td>2</td>
</tr>
<tr>
<td>Rich solution loading (mol/mol)</td>
<td>0.509-0.4882</td>
</tr>
<tr>
<td>Lean solution loading</td>
<td>0.473-0.347</td>
</tr>
<tr>
<td>Average Desorber temperature (K)</td>
<td>345-365</td>
</tr>
<tr>
<td>Desorber Pressure (atm)</td>
<td>1</td>
</tr>
</tbody>
</table>
At the beginning of each run, N\textsubscript{2} and CO\textsubscript{2} were set to the desired partial pressures and concentrations before being introduced into the bottom of the absorber column through the gas flow meter which controlled the gas flows individually. Cooling water circulated through the condenser from the cold water bath. The MEA/MEA-MDEA solution from the feed tank was let into the top of the column with the help of a constant liquid flow pump. This ensured that the column operated under contact counter-current flow, allowing CO\textsubscript{2} to be absorbed by providing maximum driving force for mass transfer. The treated gas escaped through the top of the column while the rich solution exit at the bottom of the column after which it passed through the lean/rich heat exchanger and then a hot water heater before flowing into the desorber column. Here the temperature of the desorber is at elevated temperature, allowing desorption of CO\textsubscript{2} to occur. After desorption, the desorbed CO\textsubscript{2} escapes through the top of the column and the lean amine is recirculated back into the absorber. Figure 3.4-1 and 3.4-2 shows the parking materials and experimental setup used to obtain the experimental data. The structured packing was used to ensure even distribution at the top of the column, while the inert marbles were used as a support and to ensure that plug flow condition existed in the reactor.

3.4.1 CO\textsubscript{2} Loading Test

The CO\textsubscript{2} loading tests were performed with the Chittick apparatus. The rich and lean amine solutions of 2ml were first pipetted into a 250ml Erlenmeyer flask, before adding 2-4 drops of methyl orange indicator. Approximately 10ml of distilled water is then added to dilute the sample. The sample flask filled with solution is then properly connected and fitted with a rubber cock connected to the Chittick apparatus.
before finally sealed with Teflon tape to avoid any leakages. The 1M HCl acid contained in the burette is then added dropwise into the flask until the end point indicted as a pink solution is reached. The HCl volume is then recorded as $V_{HCl}$, which is the volume of HCl added to the flask to displace the CO$_2$ contained in the amine. The removed CO$_2$ gas is recorded as $V_{CO_2}$. From this, the concentration and CO$_2$ loading of the amine can be calculated:

$$C_{amine} = \frac{c_{HCl} \cdot V_{HCl}}{2} = 0.5C_{HCl}V_{HCl} \quad 3.1$$

$$loading, \alpha = \frac{V_{CO_2} - 2 \cdot V_{HCl}}{24.45 \cdot V_{HCl}} \quad 3.2$$
Figure 3.4-2: Schematic of the experimental Setup
Each run was operated until steady state conditions were achieved. Depending on the conditions, this normally took approximately 1-2 hours. At steady state, the concentrations of CO$_2$ in the gas phase and temperature profile were measured along the length of the column using IR gas analyzer and thermocouples, respectively. To ensure that the CO$_2$ absorption rates calculated from the CO$_2$ concentration profile were certified, the CO$_2$ rich solution at the bottom of the column was simultaneously sampled and further used for analyzing the amount of absorbed CO$_2$ in the liquid phase. Using the Chittick apparatus, the CO$_2$ content in the sampled liquid were used to calculate the CO$_2$ loading of the amine solution. Each experimental run was verified by calculating the mass balance error using the formula:

$$\text{Mass balance error} = \left( \frac{\text{absorbed CO}_2 - \text{removed CO}_2}{\text{absorbed CO}_2} \right) \times 100\%$$

An error less than 10% as regarded as an acceptable test run.

3.3.2. Equilibrium Solubility of CO$_2$

The solubility experiments were carried out for blended MEA-MDEA (5/2M) solvent at 313K and 358K. The apparatus and experimental technique are similar to that used in the works of Tontiwachwuthikul et al$^9$ and Sema et al$^{10}$. The main features of the setup were gas cylinders, temperature controllable hot water bath (Cole-Parmer, temperature range 0-100°C, accuracy $\pm0.01^\circ$C), saturation cell, gas flow meters (Aalborg GFM-17 gas flow meters, ranges from 5mL/min to 5L/min with an accuracy of $\pm0.15\%$), and an absorption reactor. The operating conditions are given in table 3.5-2. The CO$_2$ tank containing desired % of CO$_2$ was fed at atmospheric pressure into a saturation cell before flowing into the lean amine solution, which was initially prepared and fed into the absorption reactor. The water saturated stream from the
absorption reactor is connected to a condenser which recovers all condensable components back into the reactor. Water was fed steadily with cold water to minimise the loss of amine thereby keepings its concentration constant. The water bath was kept at the desired temperature and properly insulated to avoid heat loss. The liquid samples were taken every two hours for CO$_2$ loading measurement. This was done at a 2-h interval to ensure that equilibrium loading was reached at the set temperature. Chittick titration apparatus involving 1M HCl solution and methyl orange indicator were used for the loading test. The obtained result and experimental setup are shown in Figures 3.5-3 and 3.5.4, respectively.
Figure 3.4-3: Experimental setup for CO$_2$ solubility (CO$_2$+MEA+MDEA+H$_2$O system)
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas Composition</td>
<td>3, 5, 15, 30 and 100% CO₂</td>
</tr>
<tr>
<td>Inlet gas flowrate</td>
<td>SLPM</td>
</tr>
<tr>
<td>Amine circulation rate (mol/min)</td>
<td>60</td>
</tr>
<tr>
<td>MEA/MDEA concentration (mol/dm³)</td>
<td>5/2</td>
</tr>
<tr>
<td>Rich solution loading (mol/mol)</td>
<td>0.509-0.4882</td>
</tr>
<tr>
<td>Lean solution loading</td>
<td>0.473-0.347</td>
</tr>
<tr>
<td>Solubility (water bath) temperature (K)</td>
<td>313 and 358</td>
</tr>
<tr>
<td>Absorption Pressure (atm)</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 3.4-4: VLE model at 358K for MEA-MDEA-CO$_2$ absorption-desorption
CHAPTER 4: DEVELOPMENT OF MATHEMATICAL MODELS FOR CO₂ DESORPTION

The development of a mathematical model for CO₂ desorption in aqueous amine solution is presented in this chapter. The power law model was expressed as a pseudo first order reaction in terms of CO₂ in the rich amine feed into the desorber. The models were developed for the general case in which the solutions might be a single (MEA) or blended (MEA-MDEA) amine system. The power law models show the general dependence and sensitivity of reaction rate on reactant concentration. Mechanistic models are comprehensive reaction models which take into account all the elementary reactions, reacting species, and their concentrations. These models were developed and used to fit the experimental data. The model parameters and physical properties needed to solve the equation model were identified.

4.1 Reaction Mechanism

The CO₂ desorption models applies to the following aqueous amine systems:

1. CO₂ + MEA + H₂O

2. CO₂ + MEA + MDEA + H₂O

In accordance with amine literature, MEA is represented as \( RNH₂ \) were \( R \) denotes = \( CH₂CH₂OH \). MDEA is represented as \( R₁R₂R₃N \) where \( R₁ = R₂ = CH₂CH₂OH \) and \( R₃ = CH₃ \).
4.1.1 Reactions Mechanism for CO$_2$+ MEA+ H$_2$O System (Base Case)

When CO$_2$ is absorbed or desorbed into MEA the following reactions occur:

**MEA Zwitterion formation**

\[
CO_2 + RNH_2 \overset{k_{1}}{\rightleftharpoons} RNH_2^+ COO^- \quad 1.2
\]

**MEA Carbamate formation and breakdown**

\[
RNH_2^+ COO^- + H_2O \overset{k_{2}}{\rightleftharpoons} H_3O^+ + RNHCOO^- \quad 1.4
\]

\[
RNH_2^+ COO^- + OH^- \overset{k_{3}}{\rightleftharpoons} H_2O + RNHCOO^- \quad 1.5
\]

\[
RNH_2^+ COO^- + RNH_2 \overset{k_{4}}{\rightleftharpoons} RNH_3^+ + RNHCOO^- \quad 1.6
\]

The lean amine had significant concentration of HCO$_3^-$ and CO$_3^{2-}$. Therefore, they are considered in the deprotonation reaction.

\[
RNH_2^+ COO^- + HCO_3^- \overset{k_{5}}{\rightleftharpoons} H_2CO_3 + RNHCOO^- \quad 4.1
\]

\[
RNH_2^+ COO^- + CO_3^{2-} \overset{k_{6}}{\rightleftharpoons} HCO_3^- + RNHCOO^- \quad 4.2
\]

**MEA protonation:**

\[
RNH_2 + H_2O \overset{k_{7}}{\rightleftharpoons} RNH_3^+ + OH^- \quad 4.3
\]

\[
RNH_2 + H^+ \overset{k_{8}}{\rightleftharpoons} RNH_3^+ \quad 4.4
\]

**MEA deprotonation:**

\[
RNH_3^+ + OH^- \overset{k_{9}}{\rightleftharpoons} RNH_2 + H_2O \quad 4.5
\]

\[
RNH_3^+ + H_2O \overset{k_{10}}{\rightleftharpoons} RNH_2 + H_3O^+ \quad 4.6
\]

**Water ionization:**

\[
H_2O \overset{k_{11}}{\rightleftharpoons} OH^- + H^+ \quad 4.7
\]

**Physical absorption of CO$_2$**

\[
CO_2(g) \overset{k_{12}}{\rightleftharpoons} CO_2(aq) \quad 4.8
\]

**Bicarbonate formation of CO$_2$**

\[
CO_2 + H_2O \overset{k_{13}}{\rightleftharpoons} HCO_3^- + H_3O^+ \quad 4.9
\]
\[ CO_2 + OH^- \xrightleftharpoons[k_{-14}]{k_{14}} HCO_3^- \]  

4.10

In the above reactions the \( k' \)'s represent rate constants and \( K' \)'s represent equilibrium constants.

4.1.2 Reaction Mechanism for CO\(_2\) + MEA + MDEA + H\(_2\)O System

When CO\(_2\) is absorbed or desorbed into MEA-MDEA, reactions 1.2, 1.4-1.6, 4.1-4.10 are the same as those in presented in the base case. The only addition is the addition of tertiary amine (MDEA) to the deprotonation and protonation reactions, and the MDEA catalyzed hydrolysis reaction.

MDEA hydrolysis reaction

\[ R_1R_2R_3N + H_2O + CO_2 \xrightleftharpoons[k_{15}k_{16}]{k_{15}k_{16}} HCO_3^- + R_1R_2R_3NH^+ \]  

4.11

MDEA carbamate formation and breakdown

\[ RNH_2^+ COO^- + R_1R_2R_3N \xrightleftharpoons[k_{15}k_{16}]{k_{15}k_{16}} HCO_3^- + R_1R_2R_3NH^+ \]  

4.12

MDEA protonation

\[ R_1R_2R_3N + H_2O \xrightarrow{k_{17}k_{18}} R_1R_2R_3NH^+ + OH^- \]  

4.13

MDEA deprotonation

\[ R_1R_2R_3NH^+ + OH^- \xrightarrow{k_{19}k_{20}} R_1R_2R_3N + H_2O \]  

4.16

\[ R_1R_2R_3NH^+ + H_2O \xrightarrow{k_{21}k_{22}} R_1R_2R_3N + OH^- \]  

4.17
4.2 Rates of Reactions over Solid Acid Catalysts

In the above mention reactions, all reactions are considered as reversible reactions. These reactions are further categorized into instantaneous equilibrium reactions (reactions involving proton transfer) and kinetically controlled finite reactions. The rate expression for the finite reactions will be presented in this section.

The overall finite desorption mechanism of the CO₂ + MEA+ H₂O used for the model development is described in the equation:

\[ RNHCOO^- + B^+ \leftrightarrow RNH_2 + CO_2 + B \]  \hspace{1cm} 4.18

\[ HCO_3^- + B^+ \leftrightarrow CO_{2(aq)} + H_2O + B \]  \hspace{1cm} 4.19

\[ HCO_3^- \leftrightarrow CO_{2(aq)} + OH^- \]  \hspace{1cm} 4.20

\[ RNHCOO^- + HCO_3^- + B^+ \leftrightarrow RNH_2 + B + 2CO_2 + OH^- \]  \hspace{1cm} 4.21

Where \( B \) is any base present in the system and \( B^+ \) is the corresponding conjugate acid. In this work the possible bases and conjugate acids are MEA, MDEA, OH⁻, H₂O, HCO₃⁻, CO₃²⁻ and MEAH⁺, MDEAH⁺, H₂O, H₃O⁺, H₂CO₃, HCO₃⁻.

The concentrations of \( H_3O^+ \), and \( H_2CO_3 \) were considered to be relatively small and were therefore neglected.

For convenience let [C] represent carbamate and concentration

Carbamate breakdown reaction

\[ r_{CO2-MEA} = [C] \times (k_{-2}[H_3O^+] + k_{-3}[H_2O] + k_{-4}[RNH_2^+] + k_{-6}[HCO_3^-]) \]  \hspace{1cm} 4.22

Bicarbonate breakdown reaction
\[ r_{HCO_3} = [HCO_3^-] \ast (k_{13}[H_3O^+] + k_{14}) \]  \hfill 4.23

Since it is difficult to know the amount of \( HCO_3^- \) that contributes to deprotonation of \( RNH_2^+ \) and the amount that reacts with \( H_3O^+ \) and also quite impossible to know \( RNH_2^+ \) that reacts with \( OH^- \) and \( H_2O \) and the fraction that contributes to carbamate breakdown, the power law model will be written in terms of product formation which incorporates the formation of \( CO_2 \) from \( HCO_3^- \) and \( RNHCOO^- \), (i.e. \( r_{CO_2} = r_{RNHCOO^-} + r_{HCO_3^-} \)).

The \( CO_2 \) production rate is written as:

\[ r_{CO_2-amine} = -k_{CO_2}[CO_2 - amine] \]  \hfill 4.24

### 4.2.1 Power law model

An empirical power law model in terms of \( CO_2 \) desorption rate was based on this overall reaction with respect to \( CO_2 \) and is represented in the form:

\[ r_{CO_2-MEA} = -k_a \exp\left(-\frac{E_a}{RT}\right)[CO_2 - amine]^n \]  \hfill 4.25

Equation 4.25 shows the general dependence of desorption rate on the concentration of reacting species expressed in the Arrhenius form.

### 4.2.2 Mechanistic model

The rate of heterogeneous reaction is proportional to the amount of the chemisorbed molecules. It is therefore important to relate the reactant fluid phase concentrations to their corresponding fractional coverage. The developed kinetic
models were based on the specific role of the catalyst and all chemical species taking part in the chemical reactions. According to the literature\cite{112} certain assumptions need to be made to allow for simplicity of the model development. These assumptions are as follows:

- Reactants are present in a single fluid phase
- All surface sites have the same adsorption energy
- There are no interactions between adsorbed molecules

The developed rate models, their derivation and assumptions for MEA and MEA-MDEA are given in Table 4.2-1 and 4.2-2

As explained in chapter 2, the introduction of catalyst to the desorber system increases the rate of reaction alongside lowering the activation energy.

The high alkalinity of MEA makes it difficult for $\text{MEA}^+$ to release its proton to $H_2O$. This high heat of regeneration consumes approximately $78.2 \text{ kJ/mol at } (90^\circ\text{C})^{68}$. Conversely, the presence of a stronger base—$HCO_3^-$ reduces the energy requirement to a value of $21.9 \text{ kJ/mol}^{68}$.

\[
\text{MEA}^+ + H_2O \leftrightarrow \text{MEA} + H_3O^+ \quad \Delta G \sim 78.2 \text{ kJ/mol (90°C)} \quad 2.1
\]

\[
\text{MEA}^+ + HCO_3^- \leftrightarrow \text{MEA} + H_2CO_3 \quad \Delta G \sim 21.9 \text{ kJ/mol (90°C)} \quad 2.2
\]

The catalyst characteristics served as a guideline for developing the mechanistic models. The model was developed using LHHW formulation to describe the surface reaction of protonated amine$RNH_2$, $RNH_3^+$, and carbamate ion, $RNHCOO^-$. 
4.2.2.1  $\gamma - Al_2O_3$ Catalyst Mechanism with MEA

The presence of oxide anion-$AlO_2^-$ active site in $\gamma - Al_2O_3$ allows the catalyst to attack and withdraw the proton, $H^+$ found in $RNH_3^+$. It assumed that the $AlO_2^-$ is a stronger base and therefore reduces the energy required to deprotonate $MEAH^+$. MEAH$^+$ is initially chemisorbed on the catalyst surface followed by the transfer of the deprotonated proton from the catalyst active site to $HCO_3^-$ and/or $RNHCOO^-$. The attached free amine ($AlO_2RNH_2$) then desorbs from the active. Another implicit assumption was that the chemical reversibility of the reaction between adsorbed $MEAH^+$ and $MEA - COO^-$ is negligible due to the high equilibrium constant ($K_2$) obtained at the highest operating temperature.

The proposed catalytic desorption is as follows:

Adsorption of protonated MEA on the catalyst active site

\[ RNH_3^+ + AlO_2^- \leftrightarrow HAlO_2RNH_2 \]  

4.26

Surface reaction between adsorbed $RNH_3^+$ and bicarbonate ion

\[ HAlO_2RNH_2 + HCO_3^- \leftrightarrow AlO_2RNH_2 + CO_2 + H_2O \]  

4.27

Surface reaction between adsorbed $RNH_3^+$ and carbamate ion

\[ HAlO_2RNH_2 + RNHCOO^- \leftrightarrow AlO_2RNH_2 + CO_2 + H_2O + RNH_2 \]  

4.28

Desorption of MEA from the catalyst active site.

\[ AlO_2RNH_2 \leftrightarrow RNH_2 + AlO_2^- \]  

4.29
Each elementary reaction is assumed to be the rate determining step (RDS) and rate expression is developed for each case as shown in table 4.2-1(a)-(c) and 4.2.2 (a) and (b).

4.2.2.2 $\gamma-Al_2O_3$ Catalyst Mechanism with MEA-MDEA

Tertiary amine MDEA is a weaker base than MEA and is therefore easier to deprotonate $MDEAH^+$ than $MEA^+$. Consequently, the concentration of $MDEAH^+$ is lowest at the bottom of the desober column were the temperature is the hottest. Shi et al$^{68}$ proposed a multi-step process for MEA-MDEA reaction as follows:

$$R_1R_2R_3N + RNH_3^+ \leftrightarrow R_1R_2R_3NH^+ + RNH_2$$  \hspace{1cm} 4.30

$$R_1R_2R_3NH^+ + H_2O \leftrightarrow R_1R_2R_3N + H_3O^+ \text{ (without bicarbonate)}$$  \hspace{1cm} 4.31

$$R_1R_2R_3NH^+ + HCO_3^- \leftrightarrow R_1R_2R_3N + H_3O^+ CO_2 + H_2O \text{ (with bicarbonate)}$$  \hspace{1cm} 4.32

He suggested that the role of MDEA is to split the energy of difficult reaction 2.1 into two easier reactions, as it is easier for $RNH_3^+$ to release its proton to $R_1R_2R_3N$ or $HCO_3^-$ than to water. Also the overall reaction rate is seen to increase as the energy efficiency increases with little wastes on water vaporization$^{61}$.

The mechanistic model for MEA-MDEA includes all the reactions occurring in MEA. The only difference is the addition of $R_1R_2R_3NH^+$ to the reaction mechanism

The proposed catalytic desorption is as follows:

Adsorption of protonated MDEA on the catalyst active site

$$R_1R_2R_3NH^+ + AlO_2^- \leftrightarrow HAIO_2 R_1R_2R_3N$$  \hspace{1cm} 4.33
Surface reaction between adsorbed $R_1R_2R_3NH^+$ and bicarbonate ion

$$\text{HAIO}_2R_1R_2R_3N + \text{HCO}_3^- \leftrightarrow \text{AlO}_2R_1R_2R_3N + \text{CO}_2 + \text{H}_2\text{O}$$  

Surface reaction between adsorbed $R_1R_2R_3NH^+$ and carbamate ion

$$\text{HAIO}_2R_1R_2R_3N + \text{RNHCOO}^- \leftrightarrow \text{AlO}_2R_1R_2R_3N + \text{CO}_2 + \text{H}_2\text{O} + \text{RNH}_2$$

Desorption of MEA from the catalyst active site.

$$\text{AlO}_2R_1R_2R_3N \leftrightarrow R_1R_2R_3N + \text{AlO}_2^-$$

4.2.2.3 HZSM-5 Catalyst Mechanism with MEA

In the case of HZSM-5, the presence of both Lewis and Brønsted acid sites allowed for the development of a model which takes into account the presence of both acid sites, thus allowing a dual site mechanism.

Carbamate breakdown:

$$\text{RNHCOO}^- + \text{H}_3\text{O}^+ \leftrightarrow \text{Zwitterion} \leftrightarrow \text{MEA} + \text{CO}_2 + \text{H}_2\text{O} \quad \Delta G \sim 15.47 \text{ kJ/mol}$$

2.2

Carbamate breakdown is a complex reaction but requires less energy. It however needs a large amount of free protons, and depends greatly on reaction 2.1, as most of the protons are attached to $\text{MEAH}^+ / \text{MDEAH}^+$.

It was assumed that $\text{RNH}_3^+$ chemically absorbs on the Lewis acid site while $\text{RNHCOO}^-$ chemisorbs on the Brønsted acid site withdrawing its proton, resulting in a dual site adsorption. The protonated Lewis active site transfers this proton to the
deprotonated Brønsted acid site. This mechanism is seen to provide a pathway with lower activation energy as is shown in the obtained parameters chapter 5.

Adsorption of $RNH_3^+$ on the Lewis active site

$$RNH_3^+ + ALO_2^- \leftrightarrow HAlO_2RNH_2$$  \hspace{1cm} 4.37

Adsorption of protonated carbamate ion on the Brønsted active site

$$RNH_2 - COO^- + H^+_{(s)} \leftrightarrow RNHCOO^- H^+_{(s)}$$  \hspace{1cm} 4.38

Surface reaction between adsorbed $RNH_3^+$ with adsorbed carbamate ion, (protonated Lewis gives proton back to proton deficient Brønsted active site)

$$HAlO_2RNH_2 + RNHCOO^- H^+_{(s)} \leftrightarrow AlO_2RNH_2 + CO_2 + RNH_2^- H^+_{(s)}$$  \hspace{1cm} 4.39

Desorption of MEA from the catalyst active site.

$$AlO_2RNH_2 \leftrightarrow RNH_2 + AlO_2^-$$  \hspace{1cm} 4.40

$$RNH_2^- H^+_{(s)} \leftrightarrow RNH_2 + H^+_{(s)}$$  \hspace{1cm} 4.41

4.2.2.4 HZSM-5 Catalyst Mechanism with MEA-MDEA

The same process explained in section 4.2.2.2 applies to zeolite catalyst. The desorption process is given below:

Adsorption of protonated MDEA on the Lewis active site

$$R_1R_2R_3NH^+ + AlO_2^- \leftrightarrow HAlO_2R_1R_2R_3N$$  \hspace{1cm} 4.42

Adsorption of protonated carbamate ion on the Brønsted active site

$$RNH - COO^- + H^+_{(s)} \leftrightarrow RNHCOO^- H^+_{(s)}$$  \hspace{1cm} 4.43
Surface reaction between adsorbed $RNH_3^+$ with adsorbed carbamate ion, (protonated Lewis gives proton back to proton deficient Brønsted active site)

$$HAIO_2R_1R_2R_3N +RNHCOO^-H_2^+ \leftrightarrow AI_2O_2R_1R_2R_3N +CO_2 +RNH_2^--H_2^+$$  4.44

Desorption of MDEA from the catalyst active site.

$$AI_2O_2R_1R_2R_3N \leftrightarrow R_1R_2R_3N +AI_2O_2^-$$  4.45

$$RNH_2^-H_2^+ \leftrightarrow RNH_2 + H_2^+$$  4.46

For convenience, the active sites will be represented as $S$ and the amines will be written as

$RNH_2 = MEA$ and $R_1R_2R_3N = MDEA$

<table>
<thead>
<tr>
<th>Model</th>
<th>Proposed Mechanism</th>
<th>Description</th>
<th>Rate expression</th>
<th>Eq #</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 LHHW</td>
<td><strong>MEAH</strong>$^-$ + (s) $\leftrightarrow$ <strong>MEAH</strong>$^+$ (s)</td>
<td>Single site non-dissociative adsorption, followed by biomolecular surface reaction as RDS</td>
<td>$r = k_c \exp\left(-\frac{E_A}{RT}\right) \cdot \frac{[H^+] \cdot [C]}{1 + K_1[C] + K_1 K_3[A]}$</td>
<td>4.47</td>
</tr>
<tr>
<td></td>
<td><strong>MEAH</strong>$^-$ + <strong>MEACOO</strong>$^-$ $\leftrightarrow$ <strong>MEA</strong>$^-$ + <strong>CO_2</strong></td>
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<td></td>
<td><strong>MEA</strong>$^-$ $\leftrightarrow$ <strong>MEA</strong> + (s)</td>
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<tr>
<td>M1 LHHW</td>
<td><strong>MEAH</strong>$^-$ + (s) $\leftrightarrow$ <strong>MEAH</strong>$^+$ (s)</td>
<td>Single site non-dissociative adsorption, followed by biomolecular surface reaction as RDS</td>
<td>$r = k_c \exp\left(-\frac{E_A}{RT}\right) \cdot \frac{[H^+] \cdot [B]}{1 + K_1[C] + K_1 K_3[A]}$</td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td><strong>MEAH</strong>$^-$ + <strong>HCO_3^-</strong> $\leftrightarrow$ <strong>MEA</strong>$^-$ + <strong>CO_2</strong></td>
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<td></td>
<td><strong>MEA</strong>$^-$ $\leftrightarrow$ <strong>MEA</strong> + (s)</td>
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<tr>
<td>M1 LHHW</td>
<td><strong>MEACOO</strong>$^-$ + (s) $\leftrightarrow$ <strong>MEACOO</strong>$^-$ (s)</td>
<td>Single site non-dissociative adsorption, followed by biomolecular surface reaction as RDS</td>
<td>$r = k_c \exp\left(-\frac{E_A}{RT}\right) \cdot \frac{[H^+] \cdot [C]}{1 + K_1[C] + K_1 K_3[A]}$</td>
<td>4.49</td>
</tr>
<tr>
<td>LHHW HZSM-5</td>
<td><strong>MEACOO</strong>$^-$ (s) + <strong>MEA</strong>$^+$ $\leftrightarrow$ <strong>MEA</strong>$^-$<strong>COOH</strong>$^-$ (s) + <strong>MEA</strong></td>
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<td></td>
<td><strong>MEA</strong>$^-$<strong>COOH</strong>$^-$ (s) $\leftrightarrow$ <strong>MEA</strong>$^+$ + **COO$$^-$ (s)</td>
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<td></td>
<td><strong>MEA</strong>$^+$ + **COO$$^-$ (s) $\leftrightarrow$ <strong>MEA</strong>$^-$ (s) + <strong>CO_2</strong></td>
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<tr>
<td></td>
<td><strong>MEA</strong>$^-$ (s) $\leftrightarrow$ <strong>MEA</strong>$^+$ (s)</td>
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<tr>
<td>Model</td>
<td>Proposed Mechanism</td>
<td>Description</td>
<td>Rate expression</td>
<td>Eq #</td>
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<tr>
<td>M2 LHHW HZSM-5</td>
<td>MEAH⁻ + (s) ↔ MEAH⁺ (s) &lt;br&gt; MEAH⁺(s) + HCO₃⁻ ↔ MEA⁺(s) + CO₂ &lt;br&gt; MEA⁺(s) ↔ MEA + (s)</td>
<td>Single site non-dissociative adsorption, followed by surface reaction as RDS</td>
<td>[ r = K_0 \exp \left( -\frac{E_A}{RT} \right) \frac{[B] \cdot [H]}{1 + K_1[C] + K_1 K_3[A]} ]</td>
<td>4.50</td>
</tr>
<tr>
<td>M3 LHHW HZSM-5</td>
<td>MEAH⁺ + (s) ↔ MEAH⁺(s) &lt;br&gt; MEA - COO⁻ + (S) ↔ MEA - COO⁻(s) &lt;br&gt; MEAH⁺(s) + MEA - COO⁻(s) ↔ MEA⁺(s) + CO₂ + MEA⁺(s) &lt;br&gt; 2 MEA⁺(s) ↔ 2MEA + (s)</td>
<td>Dual site adsorption followed by non-dissociation bimolecular reactions as RDS</td>
<td>[ r = K_0 \exp \left( -\frac{E_A}{RT} \right) \frac{[H^+] \cdot [C]}{\left(1 + K_1[C] + K_2[H] + K_3^{1/4}[A]\right)^2} ]</td>
<td>4.51(a)</td>
</tr>
<tr>
<td>M4 LHHW HZSM-5</td>
<td>MEAH⁺ + (s) ↔ MEAH⁺(s) &lt;br&gt; HCO₃⁻(s) + (S) ↔ HCO₃⁻(s) &lt;br&gt; MEAH⁺(s) + HCO₃⁻(s) ↔ MEA⁺(s) + CO₂ + H₂O(s) &lt;br&gt; MEA⁺(s) ↔ MEA + (s) &lt;br&gt; H₂O(s) ↔ H₂O + (s)</td>
<td>Dual site adsorption followed by non-dissociation bimolecular reactions as RDS</td>
<td>[ r = K_0 \exp \left( -\frac{E_A}{RT} \right) \frac{[H^+] \cdot [B]}{\left(1 + K_1[C] + K_2[H] + K_3[A]\right)^2} ]</td>
<td>4.51(b)</td>
</tr>
<tr>
<td>Model</td>
<td>Proposed Mechanism</td>
<td>Description</td>
<td>Rate expression</td>
<td>Eq #</td>
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</tbody>
</table>
| M3 LHHW (γ-Al₂O₃) | \( \text{HCO}_3^- + (S) \leftrightarrow \text{HCO}_3(S) \)  \
| | \( \text{HCO}_3(S) \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}(S) \text{MEA}^+ + \text{MEA}^- \)  \
| | \( \text{CO}_3(S) \leftrightarrow \text{MEA} + \text{CO}_2 + \text{H}_2\text{O}(S) \text{MEA}^- \)  \
| | \( \text{H}_2\text{O}(S) \leftrightarrow \text{H}_2\text{O}(s) \) | Single adsorption followed by dissociation desorption reactions as RDS | \( r = K_0 \exp \left( -\frac{E_a}{RT} \right) \times \left\{ \frac{[B]}{\left[ 1 + K_1[C] + K_2[H] + K_2[W] \right]} \right\} \) | 4.51(c) |
| M4 LHHW HZSM-5 | \( \text{MEA}^+ + (S) \leftrightarrow \text{MEA}^+(S) \)  \
| | \( \text{MEA}^+(S) + \text{MEACOO}^- \leftrightarrow \text{MEA}(S) + \text{MEA} + \text{CO}_2 \)  \
| | \( \text{MEA}(S) \leftrightarrow \text{MEA}(s) \)  \
| | \( \text{H}_2\text{O}(S) \leftrightarrow \text{H}_2\text{O}(s) \) | Single site adsorption followed by non-dissociation bimolecular reactions as RDS | \( r = K_0 \exp \left( -\frac{E_a}{RT} \right) \times \left\{ \frac{[\text{H}^+][\text{C}]}{\left[ 1 + K_1[\text{C}] + K_2[\text{A}] \right]} \right\} \) | 4.52 |
Table 4.2-2(a): Rate models based on LHHW mechanism for MEA+MDEA + CO$_2$ +H$_2$O

<table>
<thead>
<tr>
<th>Model</th>
<th>Proposed Mechanism</th>
<th>Description</th>
<th>Rate expression</th>
<th>Eq #</th>
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<tbody>
<tr>
<td>M1</td>
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<tr>
<td>LHHW</td>
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<tr>
<td>($\gamma$-Al$_2$O$_3$)</td>
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<tr>
<td>M1</td>
<td>MDEAH$^+$ + (s) $\leftrightarrow$ MDEAH$^+$ (s)</td>
<td>Single site non-dissociative adsorption, followed by biomolecular surface reaction as RDS</td>
<td>$r = K_0 \exp\left(-\frac{E_A}{RT}\right) \times \left{\frac{[H^+] \times [C]}{1 + K_1[C] + K_4[A]}\right}$</td>
<td>4.53(a)</td>
</tr>
<tr>
<td></td>
<td>MDEAH$^+$ + MEAO$^-$ $\leftrightarrow$ MDEA$_{av}$, MEA+ CO$_2$</td>
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<tr>
<td></td>
<td>MDEA$_{av}$ $\leftrightarrow$ MEA + (s)</td>
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<tr>
<td>M2</td>
<td>MDEAH$^+$ + (s) $\leftrightarrow$ MDEAH$^+$ (s)</td>
<td>Single site non-dissociative adsorption, followed by surface reaction as RDS</td>
<td>$r = K_0 \exp\left(-\frac{E_A}{RT}\right) \times \left{\frac{[C] \times [H]}{1 + K_4[C] + K_4[A]}\right}$</td>
<td>4.53(b)</td>
</tr>
<tr>
<td>LHHW</td>
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<tr>
<td>($\gamma$-Al$_2$O$_3$)</td>
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<tr>
<td>M2</td>
<td>MDEAH$^+$ + HCO$<em>3^-$ $\leftrightarrow$ MDEA$</em>{av}$ + CO$_2$ +H$_2$O</td>
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<tr>
<td></td>
<td>MDEA$_{av}$ $\leftrightarrow$ MDEA + (s)</td>
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<tr>
<td>Model</td>
<td>Proposed Mechanism</td>
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</tbody>
</table>
| M3    | MDEAH\(^+\) + (s) ⇌ MDEAH\(^{+}\)\((s)\)  
MEA - COO\(^-\) + (S) ⇌ MEA - COO\(^{-}\)\((s)\)  
MDEAH\(^{+}\)\((s)\) + MEA - COO\(^{-}\)\((s)\) ⇌ MDEA\((s)\) + CO\(_2\) + MEA\((s)\)  
MEA\((s)\) ⇌ MEA + (s)  
MDEA\((s)\) ⇌ MDEA + (s) | Dual site adsorption followed by non-dissociation bimolecular reactions as RDS | \[ r = K_o \exp \left( -\frac{E_A}{RT} \right) \times \left\{ \frac{[H^+] \cdot [C]}{\left( 1 + K_1[C] + K_2[H] + K_3 1^{1/4}[A]^2 \right)^2} \right\} \] | 4.54(a) |
| M4    | MDEAH\(^+\) + (s) ⇌ MDEAH\(^+\)\((s)\)  
HCO\(^-\) + (S) ⇌ HCO\(^{-}\)\((s)\)  
MDEAH\(^{+}\)\((s)\) + HCO\(^{-}\)\((s)\) ⇌ MDEA\((s)\) + CO\(_2\) + H\(_2\)O\((s)\)  
MDEA\((s)\) ⇌ MDEA + (s) | Dual site adsorption followed by non-dissociation bimolecular reactions as RDS | \[ r = K_o \exp \left( -\frac{E_A}{RT} \right) \times \left\{ \frac{[H^+] \cdot [B]}{\left( 1 + K_1[C] + K_2[H] + K_3 1^{1/4}[A]^2 \right)^2} \right\} \] | 4.54(b) |
As discussed in chapter 2, the bulk concentration of all the chemicals species present in the desorption reaction are needed to obtain the mechanistic rate model which describes the CO\textsubscript{2} desorption rate. These were obtained using the mass balance equation. These concentrations were compared to that obtained from the ion speciation plot generated from ASPEN NRTL system model. Both methods produced similar results.

CO\textsubscript{2} + MEA + H\textsubscript{2}O system balance

MEA balance:

\[
[MEA] + [MEAH^+] + [MEA - COO^-] = [MEA]_o
\]

4.55

Carbon balance:

\[
[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] = ([MEA]_o \cdot \alpha
\]

4.56

Charge Balance:

\[
[MEAH^+] + [H_3O^+] = [HCO_3^-] + 2[CO_3^{2-}] + [RNHCOO^-] + [OH^-]
\]

4.57

CO\textsubscript{2} + MEA+MDEA+H\textsubscript{2}O system balance

MEA balance:

\[
[MEA] + [MEAH^+] + [MEA - COO^-] = [MEA]_o
\]

4.58

MDEA balance:

\[
[MDEA] + [MDEAH^+] = [MDEA]_o
\]

4.59
Total carbon balance:

\[
[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [MEACOO^-] + ([MEA]_o + [MDEA]_o) \alpha \tag{4.60}
\]

Charge Balance:

\[
[MEA H^+] + [MDEA H^+] + [H_3O^+] = [HCO_3^-] + [CO_3^{2-}] + [MEACOO^-] + [OH^-] \tag{4.61}
\]

Knowing that \(RNHCOO^-\) and \(HCO_3^-\) reacts with \(RNH_3^+\) to produce CO\(_2\). As shown in equations 2.2 and 4.1. The amount of \(RNH_3^+\) that reacts with each of this ion has to be quantified. This is done by taking the ratio of abundance of both \(RNHCOO^-\) and \(HCO_3^-\) and quantifying their contribution to the total rate of CO\(_2\) desorption. This was also done in the case of blended solvents (MEA-MDEA).

\[
RNH_3^+ + HCO_3^- \leftrightarrow MEA + H_2CO_3 \tag{2.2}
\]

\[
RNH_3^+ + RNHCOO^- \leftrightarrow 2RNH_2 + CO_2 \tag{4.1}
\]
5.1 Catalyst characterisation

The BET surface area, pore volume and average pore size are of great importance in catalyst performance and evaluation. These physical properties were measured for all catalysts (γ-Al₂O₃, HZSM-5, SiO-Al₂O₃ and HY Zeolite). The results are presented in Table 5.1-1. The adsorption and desorption BET isotherms were seen to take the sharp of the type IV isotherm as classified by IUPAC classification, indicating the presence of relatively large mesopore area (MSA) in comparison to the micropore area in HZSM-5 and γ-Al₂O₃ as shown in figure 5.1-1.
Table 5.1-1: Structural properties of catalyst

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (mL/g)</th>
<th>Average Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>414.10</td>
<td>0.29</td>
<td>3.11</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>381.94</td>
<td>0.470</td>
<td>4.54</td>
</tr>
<tr>
<td>SiO-Al₂O₃</td>
<td>613.45</td>
<td>0.44</td>
<td>5.21</td>
</tr>
<tr>
<td>HY zeolite</td>
<td>615.49</td>
<td>0.52</td>
<td>3.43</td>
</tr>
</tbody>
</table>
Figure 5.1-1: BET surface area and pore size distribution
It is well known in the literature that only the physical characteristic alone cannot be used to evaluate catalyst performance. Other critical chemical characteristics are needed which include the Brønsted/Lewis acid ratio and the acid site strength. The Fourier Transformed Infrared Spectroscopy (FTIR) experiments were carried out to quantify the amount and ratio of Lewis (L) and Brønsted (B) acid sites in both HZSM-5 and γ-Al₂O₃ catalysts as well as all the other catalysts. The obtained results indicated the presence of Brønsted and Lewis acid sites in HZSM-5 and HY catalyst. In contrast, γ-Al₂O₃ and SiO-Al₂O₃ had just Lewis acid and Brønsted acid sites respectively. Similar trends were observed in the works of Pathak et al and other works reported in the literature. The acidic sites and strength for both catalysts (γ-Al₂O₃ and HZSM 5) were identified via TPD experiments with ammonia. The results are presented in Figure 5.1-2. The acidic strength was measured as a function of desorption temperature. The acid strength is reported to increase as the desorption temperature increases. According to literature, the acidic sites can be classified into three groups: weak, intermediate and strong acid sites which occurs at helium desorption temperatures ranges of 20-200°C, 200-350°C and 350-550°C, respectively. A high desorption intensity indicates a large number of acid sites and vice versa. The TPD curves for HZSM-5 and γ-Al₂O₃ have three major peaks. The first peak is located at 130°C and the second and third peaks are located at 320°C and 430°C, corresponding to the presence respectively of weak, intermediate and strong acid sites. It can be seen that the intensity of the peak at 150°C is lower than at 340°C and 450°C. This indicates the presence of a smaller number of weak acid sites as compared to the number of intermediate and strong acid sites present in HZSM-5. Similar observations were seen in the work of Pathak et al. On the other hand, the TPD result for γ-Al₂O₃ indicates the presence of low intensity weak acid sites peak at
150°C, medium intensity intermediate acid site at 320°C and high intensity strong acid sites peak at 430°C.

The composition, purity and crystalline structure of HZSM-5 and γ-Al₂O₃ catalysts were identified via X-ray diffraction (XRD). The XRD patterns for HZSM-5 and γ-Al₂O₃ shows the presence of crystalline structure (Figure 5.1-3). Such observations were seen in literature¹¹⁴,¹²⁰,¹²¹.
Figure 5.1-2: TPD pattern of $\gamma$-$\text{Al}_2\text{O}_3$ and HZSM-5 catalyst.

Figure 5.1-3: XRD pattern of $\gamma$-$\text{Al}_2\text{O}_3$ and HZSM-5 catalyst
5.2 Kinetic Study

5.2.1 Evaluation of Possible Heat and Mass Transfer Limitations

Intrinsic kinetic data are obtained only in the absence of heat and mass transfer limitations. Since these transfer limitations tend to occur at higher temperature due to the increase in reaction rate, it is important to determine to what extent their existence affect the reaction rate. Using the correlations available in literature, the possible effect of heat and mass limitations on reaction rates were examined at the highest reaction temperature-368K as reported in the works of Ibrahim and Idem\textsuperscript{122}.

5.2.1.1 Heat Transport Effect

Internal pore heat transfer effect was estimated using the Prate analysis given by

\[
\Delta T_{\text{particle, max}} = \frac{D_{\text{eff}} (C_{AS} - C_{AC}) \Delta H_{\text{rxn}}}{\lambda_{\text{eff}}} \tag{5.1}
\]

The value of \(\Delta T_{\text{particle, max}}\) should be less than 1\(^\circ\)C for a negligible effect of heat transfer limitation. Where the upper limit to temperature variation between pellet centre and pellet surface is \(\Delta T_{\text{particle, max}}\), and \(\Delta H_{\text{rxn}}\) is the heat of reaction. \(C_{AS}\) and \(C_{AC}\) are the concentrations at the pellet surface and centre, which are assumed to be the bulk concentration and zero respectively\textsuperscript{123}. \(D_{\text{eff}}\) is the effective mass diffusivity obtained from \(D_{\text{eff}} = \frac{\varepsilon D_{AB}}{\tau}\textsuperscript{124}\). Here \(D_{AB}\) is the bulk diffusivity of component A (CO\textsubscript{2}) in B (rich solvent) and was estimated using Brokaw equation\textsuperscript{125}. The value of \(D_{AB}\) at maximum temperature was found to be \(6.8 \times 10^{-08}\) m\(^2\)/s. \(D_{\text{eff}}\) was estimated to be \(6.85 \times 10^{-09}\) m\(^2\)/s. \(\varepsilon\) is the void fraction, calculated using the formula \(\varepsilon = 0.38 + \ldots\)
0.073[1 + ((\frac{\text{d}}{\text{dp}} - \frac{2}{d})^2)^{126} \text{ where } d \text{ and } d_p \text{ are the reactor diameter and catalyst diameter, respectively. } \tau \text{ is the tortuosity factor. } \lambda_{eff} = \text{ effective thermal conductivity and is calculated using the equation } \frac{\lambda_{eff}}{\lambda} = 5.5 + 0.05N_{Re}^{127} \text{ for PBTRs. } \lambda \text{ is the molecular thermal conductivity calculated using the correlation of Wassiljewa}^{125} \text{ and obtained to be } 1.57 \times 10^{-7} \text{kJm}^{-1}\text{s}^{-1}\text{K}^{-1}. \text{ The effective thermal conductivity, } \lambda_{eff} \text{ was found to be } 9.05 \times 10^{-7} \text{kJm}^{-1}\text{s}^{-1}\text{K}^{-1}. \text{ A value of 3.4K was obtained which is less than } 1^\circ\text{C. This shows that there is no internal pore heat transfer resistance.}

The correlation adapted from (Idem and Ibrahim)\textsuperscript{122} \text{ was used to account for the heat-transfer limitation across the gas film as shown in Equation 5.2.}

\[
\Delta T_{film,max} = \frac{L_c(-r_{A,obs})\Delta H_{rxn}}{h}
\]

Where \(\Delta T_{film,max}\) is the upper limit temperature difference between the pellet surface and the gas phase, \(L_c\) is the characteristic length, \(-r_{A,obs}\) is the observed reaction rate, and \(h\) is the heat-transfer coefficient [estimated from the correlation \(J_H = J_D = (\frac{h}{C_p\mu})N_{pr}^{2/3}\), where \(J_H\) is the heat-transfer \(J\) factor, \(N_{pr} = C_p\mu/\lambda\), \(N_{Pr}\) is Prandtl number and \(\lambda\) is the molecular thermal conductivity]. The \(J_D\) factor is given by the following correlations: \(J_D = (0.4548/\varepsilon_P)N_{Re}^{-0.4069}\) (40) = \((k_c/v)N_{sc}^{2/3}\) \textsuperscript{126}. Where \(N_{Re} = \frac{d_p\mu_p}{\mu(1-\varepsilon)}\). \(k_c\) is the mass-transfer coefficient obtained as \(2.44 \times 10^{-5} \text{m/s}\). The heat transfer coefficient, \(h\), was determined to be \(1338.18 \text{kJm}^{-2}\text{s}^{-1}\text{K}^{-1}\). A value of \(7.8 \times 10^{-3} \text{K}\) was obtained for \(\Delta T_{film,max}\).
A more rigorous criterion which determines the onset of the heat-transport limitation during reaction$^{128}$ was also used to further ascertain the insignificance of heat-transfer resistance in the rate of the reaction, as shown in equation 5.3.

$$\frac{r_{A,obs} \rho_b R_c E \Delta H_{\text{rnx}}}{hT^2 R} < 0.15$$  \hspace{1cm} 5.3

By substituting the values for the terms on the left-hand side (LHS) of equation 5.3, a value which is much less than 0.15 was obtained for both catalysts, thereby proving the absence of any heat-transport limitation. These values for $\Delta T_{\text{film, max}}$ and Mears criterion are reported in Tables 5.2-1 and 5.2-2.
Table 5.2-1: Heat transport effect for CO₂ + MEA system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Diameter (m)</th>
<th>$\Delta T_{\text{particle,max}}$ (K)</th>
<th>$\Delta T_{\text{film,max}}$ (K)</th>
<th>Mears Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma - Al_2O_3$</td>
<td>0.003</td>
<td>3.45</td>
<td>$7.8 \times 10^3$</td>
<td>$8.51 \times 10^{-4}$</td>
</tr>
<tr>
<td>H-ZSM 5</td>
<td>0.0025</td>
<td>5.19</td>
<td>$6.6 \times 10^{-3}$</td>
<td>$6.31 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 5.2-2: Heat transport effect for CO₂ + MEA + MDEA system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Diameter (m)</th>
<th>$\Delta T_{\text{film,max}}$ (K)</th>
<th>Mears Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma - Al_2O_3$</td>
<td>0.003</td>
<td>4.36</td>
<td>$8.39 \times 10^{-6}$</td>
</tr>
<tr>
<td>H-ZSM 5</td>
<td>0.0025</td>
<td>6.32</td>
<td>$5.72 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
5.2.1.2 Mass Transfer Effects

The internal pore mass transfer resistance was calculated using Weisz–Prater criterion as given:

\[
C_{wp,ipd} = \frac{-r_{A,obs}D_c R_c^2}{D_{eff} C_{AS}}
\]

(5.4)

\(C_{wp,ipd}\) is defined as the Weisz-Prater criterion for internal pore diffusion, \(\rho_c\) is the pellet density, \(R_c\) is the obtained values for \(\gamma - \text{Al}_2\text{O}_3\) and HZSM-5 were far less than 1, indicating that the concentration at the catalysts surface is almost the same as that in the catalyst pore. These results indicate the absence of internal mass transfer diffusion\(^{124}\). The effect of film mass transfer limitations was determined by estimating the ratio of observed rate to the rate of film resistance. Equation illustrates this criterion:

\[
\frac{\text{observed rate}}{\text{rate if film transfer controls}} = \frac{-r_{A,obs}d_b}{K_cC_{As} b} < 0.15
\]

(5.5)

The obtained value for the given ratio indicates that film transfer rate is less than the observed rate. Therefore, the film resistance should not influence the reaction rate\(^{123}\). A more rigorous set of criteria was applied in order to ensure the absence of mass transport limitation in the film. This Mears’ criterion\(^{124}\) considers the mass transfer limitations during kinetic data collection and given as:

\[
\frac{-r_{A,obs}D_c R_c n}{K_cC_A} < 0.15
\]

(5.6)

The summary of mass transfer limitations is given in Table 5.2-3. The results show the absence of internal and external mass transfer limitations. Also, in order to
ensure plug flow conditions, absence of back mixing and channeling certain relevant criterion\textsuperscript{129} and \textsuperscript{130} were adopted. These criteria include:

\begin{align*}
(1) \quad & \frac{\text{Catalyst bed height}}{\text{Catalyst Particle size}} = \frac{L}{d_p} \geq 50, \\
(2) \quad & \frac{\text{Catalyst bed diameter}}{\text{Catalyst Particle size}} = \frac{d}{d_p} \geq 10,
\end{align*}

In this work, both requirements were met, indicating that the system operates under plug flow conditions as shown in Table 5.2-4.
Table 5.2-3: Mass transfer limitations for CO\textsubscript{2}+MEA+H\textsubscript{2}O system

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Film mass transfer resistance \cite{5}</th>
<th>Mass transfer limitation in the film \cite{6}</th>
<th>Internal Mass transfer limitations \cite{7}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma - \text{Al}_2\text{O}_3 )</td>
<td>(-r_{A,obs}' d_b / K_C C_{AS} )</td>
<td>(-r_{A,obs}' P_b R_c n / K_C C_A &lt; 0.15)</td>
<td>( C_{wp,ipd} = ) (-r_{A,obs}' P_c R_c^2 / D_{eff} C_{AS} &lt; 1 )</td>
</tr>
<tr>
<td>( H - \text{ZSM 5} )</td>
<td>( 1.27 \times 10^{-3} )</td>
<td>( 3.44 \times 10^{-3} )</td>
<td>( 0.134 )</td>
</tr>
<tr>
<td>( H - \text{ZSM 5} )</td>
<td>( 8.7 \times 10^{-4} )</td>
<td>( 1.56 \times 10^{-3} )</td>
<td>( 0.451 )</td>
</tr>
</tbody>
</table>

Table 5.2-4: Plug flow conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>L/d(p)</th>
<th>d/d(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma - \text{Al}_2\text{O}_3 )</td>
<td>355.7</td>
<td>17</td>
</tr>
<tr>
<td>H-ZSM 5</td>
<td>426.8</td>
<td>20.4</td>
</tr>
</tbody>
</table>
5.3 Effect of Various Parameters on Catalyst Performance

The catalyst performance can be evaluated in terms of catalyst activity and selectivity. In general terms, catalyst activity is usually expressed in terms of reaction rate, with higher reaction rate indicating higher catalyst performance. Catalytic activity can also be expressed in terms of conversion. In this work, the catalytic activity was evaluated in terms of carbamate and bicarbonate conversion to CO$_2$ and the rate at which the conversion occurs. The kinetic performance of the catalyst was further expressed in terms of activation energy, $E_A$, and rate constants $K_r$. The conversion of is expressed as:

$$X_{CO_2} = \frac{CO_{2,\text{in}} - CO_{2,\text{out}}}{CO_{2,\text{in}}}$$

For supported catalyst, defining activity in terms of catalyst active sites is more useful as most of the reactions occurs on the active site. Hence, the activity was further expressed in terms of turnover frequency (TOF). TOF expresses the catalytic activity in terms of total amount of moles transformed into desired products per mole of active site per unit time. A larger TOF indicates higher catalytic activity.

$$\text{TOF} = \frac{Moles \ of \ desired \ product \ (total \ number \ of \ moles \ reacting)}{total \ number \ of \ active \ sites \ * \ unit \ time} = \text{time}^{-1} (s^{-1})$$

The results for TOF are shown in appendix A5.

In the absence of heat and mass limitations, intrinsic experimental rates were calculated using the equal area differentiation technique which was obtained from the plots of conversion, $X$ (i.e. CO$_2$ desorbed) vs. weight of catalyst per amine flow rate ($W/F_{\text{Amine}}$):

$$r_A = \frac{dX_{CO_2}}{d(W/F_{\text{Amine}})}$$

5.7
5.3.1 Effect of varying \( W/F_{\text{Amine}} \) and catalyst Ratio

Changing mass of catalyst, \( W \), while keeping amine flow rate constant \( (F_{\text{Amine}}) \), showed that the reaction rate increases with catalyst weight. As described by the Maxwell Boltzmann theory, the increase in temperature and catalyst weight increases the average number of molecules with higher kinetic energy, thus allowing the reaction to occur at a faster rate and lower activation energy. This same effect was seen as the temperature and catalyst weight were varied as presented in figures 5.3-1 and 5.3-2.
Figure 5.3-1: Variation of catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant MEA flow rate 60 ml/min
Figure 5.3-2: Variation of catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant MEA-MDEA flow rate 60 ml/min
Figure 5.3-3: Comparison of MEA and MEA-MDEA system γ-Al₂O₃. Catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant amine flow rate (60 ml/min)
Figure 5.3-4: Comparison of MEA and MEA-MDEA system HZSM-5 Catalyst weight (0-200g) and temperature (348K, 358K, and 368K) at constant amine flow rate (60 ml/min)
As explained earlier, $\gamma$-$\text{Al}_2\text{O}_3$ weakens the N-C bond present in the carbamate ion, resulting in the dissociative chemisorption of the carbamate ion, while the oxide anion-$\text{AlO}_2^-$ deprotonates $\text{MEA}^+$/MDEA$^+$ by attacking $H^+$ found in $\text{MEA}^+$/MDEA$^+$. On the other hand, HZSM-5 having both Lewis and Brønsted acid sites acts as both a proton donor and receiver, thus having the ability to assist in $\text{MEA}^+$ deprotonation and carbamate breakdown. Also, the available proton in HZSM-5 is transferred to bicarbonate ions, thus increasing the amount of desorbed CO$_2$. This explains the higher conversion and lower activation energy observed in CO$_2$ desorption in the presence of HZSM-5 in comparison to $\gamma$-$\text{Al}_2\text{O}_3$. The temperature effect can be seen at 0g catalyst weight for all temperatures (348, 358 and 368K). As earlier stated, increase in temperature increases the fraction of particles with higher energy. At 75°C (348K) the influence of the catalyst is less effective and minimal on the reaction rate. The acid strength becomes an important factor to consider. The TPD result shows that HZSM-5 has high intensity strong acid site which contributes to its slightly higher efficiency at 345K. For MEA-MDEA at 368K (Figure 5.3-2), we see that the conversions for both $\gamma$-$\text{Al}_2\text{O}_3$ and HZSM-5 are similar, this can be explained by the temperature effect. At 365K, most of the protons attached to MDEA$^+$ are deprotonated and available to assist in the deprotonation of CO$_2$, thus reducing the effect of both catalyst.

Tables 5.3-1 and 5.3-3 shows the percentage contribution of MEACOO$^-$ and $\text{HCO}_3^-$ to the total concentration of desorbed CO$_2$. It can be seen that for MEA system, a larger fraction of $\text{HCO}_3^-$ present in the reactant solution breaks down to form CO$_2$ and H$_2$O. However, as the catalyst and temperature increases, a larger percentage of this contribution comes from MEACOO$^-$. In MEA-MDEA system, MEACOO$^-$ contributes to a larger percentage than $\text{HCO}_3^-$. In addition to the catalyst and temperature effect,
the solvent effect greatly contributes to the higher percentage of $\text{MEACOO}^-$ breakdown. $\text{MDEAH}^+$ being a weaker base than $\text{MEAH}^+$ easily gives its proton to water which provides the necessary proton needed for $\text{MEACOO}^-$ breakdown.

Tables 5.3-3 and 5.3-4 Shows the percentage conversion of $\text{MEACOO}^-$ and $\text{HCO}_3^-$ to CO$_2$. In the initial stage, as temperature and catalyst weight increases $\text{HCO}_3^-$ and $\text{MEACOO}^-$ conversion also increases with a larger conversion fraction seen in the case of $\text{HCO}_3^-$. This is as a result of less energy requirement needed to split $\text{HCO}_3^-$ into CO$_2$ and H$_2$O.

5.3.2 Effect of Feed flow rate

Amine flow rate was varied while keeping $W/F_{\text{Amine}}$ constant. It is to be expected that conversion would increase with increase in amine flowrate, as there is more contact between the liquid and solid acid catalyst, thus increasing the desorption rate. However, such trend was not seen as the flow rate was varied from 50-80 ml/min (Figure 5.3-5). This can be explained by the desorber height limitation. With an absorber height of 1.067 m, a loading range of 0.476-0.489 mol amine/mol CO$_2$ was obtained at 70 and 80 mol/min, indicating that equilibrium loading was not achieved due to the short time spent in the desorber. At 50 ml/min the amine flow rate was too low thereby introducing the effect of mass transfer limitation. Also, at this rate, the amine comes in contact with or wets just a fraction of the catalyst surface thereby using just a portion of the catalyst. The optimum flow rate which utilizes most of the catalyst surface area was achieved at 60 ml/min. The same trend was seen for both catalysts.
Figure 5.3-5: Effect of MEA flow rate (50, 60, 70, 80 ml/min) on Conversion, $X$ at different catalyst weight (0-300g) at 358K.
Table 5.3-1: Percentage contribution of MEACOO$^-$ and HCO$_3^-$ to the total concentration of desorbed CO$_2$ for MEA system

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Weight of Catalyst</th>
<th>% Contribution of MEACOO$^-$ to total concentration of desorbed CO$_2$</th>
<th>% Contribution of HCO$_3^-$ to total concentration of desorbed CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>HZSM-5</td>
</tr>
<tr>
<td>348.15</td>
<td>0</td>
<td>6.09</td>
<td>6.09</td>
</tr>
<tr>
<td>348.15</td>
<td>0.05</td>
<td>17.79</td>
<td>18.34</td>
</tr>
<tr>
<td>348.15</td>
<td>0.1</td>
<td>26.12</td>
<td>25.93</td>
</tr>
<tr>
<td>348.15</td>
<td>0.15</td>
<td>26.50</td>
<td>29.58</td>
</tr>
<tr>
<td>348.15</td>
<td>0.2</td>
<td>36.09</td>
<td>36.39</td>
</tr>
<tr>
<td>368.15</td>
<td>0</td>
<td>45.95</td>
<td>37.59</td>
</tr>
<tr>
<td>368.15</td>
<td>0.05</td>
<td>53.27</td>
<td>58.56</td>
</tr>
<tr>
<td>368.15</td>
<td>0.1</td>
<td>57.41</td>
<td>59.65</td>
</tr>
<tr>
<td>368.15</td>
<td>0.15</td>
<td>60.91</td>
<td>65.00</td>
</tr>
<tr>
<td>368.15</td>
<td>0.2</td>
<td>63.30</td>
<td>66.17</td>
</tr>
<tr>
<td>378.15</td>
<td>0</td>
<td>65.55</td>
<td>62.39</td>
</tr>
<tr>
<td>378.15</td>
<td>0.05</td>
<td>69.75</td>
<td>68.99</td>
</tr>
<tr>
<td>378.15</td>
<td>0.1</td>
<td>72.45</td>
<td>70.94</td>
</tr>
<tr>
<td>378.15</td>
<td>0.15</td>
<td>73.06</td>
<td>72.61</td>
</tr>
<tr>
<td>378.15</td>
<td>0.2</td>
<td>75.23</td>
<td>75.23</td>
</tr>
</tbody>
</table>
Table 5.3-2: Percentage conversion of MEACOO⁻ and HCO₃⁻ to CO₂ for MEA System

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Catalyst weight (kg)</th>
<th>% Conversion of MEACOO⁻ to CO₂</th>
<th>% Conversion of HCO₃⁻ to CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>γ-Al₂O₃</td>
<td>HZSM-5</td>
</tr>
<tr>
<td>348.15</td>
<td>0</td>
<td>0.321</td>
<td>0.321</td>
</tr>
<tr>
<td>348.15</td>
<td>0.05</td>
<td>1.329</td>
<td>1.389</td>
</tr>
<tr>
<td>348.15</td>
<td>0.1</td>
<td>2.421</td>
<td>2.392</td>
</tr>
<tr>
<td>348.15</td>
<td>0.15</td>
<td>2.479</td>
<td>2.988</td>
</tr>
<tr>
<td>348.15</td>
<td>0.2</td>
<td>4.280</td>
<td>4.347</td>
</tr>
<tr>
<td>368.15</td>
<td>0</td>
<td>6.977</td>
<td>4.626</td>
</tr>
<tr>
<td>368.15</td>
<td>0.05</td>
<td>9.833</td>
<td>12.579</td>
</tr>
<tr>
<td>368.15</td>
<td>0.1</td>
<td>11.919</td>
<td>13.243</td>
</tr>
<tr>
<td>368.15</td>
<td>0.15</td>
<td>14.055</td>
<td>17.117</td>
</tr>
<tr>
<td>368.15</td>
<td>0.2</td>
<td>15.761</td>
<td>18.140</td>
</tr>
<tr>
<td>378.15</td>
<td>0</td>
<td>17.595</td>
<td>20.079</td>
</tr>
<tr>
<td>378.15</td>
<td>0.05</td>
<td>21.764</td>
<td>15.081</td>
</tr>
<tr>
<td>378.15</td>
<td>0.1</td>
<td>25.153</td>
<td>20.921</td>
</tr>
<tr>
<td>378.15</td>
<td>0.15</td>
<td>26.003</td>
<td>22.957</td>
</tr>
<tr>
<td>378.15</td>
<td>0.2</td>
<td>29.414</td>
<td>25.153</td>
</tr>
</tbody>
</table>
Table 5.3-3: Percentage contribution of $\text{MEACOO}^-$ and $\text{HCO}_3^-$ to the total concentration of desorbed $\text{CO}_2$ for MEA-MDEA system

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Catalyst weight (kg)</th>
<th>% contribution of $\text{MEACOO}^-$ to total concentration of desorbed $\text{CO}_2$</th>
<th>% contribution of $\text{HCO}_3^-$ to total concentration of desorbed $\text{CO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>HZSM-5</td>
<td>$\gamma$-$\text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>348.15</td>
<td>0</td>
<td>78.227</td>
<td>78.192</td>
</tr>
<tr>
<td>348.15</td>
<td>0.05</td>
<td>79.312</td>
<td>79.686</td>
</tr>
<tr>
<td>348.15</td>
<td>0.1</td>
<td>81.666</td>
<td>82.145</td>
</tr>
<tr>
<td>348.15</td>
<td>0.15</td>
<td>82.777</td>
<td>83.192</td>
</tr>
<tr>
<td>348.15</td>
<td>0.2</td>
<td>83.369</td>
<td>84.497</td>
</tr>
<tr>
<td>368.15</td>
<td>0</td>
<td>87.890</td>
<td>87.177</td>
</tr>
<tr>
<td>368.15</td>
<td>0.05</td>
<td>89.414</td>
<td>88.952</td>
</tr>
<tr>
<td>368.15</td>
<td>0.1</td>
<td>89.678</td>
<td>89.509</td>
</tr>
<tr>
<td>368.15</td>
<td>0.15</td>
<td>90.092</td>
<td>90.407</td>
</tr>
<tr>
<td>368.15</td>
<td>0.2</td>
<td>90.835</td>
<td>91.173</td>
</tr>
<tr>
<td>378.15</td>
<td>0</td>
<td>87.538</td>
<td>87.547</td>
</tr>
<tr>
<td>378.15</td>
<td>0.05</td>
<td>89.591</td>
<td>89.853</td>
</tr>
<tr>
<td>378.15</td>
<td>0.1</td>
<td>90.477</td>
<td>90.770</td>
</tr>
<tr>
<td>378.15</td>
<td>0.15</td>
<td>91.296</td>
<td>91.603</td>
</tr>
<tr>
<td>378.15</td>
<td>0.2</td>
<td>91.993</td>
<td>92.328</td>
</tr>
</tbody>
</table>
Table 5.3-4: Percentage conversion of MEACOO⁻ and HCO₃⁻ to CO₂ for MEA-MDEA System

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Catalyst weight (kg)</th>
<th>% Conversion of MEACOO⁻ to CO₂</th>
<th>% Conversion of HCO₃⁻ to CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ-Al₂O₃</td>
<td>HZSM-5</td>
<td>γ-Al₂O₃</td>
</tr>
<tr>
<td>348.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.242</td>
<td>3.118</td>
<td>24.354</td>
</tr>
<tr>
<td>0.05</td>
<td>4.318</td>
<td>4.651</td>
<td>30.412</td>
</tr>
<tr>
<td>0.1</td>
<td>7.059</td>
<td>7.634</td>
<td>42.824</td>
</tr>
<tr>
<td>0.15</td>
<td>8.611</td>
<td>9.168</td>
<td>48.420</td>
</tr>
<tr>
<td>0.2</td>
<td>9.517</td>
<td>11.355</td>
<td>51.316</td>
</tr>
<tr>
<td>368.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>19.178</td>
<td>17.140</td>
<td>71.446</td>
</tr>
<tr>
<td>0.05</td>
<td>24.168</td>
<td>22.413</td>
<td>77.368</td>
</tr>
<tr>
<td>0.1</td>
<td>25.173</td>
<td>24.412</td>
<td>78.348</td>
</tr>
<tr>
<td>0.15</td>
<td>26.854</td>
<td>28.100</td>
<td>79.859</td>
</tr>
<tr>
<td>0.2</td>
<td>30.231</td>
<td>31.810</td>
<td>82.482</td>
</tr>
<tr>
<td>378.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>18.190</td>
<td>18.121</td>
<td>70.014</td>
</tr>
<tr>
<td>0.05</td>
<td>24.838</td>
<td>25.750</td>
<td>78.028</td>
</tr>
<tr>
<td>0.1</td>
<td>28.540</td>
<td>29.784</td>
<td>81.230</td>
</tr>
<tr>
<td>0.15</td>
<td>32.605</td>
<td>34.181</td>
<td>84.058</td>
</tr>
<tr>
<td>0.2</td>
<td>36.689</td>
<td>38.753</td>
<td>86.361</td>
</tr>
</tbody>
</table>
5.3.3 Estimation of the Values of the Parameters of the Rate Models and Validation

The Power law and mechanistic model parameters were based on the minimization of the sum of the residual squares of the reaction rates by the Gauss-Newton and Levenberg-Marquardt algorithms by applying the nonlinear regression software (NLREG). The Activation energies were obtained from Arrhenius equation by plotting \( \ln k \) vs. \( (1/T) \) as is shown in figure 5.3.3-6 and 5.3.3-7. The obtained parameters are presented in Table 5.3.3-5 and 5.3.3.6.

\[ \gamma-Al_2O_3 \] and HZSM-5 catalyst increases the rate of desorption of CO\(_2\) either by increasing the frequency of collision between the reacting molecules which is represented by the pre-exponential factor, \( k_o \), or by providing an alternative pathway with a lower activation energy, \( E_A \). The order of reaction, \( n \), which shows to what extent the rate of reaction depends on reactant concentration was 1 overall for both catalysts and solvent type. The pre-exponential factor, \( k_o \), of \( \gamma-Al_2O_3 \) was seen to be higher than that of HZSM-5. This can be explained using the physical properties of the catalysts. \( \gamma-Al_2O_3 \) has larger pore size and volume than HZSM-5. This allows molecules to collide more frequently thus increasing the pre-exponential factor.
Figure 5.3-6: Arrhenius plot (CO$_2$+MEA+$H_2O$ system)
Figure 5.3-7: Arrhenius plot (CO2+MEA+ MDEA+H₂O system)
On the other hand, the activation of HZSM-5 was seen to be lower than that of γ-Al₂O₃ for both solvents. This can be explained on the basis of the chemical activity of the catalysts. The Brønsted to Lewis acid site ratio of HZSM-5 was seen to be higher than that of γ-Al₂O₃, with a ratio of 1.587 for HZSM-5 and 0.667 for γ-Al₂O₃. The Brønsted acid sites provided an alternative pathway with lower activation energy compared to the Lewis acid sites, thereby increasing the fraction of molecules with kinetic energy higher than the activation energy. HZSM-5 achieves this potentially by directly transferring its available proton to the carbamate and bicarbonate ions, thereby decreasing the amount of energy required to desorb CO₂.

As mentioned by Shi et al. tertiary amine MDEA is a weaker base than MEA and is therefore easier to deprotonate $MDEA^+$ than $MEA^+$. Consequently, the solvent effect plays an important role in increasing the conversion and reducing the activation energy alongside the catalyst contribution as shown in figures 5.3-1 to 5.3-4 (Conversion) and 5.3.3-1 and 5.3.3-2 (Activation energy).
Table 5.3-5: Parameter estimation for CO₂+ MEA+ H₂O system for γ-Al₂O₃ and HZSM-5

<table>
<thead>
<tr>
<th>Parameters</th>
<th>γ − Al₂O₃</th>
<th>HZSM-5</th>
<th>M1 γ − Al₂O₃</th>
<th>M2 γ−Al₂O₃</th>
<th>M1 HZSM-5</th>
<th>M2 HZSM-5</th>
<th>M3 HZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>0.98 ~ 1</td>
<td>0.6 ~ 1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>kₒ</td>
<td>3.4 × 10⁶</td>
<td>2.2 × 10⁵</td>
<td>7.7 × 10¹²</td>
<td>2.7 × 10¹⁵</td>
<td>2.3 × 10¹²</td>
<td>3.7 × 10¹¹</td>
<td>1.0 × 10⁸</td>
</tr>
<tr>
<td>Ea (J/mol)</td>
<td>8.02 × 10⁴</td>
<td>7.1 x 10⁴</td>
<td>9.87 x 10⁴</td>
<td>1.1 x 10⁵</td>
<td>7.23 x 10⁴</td>
<td>7.5 x 10⁴</td>
<td>5.1 x 10⁴</td>
</tr>
<tr>
<td>K₁</td>
<td>n/a</td>
<td>n/a</td>
<td>2.5 × 10⁴</td>
<td>8.5 × 10²</td>
<td>7.1 x 10⁶</td>
<td>4.5 x 10⁴</td>
<td>4.3 x 10³</td>
</tr>
<tr>
<td>K₂</td>
<td>n/a</td>
<td>n/a</td>
<td>4.31 x 10³</td>
<td>0.36 x 10¹</td>
<td>2.7 x 10⁶</td>
<td>2.1 x 10⁵</td>
<td>8.0 x 10⁻³</td>
</tr>
<tr>
<td>K₃</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>6.98 x 10⁴</td>
</tr>
<tr>
<td>AAD</td>
<td>5.1%</td>
<td>9.5%</td>
<td>4.0%</td>
<td>5.4%</td>
<td>10.7%</td>
<td>9.2%</td>
<td>11.1%</td>
</tr>
</tbody>
</table>

POWER LAW MODEL

MECHANISTIC MODEL


Table 5.3-6 Parameter estimation for CO\(_2\) + MEA + MDEA + H\(_2\)O system for γ-Al\(_2\)O\(_3\) and HZSM-5

<table>
<thead>
<tr>
<th>Parameters</th>
<th>γ-Al(_2)O(_3)</th>
<th>HZSM-5</th>
<th>M1 γ − Al(_2)O(_3)</th>
<th>M1 HZSM-5</th>
<th>M2 γ − Al(_2)O(_3)</th>
<th>M2 HZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>0.989</td>
<td>0.613</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>k(_o)</td>
<td>3.4 x 10(^6)</td>
<td>2.2 x 10(^5)</td>
<td>1.74 x 10(^{11})</td>
<td>1.03 x 10(^{10})</td>
<td>1.03 x 10(^{10})</td>
<td>2.2 x 10(^8)</td>
</tr>
<tr>
<td>Ea (J/mol)</td>
<td>8.02 x 10(^4)</td>
<td>7.1 x 10(^4)</td>
<td>6.49 x 10(^4)</td>
<td>6.6 x 10(^4)</td>
<td>7.25 x 10(^4)</td>
<td>7.1 x 10(^4)</td>
</tr>
<tr>
<td>K(_1)</td>
<td>n/a</td>
<td>n/a</td>
<td>8.5 x 10(^4)</td>
<td>3.7 x 10(^2)</td>
<td>3.68 x 10(^2)</td>
<td>1.35 x 10(^3)</td>
</tr>
<tr>
<td>K(_2)</td>
<td>n/a</td>
<td>n/a</td>
<td>7.0 x 10(^3)</td>
<td>1.6 x 10(^2)</td>
<td>2.5 x 10(^{-2})</td>
<td>3.6 x 10(^{-2})</td>
</tr>
<tr>
<td>AAD</td>
<td>5.1%</td>
<td>9.5%</td>
<td>10.7%</td>
<td>13.7%</td>
<td>8.8%</td>
<td>10.0%</td>
</tr>
</tbody>
</table>
As the temperature increases, the concentration of desorbed CO$_2$ increases, thus increasing the order at which the reaction rate depends on concentration. All models were validated by determining the absolute average deviation (AAD %) between the experimental rate and predicted rate obtained from the proposed models. Also a parity chart which depicts how well the predicted rates fit the experimental rate data was plotted as shown in Figures 5.3.3-8 to 5.3.3-10. It can be seen that the experimental and predicted rates are in close correlation. Furthermore, a restriction that an acceptable model should have an AAD% $\leq$ 15% and the corresponding activation energy should be closer in value to that of the power law model was applied in order to eliminate unrealistic models.
Figure 5.3-8: Parity chart for all developed models (MEA and MEA-MDEA system)
Figure 5.3-9: Parity chart for all developed models involving bicarbonate ion (MEA system)
Figure 5.3-10: Parity chart for all developed models involving bicarbonate ion (MEA system) and (MEA-MDEA system)
Even though all kinetic parameters were positive and fitted the data very well, they were further subjected to a thermodynamic scrutiny to determine the true models. This was achieved by ensuring that the rate constant and equilibrium constants of each proposed models were thermodynamically consistent. Thermodynamic equilibrium constants for each proposed model were regressed at each temperature (348, 358, and 368K) and the obtained parameters were further used to obtain the enthalpy, entropy and Gibbs free energy. The variation in equilibrium constants with temperature can be easily explained by Le Chatelier’s principle which shows that for an endothermic reaction the equilibrium constant increases with increases in temperature. The Van’t Hoff equation was used to calculate the enthalpy and entropy of reaction as in Equation 5.8.

\[
\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5.8}
\]

The Van’t Hoff plot, which is a plot of \( \ln K_{eq} \) Vs \( 1/T \) gives a linear relationship, with the slope given as \(-\frac{\Delta H}{R}\) and the intercept as \(\frac{\Delta S}{R}\).

The Gibbs free energy at each temperature was obtained using the Gibbs Equation:

\[
\Delta G = -RT\ln K_{eq}. \tag{5.9}
\]

The equilibrium constant, \( K_{eq} \) increases with increasing temperature. A negative slope indicates an endothermic reaction, making the enthalpy and entropy of reaction positive (i.e. \( \Delta H > 0 \) and \( \Delta S > 0 \)). The positive value \( \Delta H \) shows it to be an endothermic reaction and absorbs a lot of heat. \( \Delta S > 0 \) indicates an increase in the degree of randomness of the system as the temperatures rises. On the other hand, the negative values of \( \Delta G \) indicates a spontaneity of the process at a high temperature. It can be seen that \( \Delta G \) becomes more negative as temperature increases, indicating that
CO₂ desorption is more spontaneous at higher temperature illustrating the strong temperature effect of the reaction as compared to catalyst effect at higher temperatures. This thermodynamic consistency was only observed for the M1-γ-Al₂O₃, M1-HZSM-5 and M3-HZSM-5 models as presented in Table 5.3.3-7.
Table 5.3-7 Thermodynamic scrutiny for CO$_2$+MEA+H$_2$O system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>T (K)</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$</td>
<td>$K_2$</td>
<td>$K_3$</td>
<td>$K_1$</td>
</tr>
<tr>
<td>M1: $\gamma$-Al$_2$O$_3$</td>
<td>26375.3</td>
<td>23831.2</td>
<td>n/a</td>
<td>120.9</td>
</tr>
<tr>
<td>M1: HZSM-5</td>
<td>1159.2</td>
<td>9660.0</td>
<td>n/a</td>
<td>107.8</td>
</tr>
<tr>
<td>M2: HZSM-5</td>
<td>4929.4</td>
<td>17841.8</td>
<td>4763.9</td>
<td>30.7</td>
</tr>
</tbody>
</table>
5.4 Statistical Analysis

Statistical analysis for the experimental data of carbamate conversion to CO₂ was carried out using five acid catalysts (HZSM-5, γ-Al₂O₃, SiO-Al₂O₃ and HY of widely varying characteristics) as well as an inert parking scenario. This was done to determine which catalyst property aids most in the desorption of CO₂ from CO₂-rich MEA solution. The catalyst properties used in the analysis are presented in table 5.9. The fixed parameters were temperature (365K), catalyst weight (150g) and flowrate (60ml/min). The conversion for each catalyst were plotted against catalyst weight (figure 5.4-1)

It can be seen from figure 5.4-1 that the kinetic parameter expressed in terms of conversion is highest in HZSM-5 and lowest in the blank (no catalyst) run, and is given in decreasing order as (HZSM-5> γ-Al₂O₃> SiO-Al₂O₃ > HY> no catalyst. This trend can be explained by certain critical catalyst properties such as the Brønsted / Lewis acid ratio (B/L), acid strength and total acid sites. The corresponding values are given in table 5.4-1. As stated in literature, the Si/Al ratio influences the catalyst strength and total (Lewis and Brønsted) acidity\textsuperscript{133,134}. An increase in the Si/Al ratio increases the acid strength, while the surface acidity decreases with the decrease in the aluminum content of the catalyst\textsuperscript{133,134}. Another important factor which determines the fraction of active sites available for reaction is the Mesopore surface area (MSA). From our BET analysis, the MSA value is highest in HZSM-5 (322.87 m\textsuperscript{2}/g) and lowest in HY (122.45 m\textsuperscript{2}/g). This explains the relatively high acid strength and lower acidity found in HZSM-5. Despite the high B/L ratio found in HY and SiO-Al₂O₃ catalyst, the conversion values were lower than that of γ-Al₂O₃. This is as a result of the low acid strength in comparison to γ-Al₂O₃.
Figure 5.4-1: Conversion for different acid catalyst.
Table 5.4-1: Si/Al ratio, ratio (Pore size/pore volume), total acid site, acid strength, B/L ratio and conversion for 5M MEA at 368K.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Uncontrolled variable (factors)</th>
<th>Response Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si/Al ratio</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ratio (Pore size/pore Volume)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(nm/cm³/g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total acid sites (μmol/g)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acid strength</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experimental Conversion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Predicted Conversion</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>38</td>
<td>9.66</td>
</tr>
<tr>
<td></td>
<td>10549.72</td>
<td>0.5707</td>
</tr>
<tr>
<td></td>
<td>1.587</td>
<td>0.1707</td>
</tr>
<tr>
<td></td>
<td>0.1791</td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>N/A</td>
<td>10.47</td>
</tr>
<tr>
<td></td>
<td>3717.47</td>
<td>0.4830</td>
</tr>
<tr>
<td></td>
<td>0.667</td>
<td>0.1513</td>
</tr>
<tr>
<td></td>
<td>0.1480</td>
<td></td>
</tr>
<tr>
<td>SiO₂-Al₂O₃</td>
<td>1.5</td>
<td>6.52</td>
</tr>
<tr>
<td></td>
<td>665.36</td>
<td>0.2250</td>
</tr>
<tr>
<td></td>
<td>3.78</td>
<td>0.1422</td>
</tr>
<tr>
<td></td>
<td>0.1376</td>
<td></td>
</tr>
<tr>
<td>HY</td>
<td>2.6</td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td>32045.93</td>
<td>0.431</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.1472</td>
<td></td>
</tr>
<tr>
<td>Blank (no catalyst)</td>
<td>N/A</td>
<td>0</td>
</tr>
</tbody>
</table>
A scatterplot matrix of the variables was plotted (figure 5.4-2) and used to compare the relationships between the variables. It could be observed that all the explanatory variables are someway related to conversion. Correlation analysis was then used to measure the significance of the relationship between conversion with each of these variables – BET, acid strength, (B/L), total acid site and ratio of pore size to volume factors. In all the analysis significance level was taken to be 0.05 (i.e., if the p-value is less than 0.05, the null hypothesis was rejected or concluded to be statistically significant). Statistical Analysis was carried out using statistical package, Minitab (version 17.1.0).

Based on the observation, a fit regression analysis was performed to model the relationship between the predictors and response variable. A stepwise forward section method was applied to strengthen the model coefficients. From the regression analysis, it could be seen that the corresponding p-values of acid strength*B/L (0.018), and ratio of pore size to volume (0.006) were less than 0.05, indicating a significant contribution. The p-values of the BET, B/L, acid strength, total acid site, BET*B/L and acid strength*BET factors were greater than the significance level 0.05. One thing to be noted is that the insignificance of this variables might be due to the less sample sizes.

\[
\text{Conversion} = 0.011989 \text{Ratio} + 0.06993 \text{BL*Acid Strength} \quad 5.10
\]

The regression equation (5.10), indicates that the acid strength, ratio of pore size to pore volume, and B/L factors significantly contributes in the CO\(_2\) desorption process.
Figure 5.4-2: Matrix Scatter plot of all variables
6.1 Conclusions

- The desorption kinetics of CO$_2$ from loaded aqueous MEA and MEA-MDEA solutions were studied over $\gamma$-Al$_2$O$_3$ and HZSM-5 catalysts as a function amine flow rates and reaction temperature in a tubular packed-bed reactor. LHHW formulations were used to develop kinetic models which were used to describe the experimental kinetic data for CO$_2$ desorption.

- The kinetic performance was evaluated in terms of conversion (i.e. %CO$_2$ desorbed), activation energy and rate constants. The optimum operating conditions to obtain maximum conversion over HZSM-5 and $\gamma$-Al$_2$O$_3$ was achieved at 85°C at 60ml/min.

- HZSM-5 catalyst gave lower activation energies in comparison to $\gamma$-Al$_2$O$_3$ for both solvents and is presented in the Arrhenius form in the power law models as:

\[
\begin{align*}
\text{rate}_{\text{CO}_2-\text{MEA- } \gamma\text{Al}_2\text{O}_3} & = 3.4 \times 10^6 \text{exp} \left(- \frac{8.02 \times 10^4}{RT} \right) \times [\text{CO}_2]^{0.98} \\
\text{rate}_{\text{CO}_2-\text{MEA-HZSM } 5} & = 2.2 \times 10^5 \text{exp} \left(- \frac{7.09 \times 10^4}{RT} \right) \times [\text{CO}_2]^{0.63} \\
\text{rate}_{\text{CO}_2-\text{MEA-MDEA- } \gamma\text{Al}_2\text{O}_3} & = 1.7 \times 10^3 \text{exp} \left(- \frac{6.7 \times 10^4}{RT} \right) \times [\text{CO}_2]^{0.6} \\
\text{rate}_{\text{CO}_2-\text{MEA-MDEA-HZSM } 5} & = 3.36 \times 10^2 \text{exp} \left(- \frac{6.1 \times 10^4}{RT} \right) \times [\text{CO}_2]^{0.49}
\end{align*}
\]

- Comprehensive mechanistic rate models involving single and dual site mechanism based on LHHW model was found to best describe the experimental rates with an AAD <15%, were obtained. The results showed that HZSM-5 catalyst provides faster kinetics in terms of rate constant and
conversion with lower activation energy in comparison with $\gamma$-Al$_2$O$_3$. The final rate expressions after substituting obtained parameters are of the form:

$$r_{AA_{MM1-\gamma Al_2O_3}} = 7.7 \times 10^{12} \exp \left( -\frac{9.87 \times 10^4}{RT} \right) \left\{ \frac{[H^+]\cdot[C]}{1+2.5 \times 10^6[C]+4.3 \times 10^3+4.7 \times 10^3[A]} \right\}$$

$$r_{AM_{M2 HZSM5}} = 2.3 \times 10^{12} \exp \left( -\frac{7.23 \times 10^4}{RT} \right) \left\{ \frac{[H^+]\cdot[C]}{\left( 1+1.2 \times 10^5[C]+7.2 \times 10^4[H]+(2.7 \times 10^6)^{1/4}[A] \right)^2} \right\}$$

$$r_{AA_{MM1-\gamma Al_2O_3}} = 1.88 \times 10^9 \exp \left( -\frac{6.49 \times 10^4}{RT} \right) \left\{ \frac{[H^+]\cdot[C]}{1+8.2 \times 10^4[C]+7.0 \times 10^3[A]} \right\}$$

$$r_{AM_{M2 HZSM5}} = 1.03 \times 10^{10} \exp \left( -\frac{6.6 \times 10^4}{RT} \right) \left\{ \frac{[H^+]\cdot[C]}{\left( 1+1.59 \times 10^2[C]+(3.7 \times 10^2)^{1/4}[A] \right)^2} \right\}$$

- A statistical analysis using four catalysts (HZSM-5, $\gamma$-Al$_2$O$_3$, silica-alumina, and HY of widely varying characteristics) as well as an inert parking scenario showed that catalyst performance on CO$_2$ desorption from CO$_2$-rich MEA solution depended strongly on the acid strength*B/L ratio and ratio of pore size to pore volume.
6.2 Recommendations

It has been demonstrated in this research that the addition of catalysts such as (HZSM-5, γ-Al₂O₃, silica-alumina, and HY) to the desorber CO₂ unit reduces regeneration energy associated with CO₂ desorption by increasing the reaction rate and conversion, alongside reducing the activation energy. It was seen that the catalyst with higher acid strength bearing both Brønsted and Lewis acid sites contributed more to the desorption rate. The following investigations are recommended for future research:

- Investigations should be done to produce new catalysts with high Brønsted to Lewis acid ratio and higher acid strength. This would greatly accelerate the desorption rate
- More work should be done on the catalyst performance in terms of catalyst stability studies with regards to Time on Stream (TOS)
- The major problem related the operation of heterogeneous catalytic system is the loss of the activity of catalyst which is known to increase overtime and is inevitable. Therefore it’s important to investigate on the chemical and physical aspects as well as the kinetics of the catalytic deactivation and regeneration process. This will help in the design of deactivation-resistant catalyst.
- This study was done at 15% CO₂ partial pressure which is equivalent to the CO₂ partial pressure emitted from coal fired plants. Studies involving the reaction rate and kinetic models at various CO₂ partial pressures including 10% CO₂ (natural gas reboiler) and 30% CO₂ (reformate gas, from production of hydrogen) is suggested for the development of kinetic data needed for industrial applications.
The developed mechanistic models are valid only at 60ml/min amine flow rate. A more comprehensive model accounting for amine flowrates should be developed.

The analysis of kinetic data using integral reactor is quite difficult. Differential reactors are preferable for collecting and analyzing kinetic data. Therefore studies should be done using differential reactor and then comparing results to that obtained using integral reactor.
CHAPTER 7: REFERENCES


38. DOE N. *NETL Carbon Dioxide Capture and Storage RD&D Roadmap.*


58. NETL U. Engineering feasibility of CO₂ capture on an existing us coal-fired power plant.


Appendix A: Standard Operating Procedure for running the 2-inch Pilot Plant for Kinetic Analysis

The experiments were performed in complete absorber – desorber CO₂ capture pilot plant unit. Both the absorber and desorber columns in the unit were of 2-inch internal diameter and 3.5 ft. total height. The packing materials and operating parameters used for this experimental set are shown in figure and table 3.5-1. A detailed process flow diagram of the experimental setup is shown in appendix A2. Experimental kinetic data for CO₂ desorption were obtained in a catalytic packed bed tubular reactor (i.e. desorber) at three temperatures (348K, 358K, and 368K), with 5M MEA and 5M/2M MEA-MDEA concentrations and CO₂ loading ranging from ~ 0.41-0.5 mol CO₂/mol amine, for different ratios of catalyst weight/amine flow rate (W/Fₜₐₜ).

At the beginning of each run, N₂ and CO₂ were set to the desired partial pressures and concentrations (15% CO₂, balanced up with N₂). The feed gas is then passes through a saturation cell before being introduced into the absorber column at 15SLPM. The flow rate is controlled by the gas flow meter. Lean MEA/ MEA-MDEA solution from the feed tank is let into the top of the column with the help of a constant liquid flow pump. This is to ensure that the column operated under contact counter-current flow, allowing CO₂ to be absorbed by providing maximum driving force for mass transfer. The treated gas escapes through the top of the absorber column into a condenser were cooling water is constantly supplied. The rich solution exist the bottom of the absorber column at about 30°C and flows through the lean/rich heat exchanger were it is preheated to 50°C. Hot steam is supplied by a hot oil bath is used to supply hot steam which comes in contact with the preheated rich amine solvent, heating it up to the desired desorption temperature (75°C, 85°C, and 95°C) and then introducing it the top of desorber column from where it flows down the packed catalytic bed. The
elevated temperature, supplies the sensible heat, heat of vaporization and heat of absorption needed to desorb of CO\textsubscript{2}. After desorption, the desorbed CO\textsubscript{2} escapes through the top of the column and the lean amine is recirculated back into the absorber. The vaporized solvent and water are condensed in the overhead condenser and returned to the feed tank. Thermocouples and concentration measurements are located along the length of the absorber and desorber column and were used to constantly read the gas phase CO\textsubscript{2} concentration and temperature profiles. Concentration of desorbed CO\textsubscript{2} gas was measured constantly with a CO\textsubscript{2} gas analyzer. The plant is allowed to run for about 4 hours before equilibrium is achieved. Rich and lean samples are collected at intervals to check the CO\textsubscript{2} loading. This is done to know when steady state is achieved. At steady state, the gas flowrate, temperature and pressure of the gas flowing into and out of the absorber are recorded. Also the CO\textsubscript{2} off gas concentration, equilibrium loading as well as the temperature and concentration profiles along both columns are recorded. These recorded raw data are then used to analyze kinetics of CO\textsubscript{2} desorption. Figure 3.5-1 and 3.5-2 shows the parking materials and experimental setup used to obtain the experimental data.
Appendix A1: A typical Process flow diagram (PFD)- (LABVIEW SOFTWARE)

Figure A.2: Process flow diagram (PFD)
Appendix A2: Determination of solution Concentration

The concentration of the solution is checked at intervals to ensure that solution does not change significantly in the course of the experiment. Titration analysis is used to determine the concentration of the solution. A known sample volume of the rich and lean amine is titrated with Hydrochloric acid (HCl) using methyl orange as indicator. The $C_1V_1=C_2V_2$

Where

$C_1$ = solution concentration (mol/L) (unknown, to be determined)

$V_1$ = solution sample volume (ml) – 2ml

$C_2$ = HCl concentration (mol/l) (1mol/L)

$V_2$ = HCl volume from titration (ml) – 10ml

$$C_1 = \frac{C_2V_2}{V_1} = \frac{1\text{mol/L} \times 10\text{ml}}{2\text{ml}} = 5.0\text{mol/L}$$

Appendix A3: Determination of CO$_2$ loading

CO$_2$ loading was calculated for both rich and lean amine. This was done with the Chittick apparatus. As explained in the experimental section, 2ml of sample was collected and used for titration. As the CO$_2$ content was released from the rich/lean sample, the liquid in the graduated tube was displaced. The displaced volume of the liquid which is equal to the volume of CO$_2$ released was used to calculate the CO$_2$ loading in each sample.

The following equation was used:

$$C_{amine} = \frac{C_{HCl} \times V_{HCl}}{2} = 0.5C_{HCl}V_{HCl}$$  \hspace{1cm} 3.1

$$loading, \alpha = \frac{V_{CO_2}-2V_{HCl}}{24.45 \times V_{HCl}}$$  \hspace{1cm} 3.2

$C_{amine}$= $C_2$ (calculated in appendix 4a) – 5mol/L

$V_{CO_2}$=143ml

$V_{HCl}$= 10ml

$$loading, \alpha = \frac{143\text{ml}-(2 \times 10\text{ml})}{24.45 \times 10\text{ml}} = 0.50 \text{ mol CO}_2/\text{mol amine}$$
Appendix A4: Mass Balance Error

At the end of each run, a mass balance error calculation was done to ensure that the run was carried with no significant error (< 10%). The error was calculated by comparing the amount of CO$_2$ at the inlet and outlet of the gas side is the same with that of the liquid side CO$_2$ loading production. A typical example of the mass balance calculation is shown below (0.2kg y - Al$_2$O$_3$ weight, 345K, 60ml/mine):

\[ \text{Mass balance error} = \frac{\text{Absorbed CO}_2 - \text{loading CO}_2 \text{ production}}{\text{Absorbed CO}_2} \times 100\% \]

**Absorbed CO$_2$ = CO$_2$ in - CO$_2$ out**

CO$_2$ in = Inlet mass flowrate of CO$_2$

= Inlet flowrate of CO$_2$ ÷100 ÷ Gas volume x Molecular weight of CO$_2$ x 60

= 2.243 SLPM ÷100 ÷ 24.47 ÷ 44.1 ÷ 60 = 0.242kg/hr.

CO$_2$ out = Outlet mass flowrate of CO$_2$

= Outlet flowrate of CO$_2$ ÷100 ÷ Gas volume x Molecular weight of CO$_2$ x 60

= 1.949 SLPM ÷100 ÷ 24.47 ÷ 44.1 ÷ 60 = 0.2103kg/hr.

Absorbed CO$_2$ = CO$_2$ in - CO$_2$ out = 0.242 kg/hr - 0.2103kg/hr. = 0.0318 kg/hr

**Loading CO$_2$ production:**

(Rich loading x rich amine concentration – lean loading x lean amine concentration) x amine flowrate x Molecular weight of CO$_2$ x 60 /1000000

= 0.5 x 5 – 0.4662 x 5 x 61ml/min x 44.1 g/mol x 60/1000000

= 0.0296 kg/hr

\[ \text{Mass balance error} = \frac{\text{Absorbed CO}_2 - \text{loading CO}_2 \text{ production}}{\text{Absorbed CO}_2} \times 100\% \]

= 6.92%
Appendix A5: Packed column experimental data: Recorded data

*Table A.5 (a): Experimental data for typical run (0.2kg γ-Al2O3 weight, 345K, 60ml/min amine flow rate MEA system)*

<table>
<thead>
<tr>
<th>Variables</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Gas Flow rate Reading:</td>
<td>14.9</td>
<td>slpm</td>
</tr>
<tr>
<td>Meter Temperature:</td>
<td>23.2</td>
<td>°C</td>
</tr>
<tr>
<td>Meter Pressure:</td>
<td>17.0</td>
<td>psia</td>
</tr>
<tr>
<td>Outlet Gas Flow rate Reading:</td>
<td>14.5</td>
<td>slpm</td>
</tr>
<tr>
<td>Meter Temperature:</td>
<td>26.3</td>
<td>°C</td>
</tr>
<tr>
<td>Meter Pressure:</td>
<td>13.9</td>
<td>psia</td>
</tr>
<tr>
<td>Rotameter Amine Flow rate:</td>
<td>52</td>
<td>ml/min</td>
</tr>
<tr>
<td>Temperature</td>
<td>23.56</td>
<td>°C</td>
</tr>
<tr>
<td>Density</td>
<td>1.1450</td>
<td>g/ml</td>
</tr>
<tr>
<td>Actual Flow rate:</td>
<td>61.00</td>
<td>ml/min</td>
</tr>
<tr>
<td>Lean Amine Concentration:</td>
<td>5.00</td>
<td>mol/L</td>
</tr>
<tr>
<td>Lean Loading:</td>
<td>0.46</td>
<td>mol/mol</td>
</tr>
<tr>
<td>Rich Amine Concentration:</td>
<td>5.0000</td>
<td>mol/L</td>
</tr>
<tr>
<td>Rich Loading:</td>
<td>0.5030</td>
<td>mol/mol</td>
</tr>
<tr>
<td>Loading CO2 Production:</td>
<td>0.0296</td>
<td>kg/hr</td>
</tr>
</tbody>
</table>
Table A.5(b): Experimental data for typical run (0.2kg γ-Al2O3 weight, 345K, 60ml/min amine flow rate MEA system), temperature and concentration profile

<table>
<thead>
<tr>
<th>Height, m</th>
<th>Absorber Temperature profile, °C</th>
<th>Stripper Concentration Profile CO2</th>
<th>Absorber Temperature Profile, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas outlet</td>
<td>24.3</td>
<td>13.1</td>
<td>29.33</td>
</tr>
<tr>
<td>42</td>
<td>23.6</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>25.3</td>
<td>13.1</td>
<td>78.92</td>
</tr>
<tr>
<td>30</td>
<td>25.7</td>
<td>13.9</td>
<td>77.21</td>
</tr>
<tr>
<td>24</td>
<td>25.92</td>
<td>14.1</td>
<td>76.29</td>
</tr>
<tr>
<td>18</td>
<td>25.97</td>
<td>14.2</td>
<td>74.18</td>
</tr>
<tr>
<td>12</td>
<td>25.94</td>
<td>14.4</td>
<td>73.17</td>
</tr>
<tr>
<td>6</td>
<td>25.72</td>
<td>14.4</td>
<td>72.10</td>
</tr>
<tr>
<td>0</td>
<td>21.27</td>
<td>14.7</td>
<td>71.86</td>
</tr>
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</table>
Appendix A6: Calculation of Turnover Frequency (TOF).

TOF expresses the catalytic activity in terms of total number of moles reacting to form desired products per mole of total active site per unit time.

$$\text{TOF} = \frac{\text{Moles of desired product}}{\text{Moles of desired product} \times \text{total number of moles reacting}} = \frac{1}{\text{time}} \ (s^{-1})$$

TOF of all experimental runs were calculated and expressed in $s^{-1}$.

Table A.6-1: Turnover frequency for MEA – γ-Al₂O₃ and HZSM-5 system

<table>
<thead>
<tr>
<th>Weight of Catalyst (kg)</th>
<th>γ-Al₂O₃</th>
<th>HZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>55.22</td>
<td>19.74</td>
</tr>
<tr>
<td>0.1</td>
<td>34.26</td>
<td>12.02</td>
</tr>
<tr>
<td>0.15</td>
<td>23.06</td>
<td>8.77</td>
</tr>
<tr>
<td>0.2</td>
<td>21.92</td>
<td>7.78</td>
</tr>
<tr>
<td>0.05</td>
<td>136.47</td>
<td>55.97</td>
</tr>
<tr>
<td>0.1</td>
<td>76.76</td>
<td>28.92</td>
</tr>
<tr>
<td>0.15</td>
<td>56.87</td>
<td>22.87</td>
</tr>
<tr>
<td>0.2</td>
<td>46.02</td>
<td>17.86</td>
</tr>
<tr>
<td>0.05</td>
<td>230.73</td>
<td>62.99</td>
</tr>
<tr>
<td>0.1</td>
<td>128.35</td>
<td>39.51</td>
</tr>
<tr>
<td>0.15</td>
<td>87.73</td>
<td>28.11</td>
</tr>
<tr>
<td>0.2</td>
<td>72.28</td>
<td>22.56</td>
</tr>
<tr>
<td>Weight of Catalyst (kg)</td>
<td>Turnover frequency (TOF), $\text{min}^{-1}$</td>
<td>$\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>------------------------</td>
<td>--------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>0.05</td>
<td></td>
<td>50.44</td>
</tr>
<tr>
<td>0.1</td>
<td></td>
<td>40.07</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>32.16</td>
</tr>
<tr>
<td>0.2</td>
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<td>26.47</td>
</tr>
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</tr>
<tr>
<td>0.1</td>
<td></td>
<td>111.20</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>81.83</td>
</tr>
<tr>
<td>0.2</td>
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<td>63.08</td>
</tr>
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<td>0.05</td>
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<td>257.23</td>
</tr>
<tr>
<td>0.1</td>
<td></td>
<td>146.35</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>110.46</td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>92.52</td>
</tr>
</tbody>
</table>
Appendix A7: Calculation of Experimental data.

The experimental rates were calculated using two different methods: (i) Derivatives of $X_{CO_2}$ versus $W/F_{Ao}$ curves (5.3-1 and 5.3-2). The curves were generated using Excel Solver Add-in Software. (ii) Equal area graphical differentiation technique.

Steps for method (ii):

(a) Tabulate $W/F_{Ao}$ and $X_{CO_2}$

(b) Calculate $\Delta W/F_{Ao}$ and $\Delta X_{CO_2}$ for each interval

(c) Calculate $x_{CO_2}/W/F_{Ao}$ as an estimate of average slope

(d) Plot obtained value as an histogram versus $W/F_{Ao}$

(e) Draw smooth curve that best describe the area under the histogram

(f) Read the estimated values from $dx_{CO_2}/dW/F_{Ao}$ at all points.

These two methods were used and compared due to the sensitivity in obtaining intrinsic experimental rates.

<table>
<thead>
<tr>
<th>Weight of Catalyst (g)</th>
<th>Equal Area Graphical Technique (Experimental rate)</th>
<th>Derivatives of $X_{CO_2}$ versus $W/F_{Ao}$ curves (Experimental rate)</th>
<th>% Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.2E-05</td>
<td>1.0E-05</td>
<td>10.8</td>
</tr>
<tr>
<td>50</td>
<td>1.1E-05</td>
<td>9.58E-06</td>
<td>12.9</td>
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<tr>
<td>100</td>
<td>1.1E-05</td>
<td>9.168E-06</td>
<td>8.3</td>
</tr>
<tr>
<td>150</td>
<td>8.4E-06</td>
<td>8.742E-06</td>
<td>4.1</td>
</tr>
<tr>
<td>200</td>
<td>8.2E-06</td>
<td>8.29E-06</td>
<td>1.16</td>
</tr>
</tbody>
</table>

The % deviation shows that both methods can be used to obtain intrinsic experimental data. However, the equal area graphical technique accounts for error, allowing for compensation of bad data.
Appendix A8: Recorded Experimental data

Table A.8-1: Experimental data for MEA – γ-Al₂O₃ system

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Experimental rate x10⁸ (kmol. kgcat⁻¹ s⁻¹)</th>
<th>( C_{\text{carbamate}} ) (kmol l⁻¹) x 10⁸</th>
<th>( C_{\text{MEAH}} ) (kmol l⁻¹) x 10⁸</th>
<th>( C_{\text{bicarbonate}} ) (kmol l⁻¹) x 10⁸</th>
<th>Catalyst Weight (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>348</td>
<td>1.00E+04</td>
<td>2.28E+09</td>
<td>2.45E+09</td>
<td>1.26E+08</td>
<td>0</td>
</tr>
<tr>
<td>348</td>
<td>9.07E+03</td>
<td>2.26E+09</td>
<td>2.40E+09</td>
<td>9.85E+07</td>
<td>0.05</td>
</tr>
<tr>
<td>348</td>
<td>8.16E+03</td>
<td>2.24E+09</td>
<td>2.36E+09</td>
<td>8.23E+07</td>
<td>0.1</td>
</tr>
<tr>
<td>348</td>
<td>7.25E+03</td>
<td>2.23E+09</td>
<td>2.36E+09</td>
<td>8.16E+07</td>
<td>0.15</td>
</tr>
<tr>
<td>348</td>
<td>6.39E+03</td>
<td>2.19E+09</td>
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<td>6.55E+07</td>
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</tr>
<tr>
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<td>2.13E+09</td>
<td>2.23E+09</td>
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<tr>
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<td>2.07E+09</td>
<td>2.15E+09</td>
<td>4.16E+07</td>
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</tr>
<tr>
<td>358</td>
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### Table A.8-2: Experimental data for MEA+ CO$_2$+H$_2$O HZSM-5 system

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<tr>
<th>T (K)</th>
<th>Experimental rate $\times 10^8$ ($\text{kmol kgcat}^{-1} \text{s}^{-1}$)</th>
<th>$C_{\text{carbamate}}$ ($\text{kmol} \text{ l}^{-1} \times 10^8$)</th>
<th>$C_{\text{MEAH}}$ ($\text{kmol} \text{ l}^{-1} \times 10^8$)</th>
<th>$C_{\text{bicarbonate}}$ ($\text{kmol} \text{ l}^{-1} \times 10^8$)</th>
<th>Catalyst Weight (kg)</th>
</tr>
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Table A.8.3: Experimental data for MEA+MDEA+CO₂ – γ-Al₂O₃ system

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<th>T (K)</th>
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<th>( C_{\text{MDEA}^{+}} ) ( \text{kmol} \text{ l}^{-1} ) x 10⁸</th>
<th>( C_{\text{MEA}^{+}} ) ( \text{kmol} \text{ l}^{-1} ) x 10⁸</th>
<th>( C_{\text{carbamate}} ) ( \text{kmol} \text{ l}^{-1} ) x 10⁸</th>
<th>( C_{\text{bicarbonate}} ) ( \text{kmol} \text{ l}^{-1} ) x 10⁸</th>
<th>Catalyst Weight (kg)</th>
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Table A.8-4: Experimental data for MEA+MDEA+CO₂ – HZSM-5 system

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<th>(C_{\text{bicarbonate}}) ((kmol \ l^{-1}) \times 10^8)</th>
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Appendix B: Calculation of Heat and Mass Transfer Limitations

Appendix B1: Calculation of Diffusion Coefficient of CO$_2$ in MEA ($D_{CO2-MEA}$) and effective diffusivity $D_{eff}$

The diffusion coefficient of CO$_2$ in MEA solution was estimated by N$_2$O analogy.

$$D_{CO2,H2O} = 2.35 \times 10^{-6} \exp \left( \frac{-2119}{T} \right) \quad \text{B1}$$

$$D_{N2O,H2O} = 5.07 \times 10^{-6} \exp \left( \frac{-2371}{T} \right) \quad \text{B2}$$

First CO$_2$ diffusion coefficients of CO$_2$ and N$_2$O in H$_2$O were determined at the highest experimental operating condition were heat and mass transfer limitations are likely to occur (368K). Equations 8.1 and 8.2 are adopted from Versteeg et al $^{135,136}$.

$$D_{N2O,\mu_{MEA}} \gamma = D_{N2O,\mu_{H2O}} \mu_{H2O} \quad \text{B3}$$

Equation B3 was used to estimate the diffusion of N$_2$O into aqueous MEA.

$$D_{CO2,H2O} = 2.35 \times 10^{-6} \exp \left( \frac{-2119}{368} \right) = 7.436 \times 10^{-9} \frac{m^2}{s}$$

$$D_{N2O,H2O} = 5.07 \times 10^{-6} \exp \left( \frac{-2371}{T} \right) = 8.0912 \times 10^{-9} \frac{m^2}{s}$$

$$D_{N2O} = \frac{D_{N2O,H2O} \mu_{H2O}}{\mu_{MEA}} = \frac{0.0912 \times 10^{-9} \frac{m^2}{s} \times 297.8 (\mu \text{ Pa.s})}{\mu_{MEA}}$$

Where $\gamma$ is 0.5 in MEA, $\mu$= dynamic viscosity of fluid

Weiland equation was used obtain the dynamic viscosity of MEA $\mu_{MEA}$:

$$\mu_{\phi_{H2O}} = \exp \left( \frac{[(a\alpha+b)\Omega+(c\alpha+d)][(a(e\alpha+fT+g)+1]a}{T^2} \right)$$

$$\mu_{MEA} = 297.8 \exp \left[ \frac{[(0.05\%+0)368+(21.28 \times 0.30\%+0.273)][0.015(0.01015 \times 0.30\%+0.0093 \times 368 + -2.289)+1]30\%}{368^2} \right]$$

$$\mu_{MEA} = 921.30 \mu \text{ Pa.s}$$

Therefore $D_{N2O} = \frac{0.0912 \times 10^{-9} \frac{m^2}{s} \times 297.8 (\mu \text{ Pa.s})}{921.30^{0.5} \mu \text{ Pa.s}} = 7.414 \times 10^{-9} \frac{m^2}{s}$
The diffusivity of CO\(_2\) in MEA can then be calculated using the following equation:

\[
D_{\text{CO}_2} = \frac{D_{\text{CO}_2, \text{H}_2\text{O}}}{D_{\text{N}_2, \text{H}_2\text{O}}} \times D_{\text{N}_2, \text{O}} = \frac{7.436 \times 10^{-9} \text{m}^2}{8.0912 \times 10^{-9} \text{m}^2} \times 7.414 \times 10^{-8} \text{m}^2 = 6.81 \times 10^{-8} \text{m}^2
\]

**Calculation of \(D_{\text{eff}}\)**

\(\varepsilon\) = void fraction, \(d\) = reactor diameter, \(d_p\) = particle size (0.003 m \(\gamma - Al_2O_3\) and 0.025 m for HZSM-5)

MEA \(\Delta H_{\text{desp}}\) = -91.62 KJ/mol Estimated from work of Anusha et al \(^6\)

\[
D_{\text{eff}} = \frac{\varepsilon D_{\text{CO}_2}}{\tau}
\]

\(\tau\) = tortuosity factor = \(\frac{\text{Actual distance a moleclue travel between two points}}{\text{shortest distance between two points}}\) = 8\(^{124}\)

\(\varepsilon\) = void fraction (the ratio of the volume occupied by voids to the total catalyst bed volume). Calculated using the formula given by Geankopolis\(^{126}\).

\[
\varepsilon = 0.38 + 0.073\left[1 + \left(\frac{d}{d_p} - 2\right)^2\right] = 0.38 + 0.073\left[1 + \left(\frac{0.025 - 2}{0.003}ight)^2\right] = 0.8056 \ (\gamma - Al_2O_3)
\]

0.836 (HZSM-5)

\[
D_{\text{eff}} = \frac{\varepsilon D_{\text{CO}_2}}{\tau} = \frac{0.8056 \times 6.81 \times 10^{-8} \text{m}^2}{8} \times 10^{-9} \text{m}^2 = 6.85 \times 10^{-9} \text{m}^2 \ (\gamma - Al_2O_3), \quad 7.12 \times 10^{-9} \text{m}^2
\]

(HZSM-5)
Appendix B1: Calculation of Mass transfer coefficient, \(K_c\)

Mass transfer coefficient was calculated using the correlation for packed given in Perry and Green, 1997.\(^{125}\)

\[
N_{sh} = 0.91\Psi(N_{Re})^{0.49}N_{SC}^{3/3}
\]

\[
N_{Re} = \frac{d_p\nu\rho}{\mu(1-\varepsilon)} \quad \text{and} \quad N_{SC} = \frac{\mu}{\rho D_{CO2}} \quad \text{and} \quad N_{sh} = \frac{K_c d_p}{D_{CO2}}
\]

Here

\(N_{Re}\) = Reynold’s number, \(d_p\) = particle size, \(V_s\) = superficial velocity

\(\rho\) = Density of fluid, 32.67 \(kmol/m^3\) (910 \(Kg/m^3\) MEA), 23.5 \(kmol/m^3\) (MEA-MDEA) from ASPEN

\(\mu\) = Dynamic viscosity of fluid =1.3 m \(Pa.S\) at 80°C (Obtained from work of Weiland et al\(^{76}\))

\(\Psi\) = shape factor (1 for particle)

\(D_{CO2}\) = Diffusion coefficient of \(CO_2\) in MEA = \(6.81 \times 10^{-8} \ m^2/s\) (calculated in Appendix B1)

\(N_{SC}\) = Schmidt number, \(N_{sh}\) = Sherwood number

\(K_c\) = Mass transfer coefficient

\(d_p\) = particle size

Cross-sectional area =

Calculating \(V_s\):

\[
V_s = \text{superficial velocity} = \frac{\text{volumetric fluid flow} \ Q}{\text{Cross section Area} \ A} = \frac{60ml \times 10^{-6} \ m^3}{2.04 \times 10^{-3} \ m^2} = 4.901 \times 10^{-4} \ m/s
\]

Calculating \(N_{Re}\):

\[
N_{Re} = \frac{d_p\nu\rho}{\mu(1-\varepsilon)} = \frac{0.003m \times 4.901 \times 10^{-4} \ m/s \times 910 \ Kg/m^3}{1.3 \times 10^{-3} \ Pas (1-0.8056)} = 5.29 (\gamma - Al_2O_3), \ 5.23 (HZSM-5)
\]
Calculating $N_{SC}$:

$$N_{SC} = \frac{\mu}{\rho D_{CO2}} = \frac{1.3 \times 10^{-3}}{910 \times 9.81 \times 10^{-8} \frac{m^2}{s}} = 20.98$$

Calculating $N_{sh}$:

$$N_{sh} = 0.91 \Psi (N_{Re})^{0.49} N_{SC}^{1/3} = 0.91 \times 1 \times (5.29)^{0.49} \times (20.98^{1/3}) = 5.68$$

We know that:

$$N_{sh} = \frac{K_c d_p}{D_{CO2}}; \ K_c = \frac{N_{sh} x D_{CO2}}{d_p} = \frac{5.85 \times 6.81 \times 10^{-8} \frac{m^2}{s}}{0.003m} = 1.288 \times 10^{-4} m/s (\gamma - Al_2O_3),$$

$$1.59 \times 10^{-4} m/s (HZSM-5)$$
Appendix B2: Calculation of effective thermal conductivity $\lambda_{eff}$

$$\frac{\lambda_{eff}}{\lambda} = 5.5 + 0.05 N_{Re} \text{ (Walas et al correlation) }$$

So, $\lambda_{eff} = \lambda (5.5 + 0.05 N_{Re})$

Here $\lambda$ = thermal conductivity, $N_{Re}$ = Reynold’s number calculated from $N_{Re} = \frac{d_p v_p \rho}{\mu (1-\epsilon)} = 5.29$

Bridgman’s equation can be used to calculate thermal conductivity of the liquid reactant:

$$\lambda = 3.0 \left( \frac{N}{V} \right)^{2/3} K_B V_s$$

Where

$K_B$ = Boltzmann Constant ($1.381 \times 10^{-23} J/K$)

$V_s$ = Superficial Velocity. Calculated in appendix B2 ($4.901 \times 10^{-4} m/s$)

$V$ = molar volume; \( \frac{\text{Molecular Weight}}{\text{mass density}} \frac{(M_w)}{(\rho)} = \frac{26.695 g/mol}{0.946 g/cm^3} = 28 cm^3/mol \text{ (MEA system), } 48.5 cm^3/mol \text{ (MEA-MDEA system) }$

$N = \text{Avogadro’s number} (6.02 \times 10^{23})$

$$\lambda = 3.0 \left( \frac{6.02 \times 10^{23}}{2.8 \times 10^{-5} \frac{m^3}{mol}} \right)^{2/3} \times 1.381 \times 10^{-23} f/K \times 4.901 \times 10^{-4} m/s$$

$\lambda_{MEA} = 1.57 \times 10^{-7} W/m/K.$

$$\lambda_{MEA-MDEA} = 1.09 \times 10^{-7} W/m/K$$

Therefore

$$\lambda_{eff} = \lambda (5.5 + 0.05 N_{Re})$$

$$\lambda_{eff} = 1.57 \times 10^{-7} W/m/K (5.5 + 0.05 \times 5.29) = 9.050 \times 10^{-7} W/m/K \text{ (MEA system) }$$

$$\lambda_{eff} = 6.28 \times 10^{-7} W/m/K \text{ (MEA-MDEA system) }$$
Appendix B3: Calculation of heat transfer coefficient \( (h) \)

\[
J_H = J_D = \left( \frac{h}{C_p V_d \rho} \right) N_{pr}^{2/3}
\]

\( J_H \) = heat transfer J factor

\( C_p \) = heat capacity of feed stream at 365 K (85.2097 KJ/kg/K), obtained from ASPEN

\( N_{pr} \) = Prandlt number \( = \frac{C_p \mu}{\lambda} \)

\( V_s \) = superficial velocity \( 4.901 \times 10^{-4} \text{m/s} \) (calculated in appendix B2)

\( \mu = \text{feed viscosity} \ 1.3 \text{ m Pa.s} \)

\( \lambda = \text{thermal viscosity} \ 1.57 \times 10^{-7} \text{ W/m/K}, \)

\[
N_{pr} = \frac{C_P \mu}{\lambda} = \frac{85.2097 \text{ kJ/kg/K} \times 1.3 \times 10^{-3} \text{ kg m}^{-1} \text{s}^{-1}}{2.6 \times 10^{-1} \text{ kJ m}^{-1} \text{s}^{-1} \text{K}^{-1}} = 0.426
\]

\[
J_H = J_D = \left( \frac{0.4548}{\varepsilon} \right) N_{Re}^{-0.4069} = 0.2867 \ (\gamma - Al_2O_3) \cdot 0.277 \ (\text{HZSM-5})
\]

\( \varepsilon \) = void fraction (Calculated in appendix B1)

Now,

\[
J_H = J_D = \left( \frac{h}{C_p V_d \rho} \right) N_{pr}^{2/3} = h = \frac{J_H}{N_{pr}^{2/3}} \times C_p V_d \rho = 19.24 \frac{kJ}{m^2 \cdot s \cdot K}
\]
Appendix B4: Calculation of internal pore heat transfer resistance ($\Delta T_{\text{particle, max}}$)

Particle heat transfer:

$$\Delta T_{\text{particle, max}} = \frac{D_{\text{eff}}(C_{AS} - C_{AC})\Delta H_{\text{rxn}}}{\lambda_{\text{eff}}}$$

Here $C_{AC}$ = concentration at center, $= 0$ and $C_{AS} = 5$ kmol/m$^3$

$\Delta H_{\text{rxn}} = \Delta H_{\text{desp}} = -91.62$ KJ/mol

$D_{\text{eff}} = 6.85 \times 10^{-9}$ m$^2$/s

$\lambda_{\text{eff}}$ = effective thermal conductivity = $9.050 \times 10^{-7}$ kJ.m$^{-1}$s$^{-1}$K$^{-1}$

$$\Delta T_{\text{particle, max}} = \frac{6.85 \times 10^{-9} \text{ m}^2/\text{s} \times (5 - 0) \text{ mol. m}^3 \times 91.62 \text{ kJ/mol}}{9.050 \times 10^{-7} \text{ kJ. m}^{-1} \text{s}^{-1} \text{ K}^{-1}}$$

$\Delta T_{\text{particle, max}} = 3.467 K ( \gamma - Al_2O_3), 5.19 K$ (HZSM-5)
Appendix B5: Calculation of external film heat transfer resistance ($\Delta T_{\text{film,max}}$)

Calculating film transfer:

$$\Delta T_{\text{film,max}} = \frac{L(-r_{A,obs})\Delta H_{rxn}}{h}$$

Here $L = \frac{Rc}{3} = 0.003 \text{ m}/3 = 1 \times 10^{-3} \text{m (}\gamma \text{Al}_2\text{O}_3\text{)}, 8.33 \times 10^{-4} \text{m (HZSM-5)}$

$\Delta H_{rxn} = \Delta H_{\text{desp}} = -91.62\text{kJ/mol}$

$-r_{A,obs} = -r'_{A,obs} \times \rho_b$

$\rho_b = \text{catalyst bulk density} = \frac{\text{catalyst weight}}{\text{volume of catalyst bed}} = \frac{W}{V_{\text{bed}}}$

$V_{\text{bed}} = \pi \left( \frac{d}{2} \right)^2 H_{\text{bed}}$

$H_{\text{bed}} = \text{bed height} (1.067\text{m})$

$d = \text{bed diameter} (0.051\text{m})$

$V_{\text{bed}} = \pi \left( \frac{0.051}{2} \right)^2 1.067 = 0.00218 \text{m}^3$

$catalyst bulk density = \frac{100 \times 10^{-3} \text{kg}}{0.00218 \text{m}^3} = 68.78 \text{kg/m}^3$

$\rho_c = \text{catalyst particle density} = \frac{\rho_b}{\varepsilon}$

$\rho_c = \frac{68.78 \text{kg/m}^3}{0.8056} = 85.38 \text{kg/m}^3 (\gamma - \text{Al}_2\text{O}_3), 82.27 \text{kg/m}^3 (\text{HZSM-5})$

$-r_{A,obs} = 2.39 \times 10^{-5} \text{kmol.kgcat}^{-1}\text{s}^{-1} \times 68.78 \text{kg/m}^3 = 1.64 \times \text{mol/m}^3\cdot\text{s}$

$h = 19.24 \frac{\text{kJ}}{\text{m}^2\cdot\text{s}\cdot\text{K}}$

$$\Delta T_{\text{film,max}} = \frac{1 \times 10^{-3} \text{m} \left(1.64 \times \frac{\text{mol}}{\text{m}^3\cdot\text{s}}\right) 91.62\text{kJ/mol}}{19.24 \frac{\text{kJ}}{\text{m}^2\cdot\text{s}\cdot\text{K}}}$$

$\Delta T_{\text{film,max}} = 7.83 \times 10^{-3} \text{K} (\gamma - \text{Al}_2\text{O}_3), 6.57 \times 10^{-3} \text{K} (\text{HZSM-5})$
Appendix B6: Calculation of Mears’ Criteria for heat transport limitation

\[
\frac{r_{A,obs}\rho_b R_c E \Delta H_{rxn}}{hT^2 R} < 0.15
\]

\[
r_{A,obs} = 2.39 \times 10^{-5} \text{ kmol.kgcat}^{-1}s^{-1}(\gamma - Al_2O_3), \quad 2.41 \times 10^{-5} \text{ kmol.kgcat}^{-1}s^{-1} (\text{HZSM-5}) \quad \text{(Data from experimental run at T=365K, catalyst weight 100g)}
\]

\[
\rho_b = \text{catalyst bulk density} = \frac{100 \times 10^{-3} \text{kg}}{0.00218 \text{m}^3} = 68.78 \text{ kg/m}^3
\]

\[E = \text{Activation energy} \quad 80255 \text{J/mol (} \gamma - Al_2O_3\text{)}, \quad 70851.908 \text{J/mol (HZSM-5)}
\]

\[H_{rxn} = \text{heat of reaction} = \Delta H_{deep} = -91.62 \text{KJ/mol}
\]

\[T = 365K
\]

\[R_c = \text{radius of catalyst} \quad 1.5 \times 10^{-3}m(\gamma - Al_2O_3), \quad 1.25 \times 10^{-3}m (\text{HZSM - 5})
\]

\[R = \text{molar gas constant} = 8.314\text{J/mol/K}
\]

\[
\frac{2.39 \times 10^{-5} \text{ kmol.kgcat}^{-1}s^{-1} \times 68.78 \text{kg/m}^3 \times 1.5 \times 10^{-3}m \times 8.0255 \times 10^4 \text{kJ/kmol} \times 91.62 \text{kJ/mol}}{19.24 \frac{\text{kJ}}{m^2 \cdot \text{s} \cdot \text{K}}} \times 365\text{K} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} x 1000 \text{kJ/K}
\]

\[= 8.51 \times 10^{-4} << 0.15 \quad (\gamma - Al_2O_3), \quad 6.31 \times 10^{-4} << 0.15 \quad (\text{HZSM-5})
\]
Appendix B7: Calculation of Weisz-Prater Criterion for internal mass diffusion

The Weisz-Prater criterion for internal diffusion limitation is given as:

\[ C_{wp,ipd} = \frac{-r_{A,obs}^p p_c R_c^2}{D_{eff} C_{AS}} \]

\[ -r_{A,obs} = 2.39 \times 10^{-5} \text{ kmol. kgcat}^{-1} \text{s}^{-1} (\gamma - Al_2O_3), \quad 2.41 \times 10^{-5} \text{ kmol. kgcat}^{-1} \text{s}^{-1} \]

(HZSM-5) (Data from experimental run at T=365K, catalyst weight 100g)

\[ \rho_c = \frac{68.78 \text{ kg/m}^3}{0.8056} = 85.38 \text{ kg/m}^3 (\gamma - Al_2O_3), \quad 82.27 \text{ kg/m}^3 (HZSM - 5) \]

\[ R_c = \text{radius of catalyst} \quad 1.5 \times 10^{-3} \text{m} (\gamma - Al_2O_3), \quad 1.25 \times 10^{-3} \text{m} (HZSM - 5) \]

\[ D_{eff} = 6.85 \times 10^{-9} \text{m}^2/\text{s} \]

\[ C_{AS} = \text{concentration of reactant A in the catalyst surface= Concentration in bulk liquid=5kmol/m}^3 \text{ (This is so because of the absence of external film resistance. So the concentration in the bulk liquid and surface of catalyst are assumed to be the same).} \]

\[ C_{wp,ipd} = \frac{-r_{A,obs}^p p_c R_c^2}{D_{eff} C_{AS}} = \frac{2.39 \times 10^{-5} \text{ kmol.kgcat}^{-1} \text{s}^{-1} \times 85.38 \frac{\text{kg}}{\text{m}^3} \times (1.5 \times 10^{-3} \text{m})^2}{6.85 \times 10^{-9} \text{m}^2/\text{s} \times 5 \text{ kmol/m}^3} \]

\[ C_{wp,ipd} = 0.134 < 1 (\gamma - Al_2O_3), \quad 0.45 < 1 (HZSM-5) \]

This shows that no concentration gradient exists within the catalyst as \( C_{wp,ipd} < 1 \) indicates the absence of internal diffusion limitations.
Appendix B8: Calculation of external film diffusion limitation (Levenspiel, 1999)

\[
\frac{\text{observed rate}}{\text{rate if film transfer controls}} = \frac{-r_{A,\text{obs}} \cdot d_{b}}{K_c C_{A,s} 6}
\]

\[ -r_{A,\text{obs}} = 2.39 \times 10^{-5}\text{ kmol.kg.cat}^{-1} \text{s}^{-1} \times 68.78 \text{ kg/m}^3 = 1.64 \times 10^{-3}\text{kmol/m}^3 \cdot \text{s(}\gamma - Al_2O_3) \]

\[ 2.41 \times 10^{-5}\text{ kmol.kg.cat}^{-1} \text{s}^{-1} \times 68.78 \text{ kg/m}^3 = 1.66 \times 10^{-3}\text{kmol/m}^3 \cdot \text{s (HZSM-5)} \] (Data from experimental run at T=365K, catalyst weight 100g)

\[ C_{A,s} = \text{concentration of reactant A in the catalyst surface= Concentration in bulk liquid=5kmol/m}^3 \]

\[ K_c = \text{mass transfer coefficient = 1.29 x 10}^{-4}\text{m/s (}\gamma - Al_2O_3), 1.59 x 10^{-4}\text{m/s (HZSM-5) –calculated in appendix B2} \]

\[
\frac{-r_{A,\text{obs}} \cdot d_{b}}{K_c C_{A,s} 6} = \frac{1.64 \times 10^{-3}\text{kmol/m}^3 \cdot \text{s} \times 0.003 \text{m}}{1.288 \times 10^{-4}\text{m/s} \times 5\text{kmol/m}^3 \cdot \text{6}}
\]

\[ 1.27 \times 10^{-3}(\gamma - Al_2O_3), 8.7 \times 10^{-4} \text{ (HZSM-5)} \]

The obtained value is far less than 1. This indicates that the observed rate is less than the mass transfer film rate. Therefore, the resistance to film mass transfer does not influence the rate of reaction absence of film mass transfer rate.
Appendix B9: Calculation of Mears’ criterion for external film diffusion limitation

\[
\frac{-r'_{A,obs} \rho_b R_c n}{K_c C_A} < 0.15
\]

\[
-r'_{A,obs} = 2.39 \times 10^{-5} \text{ kmol kg cat}^{-1} s^{-1} \times 68.78 \text{ kg/m}^3 = 1.64 \times 10^{-3} \text{ kmol/m}^3 \text{s}(\gamma - \text{Al}_2\text{O}_3),
\]

\[
2.41 \times 10^{-5} \text{ kmol kg cat}^{-1} s^{-1} \times 68.78 \text{ kg/m}^3 = 1.66 \times 10^{-3} \text{ kmol/m}^3 \text{s (HZSM-5)} \quad \text{(Data from experimental run at T=365K, catalyst weight 100g)}
\]

\[
\rho_b = \text{catalyst bulk density} = \frac{100 \times 10^{-3} \text{ kg}}{0.00218 \text{ m}^3} = 68.78 \text{ kg/m}^3
\]

\[
R_c = \text{radius of catalyst} = 1.5 \times 10^{-3} \text{ m}(\gamma - \text{Al}_2\text{O}_3), 1.25 \times 10^{-3} \text{ m (HZSM-5)}
\]

\[
n = \text{Overall order of reaction} = 0.9(\gamma - \text{Al}_2\text{O}_3), 0.6 (\text{HZSM-5})
\]

\[
C_{AS} = \text{concentration of reactant A in the catalyst surface=} \text{Concentration in bulk liquid}=5 \text{ kmol/m}^3
\]

\[
K_c = \text{mass transfer coefficient} = 1.29 \times 10^{-4} \text{ m/s} (\gamma - \text{Al}_2\text{O}_3), 1.59 \times 10^{-4} \text{ m/s}
\]

(HZSM-5) –calculated in appendix B2

\[
\frac{2.39 \times 10^{-5} \text{ kmol kg cat}^{-1} s^{-1} \times 68.78 \text{ kg/m}^3 \times 1.5 \times 10^{-3} \text{ m x 0.9}}{1.29 \times 10^{-4} \text{ m/s} \times 5 \text{ kmol/m}^3} = 3.44 \times 10^{-3} \ll 0.15(\gamma - \text{Al}_2\text{O}_3), 1.56 \times 10^{-3} \ll 0.15 (\text{HZSM-5})
\]

The left hand side (LHS) of Mears’ criterion is less than 0.15, therefore it can be said that there will be no external film resistance to mass transfer.
Appendix C: Derivation of Mechanistic Models

The Mechanistic models were written based on the Langmuir Hinshelwood Hugo Watson (LHHW) formulations and were used to describe the surface reaction.

Several mechanisms were developed in accordance to the catalyst activity. As shown in Appendix B, the experimental data were collected in the absence of heat and mass transfer limitations (Intrinsic data).

An example of a single site LHHW proposed catalytic desorption mechanism is as follows:

Adsorption of protonated carbamate ion on the Brønsted active site

\[ \text{R1: } \text{RNH}^- \text{COO}^- (s) \leftrightarrow \text{RNHCOO}^-(s) \]

Surface reaction between \( \text{RNH}_2^+ \) and adsorbed carbamate ion, \( \text{RNHCOO}^- (s) \)

\[ \text{R2: } \text{RNH} - \text{COO}^- (s) + \text{RNH}_2^+ \leftrightarrow \text{RNH} - \text{COOH} (s) + \text{RNH}_2^+ \]

\[ \text{R3: } \text{RNH} - \text{COOH} (s) \leftrightarrow \text{RNH}_2^+ - \text{COO}^- (s) \]

\[ \text{R4: } \text{RNH}_2^+ - \text{COO}^- (s) \rightarrow \text{CO}_2 + \text{RNH}_2 (s) \]

Desorption of MEA from the catalyst active site.

\[ \text{R5: } \text{RNH}_2 (s) \leftrightarrow \text{RNH}_2 + (s) \]

Each elementary reaction is assumed to be the rate determining step (RDS) and rate expression is developed for each case as.

Where \( \text{RNH} - \text{COO}^- = \text{carbamate} \), \( \text{RNH}_2^+ - \text{COO}^- = \text{Zwitterion} \) \( S \) = active site

Rate of Adsorption, \( r_A \)

Rate of adsorption is directly proportional to the concentration of carbamate and catalyst vacant active sites

\[ r_A = k_A C_c C_s \]

Rate of desorption, \( r_D \)

Rate of desorption is directly proportional to the site occupied by adsorbed carbamate.
\[ r_D = -k_D C_{CS} \]

The net rate of desorption, \( r_{AD} = r_A + r_D = k_A C_C - k_D C_{CS} \)

At equilibrium the net rate of desorption, \( r_{AD} = 0 \) i.e. \( r_A = r_D \)

Where:

- \( K_A = \text{Adsorption constant} \)
- \( K_D = \text{desorption constant} \)
- \( C_C = \text{carbamate concentration} \)
- \( C_S = \text{concentration of vacant sites} \)

The equilibrium relation for each elementary step is given as:

Equilibrium desorption constant, \( K_D = \frac{k_A}{k_D} \)

\[ r_{AD1} = k_{A1} C_C - k_{D1} C_{CS} = k_{A1} \left( C_C - \frac{C_{CS}}{K_{D1}} \right) \]

The same principle applies to reactions R2, R3, R4 and R5

\[ r_{AD2} = k_{A2} C_H + C_{CS} - k_{D2} C_{CS} = k_{A2} \left( C_H + C_{CS} - \frac{C_{MEA}}{K_{D2}} \right) \]

\[ r_{AD3} = k_{A3} C_{cab} - k_{D3} C_{zS} = k_{A3} \left( C_{cab} - \frac{C_{zS}}{K_{D3}} \right) \]

\[ r_{AD4} = k_{A4} C_{zS} - k_{D4} C_{AAS} = k_{A4} \left( C_{zS} - \frac{C_{PCO2}}{K_{D4}} \right) \]

\[ r_{AD5} = k_{A5} C_{AAS} - k_{D5} C_A C_S \]

Site balance, \( C_t = C_S + C_{cab} + C_{CS} + C_{zS} + C_{AAS} \)

- Choosing reaction 2, R2 as the RDS
- At steady state, the rate of Adsorption, Surface Reaction and Desorption of the heterogeneous reactions are equal

\[ -r_A' = r_{AD} = r_S = r_D \]

By assuming R2 as the RDS, we are saying that its reaction rate constant \( K_2 \) is small with respect to the specific rate constant of the other steps R1, R3, R4, and R5.
Consequently, the ratios \( \frac{R_1}{K_1}, \frac{R_3}{K_3}, \frac{R_4}{K_4}, \frac{R_5}{K_5} \) are very small (approximately zero). However, the ratio \( \frac{R_2}{K_2} \) is relatively large.

As \( r_2 \) is the RDS, \( r_1 = r_3 = r_4 = r_5 = 0 \)

Site balance: \( C_t = C_S + C_{cab,S} + C_{c,S} + C_{z,S} + C_{A,S} \)

The variables in the site balance equation cannot be measured, and will be replaced with measurable variables.

\[
C_{c,S} = \frac{1}{K_D} C_C C_S \\
C_{A,S} = K_D C_A C_S \\
C_{z,S} = K_D C_{A,S} P_{CO_2} = K_D C_A C_S P_{CO_2} \\
C_{cab,S} = K_D C_{z,S} = K_D C_D C_A C_P P_{CO_2} \\
C_t = C_S + \frac{1}{K_D} C_C C_S + K_D C_d C_A C_S + K_D C_D C_A C_S P_{CO_2} + K_D C_D C_A C_S P_{CO_2} \\
C_t = C_S (1 + \frac{1}{K_D} C_C + K_D C_d C_A + K_D C_D C_A P_{CO_2} + K_D C_D C_A P_{CO_2})
\]

\[
C_S = \frac{C_t}{\left(1 + \frac{C_C}{K_D} + K_D C_A \right)}
\]

Recall that \( R_2 \) is the RDS

\[
r_{AD_2} = k_{A_2} C_H + \frac{1}{K_D} C_C \frac{C_t}{\left(1 + \frac{C_C}{K_D} + K_D C_A \right)} - k_D K_D C_D C_A C_S P_{CO_2} C_MEA
\]

The term containing \( P_{CO_2} \) will be eliminated since \( K_D \) is irreversible and amine reaction do not occur in the gas phase

\[
k_{A_2} C_t \frac{C_H}{\left(1 + \frac{C_C}{K_D} + K_D C_A \right)} = k_{A_2} K_D C_t \frac{C_C H^+}{\left(K_D + C_C + K_D C_A \right)}
\]

Let \( k_D = k_{A_2} K_D C_t \) \( r_2 = k_D \frac{C_C H^+}{\left(K_D + C_C + K_D C_A \right)} \)
Expressing in the Arrhenius form:

\[ r_2 = \frac{k_0 E / RT}{(K_{B1} + C_C + K_{B2}C_A)} \]

Appendix D: Nonlinear Regression, NLREG Code with results for Power Law and Mechanistic Model

Power Law Model:

\[ 1: \text{Parameters } k, E, n; \]
\[ 2: \text{variables } T, r_A, C_H; \]
\[ 3: \text{constant } E = 8.514; \]
\[ 4: \text{Function } r_A = -k \times (\exp(-E/(R*T))) \times (CA^n); \]
\[ 5: \text{Data}; \]
\[ \text{Beginning computation...} \]

<table>
<thead>
<tr>
<th>Final Results...</th>
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</thead>
<tbody>
<tr>
<td>NLREG version 6.3</td>
</tr>
<tr>
<td>Copyright (c) 1992-2005 Phillip H. Sherrod. All rights reserved. This is a registered copy of NLREG that may not be redistributed.</td>
</tr>
<tr>
<td>Number of observations = 15</td>
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<td>Maximum allowed number of iterations = 500</td>
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<td>Convergence tolerance factor = 1.000000E-010</td>
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<tr>
<td>Number of iterations performed = 249</td>
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<tr>
<td>Final sum of squared deviations = 9.3509678E-011</td>
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<tr>
<td>Final sum of deviations = -6.3771655E-007</td>
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<tr>
<td>Standard error of estimate = 2.79137E-006</td>
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<tr>
<td>Average deviation = 2.09395E-006</td>
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<tr>
<td>Maximum deviation for any observation = 4.81674E-006</td>
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<tr>
<td>Proportion of variance explained (R^2) = 0.8776 (87.76%)</td>
</tr>
<tr>
<td>Adjusted coefficient of multiple determination (R^2) = 0.8572 (85.72%)</td>
</tr>
<tr>
<td>Durbin-Watson test for autocorrelation = 0.729</td>
</tr>
<tr>
<td>This Durbin-Watson value indicates autocorrelation or inappropriate function.</td>
</tr>
<tr>
<td>Warning: Covariance matrix could not be computed because the finite-difference Hessian was indefinite.</td>
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<tr>
<td>Analysis completed 19-Sep-2016 17:17. Runtime = 0.06 seconds.</td>
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<tr>
<td>Error</td>
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<td>Total</td>
</tr>
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</table>
Mechanistic Model:

```
1: Parameters k=1e6,K1=1e2,K2=1e1,E;
2: variables T, rA,C,H, A;
3: constant R = 8.314;
4: iteration le7;
5: Function rA=k*(exp(-(E/(R*T))))*((H*C)/(1+(K1*C)+(K2*A)));
6: Data;

Beginning computation...
```

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<tr>
<th>---- Final Results ----</th>
</tr>
</thead>
<tbody>
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<td>NLREG version 6.3</td>
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</tr>
<tr>
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<td>Maximum allowed number of iterations = 10000000</td>
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<td>Convergence tolerance factor = 1.000000E-010</td>
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<td>Number of iterations performed = 364</td>
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<tr>
<td>Final sum of squared deviations = 6.7072925E-015</td>
</tr>
<tr>
<td>Final sum of deviations = -3.773981E-008</td>
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<tr>
<td>Standard error of estimate = 2.46932E-008</td>
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<tr>
<td>Average deviation = 1.72321E-008</td>
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<tr>
<td>Maximum deviation for any observation = 4.06047E-008</td>
</tr>
<tr>
<td>Proportion of variance explained (R^2) = 0.9577 (95.77%)</td>
</tr>
<tr>
<td>Adjusted coefficient of multiple determination (R^2) = 0.9462 (94.62%)</td>
</tr>
<tr>
<td>Durbin-Watson test for autocorrelation = 1.205</td>
</tr>
<tr>
<td>Analysis completed 19-Sep-2016 17:36. Runtime = 0.06 seconds.</td>
</tr>
</tbody>
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<table>
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<th>---- Calculated Parameter Values ----</th>
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<tr>
<td>Parameter</td>
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<tr>
<td>-----------</td>
</tr>
<tr>
<td>k</td>
</tr>
<tr>
<td>K1</td>
</tr>
<tr>
<td>K2</td>
</tr>
<tr>
<td>E</td>
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<tr>
<th>---- Analysis of Variance ----</th>
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<tr>
<td>Source</td>
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<tr>
<td>--------</td>
</tr>
<tr>
<td>Regression</td>
</tr>
<tr>
<td>Error</td>
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<tr>
<td>Total</td>
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</tbody>
</table>
Appendix E: Regression Analysis: Conversion versus BET, Ratio, Total acid sites, Acid strength, B/L, ...

Forward Selection of Terms

Candidate terms: BET, Ratio, Total acid sites, Acid strength, B/L, Acid strength*BET, BET*B/L, BL*Acid Strength

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Step 2</th>
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<tbody>
<tr>
<td>Coef</td>
<td>P</td>
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<tr>
<td>Ratio</td>
<td>0.01785</td>
</tr>
<tr>
<td>BL*Acid Strength</td>
<td>0.06993</td>
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</table>

*S    0.0320961  0.0074247
R-sq  96.74%  99.88%
R-sq(adj)  95.65%  99.77%
R-sq(pred)  93.86%  98.88%

**α to enter = 0.05**

Analysis of Variance

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<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
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<tbody>
<tr>
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<td>0.047320</td>
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<td>Ratio</td>
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<td>0.009583</td>
<td>0.009583</td>
<td>173.83</td>
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<tr>
<td>BL*Acid Strength</td>
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<td>0.002980</td>
<td>54.06</td>
<td>0.018</td>
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<tr>
<td>Error</td>
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<td>0.000055</td>
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<tr>
<td>Total</td>
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<td>0.094751</td>
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Model Summary

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<th>R-sq</th>
<th>R-sq(adj)</th>
<th>R-sq(pred)</th>
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<tr>
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<td>99.88%</td>
<td>99.77%</td>
<td>98.88%</td>
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Coefficients

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<th>SE Coef</th>
<th>T-Value</th>
<th>P-Value</th>
<th>VIF</th>
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</thead>
<tbody>
<tr>
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<td>0.000909</td>
<td>13.18</td>
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<tr>
<td>BL*Acid Strength</td>
<td>0.06993</td>
<td>0.00951</td>
<td>7.35</td>
<td>0.018</td>
<td>4.32</td>
</tr>
</tbody>
</table>

Regression Equation

Conversion = 0.011989 Ratio (Pore size/pore Volume) + 0.06993 BL*Acid Strength.
Residual Plots for Conversion

Normal Probability Plot

Residual

Percent

-0.01 0.00 0.01

0 10 20 30 40 50 60 70 80 90 99

Versus Fits

Residual

0.000 0.005 0.010

-0.010 0.000 0.005

Fitted Value

0.14 0.15 0.16 0.17 0.18

Versus Order

Residual

0.000 0.005

-0.010 0.000

Observation Order

1 2 3 4 5

Histogram

Frequency

0 0.5 1.0 1.5 2.0

-0.0075 -0.0050 -0.0025 0.0000 0.0025 0.0050

Residual

-0.010 0.000 0.010