CHAPTER ONE

INTRODUCTION

1.1 AMINE PROCESSES

Carbon dioxide is responsible for over seventy percent of greenhouse emissions worldwide and the majority of carbon dioxide is emitted by utility and industrial power stations. Figure 1.1 shows the distribution of greenhouse gases in Earth's atmosphere.

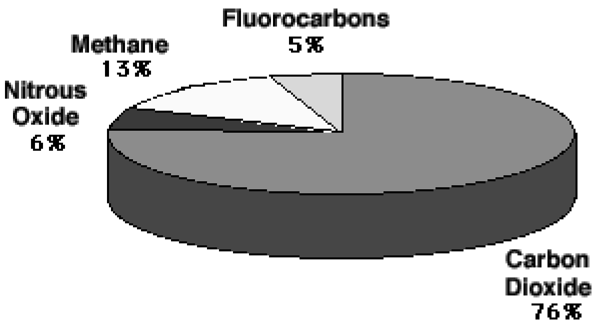

Figure 1.1: Distribution of greenhouse gases in Earth's atmosphere
(Source: www.umich.edu)

Many processes were developed for carbon dioxide capture from process gas streams, however, absorption with aqueous amine solvents remains the most commonly used technology for this purpose. Efforts are ongoing to improve this process in order to make it more economical and feasible for large scale use to reduce CO_2 emissions to the atmosphere.

The technology of treating process gas with alkanolamines in absorption/stripping systems became popular in the 1930's where this process was used for acid gas removal from natural gas and the treatment of synthesis gas. Since the 1990's, scientists have been working on developing this process to be used to reduce the presence of green house gases, typically CO_2 emissions from flue gas streams. Much attention has been focused on the reduction of CO_2 emissions from power stations burning fossil fuels since they make the largest contribution to the atmospheric build-up of CO_2.

The amine absorption/stripping process can be summarized as follows;

Prior to entering the amine absorber the acid gas will normally pass through a separator to remove solids and liquids from the gas. In some units wash water is circulated to increase the removal of solids and entrained liquid from the gas to avoid potential foaming in the absorber. The separator is usually equipped with baffles and a mist extractor (eliminator), which traps the liquid entrained in the gas before it leaves the vessel. The sour gas is then fed to the absorber where it contacts with the lean amine solution. Absorption followed by reaction between acid gas components will take place. Reacted amines known as *Rich Amine* will be fed to an amine regeneration unit. The absorber is usually a tray column with bubble caps on each tray for good liquid-gas contact. Packing column or mix of packing and tray are also used for this purpose. The sour gas enters the bottom of the contactor at a temperature between 30-40 ^{o}C and rises upwards through the bubble caps while the lean amine enters at the top of the contactor and flows downwards. In order to prevent hydrocarbon condensation the lean amine temperature is kept at 10 ^{o}C warmer than the sour gas temperature.

The CO_2 and amine solvent react to form a protonated amine and a bicarbonate anion in solution by the following reaction (Esber, 2006);

$$RNH_2 + H_2O + CO_2 \rightleftharpoons RNH_3^+ + HCO_3^-$$

The remaining flue gases are washed to remove any residual amine, and exhausted to the atmosphere. After filtration and heat recovery, the CO_2-enriched solvent is passed through a regeneration unit in which counter-current steam drives the reaction to the left, producing a stream of H_2O and CO_2. The H_2O is condensed leaving a stream of CO_2 that is over 99% pure and prepared for compression. The CO_2-lean amine solvent is recycled to the absorption tower (Herzog & Golomb, 2004).

Figure 1.2 shows a schematic diagram of the amine sweetening facilities for CO_2 capture. (Thitakamol *et al.*, 2007),

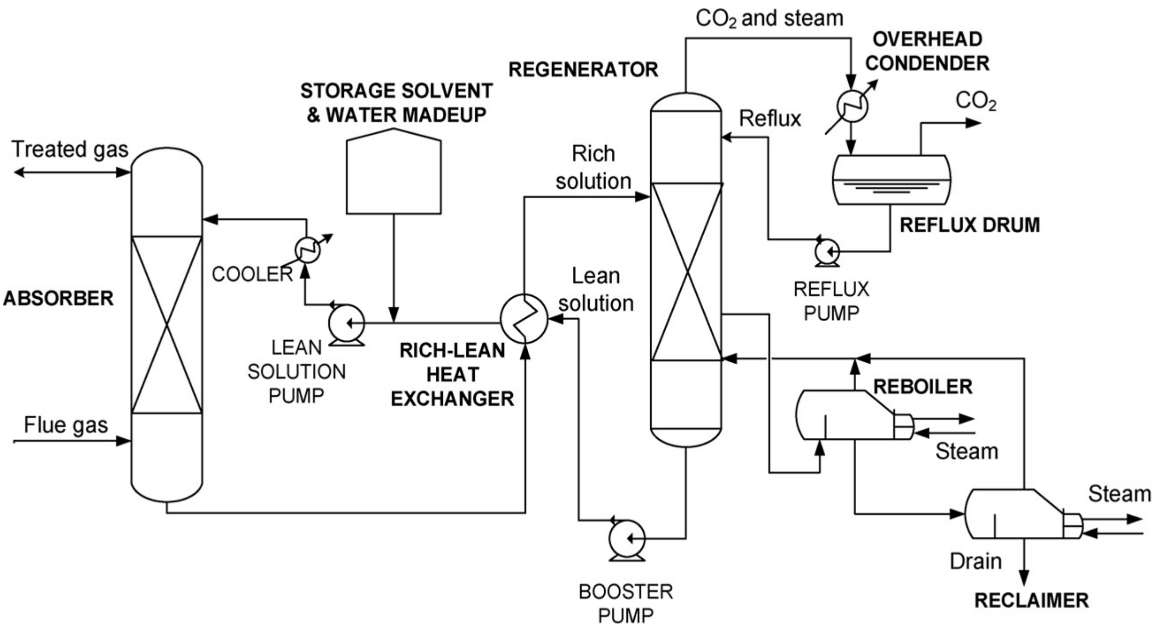

Figure 1.2: Schematic diagram of a typical absorption-based CO_2 capture unit from flue gases using amine solvents
(Source: Thitakamol *et al.* 2007)

1.2 SCOPE AND OBJECTIVES OF THE THESIS

The use of aqueous amine solvents is one of the most commonly used technologies for acid gas removal from process gas streams. One way to improve this technology is by finding solvents with better absorption properties, more specifically vapour-liquid-equilibrium data. The lack of such data for certain amine solvents in the open literature has initiated this work. MAE has been proposed by several investigators as a potential candidate for CO_2 capture. However, solubility data available in the published literature for this amine are still scarce. This work has focused on studying the equilibrium solubility of CO_2 in MAE and to quantify the performance of this amine relative to other solvents used in gas treating.

Providing sufficient solubility data and an accurate mathematical model for a CO_2-MAE-H_2O system is considered an important and vital tool that can be used by engineers for a better and more accurate screening and selection process. It will also help the design engineers in the evaluation and optimization of the different variables related to the design of process units using this amine.

The main objectives of this thesis include the following;

1. Provide CO_2 solubility data in 1.0 M, 2.0 M and 4.0 M MAE at temperatures of 30, 40 and 60 ^{o}C and CO_2 partial pressures ranging from 1 to 100 kPa. Such data are not available in the literature for this solvent.
2. Compare between the absorption of CO_2 by MAE and that by other amines at different temperatures and concentrations using data available in the literature for better and more accurate assessment and evaluation of this amine.
3. Predict the reaction equilibrium concentrations and estimate values for the equilibrium constants using data available in the literature and certain estimation techniques.
4. Derive a mathematical model that can be used to predict CO_2 loadings for this amine at a wider range of conditions.
5. Compare between the theoretical and experimental loadings of CO_2 in MAE to assess the feasibility of the proposed mathematical model for estimation.

1.3 STUDY METHOD

This study provides solubility of CO_2 in 1.0 M, 2.0 M and 4.0 M aqueous MAE at temperatures from 30 to 60 ^{o}C and CO_2 partial pressure in the range of 1 to 100 kPa.

Absorption of CO_2 in MAE was done using a single cell stirred reactor in which nitrogen and carbon dioxide gases at the required proportions are mixed with the amine solution at different temperatures. The pH is monitored with time until equilibrium is reached. The amount of CO_2 absorbed is precipitated as carbonate and determined by chemical analysis. Experimental solubility of CO_2 in MAE is compared with solubility data of other amine solutions available in the literature.

A mathematical model was derived based on the reaction mechanism proposed in the literature. This model can be applied to find the solubility of CO_2 in aqueous MAE at various conditions. The results of the proposed mathematical model are compared with the experimental data and the accuracy of the model was assessed using absolute mean percentage error and coefficient of determination.

1.4 STRUCTURE OF THE THESIS

The thesis evaluates the performance of MAE as absorbent for CO_2 in comparison with other solvents. The study consists of two parts; theoretical and experimental.

Chapter 1 introduces the process of amine technology for carbon dioxide capture and gives an outline of the study method. It also defines the scope and objectives of this thesis.

Chapter 2 is a literature review which covers the work done on different types of amine solvents with emphasis on MAE. The literature review also covers reaction mechanism, VLE studies and factors affecting solubility of CO_2 in alkanolamines.

Chapter 3 deals with the reaction mechanism of carbon dioxide with alkanolamines in general and with MAE in particular. It also describes the mathematical model proposed for predicting the solubility of carbon dioxide in MAE, including techniques used for choosing the values of the equilibrium constants, other variables and model parameters.

Chapter 4 describes the experimental procedure and the types of equipment and chemicals used for determining the CO_2 loading in MAE at different operating conditions of temperature, CO_2 partial pressure and amine concentration.

Chapter 5 lists the results of the experimental solubility data of CO_2 in MAE at different operating conditions. It also includes a comparison of the solubility data of MAE with other types of amines and a discussion of these results.

Chapter 6 presents results and discussion of the calculated CO_2 loading in MAE using the proposed mathematical model described in chapter 3. It also gives a comparison between the experimental results and the theoretical results using the coefficient of determination and the absolute mean percentage error as measures for comparison.

Chapter 7 gives the conclusion of the study and some suggestions and recommendations for future work in this field.