# CHAPTER I

# INTRODUCTION

Approximately, 90% of the world's primary energy is currently derived from the use of fossil fuels (Gupta et al., 2003). In terms of measurable reserves, the distribution is in the order of oil, natural gas and coal, respectively having shares of 38, 31, and 28% as illustrated in Figure 1.1. Although fossil fuels contribute to such a significant energy supply, an environmental concern over the emission of carbon dioxide ($CO_2$), a major greenhouse gas, can limit their use.
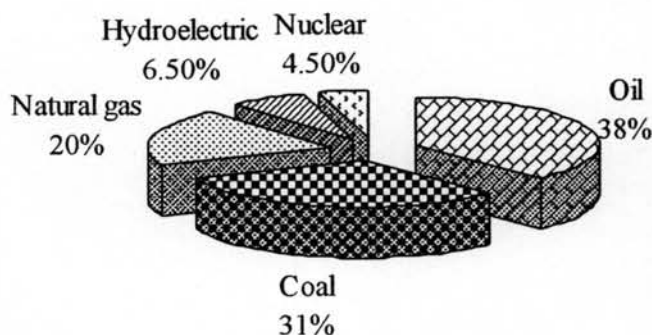


**Figure 1.1** Distribution of world's energy supply (Speight, 1994).

In a conversion process for power generation, using coal combustion as an example, $CO_2$ is produced through a series of reactions. According to Berkowitz (1994), the release of $CO_2$ is a result of the oxidation reaction of carbon monoxide (CO), initially formed by chemisorption of oxygen ($O_2$) at active sites on coal particle surfaces. $CO_2$ is either converted further to CO by impinging on the coal particles or escapes into the off-gas stream. In addition, $CO_2$ may be generated through a reaction of CO and molecules of water ($H_2O$) available within the combustion system. Carbon-oxygen reactions in coal combustion process including $CO_2$ formation steps are given in the following equations;

$$2C + O_2 \rightarrow CO \tag{1.1}$$

$$2CO + O_2 \rightarrow CO_2 \tag{1.2}$$

$$CO_2 + C \rightarrow 2CO \tag{1.3}$$

$$C + O_2 \rightarrow 2CO \tag{1.4}$$

$$H_2O + C \rightarrow CO + H_2 \tag{1.5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1.6}$$

There has been an increased use of coal for power generation in the past decades. As summarized in the literature (IEA coal research, 2001), during 1991-1998, over twice the capacity of coal-fired application was installed in non-OECD countries compared to OECD countries (Organisation for Economic Co-operation and Development). IEA coal research (2001) has also estimated that the future growth in the use of coal for power generation until the year 2020 is likely to be in North America as well as in developing countries. This rapid growth has raised a serious environmental concern due to the emission of $CO_2$. This uncontrolled emission of $CO_2$ can upset the environmental system by enhancing the greenhouse effect which can potentially cause change in global climate pattern.

## 1.1 Enhanced Greenhouse Effect and Coal-induced $CO_2$ Emission

Greenhouse effect is a term used to represent a natural occurring process essentially needed for controlling the global surface temperature to make lives on Earth possible. According to Drake (2000), when the sun emits its solar energy in the form of short wave radiation to the Earth, some of the radiation is reflected back into the space by the Earth's atmospheric layer. The layer consisting of nitrogen ($N_2$), oxygen ($O_2$), argon (Ar), water vapor ($H_2O$), $CO_2$, and traces of other greenhouse gases (i.e. methane and nitrous oxide) mostly allows the radiation to pass through and be absorbed by the Earth's surface. The exhausted radiation of long wave length infrared is then emitted back by the Earth's surface to maintain the energy balance. A small portion of this outgoing radiation is lost to space. On the other hand, most of it

does not carry enough energy to penetrate through the greenhouse gas layer. Instead, it is absorbed and reradiated back. This energy is then confined between the atmospheric layer and the surface of the Earth. As a result, the trapped energy warms the Earth's surface, thus creating unliveable environment. It is clear that the greenhouse gas layer plays a vital role in the control of the Earth's surface temperature. Drastic increases in the concentrations of these atmospheric gases could therefore trap more heat. As a result, the temperature of the Earth's surface could be raised. This impact of an increase in greenhouse gas concentration to the global temperature is a serious concern, and is known as enhanced greenhouse effect.

The emission of $CO_2$ from fossil fuel-derived power generation has become a major concern because its uncontrolled release has started to show evidence of the enhanced greenhouse effect. As summarized by Davison (2007), with the current rate of fossil fuel use, the main source of $CO_2$ emission are derived from power generation, industrial processes, transportation, and residential and commercial buildings. The contribution of each source is shown in Figure 1.2.
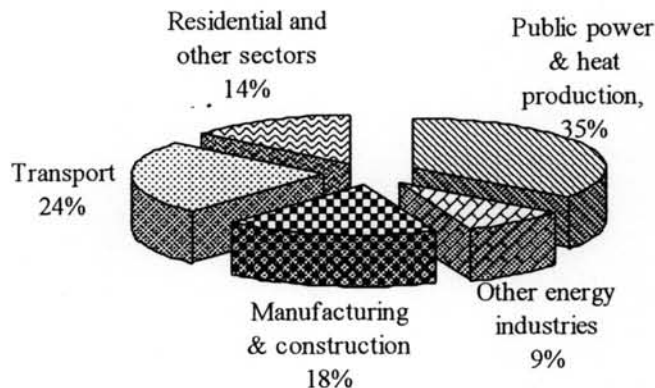


**Figure 1.2** $CO_2$ emission from fossil fuel use (Davison, 2007).

For power generation, approximately one third of $CO_2$ emission is mainly from the use of coal and natural gas (Davison, 2007). Coal alone is globally responsible for 28 - 36 % of $CO_2$ emission (Smith and Thambimuthu, 1993). With a lack of proper control technique, especially in coal-fired power generation, the

emitted $CO_2$ can aggravate the enhanced greenhouse effect causing a rise of the Earth's temperature and a change in global climate pattern. In addition, coal-fired flue gas streams to be utilized in industrial processes such as coal gasification must meet the $CO_2$ concentration targets. Table 1.1 shows $CO_2$ clean-up targets requirement for coal gasification with other industrial processes.

**Table 1.1** $CO_2$ clean-up target for various industrial processes (Astarita, 1983)

| Process | Clean-up target |
|---|---|
| Hydrogen manufacture | < 0.1% $CO_2$ |
| Ammonia Manufacture ($H_2/N_2$ mixture) | < 16 ppm $CO_2$ |
| Natural gas purification | |
| - Pipeline gas | < 1% $CO_2$ |
| - LNG feedstock | < 50 ppm $CO_2$ |
| Coal gasification | |
| - High Btu gas | 500 ppm $CO_2$ |
| - Intermediate Btu gas | 500 ppm $CO_2$ |
| - Low Btu gas | 500 ppm $CO_2$ |
| Systhesis gas for chemical ($H_2/CO$) | < 500 ppm $CO_2$ |

Several techniques could be undertaken such as improved energy efficiency and use of alternative energy sources to help reduce the $CO_2$ emission rate. Although, these approaches look promising but they still pose some concerns. For example, the use of alternative sources of energy could cause a serious disruption to the global economy if moving away from the use of fossil fuel, especially coal, is too rapid (Davison, 2007). Therefore, the capture of $CO_2$ from large point sources of coal-fired power plants in order to mitigate $CO_2$ emissions becomes the technology of choice. Within this envelope, specific technologies include oxyfuel combustion, gasification and post combustion capture by solvent absorption. In the case of low pressure-coal derived flue gas streams, absorption with chemical reaction using aqueous alkanolamine solutions has been found attractive for $CO_2$ capture demonstrated in the literature (Idem et al., 2006).

## 1.2 CO₂ Absorption Process

According to Kohl and Riesenfeld (1985), the capture technology was first developed as early as 1930 for natural gas treatment with its application having been found attractive also for coal derived flue gas purification. A simplified diagram for the $CO_2$ capture process using alkanolamine is demonstrated in Figure 1.3.

For a general description, a stream of flue gas containing a relatively high concentration of $CO_2$ is introduced into the unit at the lower section of the absorber. It flows upwards to make countercurrent contact with a stream of aqueous alkanolamine solution fed from the top section of the absorber. Alkanolamine absorbs $CO_2$ leaving the treated $CO_2$-lean gas to exit at the top of the absorber. Alkanolamine with a high concentration of $CO_2$, referred to as the "rich solution", is collected at the bottom of the absorber. The rich solution is partially heated by a heat exchanger and is subsequently fed through the top of the stripper, to contact with a stream primarily consisting of water vapor and stripped $CO_2$ from a reboiler. Heat is given up by water vapor to free $CO_2$ from the rich downcoming alkanolamine solution. The $CO_2$ exits the stripper column to a condenser and reflux accumulator to recover water and carry over alkanolamine. It is finally collected at the end of the process. The alkanolamine containing a low concentration of $CO_2$, referred to as the "lean solution", is collected in the stripper bottom and passed through the heat exchanger and a water-cooling system where it is cooled before being fed back to the absorber to complete the cycle.

### 1.2.1 Alkanolamine Solutions

In terms of conventional alkanolamines, various selections are commercially available ranging from primary to tertiary alkanolamines. The classification is categorized by the number of substituting groups attached to the nitrogen atom (N) of the molecule. For example, monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are respectively primary, secondary, and tertiary alkanolamine. Their chemical structures are given in Figure 1.4. Among the conventional alkanolamines, MEA is the most extensively

used solvent due to its high reactivity to $CO_2$ in the absorption process (Goff and Rochelle, 2004). DEA is generally preferred when impurities such as COS are present in the feed gas. Although MDEA is a low reactive alkanolamine, its use is found in the selective removal of $H_2S$ in the presence of $CO_2$.
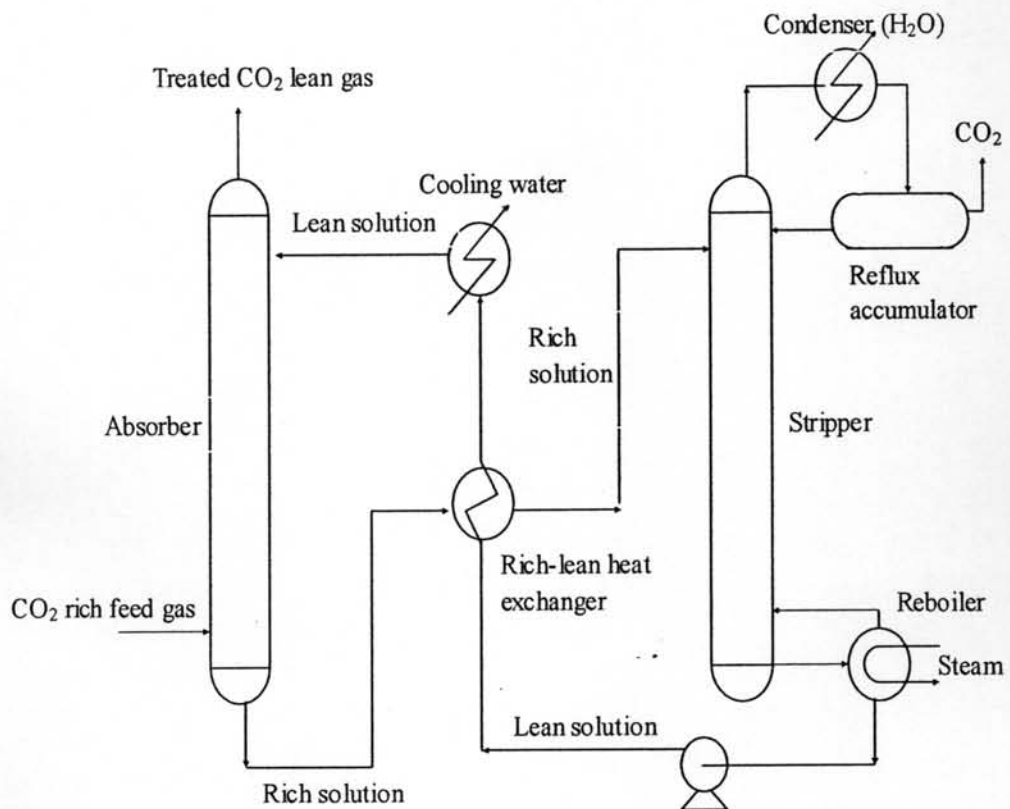


**Figure 1.3** Simplified alkanolamine-based $CO_2$ capture process.

H
 NCH₂CH₂OH        Monoethanolamine (MEA)
H

             CH₂CH₂OH
      H−N
             CH₂CH₂OH        Diethanolamine (DEA)

              CH₂CH₂OH
OHCH₂CH₂−N
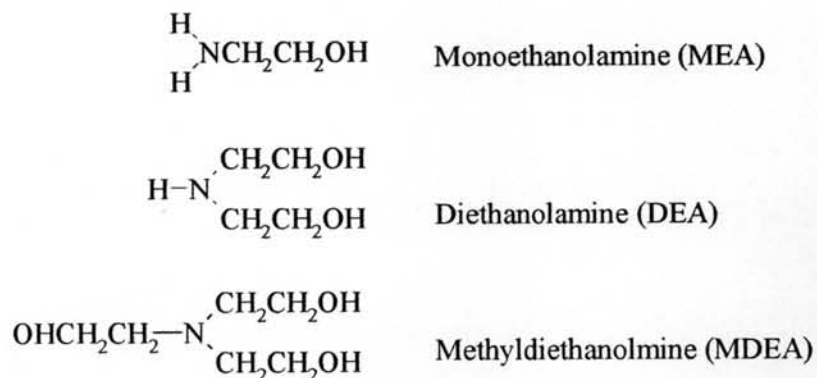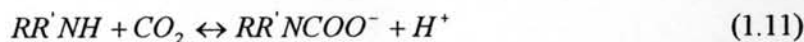              CH₂CH₂OH        Methyldiethanolmine (MDEA)

**Figure 1.4** Chemical structures of conventional alkanolamines.

In addition, certain quantities of MDEA, if mixed with MEA or DEA, could enhance the absorption capacity but reduce energy consumption of the process. Various studies have been conducted to show the benefit of using blended alkanolamines in $CO_2$ capture process. Ramachandran et al. (2006) has completed kinetic work of $CO_2$ absorption using blended MEA/MDEA. Also, a mixture of DEA and MDEA has been recently studied to obtain the $CO_2$ absorption kinetic data (Zhang, Zhang and Liu, 2002).

The advantages of alkanolamines used for capturing $CO_2$ from flue gases are summarized by Kohl and Reisenfeld (1985). According to chemical structure of alkanolamines, they at least contain one hydroxyl group (OH), which helps to reduce the vapor pressures while increasing the solubility in an aqueous solution. On the other hand, the amino group ($NH_2$) provides the necessary alkalinity to absorb $CO_2$. The mechanism of $CO_2$ absorption into alkanolamine solution is complex and not totally understood (Astarita et al., 1983). However, a generic mechanism proposed several decades ago could represent the absorption process (Danckwerts and McNeil, 1967). The absorption reaction is initiated by dissolution of $CO_2$ into water and the ionization of water followed by the formation of bicarbonate and carbonate ions by the dissolved $CO_2$ in the solution. Alkanolamine also reacts with the dissolved $CO_2$ forming carbamic acid which exists in the form of

a carbamate ion. The latter undergoes a hydrolysis reaction returning the alkanolamine and bicarbonate ion into the solution. A series of absorption reactions written in chemical equation form are shown as follows;

$$H_2O \leftrightarrow OH^- + H^+ \tag{1.7}$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{1.8}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{1.9}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{1.10}$$

$$RR'NH + CO_2 \leftrightarrow RR'NCOO^- + H^+ \tag{1.11}$$

$$RR'NH + H^+ \leftrightarrow RR'NH_2^+ \tag{1.12}$$

$$RR'NCOO^- + H_2O \leftrightarrow RR'NH + HCO_3^- \tag{1.13}$$

R represents an alkanol group. R' denotes an H for primary alkanolamines or an alkanol group for secondary alkanolamines. One exception to this mechanism is that tertiary alkanolamines do not form carbamate ions because they lack an ionizable H atom.

## 1.3 Research Motivation

Although, alkanolamine-based $CO_2$ absorption process has been used for a number of years. There still exist operational burdens that continuously upset absorption plants. One of these difficulties is that alkanolamines can undergo chemical fragmentations during the capture process. This break-down known as degradation is extremely undesirable since they result in solvent losses. As stated by Kohl and Reisenfeld (1985), the most serious solution loss is likely to be caused by alkanolamine degradation. To give a broad definition of degradation, it is a chemical change of an active alkanolamine in which it does not leave the system but is no longer available for removing $CO_2$ (Stuart and Lanning, 1994).

Alkanolamine degradation is a result of repeated use and long exposure to side reactions with $CO_2$, $O_2$, and other contaminants. In the case of coal derived flue gas streams, they often contain considerable concentration of $O_2$ as a result of combustion, in which it is known to deteriorate if brought into contact with alkanolamines (Hendricks, 1994). Typical concentrations of $O_2$ in a flue gas streams from coal-fired operation are given in Table 1.2

**Table 1.2**  Gaseous compositions of a typical coal-fired flue gas
(Chakma et al.,1995)

| Composition | Concentration (mole%) |
|---|---|
| $CO_2$ | 7 - 15 % |
| $O_2$ | 2 - 12% |
| $N_2$ | 65 - 75% |
| $H_2O$ | 5 - 15% |
| $SO_2$ | 2 - 400 ppm |
| $SO_3$ | 1 - 10 ppm |
| $NO_x$ | 1 - 400 ppm |

\* Composition was analysed after $SO_2$ scrubbing

In addition, $O_2$ also contaminates the system through alkanolamine storage tanks without a gas blanket (Stuart and Lanning, 1994). These $O_2$ quickly induce alkanolamine degradation resulting in reduction of $CO_2$ removal capacity of alkanolamines and introduce unwanted degradation products into the solution. The negative corrosive effect towards plant equipment of these degradation products have been periodically reported in the literatures (Howard and Sargent, 2001; Rooney, Bacon, and Dupart, 1996; Rooney, Dupart, and Bacon, 1997). The alkanolamine solution contaminated by these degradation products often requires a reclaiming unit to treat approximately 1 – 5% side stream of the contaminated solution to liberate the alkanolamine from the products prior to returning the solvent to the system. It has been reported that as much as 10% of contaminated alkanolamine streams need to be purified in the reclaimer, thus, increasing operational cost and energy consumption (Chakma and Tontiwachwuthikul, 1999). In some severe cases, heavily contaminated

solvents must be eventually replaced with fresh ones giving rise to additional cost of disposal and alkanolamine make-up.

Past research has provided useful information on various aspects of oxidative degradation of alkanolamines, in which the most attention has been given to the identification of degradation products (Blanc, Grall, and Demarais, 1982; Hofmeyer, Scholten, Lloyd, 1965; Strazisar, Anderson, and White, 2003) and formation of heat stable salts (Rooney and Dupart., 2000, Veldman, 2000). Also, the kinetics of the degradation has recently gained a considerable interest over the past years since this provides the elements for a better understanding of the degradation mechanism during the $CO_2$ absorption operation. A kinetic evaluation also helps in the formulation of a degradation prevention strategy which is considered to be the overall goal of degradation studies (Rochelle et al., 2002). However, its formulation is so far limited to measurement of either the concentration decline of alkanolamine reactant or production rate of a gaseous product (Chi and Rochelle, 2002; Goff and Rochelle, 2004; Lawal and Idem, 2006; Supap et al., 2001). A more favorable kinetics based on a degradation mechanism has been also proposed for the system of $MEA-O_2-H_2O$ with/without $CO_2$ and sodium metavanadate (Bello and Idem, 2006).

Although these studies that were based only on the presence of $O_2$ in the flue gas could provide useful knowledge, their application is limited to and compatible with systems only containing $O_2$ such as natural gas-fired power plant flue gases. To apply these studies to coal fired-based application in which an aqueous alkanolamine solution is used to remove $CO_2$ would give inaccurate results due to the presence of other impurities such as $SO_2$. Even though present in ppm level, as shown in Table 1.2, $SO_2$ can dissolve and be carried in the alkanolamine solution to the regeneration section of the capture process at which point a high temperature can trigger serious degradation reactions with the alkanolamine solvent. Negative effects of some sulfur-containing impurities in alkanolamine degradation have also been reported in terms of being capable of forming heat stable salts such as thiosulfate and sulfate (Smit, Van Heeringen, and Van Grinsven 2002; Veldmann, 2000). Although, the most recent kinetic study has taken into account the effect of $SO_2$ by incorporating $SO_2$ into the MEA degradation rate equation using power law

rate analysis (Uyanga and Idem, 2007). The kinetics still fails to describe the degradation roles of all species (e.g. MEA, $O_2$, $SO_2$ and $CO_2$) because its development was not based on any mechanism.

### 1.3.1 Research Objectives

The present study was conducted to establish the degradation roles of MEA, $O_2$, $SO_2$ and $CO_2$ to address this urgent need, and to achieve a more realistic scenario as used in $CO_2$ absorption from both coal- and natural gas-fired power plant flue gas streams. MEA was chosen as the solvent because of its popularity and high $CO_2$ removal capacity since it has a high reactivity and is thus able to effect a high volume of acid gas removal at a fast rate. The MEA concentration used was in the range of 3-7 $kmol/m^3$. Simulated flue gas streams, which varied in $O_2$ and $SO_2$ concentrations between 6-100% and 0-196 ppm, respectively were used to mimic the natural gas or coal derived flue gas streams. $CO_2$ loading ranging from 0-0.55 mole $CO_2$/mole MEA was selected so they could represent the actual values found in $CO_2$ capture process. As well, the degradation temperatures of 328-393 K were also chosen in accordance with the absorption/regeneration conditions used in a typical $CO_2$ capture unit. The objectives of the present study are given as follows:

1.3.1.1 Analysis of MEA and its oxidative degradation products during $CO_2$ absorption from flue Gases: A comparative study of GC-MS, HPLC-RID and CE-DAD analytical techniques and possible optimum combinations

The establishment of the roles of the degradation species required the development of an adequate analytical technique that must be able to effectively identify and monitor a wide variety of the products typically formed within the degradation systems. Prominence was therefore given to the establishment of analytical techniques in the current study. The objective was to develop improved methods as well as explore the best combinations of gas chromatographic, liquid chromatographic and capillary electrophoresis analytical techniques to completely characterize the oxidative degradation of two aqueous monoethanolamine systems, MEA-$H_2O$-$O_2$ and MEA-$H_2O$-$O_2$-$CO_2$. In the GC-MS technique, 3 different chromatographic columns of different stationary phase polarity were evaluated for

separation, detection, identification, and quantification of MEA and its degradation products for both systems. On the other hand, in the HPLC technique, 2 different columns and 2 different mobile phases were evaluated for the same purpose. The capillary electrophoresis technique (CE) with selected electrolyte solutions was also explored. Some standards were used to identify degradation products using spiking techniques. The results for all the techniques are reported in terms of compatibility of each analytical technique to separation of aqueous MEA and its oxidative degradation products as well as the best combinations of techniques to achieve this objective.

1.3.1.2 Studies of $SO_2$ and $O_2$ induced degradation of aqueous MEA solution during $CO_2$ absorption from power plant flue gas streams

This was based on developing mechanism based kinetic models for degradation of MEA in the presence of aqueous MEA, $O_2$, $SO_2$ and $CO_2$. Also, the roles of the concentrations of MEA, $O_2$, $SO_2$ and $CO_2$ and degradation temperature were evaluated. A total of four kinetic models were developed for evaluation out of which two were empirical (power law and modified power law) models while two were mechanism based (split and combined) models. The analysis of the kinetic models for the degradation of MEA was performed using 3 major criteria of model limitation in predicting MEA degradation rate, accuracy, and usability in describing the degradation mechanism.

1.3.1.3 Preliminary study of degradation prevention techniques using degradation inhibitors for MEA based $CO_2$ absorption from power plant flue gases

A number of degradation inhibitors was investigated for their effectiveness in minimizing the degradation of aqueous MEA used for the absorption of $CO_2$ from coal-fired power plant flue gases (i.e. MEA-$O_2$-$SO_2$ system). The ranges of experimental conditions were selected to duplicate the extremes that would be encountered in a $CO_2$ capture process in a coal fired power plant. Based on the ability to simultaneously scavenge $O_2$ and $SO_2$, inhibitor A was selected as a potential inhibitor for oxidative degradation of MEA for the systems with/without

$SO_2$. The inhibitor was initially evaluated to confirm its positive effect in reducing MEA degradation rate. Its concentration was then varied to search for the optimum concentration required to best retard the degradation rate of MEA.