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*Original Article*

# Degradation kinetics of monoethanolamine during $CO_2$ and $H_2S$ absorption from biogas

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**Abstract**

The rate of degradation of MEA during $CO_2$ and $H_2S$ absorption in the biogas upgrading process was examined in four degradation systems, i.e., MEA-$CO_2$, MEA-$CO_2$-$O_2$, MEA-$CO_2$-$H_2S$ and MEA-$CO_2$-$O_2$-$H_2S$. Degradation experiments were performed in a 800-ml stainless steel autoclave reactor, using MEA concentrations of 3 and 5 mol/L, $CO_2$ loadings of 0.4 and 0.5 mol $CO_2$/mol MEA, $O_2$ pressure of 200 kPa, and $H_2S$ concentrations of 84 and 87 mg/L at temperatures of 120 and 140°C. The results showed that, for the MEA-$CO_2$ system, an increase in temperature or MEA concentration resulted in a higher rate of MEA degradation. In contrast, an increase in $CO_2$ loading in the MEA-$CO_2$-$O_2$ system led to a reduction of MEA degradation. The degradation rate of the system with $O_2$ was with 8.3 times as high as that of the system without $O_2$. The presence of $H_2S$ did not appear to affect the rate of degradation in the MEA-$CO_2$-$H_2S$ system. However, for the system in which both $H_2S$ and $O_2$ were present, the MEA degradation was additionally induced by $H_2S$, thus, resulting in higher degradation rates than those of the system with $O_2$ only. The extent of degradation under the same period of time increased in the order MEA-$CO_2$, MEA-$CO_2$-$H_2S$ < MEA-$CO_2$-$O_2$ < MEA-$CO_2$-$O_2$-$H_2S$.

**Keywords:** monoethanolamine, degradation, carbon dioxide, absorption, biogas

## 1. Introduction

The current use of fossil fuels is rapidly depleting the natural reserves. The natural formation of coal and oil however, is a very slow process which takes ages. Therefore, a lot of research efforts are put into finding renewable fuels nowadays to replace fossil fuels. Renewable fuels are in balance with the environment and contribute to a far lesser extent to the greenhouse effect. Biogas, considered to be a renewable and sustainable energy source, is produced in a large number of biogas plants from a manifold of substrates like energy crops, organic wastes or agrarian residues (Deublein and Steinhauser, 2008; Lombardi and Carnevale, 2013). Biogas produced in anaerobic digestion plants is primarily composed of 55-65% of methane ($CH_4$) and 35-45% of carbon dioxide ($CO_2$) with smaller amounts of hydrogen sulfide ($H_2S$) and ammonia ($NH_3$) (Appels *et al.*, 2008; Xuan *et al.*, 2009). Trace amounts of hydrogen ($H_2$), nitrogen ($N_2$), carbon monoxide (CO), and oxygen ($O_2$) are occasionally present in the biogas (Rasi *et al.*, 2007). Conversion of the chemical energy contained in biogas to heat or electricity is possible through combustion. For many applications such as

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for heat and electricity production, or for vehicle fuels, the quality of biogas has to be improved. The main parameters that may require removal in an upgrading system are $H_2S$ and $CO_2$. $CO_2$, usually present in large quantities in biogas, is an inert gas in terms of combustion, thus decreasing the energetic content of the biogas. Depending on the composition of the organic material fermented, the $H_2S$ content of biogas can vary from 1,000 to about 3,000 ppm (Alonso-Vicario *et al.*, 2010). This contaminant, besides its bad smell, is highly non-desirable in energy-recovery processes because it converts to highly corrosive, unhealthy and environmentally hazardous sulfur dioxide ($SO_2$) and sulfuric acid ($H_2SO_4$).

Various technologies have been developed for separation of $CO_2$ from gas streams. These include absorption by chemical solvents, physical absorption, cryogenic separation, membrane separation, and biological methane enrichment (Ryckebosch *et al.*, 2011). However, the method that has been widely used on an industrial scale is chemical absorption using an aqueous solution of alkanolamines as a solvent. In this method, $CO_2$ is separated from a gas stream by passing the gas stream through a continuous scrubbing system consisting of an absorber unit and a stripper unit (regenerator). After absorbing $CO_2$ in the absorber, the $CO_2$-rich amine solution is then routed into the stripper where the temperature is raised to produce regenerated or lean amine solution that is recycled for reuse in the absorber. The absorber temperature is typically around 40-55°C, and the stripper temperature is around 100-140°C (IPCC, 2005). Although there are different types of industrially utilized alkanolamines; monoethanolamine (MEA) is a widely used solvent for $CO_2$ absorption because of its high absorption capacity, fast kinetics, high water solubility, low price, and other advantages (Mandal *et al.*, 2001; Lepaumier *et al.*, 2009). In general, MEA has the highest $CO_2$ separation rate, which leads to relatively low overall costs (Ma'mun *et al.*, 2007). Moreover, MEA can also absorb $H_2S$ in gas streams through a reversible and instantaneous reaction (Al-Baghli *et al.*, 2001). This has led to using MEA as an absorbent for simultaneous removal of $CO_2$ and $H_2S$ from gas streams such as natural gas and biogas.

A major problem associated with chemical absorption using MEA is the degradation of the solvent through irreversible side reactions with $CO_2$ and other gases in the gas streams. MEA in these processes are subject to two main types of degradation, thermal and oxidative degradation (Goff and Rochelle, 2004). Thermal degradation, also known as carbamate polymerization, occurs at stripper conditions (around 120°C for MEA) in the presence of $CO_2$. Oxidative degradation occurs in the presence of oxygen, resulting in fragmentation of the amine solvent (Goff and Rochelle, 2004). The amine degradation deteriorates the performance of the amine in the absorption process. Not only is the absorption capacity reduced, but also corrosion and foaming are induced due to the presence of degradation products, thus, forcing the solution to be eventually discarded (DeHart *et al.*, 1999; Strazisar *et al.*, 2003). The prediction of the extent and rate of amine degradation is vital in the estimation of the exact amine make-up rate needed to maintain the absorption capacity of the $CO_2$ and/or $H_2S$ removal process. It is also essential to evaluate the kinetics of the degradation process since this provides the elements for a better understanding of the degradation mechanism during the $CO_2$ and/or $H_2S$ 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.

Degradation studies of amines including MEA have been reported over the past several years (Bedell *et al.*, 2011; Lepaumier *et al.*, 2011; Zhou *et al.*, 2012). However, most of these studies have focused on the understanding of the processes of $CO_2$ capture from flue gas which contains $CO_2$, $O_2$, $SO_x$, and $NO_x$. Limited information is available on the MEA degradation occurring during $CO_2$ and $H_2S$ absorption in the biogas upgrading process. The present study was therefore conducted to evaluate the degradation of MEA in the presence of $CO_2$, $O_2$ and $H_2S$. The effects of operating parameters such as temperature, initial MEA concentration, and $CO_2$ loading were also evaluated.

## 2. Methodology

### 2.1 Materials

Concentrated MEA (research grade, 97% purity) was obtained from Fisher Scientific. For each experimental run, MEA was diluted with deionized water to the desired concentration and then standardized using 1 M Hydrochloric acid (Supap *et al.*, 2009). $CO_2$ (99.97% purity), $O_2$ (99.99% purity) and biogas, which was obtained from the wastewater treatment plant of a local swine farm, were used as feed gas.

### 2.2 Equipment

The closed vessel that was used to carry out the MEA degradation study was a 800 ml-stainless steel reactor. The reactor consisted of a gas feed port, a gas outlet port, a liquid sampling tube, a pressure gauge, a thermowell, an impeller and an electric heating jacket, as shown in Figure 1. A K-type thermocouple placed in the thermowell was used to measure the temperature of the reaction mixture, while the heating jacket, controlled by a proportional-integral-derivative temperature controller (PID), was used to supply heat to the reactor. The accuracy of the temperature control was within ±1°C.

### 2.3 Experimental procedure

Four systems were evaluated for the degradation of MEA. The first system (MEA-$CO_2$) was used to establish the contribution of $CO_2$ alone to the degradation of MEA. The second system (MEA-$CO_2$-$O_2$) was used to evaluate the contribution of both $CO_2$ and $O_2$ to the MEA degradation. The third (MEA-$CO_2$-$H_2S$) and fourth system (MEA-$CO_2$-$O_2$-

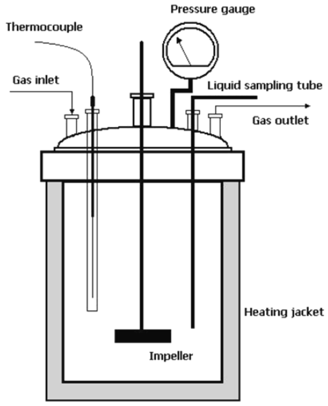


Figure 1. Schematic diagram of the reactor.

$H_2S$), respectively, were used to evaluate the first two systems, in the presence of $H_2S$.

### 2.3.1 MEA-$CO_2$ degradation system

Each experimental run was conducted using aqueous solutions of 3 and 5 mol/L MEA. These MEA concentrations are widely used for $CO_2$ capture or gas treatment in industries (Strazisar *et al.*, 2003; Lepaumier *et al.*, 2009). The MEA solution was loaded with $CO_2$ by bubbling pure $CO_2$ through the solution until the desired concentration was reached. The time needed to introduce $CO_2$ into the MEA solution depended on the desired $CO_2$ loading. This ranged from 30 to 45 minutes for $CO_2$ loading in the range of 0.4-0.5 mol $CO_2$/mol MEA. The $CO_2$ loading of the solution was determined using the aqueous HCl volumetric titration and $CO_2$ displacement technique outlined by AOAC (1990). The $CO_2$-loaded MEA solution of 500 ml was then transferred into the reactor and stirred at 350 rpm while being heated to the desired temperature (120-140°C). Once the reaction mixture reached the desired temperature, the pressure inside the reactor at this point was a combination of pressure of water vapor and non-dissolved $CO_2$. At predetermined intervals of time, samples of about 3 ml were withdrawn from the reactor through the liquid sampling valve into 5-ml sampling bottles. After each sampling, extra $CO_2$ from gas cylinder was added into the reactor to compensate for the pressure loss during the sampling process and to maintain the constant pressure of the system. To avoid further degradation, the sample was quickly quenched by running cold water over the sample bottle for several minutes and was then kept in a refrigerator at 4°C for GC analysis. Table 1 lists all of the experimental operating conditions used in this study.

### 2.3.2 MEA-$CO_2$-$O_2$ degradation system

The experimental procedure for the MEA-$CO_2$-$O_2$ degradation system was similar to that of the MEA-$CO_2$ degradation system except that $O_2$ was introduced into the system in addition to $CO_2$. After being loaded with $CO_2$, the MEA solution of 3 mol/L was transferred into the reactor. The solution was stirred and heated to the desired temperature. When the reaction mixture reached the desired temperature, $O_2$ at 200 kPa pressure was additionally introduced into the system through the gas inlet valve by opening the $O_2$ cylinder tank. The total pressure of the reactor at this point was therefore the sum of water vapor pressure, $CO_2$ vapor pressure and 200 kPa of $O_2$.

### 2.3.3 MEA-$CO_2$-$H_2S$ degradation system

The reaction was conducted using 3 mol/L MEA. The untreated biogas consisting of 61.8% of $CH_4$, 38.1% of $CO_2$ and 1,726 ppm of $H_2S$ from the chosen swine farm was used as a source of $CO_2$ and $H_2S$ for loading into the MEA solution. The biogas was bubbled into the solution until the desired $CO_2$ loading was reached. Since MEA solutions can simultaneously absorb $CO_2$ and $H_2S$, using this technique allowed these two gases to be loaded into the solution. In this study, when a $CO_2$ loading of 0.4 mol $CO_2$/mol MEA was reached a $H_2S$ concentration of 87 mg/L in the MEA solution was obtained. The solution loaded with $CO_2$ and $H_2S$ was then transferred into the reactor and the rest of the procedure was the same as that of the MEA-$CO_2$ degradation system.

### 2.3.4 MEA-$CO_2$-$O_2$-$H_2S$ degradation system

Solutions of 3 mol/L MEA with the $CO_2$ loading of 0.4 mol $CO_2$/mol MEA were used in this system. The biogas

Table 1. Experimental operating conditions.

| Parameter | conditions |
|---|---|
| MEA-$CO_2$ system | |
| temperature (°C) | 120, 140 |
| MEA concentration (mol/L) | 3, 5 |
| $CO_2$ loading (mol $CO_2$/mol MEA) | 0.4 |
| MEA-$CO_2$-$O_2$ system | |
| temperature (°C) | 120 |
| MEA concentration (mol/L) | 3 |
| $CO_2$ loading (mol $CO_2$/mol MEA) | 0.4, 0.5 |
| $O_2$ pressure (kPa) | 200 |
| MEA-$CO_2$-$H_2S$ system | |
| temperature (°C) | 120 |
| MEA concentration (mol/L) | 3 |
| $CO_2$ loading (mol $CO_2$/mol MEA) | 0.4 |
| $H_2S$ concentration (mg/L) | 87 |
| MEA-$CO_2$-$O_2$-$H_2S$ system | |
| temperature (°C) | 120 |
| MEA concentration (mol/L) | 3 |
| $CO_2$ loading (mol $CO_2$/mol MEA) | 0.4 |
| $O_2$ pressure (kPa) | 200 |
| $H_2S$ concentration (mg/L) | 84 |

was also used as a source of $CO_2$ and $H_2S$ for loading into the MEA solution. Each experimental run began by bubbling the biogas through the MEA solution until the $CO_2$ loading reached 0.4 mol $CO_2$/mol MEA, with 84 mg/L of $H_2S$ obtained in the solution. The MEA solution was then loaded into the reactor. The rest of the procedure was similar to that of the MEA-$CO_2$-$O_2$ degradation system.

### 2.4 Sample analysis

Samples from the degradation systems were analyzed using a gas chromatograph (GC model HP 7890 supplied by Hewlett-Packard Ltd., U.S.A.). An HP-Innowax column packed with the dimension of 0.25-µm thickness × 250-µm inside diameter × 30-m length was used in the GC for the separation of components. The introduction of sample into the GC column was done using an autosampler/autoinjector supplied by Hewlett-Packard Ltd. For a typical run, a 1-µL sample was injected at the GC inlet set at 250°C using a split injection mode with a split ratio of 30:1. The GC oven was initially set at 100°C and ramped to 190°C at a rate of 20°C/min and then to 240°C at a rate of 25°C/min. The samples were analyzed twice to check for reproducibility. Degradation of MEA was measured in terms of reduction in MEA over a period of time. This involved plotting of calibration curves for MEA for which known concentrations of pure MEA (ranging from 0.25-5 mol/L) were prepared. These samples were analyzed by GC to obtain peak areas. The concentrations of the pure samples were plotted against the corresponding peak areas. For each degradation sample analyzed, the GC was used to obtain the peak areas of MEA in the sample. The concentrations of MEA were then calculated using the equations obtained from the calibration curves.

For all the degradation systems investigated , the concentrations of MEA were plotted against time (concentration-time curve) to represent the kinetic data. Experimental degradation rates in terms of instantaneous rates were evaluated as slopes of the concentration-time curves. The rates were obtained as follows. Initially, a concentration-time curve was plotted for all the systems investigated. This was followed by curve fitting of the data by using an exponential function available on Microsoft Excel. The equation of the line was obtained and differentiated to obtain the rate at each instant of time. The rate data obtained was then plotted versus time to obtain the rate-time plots. The initial degradation rates at time zero were then determined from the slope of the concentration–time curve at time zero using the line of best fit equation. Therefore, the initial rates shown throughout this study involved all the concentration–time data points. The initial degradation rates were used for comparison because these values represent the conditions where the rates are unaffected by competition of the reaction products with MEA for $CO_2$, $O_2$, or $H_2S$ available in the reaction mixture (Supap *et al.*, 2009). The degradation rates were also evaluated in terms of overall rate, which was calculated using Equation 1:

$$\text{Overall degradation rate} = \frac{\Delta[MEA]}{\Delta t} \qquad (1)$$

where $\Delta[MEA]$ represents the overall change in MEA concentration and $\Delta t$ represents time taken to obtain this change. Besides, the extents of degradation of the systems at the end of experiments were compared using Equation 2:

$$\text{Extent of degradation} = \frac{[MEA]_0 - [MEA]_t}{[MEA]_0} \times 100 \qquad (2)$$

where $[MEA]_0$ and $[MEA]_t$ represent initial and remaining MEA concentrations, respectively.

## 3. Results and Discussion

### 3.1 MEA-$CO_2$ degradation system

In the MEA-$CO_2$ degradation system, the effects of operating parameters on the extent of MEA degradation to be investigated were temperature and initial MEA concentration.

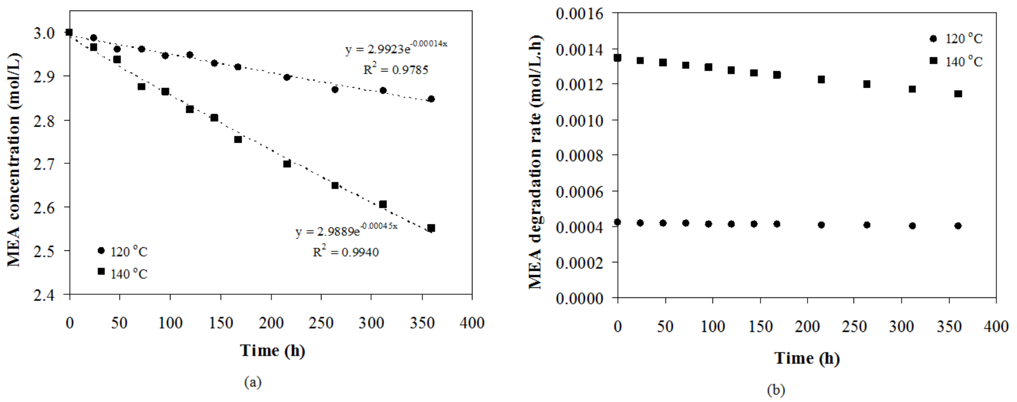
### 3.1.1 Effect of temperature

The effect of temperature was evaluated by using 3 mol/L MEA and 0.4 mol/mol $CO_2$ loading at 120 and 140°C, and the results are shown in Figure 2. It is obvious from Figure 2(a) that the MEA concentration of the run conducted at 140°C decreased more rapidly than that of the run carried out at the lower temperature of 120°C. Figure 2(b) shows that the initial MEA degradation rate (at time zero) at 140°C, which was $1.34\times10^{-3}$ mol/L·h, was approximately 3.2 times higher than that at 120°C, which was $4.19\times10^{-4}$ mol/L·h. This indicates that the rate of degradation increases with an increase in temperature. This is expected because, at a higher temperature, more products can overcome the energy barrier required for their reaction with MEA, thus, resulting in higher rates of MEA disappearance in the system.

The degradation of amines, such as MEA, at high temperatures in the presence of $CO_2$ can be categorized as thermal degradation (Davis and Rochelle, 2009). The high temperature and high $CO_2$ concentration in the solvent regeneration section of a gas absorption plant are the right conditions for thermal degradation of amines. The high temperature will break the chemical bonds of amines and increase the reaction rate of amines reacting with $CO_2$ to form high molecular weight degradation products (Carbamate polymerization), which will cause loss of amines in the system.

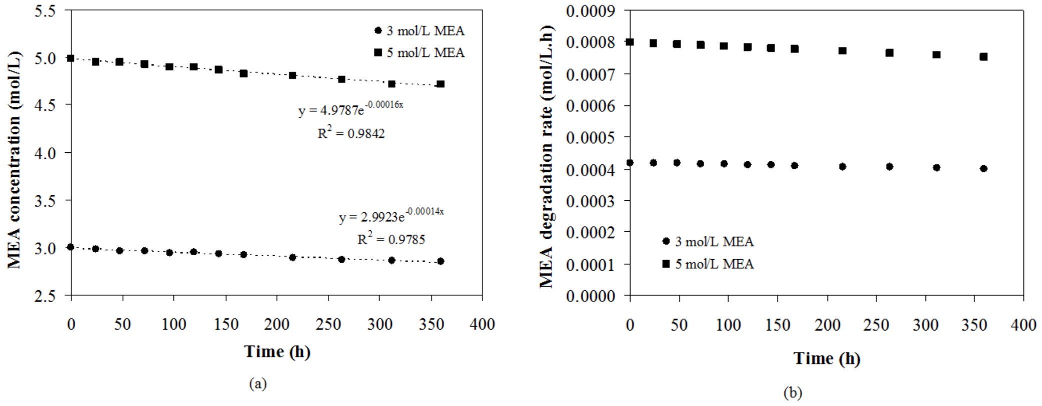
### 3.1.2 Effect of initial MEA concentration

The effect of MEA concentration was verified using experimental runs with 3 and 5 mol/L MEA and 0.4 mol/mol $CO_2$ loading at 120°C. The plots of MEA concentration and degradation rate versus time for both MEA concentrations



(a) (b)

Figure 2. (a) MEA concentration against time and (b) rate of MEA degradation against time at 120 and 140°C for the MEA-$CO_2$ system using 3 mol/L MEA and 0.4 $CO_2$ loading.



(a) (b)

Figure 3. (a) MEA concentration against time and (b) rate of MEA degradation against time for the MEA-$CO_2$ system using 3 and 5 mol/L MEA at 120°C and 0.4 $CO_2$ loading.

are given in Figure 3. Figure 3(a) shows that the concentrations of both 3 and 5 mol/L MEA decreased quite slowly with time. However, when the degradation rate was considered, Figure 3(b), the experimental run conducted with 5 mol/L MEA resulted in $7.97\times10^{-4}$ mol/L·h of initial degradation rate, which was around 90% higher than that of the run carried out with 3 mol/L MEA ($4.19\times10^{-4}$ mol/L·h). This indicates that the rate of degradation increases with an increase in initial MEA concentration because more amine is available for the degradation reaction.

## 3.2 MEA-$CO_2$-$O_2$ degradation system

### 3.2.1 Comparison of MEA-$CO_2$-$O_2$ with the corresponding MEA-$CO_2$ system

A comparison of the MEA-$CO_2$-$O_2$ system with the corresponding MEA-$CO_2$ system was made in order to obtain an understanding of the effect of the presence or absence of $O_2$ in a $CO_2$-loaded system. This was carried out by using 3 mol/L MEA with 0.4 mol/mol $CO_2$ loading, at 120°C, with and without 200 kPa of $O_2$ pressure. The concentration-time and degradation rate-time curves of the two systems are compared in Figure 4 and 5, respectively. The decrease in MEA concentration with time (Figure 4) in the system with $O_2$ was much more rapid than that without $O_2$. The degradation rate of the system with $O_2$ started with $4.27\times10^{-3}$ mol/L·h and decreased to $2.54\times10^{-3}$ mol/L·h at 360 hours (15 days) whereas that of the system without $O_2$ started with $4.19\times10^{-4}$ mol/L·h and decreased slightly to $3.98\times10^{-4}$ mol/L·h during the same period of time. These results showed that the degradation rate in the MEA-$CO_2$-$O_2$ system was with 8.3 times as high as that in the MEA-$CO_2$ system. This is consistent with the literature (Dawodu and Meisen, 1996), which shows that MEA is more prone to degradation in the presence of $O_2$ as compared to the presence of $CO_2$ only.

### 3.2.2 Effect of $CO_2$ loading

The effect of $CO_2$ loading was evaluated in experimental runs with 3 mol/L MEA and $O_2$ pressure of 200 kPa, at 120°C by comparing the results obtained using 0.4 mol/mol $CO_2$ loading with those of 0.5 mol/mol $CO_2$ loading. The plots of MEA concentration and degradation rate versus

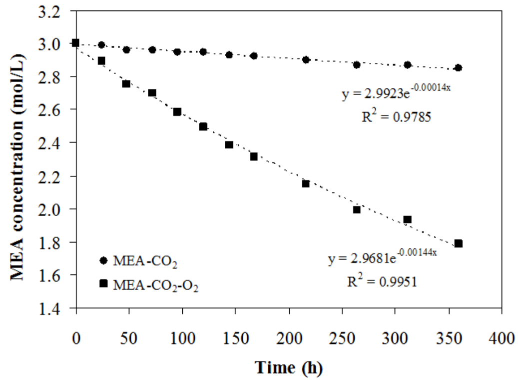


Figure 4. MEA concentration against time for the MEA-$CO_2$ and MEA-$CO_2$-$O_2$ systems using 3 mol/L MEA at 120°C and 0.4 $CO_2$ loading.

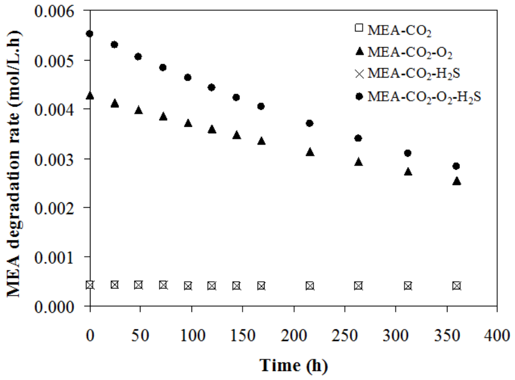
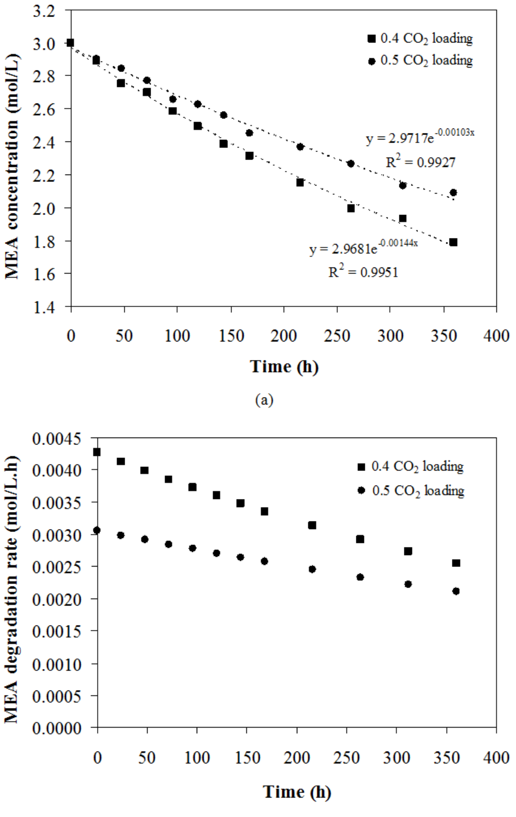


Figure 5. Rate of MEA degradation against time for the MEA-$CO_2$, MEA-$CO_2$-$O_2$, MEA-$CO_2$-$H_2S$ and MEA-$CO_2$-$O_2$-$H_2S$ systems using 3 mol/L MEA at 120°C and 0.4 $CO_2$ loading.

time are given in Figure 6. The results show that $CO_2$ loading significantly affected the degradation of MEA. The MEA degradation rate was higher at a lower $CO_2$ loading than at a higher $CO_2$ loading. As can be seen, when the $CO_2$ loading increased from 0.4 to 0.5 mol/mol, the initial degradation rate decreased by 28.3% from $4.27\times10^{-3}$ to $3.06\times10^{-3}$ mol/L·h. This is attributed to the fact that the higher $CO_2$ loading causes a reduction in the solubility of $O_2$ in the MEA solution even at a higher $O_2$ pressure (Supap *et al.*, 2009), thereby reducing the MEA degradation rate. The $CO_2$ inhibition effect obtained in this study is consistent with those obtained by other degradation studies (Rooney *et al.*, 1998).

### 3.3 MEA-$CO_2$- $H_2S$ degradation system

In order to evaluate the effect of the presence or absence of $H_2S$ in a $CO_2$-loaded system, a comparison of the MEA-$CO_2$-$H_2S$ system with the corresponding MEA-$CO_2$ system was made. This was done by using 3 mol/L MEA with 0.4 mol/mol $CO_2$ loading, at 120°C with and without 87 mg/L of $H_2S$. The curves of MEA concentration and degradation rate against time for both scenarios are shown in Figure 5 and 7, respectively. Apparently, the variations of the MEA concentration with time of the two systems in Figure 7 were insignificantly different, resulting in almost the same rate of degradation (around $4.18\times10^{-4}$ mol/L·h) as shown in Figure 5. The extents of degradation calculated after 360 hours of the MEA-$CO_2$ and MEA-$CO_2$-$H_2S$ system were 5.06 and 4.83%, respectively, which are nearly the same. This indicates that the presence of $H_2S$ does not affect the degradation rate of MEA in the $CO_2$-loaded system.



(a)

(b)

Figure 6. (a) MEA concentration against time and (b) rate of MEA degradation against time for the MEA-$CO_2$-$O_2$ system using 3 mol/L MEA, and 0.4 and 0.5 $CO_2$ loading at 120°C.

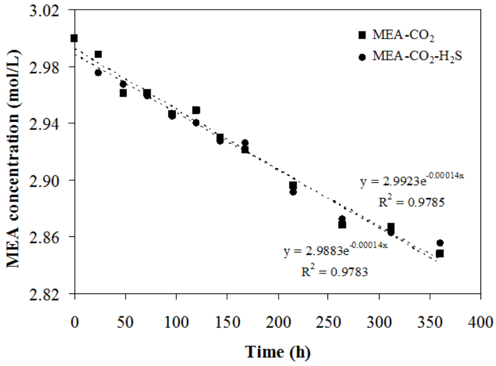


Figure 7. MEA concentration against time for the MEA-$CO_2$ and MEA-$CO_2$-$H_2S$ systems using 3 mol/L MEA at 120°C and 0.4 $CO_2$ loading.

### 3.4 MEA-$CO_2$-$O_2$-$H_2S$ degradation system

The effect of the presence or absence of $H_2S$ on the MEA degradation in the MEA-$CO_2$-$O_2$ system was verified by comparing the MEA-$CO_2$-$O_2$-$H_2S$ system with the corresponding MEA-$CO_2$-$O_2$ system. Experimental runs were carried out by using 3 mol/L MEA with 0.4 mol/mol $CO_2$ loading, 200 kPa of $O_2$ pressure at 120°C, with and without 84 mg/L of $H_2S$. The MEA concentration and degradation rate versus time were plotted as shown in Figure 5 and 8, respectively. It is evident that the concentration-time and degradation rate-time curves of the MEA-$CO_2$-$O_2$-$H_2S$ system were different from those of the MEA-$CO_2$-$O_2$ system. The initial rate of MEA degradation of the MEA-$CO_2$-$O_2$-$H_2S$ system was $5.52\times10^{-3}$ mol/L·h whereas that of the MEA-$CO_2$-$O_2$ system was $4.27\times10^{-3}$ mol/L·h. Moreover, the extents of degradation calculated after 360 hours of the MEA-$CO_2$-$O_2$-$H_2S$ system (48.8%) was approximately 1.2 times higher than that of the MEA-$CO_2$-$O_2$ system (40.5%). These results were different from those of the MEA-$CO_2$ and MEA-$CO_2$-$H_2S$ systems mentioned earlier. This indicates that, when both $O_2$ and $H_2S$ are present in the system, the MEA degradation is additionally induced by $H_2S$, thus resulting in higher degradation rates than the system with $O_2$ only. According to Kohl and Nielson (1997), there are two possible routes in which $H_2S$ is involved in the amine degradation in the presence of $O_2$; one is the reaction of $O_2$ with $H_2S$ to form elemental sulfur, which then reacts with the amines to form decomposition products, and the other is the oxidation of $H_2S$ to stronger acid anions such as thiosulfate, which further reacts with the amines to form heat stable amine salts.

Since there were four different degradation systems investigated in this study, i.e., MEA-$CO_2$, MEA-$CO_2$-$O_2$, MEA-$CO_2$-$H_2S$ and MEA-$CO_2$-$O_2$-$H_2S$ systems, it is worth summarizing the results obtained from these systems under the same conditions. Figure 9 shows the overall MEA degradation rates of all the systems using 3 mol/L MEA and 0.4 $CO_2$ loading at 120°C. The figure shows the same overall degradation rate of around $4.10\times10^{-4}$ mol/L·h for the MEA-$CO_2$ and MEA-$CO_2$-$H_2S$ systems, indicating that the presence of $H_2S$ has no effect in these systems. On the other hand, the presence of $O_2$ can apparently accelerate the degradation of MEA. The overall degradation rate of the MEA-$CO_2$-$O_2$ was about eight times higher than that of the MEA-$CO_2$ system. Although $H_2S$ did not affect the MEA-$CO_2$ system, it could increase the MEA degradation rate in the presence of $O_2$. This can be seen from Figure 5.10 that the MEA-$CO_2$-$O_2$-$H_2S$ system gave an overall rate of $4.07\times10^{-3}$ mol/L·h, which was 20.4% higher than that of the MEA-$CO_2$-$O_2$ system ($3.38\times10^{-3}$ mol/L·h)

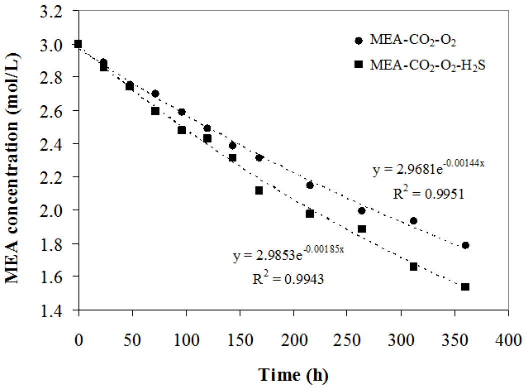


Figure 8. MEA concentration against time for the MEA-$CO_2$-$O_2$ and MEA-$CO_2$-$O_2$-$H_2S$ systems using 3 mol/L MEA, 0.4 $CO_2$ loading and 200 kPa of $O_2$ pressure at 120°C.

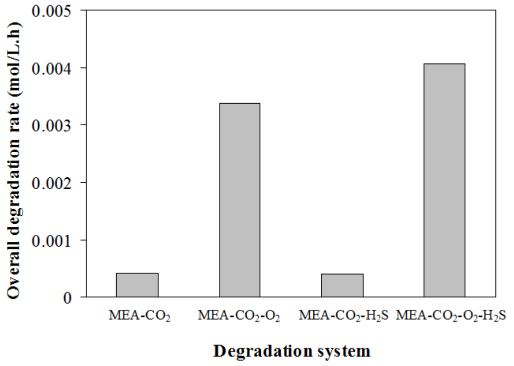


Figure 9. Overall MEA degradation rate in the different degradation systems using 3 mol/L MEA and 0.4 $CO_2$ loading at 120°C.

## 4. Conclusions

The degradation of MEA has been studied under various conditions. The effects of temperature, MEA concentration, $CO_2$ loading, $O_2$, and $H_2S$ were investigated. For the MEA-$CO_2$ system, higher temperature and MEA concentration led to a larger extent of MEA degradation. An increase in $CO_2$ loading in the MEA-$CO_2$-$O_2$ system resulted in a reduction of MEA degradation because of the ability of $CO_2$ to reduce the solubility of $O_2$ in the MEA solution. The degradation rate of the system with $O_2$ was with 8.3 times as high as that of the system without $O_2$. The presence of $H_2S$ in the MEA-$CO_2$-$H_2S$ system did not affect the rate of degradation. However, when $H_2S$ and $O_2$ were present in the system (MEA-$CO_2$-$O_2$-$H_2S$ system), the degradation rate was 20.4% higher than that of the system with $O_2$ only (MEA-$CO_2$-$O_2$ system). The extent of degradation under the same period of time increased in the order MEA-$CO_2$, MEA-$CO_2$-$H_2S$ < MEA-$CO_2$-$O_2$ < MEA-$CO_2$-$O_2$-$H_2S$.

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