ELSEVIER

GHGT-10

Mechanism of Formation of Heat Stable Salts (HSSs) and their Roles in Further Degradation of Monoethanolamine during CO_2 Capture from Flue Gas Streams

Teeradet Supap[a], Raphael Idem,[1a,*], Paitoon Tontiwachwuthikul[a]

[a]*International Test Center for CO2 Capture, 3737 Wascana Parkway, Regina, Saskatchewan, Canada, S4S 0A2*

Abstract

The roles of HSS induced acid products of MEA degradation were evaluated. The results show that formic and acetic acids, formed as a result of MEA oxidation, exist in 2 forms in equilibrium; namely, salts and amides. Specifically, these are formate and acetate, and N-(2-hydroxyethyl)formamide and N-(2-hydroxyethyl)acetamide, respectively. Glycolic acid, also formed due to MEA oxidation, is stable and exists mostly bonded with MEA to produce the glycolate HSS. Its amide is unstable, hydrolyzing back to glycolate and MEA. Oxalic acid was found as a reactive intermediate that mostly decomposed to formic acid, which in turn produced a stable N-(2-hydroxyethyl)formamide. Oxalic acid amide (N-(2-hydroxyethyl)oxamide) could also be formed but its formation was considered a minor route compared with the decomposition route. Succinic acid formed a stable imide (N-(2-hydroxyethyl)succinimide) through an intermediate amide (N-(2-hydroxyethyl)succinamide).

1. Introduction

Oxygen (O_2) induced degradation of amines used in carbon dioxide (CO_2) capture process is a well known source of heat-stable salts (HSS). HSSs contain no value in absorbing CO_2, and are also difficult to regenerate under normal regeneration conditions used in CO_2 absorption unit. In case of high concentration build-up, HSSs also cause damage to plant construction materials due to their corrosive nature [1, 2]. One of the first oxidative pathways of amine degradation using monoethanolamine (MEA) was proposed by Jefferson Chemical [3]. The pathway showed that the reaction of MEA and O_2 produced oxalic acid through α-amino acetaldehyde intermediate. Oxalic acid is also known to form a heat stable salt with MEA. Several years later, the formation routes to account for additional HSS-induced species specifically formic and acetic acids were proposed [4]. Lactate, formate and acetate were also proposed to be generated by radical-induced oxidation of diisopropanolamine (DIPA) and MEA, respectively [5, 6]. The mechanisms initially produced a peroxide radical which further reacted with O_2 and DIPA or MEA forming

---

* Corresponding author. Tel.: +1-306-585-4470; fax: +1-306-337-3112.
E-mail address: Raphael.idem@uregina.ca.

hydroperoxide. The compound later decomposed to form either lactic acid or acetic and formic acid. Although, the proposed mechanistic works were detailed, the existence of these radicals is yet to be verified. A mechanistic work on amine degradation carried out on the basis of a real amine plant sample analysis was also reported in 2003 [7]. This work employed various analytical techniques to identify the degradation products of MEA in plant samples in which pathways of some products were proposed including 2-oxazolidone, N-acetlyethanolamine, and 1-hydroxyethyl-2-piperazinone. The most recent work discussed MEA autoxidation by dioxygen (O_2) as one of the three major amine degradation pathways [8]. The formation of glycine, an intermediate which reacted further to produce glycolic acid HSS was also proposed in this work.

In the present study, we used MEA and major acidic degradation products often detected in CO_2 capture process namely, formic acid, acetic acid, glycolic acid, oxalic acid, and succinic acid. These acids have been reported to form major HSSs with MEA. The objectives set for the experiments were to understand the mechanistic roles of these acids in the oxidation process after they are formed. The roles of MEA-HSSs in further degradation process were also investigated.

2. Experiments

2.1 Chemicals and Equipment

Monoethanolamine (MEA, 99%) was used to prepare an aqueous solution of desired concentrations. Formic acid (98 %), acetic acid (99.7 %), propanonic acid (99.5 %), butyric acid (99 %), glycolic acid, oxalic acid, and succinic acid were used by adding predetermined amounts in the aqueous MEA solution. These acids were also used as standard solutions for verification of the degradation products. Other standards used included N-(2-hydroxyethyl)acetamide, N-(2-hydroxyethyl)succinimide, N, N'-Bis(2-hydroxyethyl)oxamide, N, N'-Bis-(2-hydroxyethyl)formamide. A gas mixture consisting of 6% O_2 with N_2 balance was used as feed gas. All chemicals were reagent grade and were supplied by Sigma-Aldrich, Canada except the gas mixture which was provided by Praxair, Regina, Saskatchewan, Canada. The experiments were carried out in a 0.6 L-stainless steel semi batch reactor (model 4560, Parr Instrument Co., Moline, IL) equipped with an electrical heating jacket and a magnetic-drive stirrer. A controller (Model 4836, Parr Instrument Co., Moline, IL) of ± 0.1% accuracy was used to control and monitor the process temperature and the speed of the stirrer. MEA sample were analyzed using gas chromatograph-mass spectrometer instrument (GC-MS, model 6890-5073) with a method developed in our laboratory. Capillary electrophoresis with diode array detector (CE-DAD, model HP 3D CE) was used for HSSs analysis with a literature CE method [9]. GC-MS and CE were both supplied by Agilent Canada.

2.2 Experimental Procedures

A typical experiment was carried out in 0.6 L reactor using 0.45 L aqueous solution of either mixture of 1 kmol/m^3 MEA and 0.1 kmol/m^3 acids, or 0.1 kmol/m^3 acid alone. The solution was heated to 393 K and stirred at a speed of 500 rpm respectively by electrical heating jacket and magnetic-drive stirrer. The solution was left to stabilize for a few minutes once the set temperature was reached. For some experiments which evaluated the O_2 effect, the solutions were also pressurized to 303 kPa with 6% O_2 feed gas. MEA samples were collected at predetermined time interval starting from 0 day (i.e. after set temperature stabilized or O_2 feed into the solution) to the end of the test run which normally lasted for 1 week. Samples were analyzed by GC-MS for general degradation products while CE-DAD was used to analyze for specific HSSs.

3. Results and Discussion

3.1 MEA-Formic acid

The reactions of MEA and acids were performed at 393 K using 1 kmol/m^3 MEA and 0.1 kmol/m^3 acids. O_2 was excluded from the experiments so that the interactions of the HSSs with MEA could be completely elucidated. For MEA-formic acid system, the reaction occurred instantly after mixing MEA and formic acid at room temperature and went beyond acid-base reaction converting the salt of MEA-formic acid into a new product as detected by GC-MS at 19 minutes. Based on mass spectrum analysis, this product was identified as N-(2-

hydroxyethyl)formamide consistent with the literature [7]. The mixture was subsequently run in the reactor with the condition previously described. Figures 1(a) - (d) show GC chromatograms of MEA-formic acid mixture at different reaction times. Based on GC peak area, used to determine the relative concentrations, the concentration of N-(2-hydroxyethyl)formamide labeled as peak 4 in Figure 1(a) was observed to increase with reaction time until it reached a maximum at about 4 days. Then, the peak started to drop off to stabilization at day 7 indicating the decomposition of N-(2-hydroxyethyl)formamide to MEA-formate salt. CE results also confirm this as it was used to measure formate in the mixture. Formate was found to initially decrease in peak area until approximately days 5 – 7 when its area started to increase again. The GC and CE results show that formic acid after being formed as a result of MEA oxidation, exists in 2 forms in equilibrium; (i) as formate HSS of MEA formed by the electrostatic force of MEA and formic acid, and (ii) as formamide which occurs due to covalent bonding between amino and carboxylic groups of MEA and formic acid. Our plant samples analyzed prior to the tests also showed both products in GC analysis. Figure 2 shows mechanistic roles of formic acid after MEA oxidation.
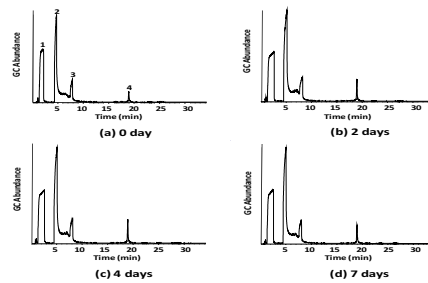

Figure 1 GC Chromatograms of MEA-formic acid mixture at different reaction times (1 kmol/m^3 MEA, 0.1 kmol/m^3 formic acid, 393 K; 1 = water; 2 =MEA; 3 = formic acid; 4 = N-(2-hydroxyethyl)formamide)
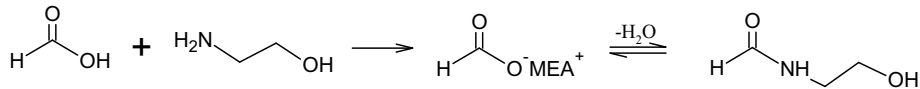

Figure 2 Role of formic acid in MEA degradation

3.2 MEA-Acetic acid

Systems of MEA-acetic acid behaved in a similar manner as that of MEA-formic acid. Figures 3(a) – (d) show GC chromatograms of MEA-acetic acid samples collected at different reaction times. N-(2-hydroxyethyl)acetamide labeled as peak 4 in Figure 3(a) was the only product identified. This amide also existed in real plant samples. Its peak area increased until a maximum and started to decrease at day 6 until it leveled off. On the other hand, CE analysis shows that acetate increased at the same time. Similar to formic acid, acetic acid existed in the system as both acetate salt of MEA and acetamide, and their reactions are given in Figure 4.

3.3 MEA-Glycolic acid

Glycolic acid was also tested similar to tests for formic and acetic acids. Figure 5 (a) – (d) shows GC chromatograms of MEA-glycolic acid samples at different times. Based on the analysis of the mass spectrum of peak 4 in Figure 5(a), the reaction product of glycolic acid and MEA was structurally analogous to amides of formic acid and acetic acid with MEA, and thus, believed to be N-(2-hydroxyethyl)glycolamide. However, N-(2-hydroxyethyl)glycolamide was much less stable than the observed N-(2-hydroxyethyl)formamide and N-(2-hydroxyethyl)acetamide because the peak almost disappeared completely after 4 days. Unlike formic and acetic acids, glycolic acid mostly took a more favorable form of glycolate salt of MEA in the system. This could explain the nonexistence of N-(2-hydroxyethyl)glycolamide in real plant samples. Additional tests also suggested high stability of glycolic acid for the reaction performed using 0.1 kmol/m^3 glycolic acid and 303 kPa of 6% O_2 at 393 K O_2. Most of the glycolic acid remained intact. Only trace amount was converted to formic acid after several days of

reaction. Decomposition of glycolic acid to formic acid could be through the formation of oxalic acid. The role of glycolic acid in MEA system is shown in Figure 6.
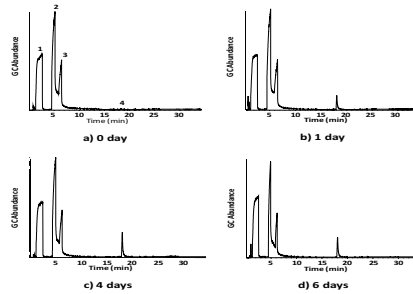

Figure 3 GC Chromatograms of MEA-acetic acid mixture at different reaction times (1 kmol/m^3 MEA, 0.1 kmol/m^3 acetic acid, 393 K; 1 = water; 2 = MEA; 3 = acetic acid; 4 = N-(2-hydroxyethyl)acetamide)
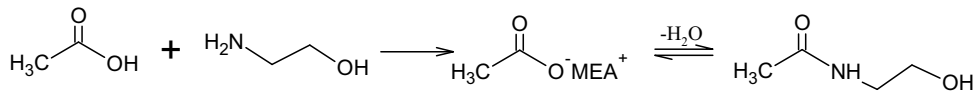

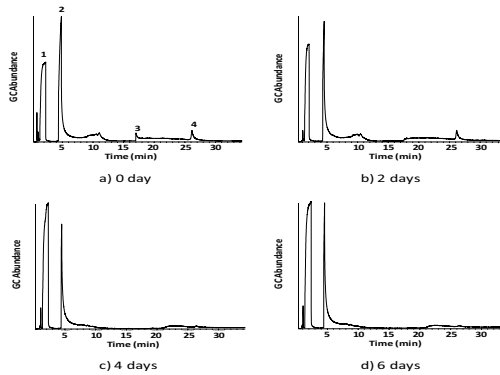Figure 4 Role of acetic acid in MEA degradation

Figure 5 GC Chromatograms of MEA-glycolic acid mixture at different reaction times (1 kmol/m^3 MEA, 0.1 kmol/m^3 glycolic acid, 393 K; 1 = water; 2 = MEA; 3 = glycolic acid; 4 = N-(2-hydroxyethyl)glycolamide)
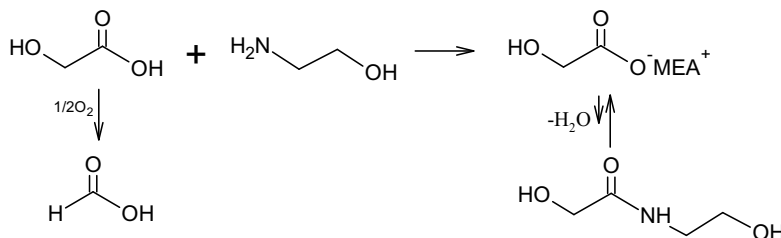

Figure 6 Role of glycolic acid in MEA degradation

3.4 MEA-Oxalic acid

Tests were also carried out for a mixture of oxalic acid and MEA. As shown in Figure 7(a) labeled as peak 3, 4, and 5, respectively, the mixture produced formic acid, N-(2-hydroxyethyl)formamide, and N, N'-Bis(2-hydroxyethyl)oxamide instantly. This indicates that oxalic acid is highly reactive, and so, it could be an intermediate in MEA oxidation. Once it is generated by MEA oxidation, one mole of oxalic acid reacts right away with 2 moles of MEA to form N, N'-Bis(2-hydroxyethyl)oxamide. The decomposition of oxalic acid also occurs simultaneously producing formic acid which in turn reacts with MEA to form N-(2-hydroxyethyl)formamide. After 1 day, N, N'-Bis(2-hydroxyethyl)oxamide peak disappeared but a new peak labeled as peak 6 emerged as shown in Figure 6(b). A quick disappearance of N, N'-Bis(2-hydroxyethyl)oxamide indicates a high instability of this amide. The decomposition of N, N'-Bis(2-hydroxyethyl)oxamide is believed to occur by hydrolysis similar to formamide, acetamide, and glycolamide. However, N, N'-Bis(2-hydroxyethyl)oxamide was not completely hydrolyzed to regenerate MEA and oxalic acid back to the system. Instead, it lost only one molecule of MEA on one side and produced a more stable N-(2-hydroxyethyl)oxamide believed to be peak 6 in Figure 7(b). The conversion of oxalic acid to its amides and formic acid was also evident as shown in the CE results given in Figure 8. Oxalate peak clearly reduced with time while a new peak at 6 min appeared after one day, and this increased in peak size until it stabilized at day 5 to 7. This peak was believed to be N-(2-hydroxyethyl)oxamide which its remaining of carboxyl group made it detectable by CE technique specifically developed for anion analysis. N, N'-Bis(2-hydroxyethyl)oxamide was not detected at 0 day simply due to its inability in acquiring a charge in CE analysis. Figure 8 also shows formate peak after one day which remained detected throughout the test period. Since oxalic acid could behave as an intermediate of formic acid, the role of O_2 in oxalic-formic conversion was also undertaken using 0.1 kmol/m^3 oxalic acid, 303 kPa of 6% O_2, and 393 K. Figure 9 shows clearly that in the presence of O_2, oxalic acid quickly degraded to formic acid. Practically, this reaction could be dominant as opposed to oxalic acid-oxamide conversion as our plant sample analysis always contained formate and N-(2-hydroxyethyl)formamide as major degradation products. On the other hand, oxalate was found in much less concentration with oxamide rarely detected, thus its formation was considered minor. The role of oxalic acid can be summarized in Figure 10.
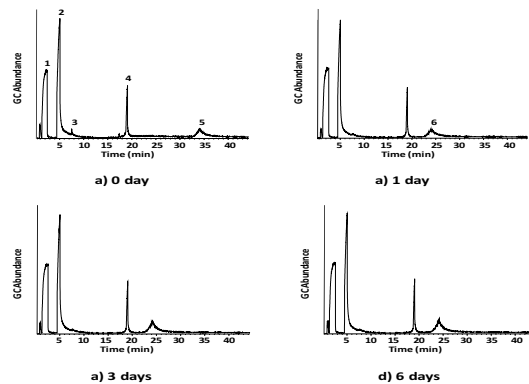

a) 0 day **a) 1 day**

a) 3 days **d) 6 days**

Figure 7 GC Chromatograms of MEA-oxalic acid mixture at different reaction times (1 kmol/m^3 MEA, 0.1 kmol/m^3 oxalic acid, 393 K; 1 = water; 2 = MEA; 3 = formic acid; 4 = N-(2-hydroxyethyl)formamide, 5 = N, N'-Bis(2-hydroxyethyl)oxamide, 6 = N-(2-hydroxyethyl)oxamide)
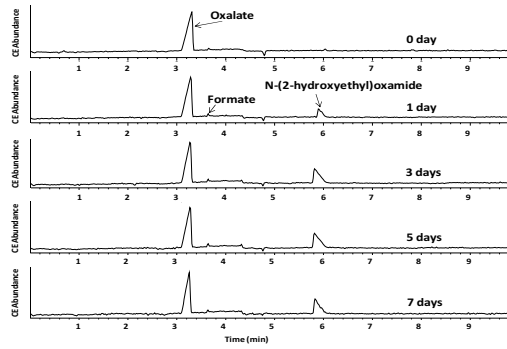
Figure 8 CE Electrophoregram of MEA-oxalic acid mixture at different reaction times
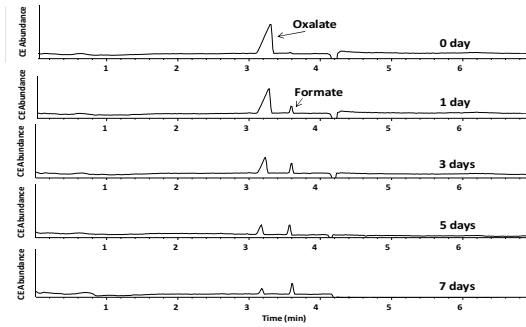(1 kmol/m^3 MEA, 0.1 kmol/m^3 oxalic acid, 393 K)

Figure 9 CE Electrophoregram of Oxalic acid-O_2 system at different reaction times
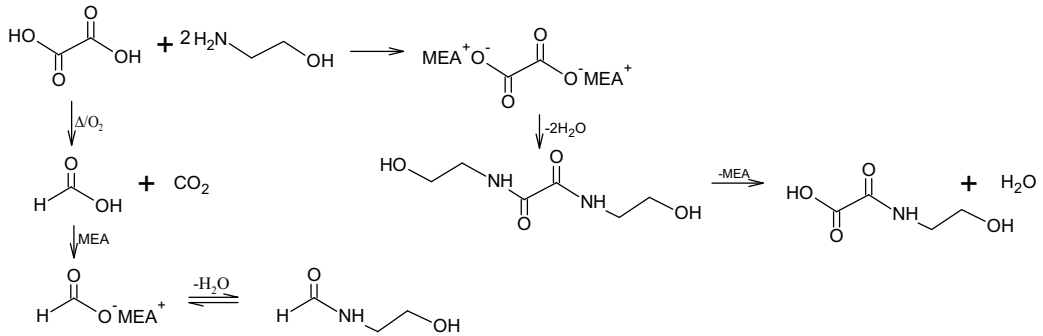(1 kmol/m^3 MEA, 0.1 kmol/m^3 oxalic acid, 393 K)

Figure 10 Role of oxalic acid in MEA degradation

3.5 MEA-Succinic acid

The reaction of succinic acid and MEA was carried out in a similar manner to all acids described earlier. Figures 11(a) – (d) show GC results at various reaction times. In Figure 11(a), the mixture produced a product right away labeled as peak 3, which was verified with a standard as N-(2-hydroxyethyl)succinimide. This was an imide in addition to N-(2-hydroxyethyl)formamide and N-(2-hydroxyethyl)acetamide detected in our plant samples. This imide peak reached its maximum height and started to fall just similar to N-(2-hydroxyethyl)formamide and N-(2-hydroxyethyl)acetamide. The CE analysis of the initial reaction times (i.e. 0 – 3 days) shown in Figure 12 also corresponded to the results of GC when succinate peak initially reduced as succinimide was formed. However, succinate peak still decreased further though GC peak as the succinimide decreased. Further decrease of N-(2-hydroxyethyl)succinimide peak could be explained by formation of a new CE peak at about 7 min. Although, this peak could not be identified due to commercial unavailability, we believed it was N-(2-hydroxyethyl)succinamide. It is well known that amide is an intermediate of imide formation. Thus, this is also the case for N-(2-hydroxyethyl)succinimide which was formed through N-(2-hydroxyethyl)succinamide intermediate. The reactions showing the role of succinic acid is given in Figure 13.
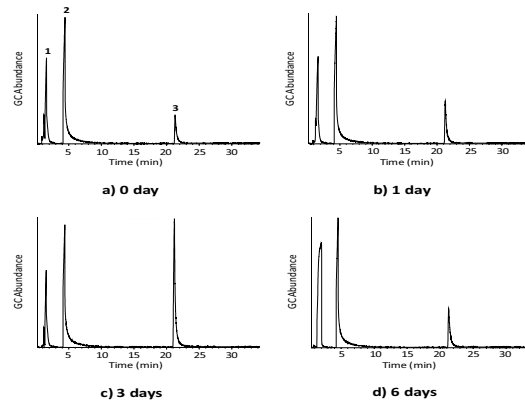

Figure 11 GC Chromatograms of MEA-succinic acid mixture at different reaction times (1 kmol/m^3 MEA, 0.1 kmol/m^3 succinic acid, 393 K; 1 = water; 2 =MEA; 3 N-(2-hydroxyethyl)succinimide)
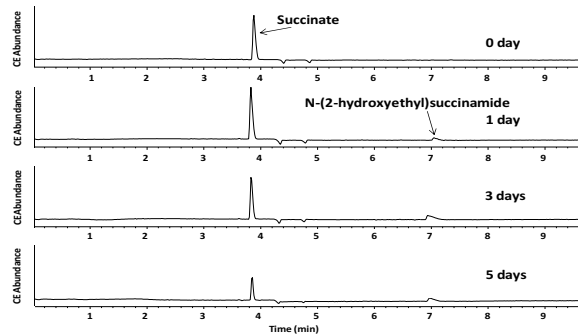

Figure 12 CE Electrophoregram of succinic acid-O_2 system at different reaction times
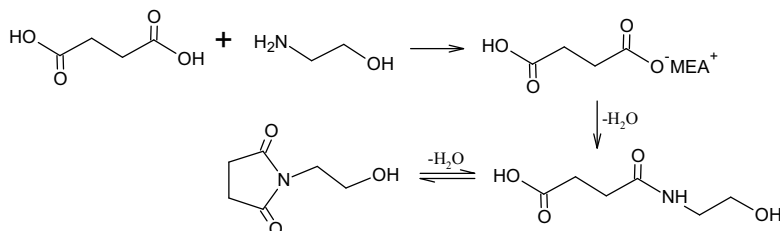(1 kmol/m^3 MEA, 0.1 kmol/m^3 succinic acid, 393 K)

Figure 13 Role of succinic acid in MEA degradation

4.   Conclusions

4.1 Formic and acetic acids exist in 2 forms in equilibrium; formate and acetate HSSs of MEA and N-(2-hydroxyethyl)formamide and N-(2-hydroxyethyl)acetamide, respectively.

4.2 Glycolic acid was found to favor HSSs formation with MEA. Its amide was found to be unstable, and mostly hydrolyzed back to glycolate and MEA.

4.3 Oxalic acid was determined to be a reactive intermediate mostly decomposing to formic acid, which in turn, produced a stable N-(2-hydroxyethyl)formamide. N-(2-hydroxyethyl)oxamide could also be formed but its formation was much less prominent.

4.4 Succinic acid formed a stable N-(2-hydroxyethyl)succinimide through an intermediate of N-(2-hydroxyethyl)succinamide.

Acknowledgements

References

[1] Tanthapanichakoon W, Veawab A, McGarvey B. Electrochemical investigation on the effect of heat-stable salts on corrosion in CO_2 capture plants using aqueous solution of MEA. Ind. Eng. Chem. Res*. 2006**;** 45**:** 2586 – 2593.

[2] Nainar M, Veawab A. Corrosion in CO_2 capture process using blended monoethanolamine and piperazine. Ind. Eng. Chem. Res*. 2009**;** 48: 9299 – 9306.

[3] Hofmeyer B.G, Scholten H.G, Lloyd W.G. Contamination and corrosion in monoethanolamine gas treating solutions. Internal Report No. 722. Michigan: The Dow Chemical Company; 1965.

[4] Rooney P. C, Dupart, M.S, Bacon, T.R. Oxygen's role in alkanolamine degradation. Hydrocarbon Process. 1998; 77: 109 - 113.

[5] Smit C.J, Van Heeringen G.J, Van Grinsven, P.F.A. Degradation of amine solvents and the relation with operational problems. Proceedings of 52nd Annual Laurance Reid Gas Conditioning Conference. Oklahoma: University of Oklahoma; 2002.

[6] Chi S, Rochelle G. T. Oxidative degradation of monoethanolamine. Ind. Eng. Chem. Res. 2002; 41: 4178-4186.

[7] Strazisar B.R., Anderson R.R., White, C.M. Degradation pathways for monoethanolamine in a CO_2 capture facility. Energy & Fuels. 2003; 17: 1034 - 1039.

[8] Bedell S.A. Amine autoxidation in flue gas CO_2 capture-mechanistic lessons learned from other gas treating processes. IGJCC. 2010; Article in press.

[9] Bord, N, Crétier G, Rocca J.-L, Bailly C, Souchez J.-P. Simultaneous determination of inorganic anions and organic acids in amine solutions for sour gas treatment by capillary electrophoresis with indirect UV detection. Journal of Chromatography A. 2005; 1100: 223 - 229.