GHGT-11

SO$_2$ effect on degradation of MEA and some other amines

Shan Zhou[a], Shujuan Wang[a]*, Chenchen Sun[a], Changhe Chen[a]

[a]Key Laboratory for Thermal Science and Power Engineering of Minister of Education, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

Abstract

SO$_2$ is the main acidic impurity in flue gas and will affect amine degradation in CO$_2$ capture process. This work introduced SO$_2$/Na$_2$SO$_3$ in various experiment conditions of MEA (monoethanolamine) oxidative degradation and evaluated the SO$_2$ effect on MEA degradation considering both oxidative and thermal degradation. 60 ppm SO$_2$ could inhibit MEA oxidative degradation by scavenging oxidative radicals in absorber condition. Higher concentration of SO$_2$ does not enhance the inhibitory effect, but will increase the corrosivity of the solution. NH$_3$ is promoted by sulfite and becomes significant in MEA thermal degradation. Thiosulfate, the disproportionation product of sulfite, is believed to be the catalyst of S$_N$2 reaction. Na$_2$SO$_3$ was used to test SO$_3^{2-}$ effect on thermal degradation of EDA (ethylenediamine), 2-PE (2-piperidineethanol) and PZ/AMP (piperazine /2-amino-2-methyl-1-propanol) solution. Alkyl structure of amines has important effect on the S$_N$2 reactions.

1. Introduction

Amine degradation is one of the main issues in chemical absorption method for CO$_2$ capture. Degradation of amine increases the corrosivity and foaming tendency of amine solution, while decreasing the absorption rate and recycle capacity. The makeup cost was estimated to contribute about 10% to the cost of CO$_2$ capture using MEA (monoethanolamine) solution [1].

SO$_2$, as an important pollutant in flue gas, has been reported to speed up amine degradation in pilot scale [2,3] and can not be stripped out at CO$_2$ stripping condition [4]. Cansolve [5] reported their integration system including a desulfurization unit and a CO$_2$ recovery unit. In this system, SO$_2$ was removed

_____

* Corresponding author. Tel.: +86-010-62788668; fax: +86-010-62770209.
E-mail address: wangshuj@tsinghua.edu.cn.

completely in the desulfurization unit, as fine desulfurization is costly. The remaining SO_2 will be converted to sulfite in CO_2 absorber, which was reported to prevent amine oxidative degradation.

In laboratory research, Na_2SO_3 was added into the amine solution as inhibitor for oxidative degradation [6-8], while SO_2 (gas) was reported to induce MEA degradation with O_2 present [9,10]. Previous work [11] suggested that SO_2 or Na_2SO_3 promoted NH_3 formation in MEA thermal degradation. The different experiment results suggest that SO_2 may have several different kinds of effect on amine degradation.

This work introduced SO_2 or Na_2SO_3 in various experiment conditions of MEA oxidative degradation and evaluated the SO_2 effect on MEA degradation based on experiment results from both oxidative and thermal degradation. Na_2SO_3 was added into three other amine solutions to test SO_3^{2-} effect on amine thermal degradation.

2. Experimental methods

2.1. Oxidative degradation experiment

Oxidative degradation experiments were performed using a 1 L stainless steel autoclave reactor. 500 mL 30 wt. % MEA solution with 0.4 CO_2 loading was used for each experiment. The agitator was always set at 1000 rpm to accelerate mass transfer. About 5 mL solution was sampled after abandoning 13 mL (dead volume). This work tried to evaluate the SO_2 effect on MEA oxidative degradation in absorber condition ($55^{o}C$), and stripper condition ($100^{o}C$) separately.

For the experiments at $55^{o}C$, the system was kept at atmosphere. 7.5 L/min simulated gas was bubbled into the solution at the bottom with 2% CO_2 to maintain the CO_2 loading in liquid phase and 20% O_2 to accelerate oxidative degradation. SO_2 concentration varied from 0 to 150 ppm. The balance gas was N_2. Since the gas flow will be saturated with water, a constant flow pump was used to add deionized water into the reactor. 1-3 mM NaCl was added into the solution, so that concentration of Cl^- could be used to correct the concentrations of MEA and degradation products.

For the experiments at $100^{o}C$, the experiment system was sealed and heated to $100^{o}C$. Then additional 250 kPa gas was added into the system. The valve of gas cylinder was kept open to maintain the total pressure. When the gas supplement was air or simulated gas, the initial added gas was as same as the gas supplement. SO_2 (gas) concentration in the simulated gas was 194 ppm, while balance gas is air. When the gas supplement was O_2, 200 kPa N_2 and 50 kPa O_2 were added into the autoclave at the beginning. Na_2SO_3 (solid) was used instead of SO_2 (gas).

2.2. Thermal degradation experiment

MEA thermal degradation experiment method has been described in the previous work [11]. The same apparatus (sealed 316L stainless steel reactors and forced convection oven from Memmert) were used in this work. Since Na_2SO_3 and SO_2 have similar effect on the MEA thermal degradation [12], Na_2SO_3 was used in this work for convenience. Carbamate always plays an important role in amine thermal degradation, while the most significant effect on MEA thermal degradation of sulfite is promoting pronated MEA degraded to NH_3. H_2SO_4 was loaded into the solution instead of CO_2 to avoid carbamates. All the experiments in this part were performed at $150^{o}C$ to accelerate the reaction and lasted 2 weeks.

2.3. Analytical methods

Acid titration method was used to confirm the amine concentration of initial solutions. Precipitate titration method was used to confirm the CO_2 loading in the initial solution. Amines and cationic

degradation products in the degraded solutions were quantitative analyzed by cationic ion chromatography (IC) (Dionex DX-120 with CG17/CS17, CSRS 4 mm and RFC30). Anionic degradation products and inorganic salt ions were analyzed by anionic IC (Dionex ICS-1000 with AG15/AS15, ASRS 4 mm and RFC30). Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Thermal-Fisher Advantage ICP-AES) was used for metal concentration dissolved in the solutions. Liquid Chromatography (LC) (Varian ProStar 320 UV/Vis detector with C18) was used for qualitative analysis.

3. Results and discussion

3.1. SO$_2$ effect on MEA oxidative degradation

This work evaluated the SO$_2$ effect on MEA oxidative degradation at 55°C by introducing SO$_2$ (gas) with simulated flue gas continuously into the solution. The emission limit of SO$_2$ is 100 mg/m^3 for new coal fired power plants and 200 mg/m^3 for existed power plants in China [13], which is about 35 ~ 70 ppm. SO$_2$ concentration in the simulated flue gas was set at 60 ppm to simulate the SO$_2$ concentration after FGD. All the experiments at 55°C lasted about 120 hours. The effect of 150 ppm SO$_2$ was also tested.

In the experiment system at 55°C, MEA volatilization is an important issue, which contributed more than 50% to the total MEA loss in this work. The analytical error of MEA caused by IC is about 3.5%, close to the MEA degradation loss in this work. MEA concentration could not tell the differences clearly. The concentrations of degradation products are used to evaluate the SO$_2$ effect here.

Formate, oxalate, acetate and glycolate are reported as the main anionic MEA oxidative degradation products [14]. Both acetate and glycolate were not concentrated, and were covered by MEA carbamate on the anionic ion chromatogram in this work. Formate, nitrite and N-(2-hydroxyethyl)oxamide were the main quantified anionic products. Since there was no standard substance of N-(2-hydroxyethyl)oxamide, the standard curve of formate on a molar basis was used to estimate the concentration of N-(2-hydroxyethyl) oxamide.

The concentrations of degradation products in the experiments without SO$_2$ and with 60 ppm, 150 ppm SO$_2$ are compared in Fig. 1. The concentrations of oxidative degradation products of MEA decreased with SO$_2$ obviously. Especially, formate and N-(2-hydroxyethyl)oxamide are not detectable during the whole experiments with 60 ppm SO$_2$. The final samples of experiments with 0 ppm SO$_2$ and 60 ppm SO$_2$ were qualitatively analyzed by LC. Degradation products are obvious in the former sample, but can't be detected in the later sample. SO$_2$ (gas) inhibits MEA oxidative degradation in the absorber condition, agreeing with Hakka et al [15].

Several researchers have reported that sulfite could inhibit MEA oxidative degradation by scavenging oxidative radicals [6, 10, 15]. The SO$_2$ bubbled into the solution was almost converted to sulfite and sulfate. With oxidation reaction going on, sulfite concentration was maintained at a relative stable level, while sulfate concentration was increasing all the time during the experiments in this work. The sulfite and sulfate concentrations in the above experiments are shown in Fig. 2.

One interesting phenomenon is that degradation products are more concentrated with 150 ppm SO$_2$ than that with 60 ppm SO$_2$ in the simulated gas, which goes against the explanation for SO$_2$ inhibiting MEA oxidative degradation. There should be some other elements or mechanisms affecting the oxidative degradation process. Since the reactor was made of stainless steel, higher concentration of SO$_2$ (150 ppm) could increase the corrosivity of MEA solution. ICP-AES was used to analyze the dissolved metal concentrations in the final samples of the above experiments, as shown in Fig. 3.

Metal' concentrations were increased with 150 ppm SO$_2$. Fe^{2+} is the most concentrated corrosion product in amine solutions, and also an important catalyst for amine oxidative degradation. The catalysis of ferrous ion may be the reason for the weakening of inhibitory effect of 150 ppm SO$_2$. This work also

investigated the effect of SO$_2$ on MEA oxidative degradation with 0.47 mmol/kg ferrous ion in the solution, as shown in Fig. 4.

The oxidative degradation products decreased with 60 ppm SO$_2$ in the experiment when 0.47 mmol/kg ferrous ion was added into the initial solution. 60 ppm SO$_2$ could still inhibit the oxidative degradation with Fe^{2+}, though the effect was weakened.
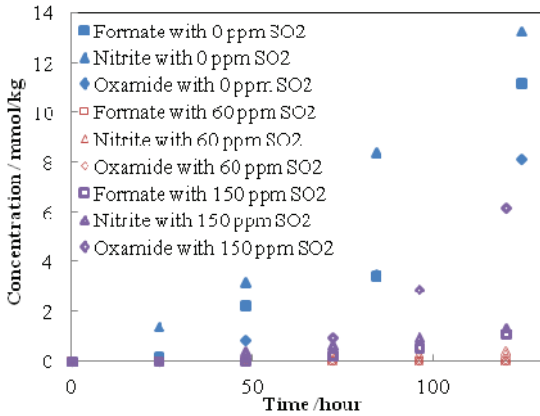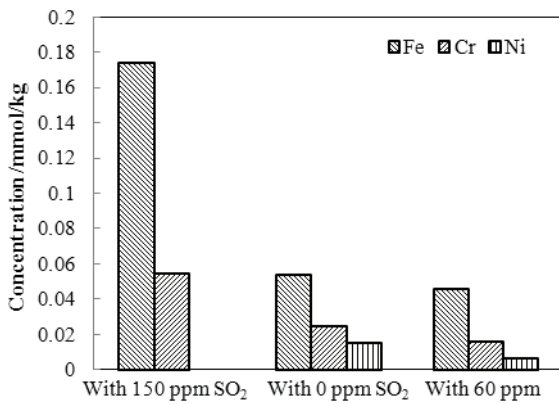

Fig. 1. SO$_2$ effect on anionic products at 55°C

Fig. 2. Sulfate and sulfite concentration at 55°C

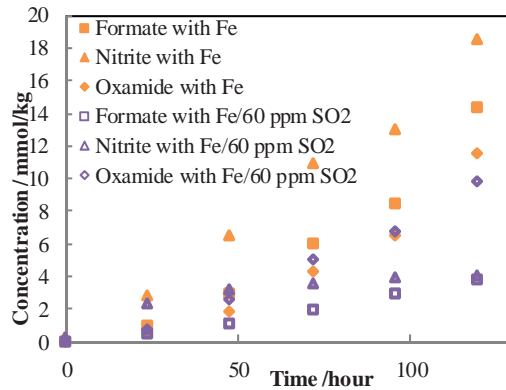Fig. 3. Dissolved metals in final samples at 55°C

Fig. 4. 60 ppm SO$_2$ effect on anionic products with Fe^{2+} catalyst

The experiment system was sealed in the oxidative degradation experiments that performed at 100°C, so that volatility of MEA and water evaporation did not affect MEA loss analysis obviously. On the contrast, O$_2$ partial pressure, one of the most important experiment conditions, could not be constant in the sealed reactor. Oxidation reaction consumed O$_2$, while N$_2$ or the gaseous degradation products accumulated in the gas phase. O$_2$ partial pressure was decreasing during the experiments. As a fact, the average O$_2$ partial pressure in the experiments with air/simulated gas supplemented was much lower than that in the experiment with O$_2$ supplemented. At the same time, the sampling process would bring more

uncertainty to the O_2 partial pressure. All the oxidative degradation experiments at 100^oC lasted 30 hours without any inter-sampling.

When the gas supplement was air/simulate gas, O_2 concentration in the supplement gas was 21%. SO_2 concentration is 194 ppm in the simulated gas compared with 0 in the air. The ratio of remained MEA after 30 hours with air supplement and simulated gas supplement are compared in Fig. 5. MEA loss was always within the analysis error range in these conditions.
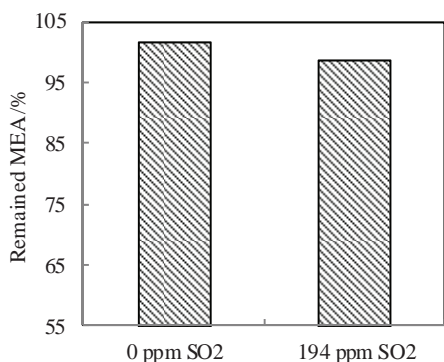

Fig. 5. 194 ppm SO_2 effect on the ratio of remained MEA at 100^oC with air supplement
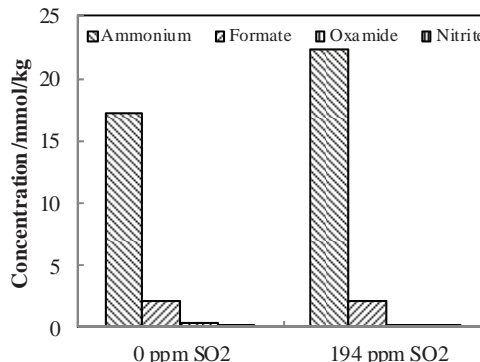
Fig. 6. 194 ppm SO_2 effect on degradation products at 100^oC with air supplement

NH_3 is the main gas gaseous product in MEA oxidative degradation [16]. It was dissolved in MEA solution and made ammonium the most concentrated product in the oxidative degradation samples at 100^oC. The concentrations of main degradation products with air supplement and simulated gas supplement are compared in Fig. 6.All the anionic degradation products' concentrations were lower than 3 mmol/kg, and not affected significantly by the SO_2 in the gas supplement.

Pure O_2 was supplied into the experiment to maintain the O_2 partial pressure and accelerate the oxidation process. Na_2SO_3 (solid) was added into MEA solution at the beginning instead of SO_2 (gas) in this condition. In 30 hours experiments, MEA loss was about 10% in the experiments with O_2 supplement. 268 mmol/kg Na_2SO_3 does not have obvious effect. The concentrations of degradation products are shown in Fig. 7. In another independent experiment, 267 mM Na_2SO_3 was proved to be almost oxidized completely in the first hour with O_2 supplement and did not show significant effect on the following MEA oxidative degradation.
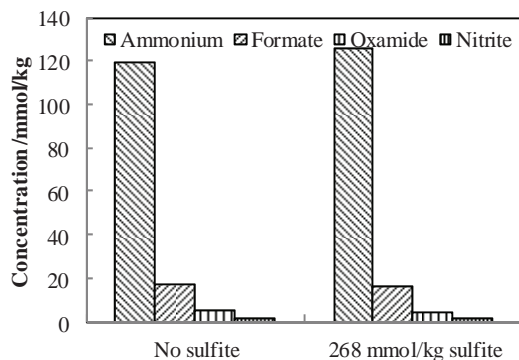

Fig. 7. 268 mmol/kg Na_2SO_3 effect on degradation products at 100^oC with O_2 supplement

In the above experiments, SO_2 does not promote MEA oxidative degradation with higher O_2 pressure than that in flue gas, while the oxidation process of sulfite scavenges the oxidative radicals and could be used to inhibit MEA oxidative degradation in the absorber condition. SO_2 may promote the amine degradation by increasing catalyst concentration in the oxidative degradation. SO_2 (gas) or Na_2SO_3 (solid) did not show significant effect on MEA oxidative degradation at 100^oC.

3.2. SO$_2$ effect on MEA thermal degradation

Previous work [11, 12] has reported that MEA thermal degradation rate did not change obviously with H_2SO_4, SO_2 or Na_2SO_3. On the other hand, sulfite was found to promote ammonia production in MEA thermal degradation process. Na_2SO_3 showed similar effect with SO_2 on MEA thermal degradation. Protonated MEA is the source of ammonia product. Bimolecular nucleophilic substitution (S_N2) reaction was used to explain this phenomenon, as shown in equation (1), where Nu: is nucleophilic reagent with lone pair electrons.

$$\text{(1)}$$
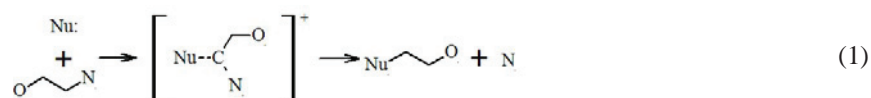
Ammonia could also be the product of MEA decomposing in stripper condition, as equation (2) [17].

$$\text{(2)}$$

Ethylene oxide (EO) and ammonia are used to produce MEA in industry. EO could also react with the other nucleophilic reagents, such as MEA and H_2O, in MEA solution readily. EO could be the intermediate product of S_N2 reactions. The hydroxyl of MEA molecule could participate in the S_N2 reactions as neighboring group.

Similar S_N2 reactions and intermolecular nucleophilic substitution reactions could be possible for other alkylol amines and diamines. Amine group could also participate in the nucleophilic substitution reactions and produce aziridinium salts. However, these intermediate products could not be proved [18].

The S_N2 reactions between MEA and the nucleophilic reagents were catalyzed with added SO_2 or Na_2SO_3, while disproportionation of sulfite was always detected at the same time. On the contrast, sulfite showed no effect on the S_N2 reaction of the quaternary with amine at 140^oC [19]. Thiosulfate may be the catalyst for the S_N2 reactions instead of sulfite.

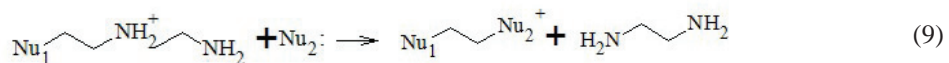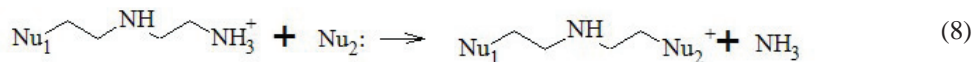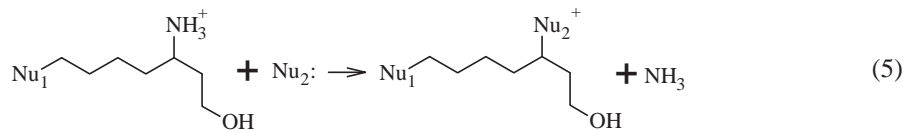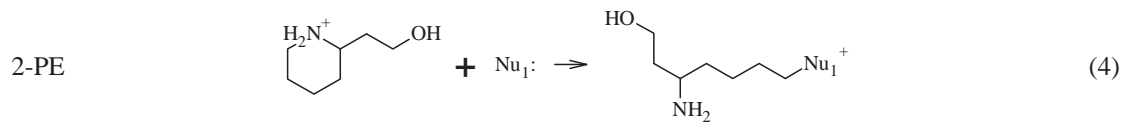### 3.3. SO$_2$ effect on thermal degradation of other amines

Table 1. Summary of thermal degradation experiments

Expt	Amine	Amine Con. (*mol/kg*)	H$_2$SO$_4$ Con. (*mol/kg*)	Na$_2$SO$_3$ Con. (*mol/kg*)
P1	EDA	2.86	1.11	0
P2	EDA	2.75	1.07	0.31
P3	2-PE	2.51	0.50	0
P4	2-PE	2.46	0.49	0.14
P5	PZ/AMP	1.86/1.25	0.98	0
P6	PZ/AMP	1.79/1.21	0.94	0.27

SO$_2$ effect on amine thermal degradation was further tested using EDA (ethylenediamine), 2-PE (2-piperidine ethanol) and PZ/AMP (piperazine /2-amino-2-methyl-1-propanol) solution. Carbamate is the key species in thermal degradation of various alkanolamines and diamines solutions with CO$_2$ loading, except PZ [18, 20]. Carbamate polymerization is much more significant than S$_N$2 reactions for these amines. Although S$_N$2 reaction is one of the main mechanisms of concentrated PZ thermal degradation, the reaction rate is pretty slow at 150°C [21].

H$_2$SO$_4$ was used to protonate amines to avoid carbamate, while Na$_2$SO$_3$ was used to introduce sulfite into the solutions. The concentrations of amines and additives are shown in Table 1.

Similar with equation (1), equation (3) to (9) could be the reaction equations for the tested amines. Ammonia is the most obvious product of the S$_N$2 reactions in which amino group are substituted. EDA is also one of the important products of S$_N$2 reactions of diamines.

EDA

(3)

2-PE

(4)

(5)

AMP

(6)

PZ

(7)

(8)

(9)
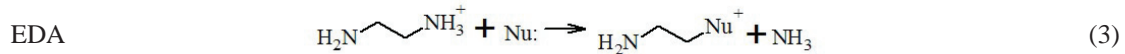
4. Conclusion

This work evaluated the SO$_2$ effect on MEA degradation considering both oxidative and thermal degradation through a series of experiments. It suggested that 60 ppm SO$_2$ could inhibit MEA oxidative degradation by scavenging oxidative radicals in absorber condition, while higher concentration of SO$_2$ (150 ppm) could increase the Fe and thus weakened the inhibitory effect. SO$_2$ or Na$_2$SO$_3$ did not show significant effect on MEA oxidative degradation at 100°C.

In MEA thermal degradation, NH$_3$ is promoted by sulfite and becomes significant. Thiosulfate, the disproportionation product of sulfite, is believed to be the catalyst of S$_N$2 reaction. Na$_2$SO$_3$ was used to test SO$_3^{2-}$ effect on thermal degradation of EDA, 2-PE and PZ/AMP solution. The S$_N$2 reactions also existed in these amines but would be effected by alkyl construction.

Acknowledgements

References

[1] Rao AB, Rubin ES. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environmental Science and Technology*, 2002, **36**(20): 4467-4475.

[2] Barchas R, Davis R. The Kerr-McGee/ABB Lummus Crest technology for the recovery of CO_2 from stack gases. *Energy Conversion and Management*, 1992, **33**(5-8): 333-340.

[3] Gao J, Wang S, Zhao B, Qi G, and Chen C. Pilot-Scale Experimental Study on the CO_2 Capture Process with Existing of SO_2: Degradation, Reaction Rate, and Mass Transfer. *Energy Fuels*, 2011, **25**(12): 5802-5809.

[4] Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwilas A, et al. Pilot plant studies of the CO_2 capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO_2 capture technology development plant and the Boundary Dam CO_2 capture demonstration plant. *Ind. Eng. Chem. Res.*, 2006. **45**: 2414-2420.

[5] Shaw D. Cansolv CO_2 capture: The value of integration. *Energy Procedia* 2009,**1**: 237-246.

[6] Goff GS, Rochelle G. Oxidation inhibitors for Cu catalyzed degradation of monoethanolamine in CO_2 capture processes. *Ind. Eng. Chem. Res.*, 2006, **45**(8): 2513-2521.

[7] Sexton AJ. *Amine Oxidation in CO_2 Capture Processes* [D]. Austin, US: Department of Chemical Engineering, The University of Texas at Austin, 2008.

[8] Supap T, Idem R, Tontiwachwuthikula P, Saiwan C. Investigation of degradation inhibitors on CO_2 capture process. *Energy Procedia*, 2011, **4**: 583-590.

[9] Uyanga IJ, Idem RO. Studies of SO2- and O2- induced degradation of aqueous MEA during CO_2 capture from power plant flue gas streams. *Ind. Eng. Chem. Res.*, 2007, **46**: 2558-2566.

[10] Supap T, Idem R, Tontiwachwuthikul P, Saiwan C. Kinetics of sulfur dioxide- and oxygen-induced degradation of aqueous monoethanolamine solution during CO_2 absorption from power plant flue gas streams. *International Journal of Greenhouse Gas Control*, 2009, **3**: 133-142.

[11] Zhou S, Wang SJ, Chen CH. Thermal degradation of MEA in CO_2 capture with acidic impurities in flue gas. *Ind. Eng. Chem. Res.*, 2012, 51(6): 2539-2547.

[12] Zhou S, Wang S, Chen C, Xu X. Thermal degradation of MEA with SO_2 in flue gas, *7th International Symposium on Coal Combustion*, July, 2011, Harbin.

[13] Ministry of Enviromental Protection of the People's Republic of China. Emission Standard of Air Pollutants for Thermal Power Plants GB13223-2011, 2011.

[14] Rooney PC, DuPart MS, Bacon TR. Oxygen's role in alkanolamine degradation. *Hydrocarbon Process: Int. Ed.*, 1998, **77**(7): 109-113.

[15] Hakka LE, Ouimet MA. Method for recovery of CO_2 from gas streams: U.S., US7056482 (B2). 2004-12-16, 2006.

[16] Sexton AJ, Rochelle GT. Reaction products from the oxidative degradation of monoethanolamine. *Ind. Eng. Chem. Res.*, 2011, **50**(2): 667-673.

[17] Talzi V. NMR determination of the total composition of commercial absorbents based on monoethanolamine. *Russian Journal of Applied Chemistry*, 2004, **77**(3): 430-434.

[19] Lepaumier H, Picq D, Carrette P-L. New amines for CO_2 capture. I. Mechanisms of amine degradation in the presence of CO_2. *Ind. Eng. Chem. Res.*, 2009, **48**(20): 9061-9067.

[19] Bedell SA, Worley CM, Al-Horr RS, McCrery DA. Quaternaries as intermediates in the thermal and oxidative degradation of alkanolamines. *Ind. Eng. Chem. Res.*, 2010, **49**(16): 7147-7151.

[20] Davis JD. *Thermal degradation of aqueous amines used for carbon dioxide capture* [D]. Austin, US: Department of Chemical Engineering, The University of Texas at Austin, 2009.

[21] Freeman SA. *Thermal degradation and oxidation of aqueous piperazine for carbon dioxide capture* [D]. Austin, US: Department of Chemical Engineering, The University of Texas at Austin, 2011.