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Oxidative Degradation of AMP/MEA Blends for Post-combustion CO₂ Capture

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Abstract

The oxidative degradation of aqueous, concentrated 2-amino-2-methyl-1-propanol (AMP)/monoethanolamine (MEA) mixture has been investigated in batch reactors at temperatures in the range of 100-140°C, and oxygen pressures in the range of 250-350 kPa. The oxidation pathway of individual AMP was proposed before attempting to investigate the oxidation of AMP/MEA blend. As compared with degradation of single MEA and AMP, no cross product was found in the degraded AMP/MEA blend under the experimental conditions. This result showed that AMP and MEA could be oxidized in parallel in the mixture. Both the overall degradation rates of MEA and AMP increased with raising temperature and oxygen partial pressure. MEA degraded faster than AMP in the blend under all the experimental conditions. The degradation rate of AMP decreased indicating MEA protects AMP from oxidation in the mixture when initial MEA concentration was increased.

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Keywords: CO₂ capture; monoethanolamine; 2-amino-2-methyl-1-propanol; oxidative degradation.

1. Introduction

Capturing carbon dioxide (CO₂) generated from fossil fuel fired power plants is an important strategy that helps mitigate global warming. The chemical absorption process is generally recognized as the most effective technology due to relatively low CO₂ partial pressure streams typically found in fossil fuel-derived flue gases [1]. One of the advancements in gas treating technology is the application of sterically hindered amines which offer advantages over conventional amines for CO₂ removal from flue gases. Primary sterically hindered alkanolamines have been disclosed as potentially alternative solvents for removal of acid gases. An example of this kind of alkanolamine is AMP, which requires less energy for solvent regeneration than conventional amines [2] and can reach loadings of 1 mol of CO₂/mol of amine

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due to formation of an unstable carbamate intermediate which is readily hydrolyzed [3,4]. A disadvantage of AMP is that it has a lower reaction rate constant for the reaction with CO₂ than that of MEA [5]. Encouragingly, it was found that addition of small amounts of other amines to an aqueous solution of AMP significantly enhances the absorption rate and enhancement factor [6-8].

We are interested in AMP/MEA blends because of the potential advantages of AMP, and MEA as the benchmark molecule. The addition of small amounts of MEA to an aqueous solution of AMP significantly enhances CO₂ absorption rate over conventional single amine solvents [6, 9]. An AMP/MEA blend requires less energy and uses lower-quality steam for solvent regeneration and carries less energy penalty as compared to MEA, blended MEA/MDEA and DEA/MDEA [10, 11].

Flue gas streams are typically composed of 5 to 7.5 % O₂, in addition to CO₂, N₂, and other impurities. The presence of O₂ at these concentrations presents a great challenge since many alkanolamines are susceptible to oxidative degradation. Alkanolamine degradation is undesirable not only because it represents a loss of solvent, but also because it may result in plant operating problems such as fouling, foaming and corrosion [12]. In this respect, benefits of new solvents depend on whether the chemical stability of the amines can be maintained. This study was therefore conducted to investigate the degradation behaviour of AMP/MEA aqueous solutions used for post-combustion CO₂ capture.

2. Experimental Methods

Analytical-reagent grade or better chemicals as well as analytical grade water were used in this work. The experiments were conducted in batch mode using a 200mL glass autoclave ('miniclave steel' type 1/200mL 10bar, obtained from Büchi Glas Ulster, Switzerland) with a stainless steel lock. The reactor was equipped with a magnetic stirrer. Pressure and temperature were monitored and controlled with a pressure gauge and a thermocouple, respectively. In order to shorten the length of experiments from months to days, the degradation runs were conducted at elevated temperatures and O₂ pressures.

In a typical experimental run, 140mL aqueous amine solution was degassed and transferred into the reactor. Subsequently, the solution was stirred at a speed of 200rpm and heated to the desired operating temperature. O₂ was then introduced into the vessel to achieve the desired partial pressure through the gas inlet valve. It was ensured that the desired O₂ partial pressure was maintained throughout the duration of the reaction by keeping the inlet valve of O₂ open at a certain value. A check valve was preset in the gas inlet tubing to avoid the gas mixture flowing backwards. Liquid samples were withdrawn from the reactor through the liquid sampling valve at appropriate predetermined intervals and stored in a refrigerator. The samples were analyzed by GC-MS, cation IC and anion IC methods after each experimental run. The analytical methods were reported in previous work [13, 14].

3. Results and Discussion

3.1 Oxidative degradation of individual MEA and AMP

MEA is the most widely studied solvent for post-combustion CO₂ capture from flue gases since it is the benchmark molecule. The reported degradation products of MEA and proposed pathways for generation of the degradation products were recently summarized by Gouedarda et al. [15]. Only one experiment was performed on MEA solution in order to verify our analysis methods in the present work. An aqueous solution of 5 mol/kg MEA was degraded under 250 kPa O₂ at 120°C. Cation IC and anion IC were performed on all the samples, while GC-MS was only performed on selected samples, since the concentrations of most of the non-ionic products was too low for quantification using GC-MS in the initial stage of the oxidations.

The key degradation compounds of MEA that have been previously reported and summarized [15] were also detected in this study. The major degradation products included ammonia, N-(2-hydroxyethyl) formamide (HEF), N-(2-hydroxyethyl)acetamide (HEA), N-(2-hydroxyethyl)imidazole (HEI) and carboxylic acids (formic acid, acetic acid, oxalic acid and glycolic acid). Additionally, nitrite, nitrate were detected at low concentrations. The presence of ammonia in degraded MEA was measured as NH_4^+ using cation IC. The formation of HEF and HEA can be explained by reactions of MEA with formic- and acetic acid, while the mechanism of HEI formation still needs further work.

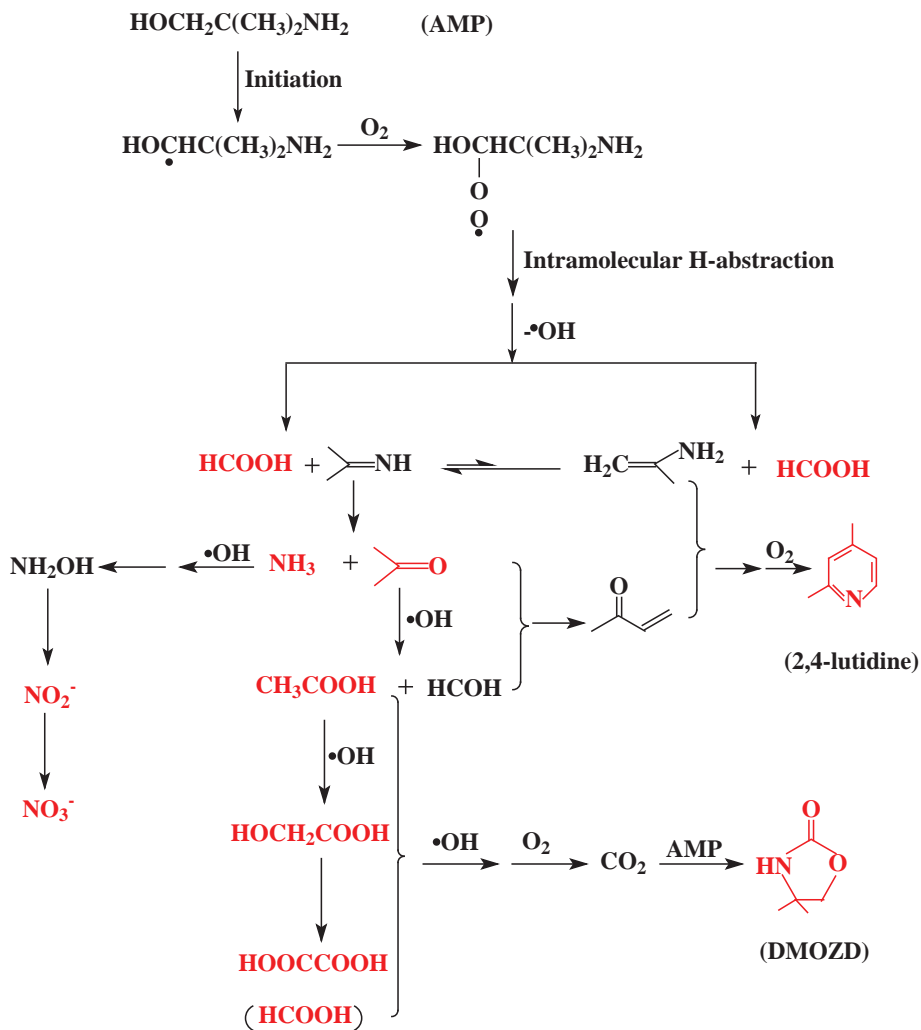


Fig.1. Scheme for AMP oxidation adapted from [13]. Compounds noted in red have been identified in the degraded reaction mixture.

In this work AMP oxidation was studied to clarify the oxidation pathway of individual AMP before attempting to understand the oxidation pathways of AMP/MEA blends. Aqueous AMP solutions with initial concentration of 3-5 mol/kg were degraded under 250-350 kPa O₂ at 100-140°C. The major degradation products of AMP included ammonia, acetone, 2, 4-lutidine, 4, 4-dimethyl-2-oxazolidinone (DMOZD) and carboxylate ions. Except for 2, 4-lutidine, all observed products belong to the same families as described for the degradation products of MEA. 2, 4-lutidine is a secondary product of AMP oxidation at elevated temperatures, which is supported by a synthesis study [13]. Based on the identified products, we have proposed a pathway for degradation of AMP as summarized in Fig.1. [13]. Oxidative degradation of AMP is believed to proceed via a radical mechanism. O₂ participating in the oxidation process is thought to be through formation of a peroxy radical, which decomposes into primary products through intramolecular hydrogen abstraction and loss of a ·OH radical.

Formation of HEF and HEA in the case of MEA suggests that carboxylic acids play one more role in further degradation of the solvent in addition to the well known heat stable salt forming reaction. Since the carboxylic acids were also found in AMP degradation, we suspect that similar reactions could occur between AMP and these acids, however, the expected amides were not found in the degraded AMP solutions. Thus it seems that the steric hindrance in AMP could be unfavourable for this reaction.

3.2. Oxidation of AMP/MEA blends

3.2.1. Overview of degradation products

For the oxidation experiments of AMP/MEA blends, the operating temperatures ranged from 100 to 140°C, the O₂ partial pressure ranged from 250 to 350 kPa, and the AMP-MEA ratio was varied as shown in Table 1. A total of eight oxidation experiments were completed with the AMP/MEA blends in the glass autoclave reactors. We detected the same degradation products under different composition, temperature and oxygen pressure, except that the relative amounts of the products varied. The oxidative degradation products in the AMP/MEA blends are similar to those observed in separately degraded AMP and MEA. In the blends the major MEA derived compounds included HEF, HEA and HEI. In comparison with degradation of single AMP and MEA samples, no new oxidative degradation product was detected in the AMP/MEA mixtures. This indicates that AMP and MEA can be oxidized in parallel in an AMP/MEA blends.

Table 1. Summary of experimental conditions with AMP/MEA blends

Expt. No.	Initial AMP conc. (mol·kg ⁻¹)	Initial MEA conc. (mol·kg ⁻¹)	Temp. (°C)	O ₂ press. (kPa)	Apparent first order reaction constant/ 10 ⁻⁷ s ⁻¹	
					MEA	AMP
AM1	4	1	120	250	13.6 ± 0.97	4.54 ± 0.53
AM2	3	2	120	250	12.7 ± 1.17	3.96 ± 0.45
AM3	2	3	120	250	7.55 ± 0.23	3.56 ± 0.09
AM4	2	3	120	350	12.2 ± 0.53	5.31 ± 0.25
AM5	3	2	140	250	19.5 ± 1.14	6.37 ± 0.68
AM6	3	2	100	250	5.37 ± 0.57	1.72 ± 0.16
AM7	4	2	120	250	10.6 ± 0.76	3.10 ± 0.32
AM8	4	4	120	250	7.07 ± 0.26	2.37 ± 0.11

It should be noted that DMOZD was detected in the degraded AMP/MEA mixtures, but no 2-oxazolidinone (OZD) was found. OZD is reactive and easily reacts with another MEA molecule to form N-(2-hydroxyethyl)-ethylenediamine (HEEDA). Subsequently HEEDA reacts with CO₂ to form N-(2-hydroxyethyl)imidazolidinone (HEIA) [16]. Hence OZD cannot accumulate in the degraded blends. Although DMOZD is much more stable than OZD due to the steric hindrance, MEA can still react with DMOZD to form 2-ethylenediamine-2-methyl-1-propanol [16]. AMP can also react with OZD in a similar way. Thus cross products can be expected to be formed in the presence of CO₂. However, further degradation products of OZD and DMOZD were not detected in this work as these degradation products are expected at low concentration because the blends were not loaded with CO₂.

3.2.2. Degradation rate

The concentration profiles for AMP and MEA in the partially degraded mixtures decreased linearly with degradation time when plotted in a semi-logarithm scale. This suggests an overall first order reaction with respect to the amines. All the calculated first order reaction constants for AMP and MEA under different experimental conditions are presented in Table 1. Although our MEA and AMP oxidation experiment could be oxygen mass transfer limited at the experimental temperatures, it does not affect the comparison of the relative degradation rates between AMP and MEA. The results show that the rate of MEA degradation was higher than that of AMP in all the different blend composition at all experimental conditions. As can be seen in Table 1, the overall rates of both AMP and MEA degradation increased with rising temperature. The generation of carboxylate ions was measured in all samples. The comparison of formate and oxalate concentration for the case of 3 mol/kg AMP-2 mol/kg MEA at 120°C and 140°C is shown in Fig. 2. Generation of both formate and oxalate was enhanced at higher temperature, as expected with increased oxidation rates of AMP and MEA. This result indicates that the enhanced degradation rates of AMP and MEA at higher temperatures are potentially true which is also reflected in increased concentration of degradation products.

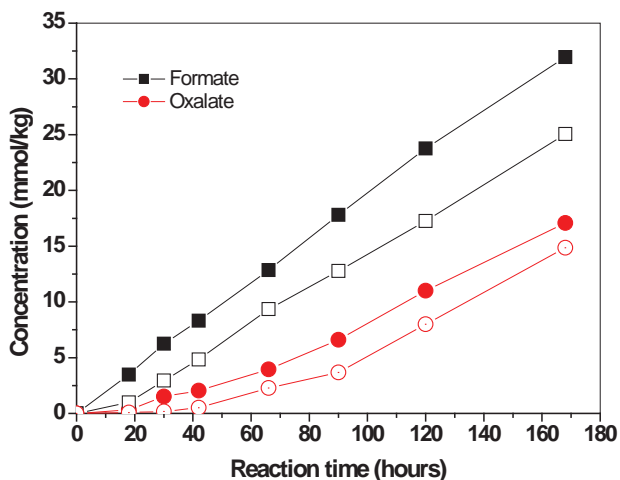


Fig.2. Effect of temperature on generation of formate (■) and oxalate (●) at 120°C (open points) or 140°C (solid points). The experiments were conducted with 3 mol/kg AMP + 2 mol/kg MEA under 250 kPa O₂.

For the case of amine oxidation, dissolved O_2 reacts with amine followed by degradation. Degradation rates of AMP and MEA are increased at increased O_2 partial pressure since concentration of dissolved O_2 in the aqueous phase is an increasing function of O_2 partial pressure. Most of the oxidation experiments were performed with an oxygen partial pressure of 250 kPa. However, in order to investigate the effect of O_2 partial pressure on AMP/MEA blend degradation, two of the eight experiments were conducted with varied O_2 pressure. As shown in Table 1, for the case of 2 mol/kg AMP and 3 mol/kg MEA degraded at 120°C , the apparent first order reaction constant for AMP increased with 49% when O_2 pressure was increased from 250 kPa to 350 kPa, and the apparent first order reaction constant for MEA increased with 61%. This result demonstrates that, as expected, O_2 partial pressure has a significant effect on both oxidation rates of AMP and MEA in blends. The oxidation of MEA and AMP could be O_2 mass transfer limited under the experimental conditions [16, 17], thus higher O_2 pressure caused higher degradation rates of MEA and AMP.

Based on the previous assumption that AMP and MEA may be oxidized in parallel in AMP/MEA blends, and that acetone, 2, 4-lutidine and DMOZD are universally found during oxidative degradation of individual AMP and AMP/MEA blends, we take these three AMP degradation products as degradation indicator. Comparison of the amount of acetone, 2, 4-lutidine and DMOZD in the blends after 168 hours reaction time is shown in Fig.3. The amount of acetone, 2, 4-lutidine and DMOZD significantly increased with raising O_2 pressure. As proposed in Fig.1, acetone is an intermediate of AMP oxidation and decomposes further in the presence of $\cdot\text{OH}$ radical. Therefore, the end result of the formation rate of acetone increased less than those of 2, 4-lutidine and DMOZD.

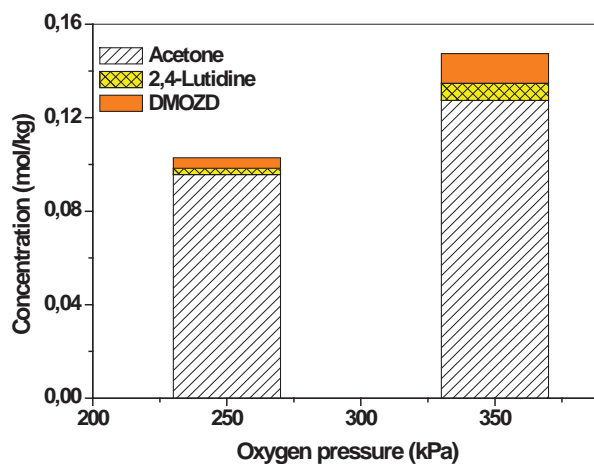


Fig.3. Comparison of the amount of formation of acetone, 2, 4-lutidine and DMOZD in 2mol/kgAMP-3 mol/kg MEA mixture after 168 hours. The experiments were conducted at 120°C and oxygen pressure of 250 kPa and 350 kPa.

Another factor explored in this work is the effect of blend composition on the oxidation of AMP in the blends. As can be seen in Table 1, the degradation rate of AMP decreased when the initial concentration of AMP was fixed at 4 mol/kg but the initial concentration of MEA was increased. Fig. 4 shows the amount of formation of acetone, 2, 4-lutidine and DMOZD at 168 hours in the AMP/MEA blends. The data clearly show that the amount of acetone, 2, 4-lutidine and DMOZD decreased with raising MEA concentration. The degradation rate of AMP and the formation rates of the indicators decreased indicating that MEA protects AMP from oxidation in the mixture when the initial MEA concentration was increased. As mentioned above, AMP and MEA could be degraded separately in the blends, but MEA degrades faster than AMP. It could be that MEA reacts faster with the autoxidation chain propagating

radicals. However, the oxidation of concentrated MEA and AMP could be O₂ mass transfer limited in the experimental conditions but above proposal could still hold true.

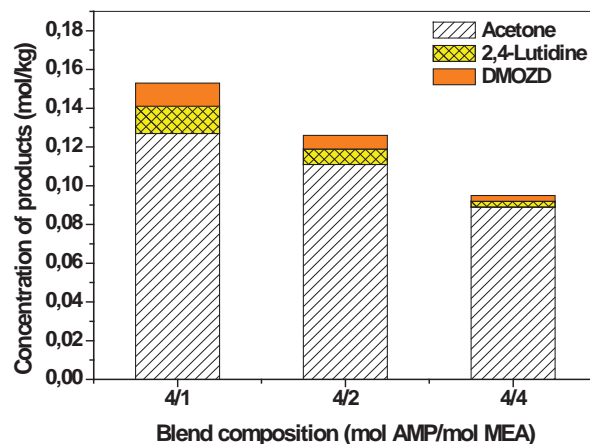


Fig.4. Generation of acetone, 2, 4-lutidine and DMOZD in degraded AMP/MEA mixtures at 168 hours and 250 kPa O₂ at 120°C.

4. Conclusion

No cross product was found in degraded AMP/MEA blends as compared with degradation of single MEA and AMP. This result indicates that AMP and MEA could be oxidized in parallel in the mixtures. As expected, both the overall degradation rates of MEA and AMP increased when raising temperature and oxygen partial pressure. MEA degraded faster than AMP in the blends under different experimental conditions. When initial MEA concentration was increased, the rate of AMP degradation decreased indicating MEA protects AMP from oxidation. The inhibition effect of MEA on AMP degradation could be due to the fact that MEA degraded faster than AMP in the blends, however, this “protecting” effect is not expected to operate in a situation with high O₂ concentration. Although thermodynamic and kinetic data have shown that AMP/MEA blend is an attractive solvent for CO₂ capture, it is not stable and needs degradation inhibition strategies for its industrial applications.

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