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Thermal degradation of morpholine in CO₂ post-combustion capture

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Abstract

Aqueous monoethanolamine (MEA) has been used as benchmark solvent in CO₂ capture systems due to its fast absorption kinetics, high cyclic capacity and low cost. However, operational challenges make MEA potentially less attractive, and therefore; there has been a high demand to develop new solvent systems, such as morpholine (MOR). Accordingly, in this work, thermal degradation studies using MEA or MOR have been conducted under stripper conditions in a post-combustion CO₂ capture system to identify operational challenges associated with amines degradation. The comparison of MEA and MOR degradation shows that MOR is more thermally stable when compared with MEA in the presence of CO₂ at stripper operating conditions studied here. Initial test results identified 1-(2-Hydroxyethyl)-2-imidazolidinone as thermal degradation of MEA, but they were not observed for MOR.

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1. Introduction

Post-combustion CO₂ capture systems employ a number of familiar gas separation techniques like absorption, adsorption, membrane separation, chemical looping combustion, cryogenic distillation and hydrate-based separation [1]. Amine-based absorption is the current state-of-the-art and most mature technology for post-combustion CO₂

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capture from coal-fired power plants [2]. However, thermal degradation of amines during the regeneration process will reduce CO₂ capacity; increases the costs of solvent make-up, reclaiming and disposal of waste. Therefore, the rate of degradation of amines used in CO₂ capture is of significance in solvent selection [3]. Thermal degradation can also present potential environmental concerns associated with unknown health effects and reactivity in the environment of several volatile degradation products [3, 4, 5, 6].

Operational challenges related to using MEA for CO₂ capture have led to research into alternative solvent systems. Morpholine (MOR) has been proposed for CO₂ capture because of its fast reaction rate and high thermal stability [4, 7]. These attractive advantages of MOR have prompted studies on the kinetics of CO₂ capture by MOR; however, they have not been investigated under comparable stripper operating conditions [3]. Accordingly, an understanding of the degradation of MOR in post combustion system conditions is presented here.

2. Materials and Experimental Method

2.1. Materials

All chemicals used in this work were commercially available from Sigma-Aldrich Company Ltd and Fisher Scientific UK Ltd. Sulphuric acid solution was prepared according to American standard (CTM-027) in an impinger to prevent any amine from escaping the system. 2-Oxazolidinone, (2-Hydroxyethyl)urea, 1-(2-Hydroxyethyl)-2-imidazolidinone solution (HEIA), N-(2-Hydroxyethyl) ethylenediamine (HEEDA) have been reported in literature as main degradation compounds formed from thermal degradation of MEA [6,8,9,10]. Therefore, these chemicals were purchased as standard samples and were used as fingerprints in the gas chromatograph (GC) for comparison with degradation samples from this work. All of the amine and other chemical solutions in this work were prepared volumetrically. Millipore Direct-Q Water Purification System provided the deionized water used in the preparation of the solutions. The system produced 18.2 MΩ·cm at 25 °C ultrapure water. The amines used for the thermal degradation study in this research work were of 99% purity and used as received.

2.2. Experimental Method

Figure 1 is a schematic representation of the apparatus for the absorption process. Firstly, CO₂ gas was bubbled via a frit tube into a 500 ml three-neck flask reactor containing 30 wt% solvent (MOR or MEA) at a flowrate of 0.2 l/min and stirred at 340 rpm with a magnetic stirrer. Amine concentration was kept at 30 wt% because of reported corrosion and operational issues [11]. Temperature in the thermal oil bath was set to 50 °C - a temperature representative of normal absorber conditions. After the desired CO₂ loading of 0.4 moles CO₂/mole MEA or MOR was achieved, the gas feed was turned off. CO₂ loading was determined by the method described by Wonder et al [12] and Buschle et al [13].

Thermal degradation experiments were carried out using 150 ml 316L stainless steel DOT-Complaint sample cylinders with valve and fittings purchased from Swagelok. Temperature and pressure were monitored using a T-type thermocouple with accuracy of ±1 °C and a SMPG 50 mm dial pressure gauge with accuracy of ±0.2% purchased from Hydrasun[®], respectively. 50 ml each of the solution were then introduced into the Swagelok thermal sample cylinders and degradation studies were carried out for 4-5 weeks at temperatures of 135 °C and 150 °C at 4 bar pressure. The cylinders were then placed in a forced convection oven at temperatures representative of stripper operating conditions (120 °C – 150 °C) [6]. A cylinder was taken out of the oven after two and four weeks; it was allowed to cool down to room temperature under ambient conditions. The contents were then transferred into glass vials and a portion of the sample diluted with deionized water – 0.1% v/v, for analytical testing. A GC (Agilent, Model 7890B series) with a flame-ionization detector (GC/FID) was used to analyze the degraded samples. The separation column used was a Durabond column, (DB-624, 30 m×0.32 mm×1.80 μm).

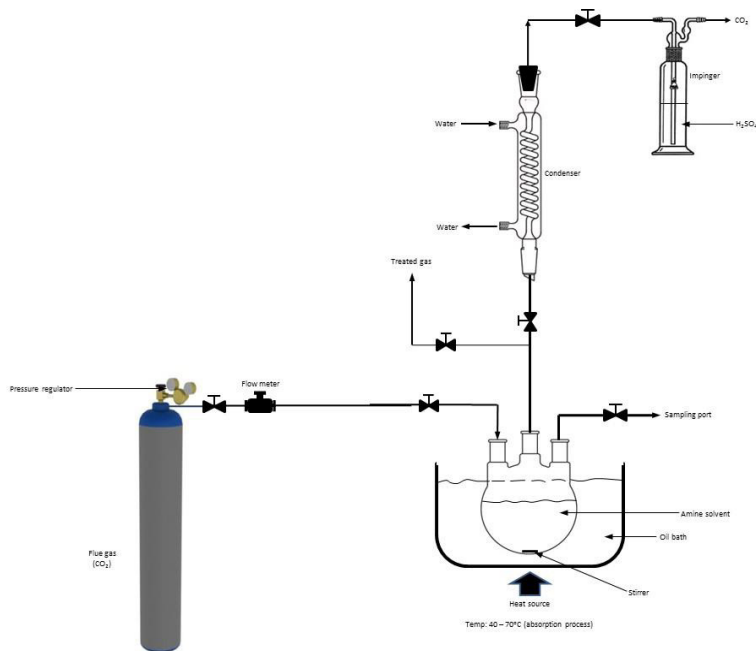


Fig. 1. CO₂ absorption apparatus.

3. Results and Discussion

Thermal degradation studies were conducted to identify potential operational and environmental challenges related to amine degradation and degradation compounds, and the results are discussed here.

3.1. MEA degradation

Table 1 shows the area percent of various peaks observed from the GC plot of 30 wt% MEA with 0.4 mol CO₂ loading subjected to degradation at 135°C for over two weeks. Degradation products, including HEIA and HEEDA were detected. The area percent for MEA decreased from 93.62% to 92.38% indicating that most of the MEA degradation occurred during the first two weeks. After two weeks, HEIA was observed and both HEIA and HEEDA were present after four weeks. The area of the HEIA compound did not change significantly between two and four weeks of thermal stress; however, the area percent of HEEDA increased up to 2.97% between two and four weeks of thermal stress. This agrees with the work reported by Davis and Rochelle [8] and Zoannou et al. [6].

2-Oxazolidinone was not detected in this work, possibly because this degradation product is said to be unstable and a precursor to the production of HEIA [8]. Davis and Rochelle [8] have also reported measurable quantities of (2-Hydroxyethyl)urea for a short interval after an initial lag period using HPLC. However, in the studies reported here, (2-Hydroxyethyl)urea was not detected by GC after two weeks and four weeks of thermal degradation of MEA. This is consistent with the GC studies conducted by Lepaumier et al. [14] and Zoannou et al. [6] who also reported that it was not possible to detect this product using GC analysis.

Table 1. Comparison of area percent for the GC peaks identified for the degradation of MEA over two and four weeks at 135°C and 4 bar.

| | MEA | HEIA | HEEDA | Unknown |
|-------------------------|-------|------|-------|---------|
| <i>After two weeks</i> | 93.62 | 4.17 | N.D. | 2.21 |
| <i>After four weeks</i> | 92.38 | 4.10 | 2.97 | 0.55 |

N.D.: Not detected

3.2. MOR degradation

Table 2 shows the area percent of various peaks observed from the GC plot of MOR samples degraded at 135 °C for two weeks with CO₂ loading of 0.4 mol CO₂. MOR did not degrade significantly even after four weeks, as observed by the area percent for MOR decreasing only slightly from 99.90% to 99.65%. After two and four weeks, 2-Oxazolidinone, HEIA and HEEDA were not detected. Therefore, when comparing the thermal degradation of MEA and MOR after two and four weeks, degradation of MOR under the same operating conditions is slower than that of MEA.

Table 2. Comparison of area percent for the GC peaks identified for the degradation of MOR over two and four weeks at 135°C and 4 bar.

| | MOR | HEIA | HEEDA | Unknown |
|-------------------------|-------|------|-------|---------|
| <i>After two weeks</i> | 99.90 | N.D. | N.D. | 0.10 |
| <i>After four weeks</i> | 99.65 | N.D. | N.D. | 0.35 |

N.D.: Not detected

4. Conclusions

A comparison of the potential operational and environmental challenges related to amine degradation and degradation compounds was performed using MEA and MOR. Amine degradation in post-combustion CO₂ capture is a slow process with MEA and MOR degrading at different rates in the presence of CO₂ at stripper operating conditions. HEIA and HEEDA were identified as thermal degradation products of MEA under the studied conditions. However, HEIA and HEEDA were not detected after two and four weeks from the thermal degradation of MOR. Therefore, the studies conducted thus far show that MOR is more thermally stable when compared with MEA. Work is still on going to determine the major degradation products formed from thermal degradation of MOR and future experiments will include evaluating the impact of impurities, such as NO_x, SO_x and H₂S on the performance of MOR. Health and environmental issues about the use of MOR for CO₂ capture will also be investigated.

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