# Degradation of Monoethanolamine Used in Carbon Dioxide Capture from Flue Gas of a Coal-fired Electric Power Generating Station

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Introduction

The development of techniques for the separation and capture of CO_2 is considered to be one of the highest priorities in the field of carbon sequestration science. This is mainly because the capture cost is expected to make up about 75% of the total costs for geological or oceanic sequestration[1], with the other 25% going into transportation and injection costs. The technology for separation of CO_2 from flue gas or from other gaseous streams using chemical absorption has existed and been in use for decades.[2,3] To date, chemical absorption is the only technique that has been used commercially to capture CO_2 from flue gas. The general method involves exposing a gas stream to an aqueous amine solution which reacts with the CO_2 in the gas by an acid-base neutralization reaction to form a soluble carbonate salt:

$$2RNH_2 + CO_2 + H_2O \,^\circ\ (RHN_3)_2CO_3 \qquad [1]$$
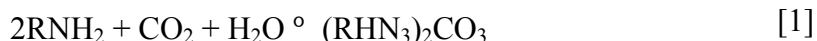
This reaction is reversible, allowing the CO_2 gas to be liberated by heating in a separate stripping column. Therefore, the major advantage to this technique is that, in the ideal situation, the amine is not consumed and may be continuously recycled through the process.

The amine used in this process is most commonly one of several alkanolamines including monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), or diisopropanolamine (DIPA). The technology was originally developed not for the purpose of carbon sequestration, but in order to "sweeten" natural gas streams by removing CO_2.[4] More recently, it was successfully adapted for recovery of CO_2 from flue gas of coal-fired electric power generating plants.[5] In this case, rather than CO_2 sequestration, the CO_2 has been used for commercial purposes such as enhanced oil recovery and the carbonation of brine as well as food industry uses. Currently there are three electric power generating stations in the U. S. that capture CO_2 from flue and six

other major flue gas CO_2 capture facilities worldwide. All nine use MEA as the chemical sorbant.[6]

There is only one operation in the world that performs CO_2 separation for the purpose of sequestration. Statoil's Sleipner plant separates about 2,800 tons of CO_2 from a natural gas stream daily using chemical absorption and injects it into a saline aquifer below the North Sea. [7] This project was made economically attractive by a Norwegian tax based on CO_2 emissions. In order for current sequestration goals to be met, it may be necessary for many fossil fuel fired power plants to adopt similar capture and sequestration capabilities. Unfortunately, such a large scale CO_2 separation program would be cost prohibitive under the current state of technology. One possible solution is to improve upon the existing technology in a way that will decrease the cost.

A significant problem with the MEA absorption technique in its current form is the degradation of the amine over time. The byproducts of MEA degradation are known to decrease the efficiency of CO_2 capture. and have also been implicated in the corrosion of machinery[8] In order to compensate for this degradation, current facilities include distillation of the amine to remove byproducts while continuously adding fresh amine to the system. Unfortunately, this leads to increased material and waste disposal costs. In addition, degradation processes have forced the use of lower concentrations of MEA (<20%) leading to larger overall equipment size, higher solvent circulation rate, and therefore increased energy requirements for CO_2 regeneration from the rich amine.[9] This increased energy requirement is especially significant since it increases the parasitic load on the power plant leading to increased fuel consumption, higher maintenance costs, and (ironically) increased CO_2 production relative to the power output of the plant.

Using current technology, it has been estimated that CO_2 capture from fossil fuel-fired power plants for geological or ocean sequestration would increase electricity costs by 50%.[9] This does not include transportation and injection costs, which would increase the economic burden even further. It is clear that CO_2 separation technology based on chemical absorption could be improved by limiting or eliminating solvent degradation. It is crucial that we learn more about the processes that lead to solvent degradation. A clear understanding of the chemical processes involved under current conditions will be necessary in order to guide the development of improved solvents or technology.

Reactions of MEA with carbon dioxide[10,11] and with oxygen[12] have been well studied over the past 50 years. It is thought that CO_2 initiated degradation begins with the formation of 2-oxazolidone:

$$HO \diagup \diagdown NH_2 + CO_2 \rightleftarrows \quad O \diagup \diagdown NH + H_2O \qquad [2]$$
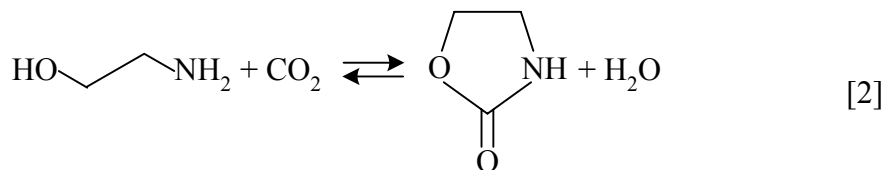
which can, in turn, react with another MEA molecule to form N-(2-hydroxyethyl)-ethylenediamine via intermediates of N,N′-di(hydroxyethyl)urea and 1-(2-hydroxyethyl)-2-imidazolidone:

$$\text{[3]}$$
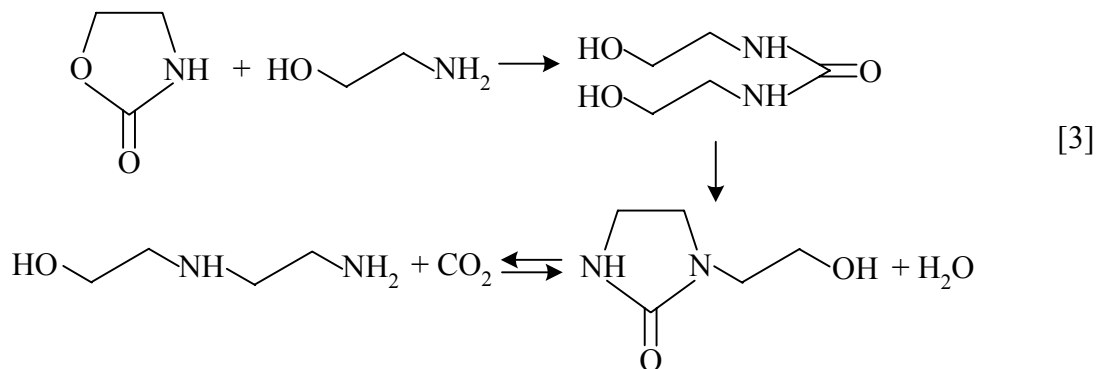
The majority of work that has been done in this area was aimed at understanding natural gas sweetening processes. However, in flue gas from a fossil fuel fired boiler, the process becomes much more complicated due to the presence of a mixture of CO_2, O_2, CO, SO_x, NO_x, and fly ash. The degradation process in this case remains poorly understood, particularly under conditions that are common to power plants.[13]

In order to begin to develop an understanding of how the degradation products are formed, the first step is to determine what the major products are under actual plant conditions. Once the formation mechanisms are elucidated, it may be possible to take steps to minimize them or prevent them from occurring.

Approach

The IMC Chemicals Facility in Trona, California is a plant that has been performing CO_2 capture from flue gas since 1978, longer than any other such plant in the world. CO_2 is separated from flue gas of a coal-fired boiler, which is used to produce electricity. In this case, the captured CO_2 is used for the carbonation of brine from Searles Lake, California for the commercial production of sodium carbonate.[5] For the current study, MEA samples were obtained from this plant in order to identify the degradation products from the CO_2 separation process. There were two samples obtained as well as a sample of the virgin concentrated MEA. The first sample was "lean" MEA. This is the material that is introduced to the absorption column where it is contacted by flue gas. The second was the reclaimer bottoms, which is the still bottoms waste that remains after the amine is distilled to remove the degradation products.

A variety of analytical techniques were used to characterize these samples. In order to identify the volatile organic compounds, the mixture was separated and analyzed using combined gas chromatography-mass spectrometry (GC-MS) and combined gas chromatography-Fourier transform infrared absorption spectrophotometry (GC-FTIR).

Two separate gas chromatographic columns were used for separation. The first was a 60 m × 0.32 mm i. d. fused silica column coated with a 0.25-μm film of 14%-(cyanopropyl-phenyl)-methylpolysiloxane (DB-1701 from J&W Scientific). This column was temperature programmed from 35 to 280°C at 1 C^o/min. The second column, a 60 m × 0.25 mm i. d. column coated with 0.25-μm modified polyethylene glycol (Nukol™ from Supelco), was temperature programmed from 50 to 200°C at 5 C^o/min. Helium carrier gas was used with initial linear velocities of 40 and 36 cm/s, respectively. In both cases, samples were introduced via a split injector held at 250°C. GC-MS experiments were done using an HP 5973 mass selective detector (MSD) and GC-FTIR experiments employed an HP 5965A infrared detector (IRD).

In addition, precise molecular masses of the organic compounds were obtained using low voltage high-resolution mass spectrometry (LVHRMS).[14] Mass spectra were acquired on a Kratos MS-50 high-resolution mass spectrometer. The ionizing voltage was set to about 11.5 electron volts in order to minimize fragmentation and therefore enhance detection of molecular ions. In this experiment, the samples were introduced to the ion source directly without prior separation.

Results

Since the focus of this study was on the MEA degradation products, the reclaimer bottoms sample, where these products were concentrated as a result of distillation provided the most important information. Portions of the total ion chromatograms obtained from GC-MS analysis of this sample on both the DB-1701 and the Nukol™ columns are shown in Figures 1 and 2, respectively. The numbered peaks are identified in table 1 along with the methods of identification. An "x" in the GC-MS or GC-FTIR column indicates a positive match from an electronic search of either MS or FTIR libraries. MS library searches were done using the NIST Mass Spectral Search Program for the NIST/NIH/EPA Mass Spectral Library.[15] FTIR searches were done using the FTIRsearch.com service.[16] The LVHRMS column indicates whether a match within 0.003 amu of the mass of the indicated molecule was present in the mass spectrum of the entire sample. Also included in Table 1 is an indication of which column or columns were used to detect each compound. The % of total area refers to the integrated peak area from the total ion chromatogram as a percentage of the total signal intensity for each column. Other than the MEA, none of the peaks shown in Figures 1 and 2 were present in identical experiments performed on the virgin MEA

The use of two separate GC columns (one intermediate and one polar stationary phase) was necessary due to the large variation in polarity of the degradation products, a result of the large number of heteroatoms present in the compounds. This is illustrated by the fact that each chromatogram (Figures 1 and 2) has some major peaks that are not present in the other.
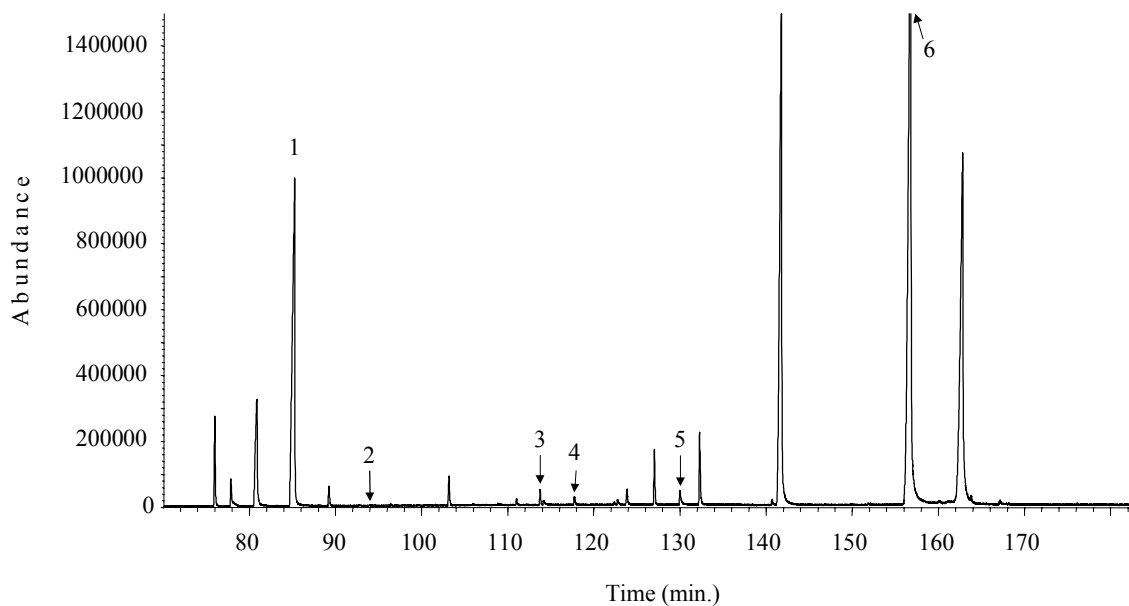
Figure 1. Portion of total ion chromatogram of the reclaimer bottoms sample obtained using the DB-1701 column. Numbered peaks are identified in Table 1. (MEA peak at 9.3 minutes not shown.)
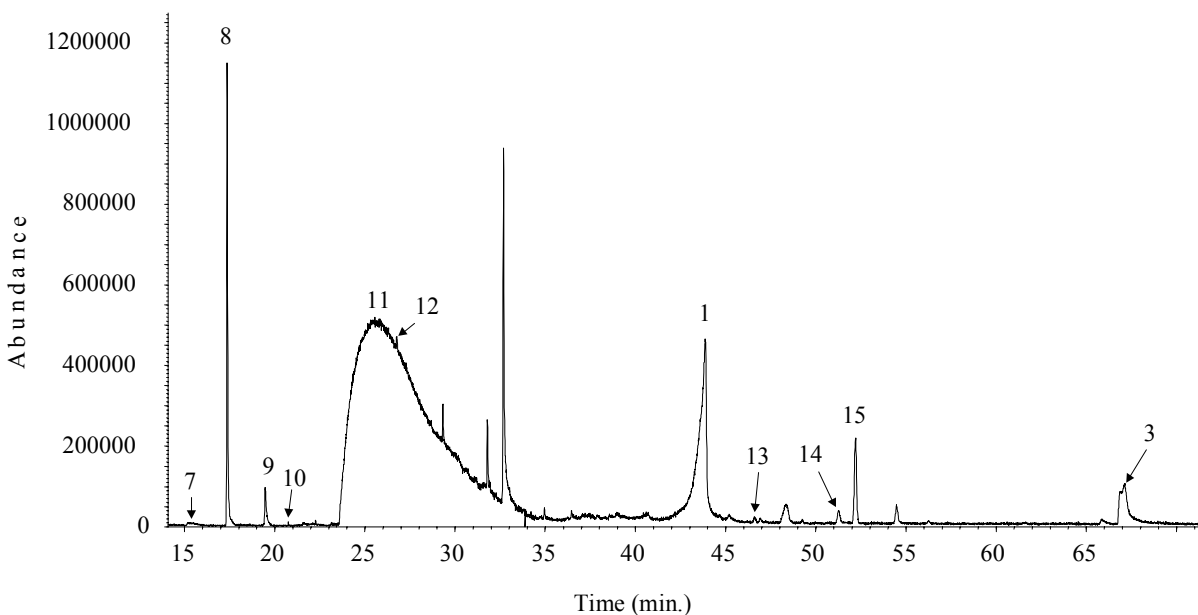

Figure 2. Portion of total ion chromatogram of the reclaimer bottoms sample obtained using the Nukol™ column. Numbered peaks are identified in Table 1.

Table 1. Identified compounds from monoethanolamine reclaimer from a CO_2 capture facility.

peak	compound	method of identification			GC column		%of total area	
		GC-MS	GC-FTIR	LVHRMS	DB-1701	Nukol	DB-1701	Nukol
1	N-acetylethanolamine ($C_4H_9NO_2$)	x		x	x	x	8.86	6.28
2	N-glycylglycine ($C_4H_8N_2O_3$)	x		x	x		<0.01	
3	N-(hydroxyethyl)-succinimide ($C_6H_9NO_3$)	x		x	x	x	0.16	*
4	N-(2-hydroxyethyl)-lactamide ($C_5H_{11}NO_3$)	x	x	x	x		0.07	
5	1-(2-hydroxyethyl)-2-imidazolidinone ($C_5H_{10}N_2O_2$)	x	x		x		0.24	
6	N,N-diacetylethanolamine ($C_6H_{11}NO_3$)		x	x	x		21.83	
7	ammonia (NH_3)	x				x		0.10
8	acetic acid ($C_2H_4O_2$)	x		x		x		2.02
9	propionic acid ($C_3H_6O_2$)	x				x		0.30
10	n-butyric acid ($C_4H_8O_2$)	x		x		x		0.01
11	monoethanolamine (C_2H_7NO)	x	x	x	x	x	*	35.18
12	2,6-dimethyl-4-pyridinamine ($C_7H_{10}N_2$)	x		x		x		0.05
13	2-imidazolecarboxaldehyde ($C_4H_4N_2O$)	x		x		x		0.05
14	1-methyl-2-imidazolecarboxaldehyde ($C_5H_6N_2O$)	x		x		x		0.17
15	2-oxazolidone ($C_3H_5NO_2$)	x		x		x		0.80

* Area percentage not calculated due to overlap with other peaks

Peaks 5 and 15 are known products of the degradation of MEA induced by CO_2 as shown in equations [2] and [3]. However, these are relatively minor components. The other two compounds from equation [3], N,N'-di(hydroxyethyl)urea and N-(2-hydroxyethyl)-ethylenediamine are not present at a detectable level. The largest identified peaks from MEA degradation products are due to N-acetylethanolamine and N,N-diacetylethanolamine (peaks 1 and 6), indicating that degradation may be dominated by a process other than simple reaction between MEA and CO_2. The acetic, propionic and butyric acid (peaks 8,9, and 10) are suspected to be present in the flue gas in small amounts as combustion products which may be captured by the MEA and may react with it. The acetylated MEA compounds show that reaction between acetic acid and MEA may be a major source of degeradation.

Future Activities

At the time of submission, positive identification of all of the major degradation products was not yet fully accomplished. In order to identify the remaining compounds as well as to provide further confirmation of the identity of the compounds listed on table 1, preparative GC will be used to isolate the compounds. Both proton and carbon-13 nuclear magnetic resonance (NMR) spectra may then be obtained for each as well as the single species LVHRMS. In addition, authentic standards of each identified compound will be obtained in order to verify gas chromatographic retention times under identical experimental conditions. The standards will also be used to determine response factors in order to calculate relative concentrations for each compound. This will provide a more complete picture of the organic MEA degradation products so that degradation pathways and mechanisms may be postulated.

The work described thus far has been aimed primarily at identifying organic molecular compounds in the MEA degradation samples. It is known that ionic species are also generated in alkanolamine degradation.[12] Identification of ionic species is currently in progress using ion chromatography (IC) as well as inductively coupled plasma emission spectrophotometry (ICP). The reclaimer sample also contained a solid residue that will be isolated and analyzed as well.

Acknowledgments

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