Chemical Engineering Science 66 (2011) 3491–3498

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

# Degradation of MMEA at absorber and stripper conditions

Helene Lepaumier[a], Andreas Grimstvedt[b], Kai Vernstad[b], Kolbjørn Zahlsen[b], Hallvard F. Svendsen[a,*]

[a] *Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway*
[b] *SINTEF Materials and Chemistry, N-7465 Trondheim, Norway*

ARTICLE INFO

*Article history:*
Received 11 November 2010
Received in revised form
2 March 2011
Accepted 5 April 2011
Available online 21 April 2011

*Keywords:*
$CO_2$ capture
Absorption
MMEA (*N*-methylethanolamine)
Oxidative degradation
Thermal degradation
Mechanisms

ABSTRACT

This study examines the degradation of *N*-methylethanolamine (MMEA) under different experimental conditions. Thermal degradation with and without $CO_2$, and oxidative degradation are investigated. Samples of the degraded solution were taken at regular intervals and analyzed. The percentage of amine loss was determined by Liquid Chromatography–Mass Spectrometry (LC–MS) while the degradation compounds were identified and quantified by Gas Chromatography–Mass Spectrometry (GC–MS). MMEA degradation at absorber and stripper conditions is compared with previous work on 2-ethanolamine (MEA). Degradation mechanisms are proposed and discussed in order to understand the differences compared to MEA.

## 1. Introduction

Global warming is a major environmental issue and one of the main causes is the increase of anthropogenic $CO_2$ emissions to the atmosphere. Main point sources are industries (19%) and power stations (26%; Metz et al., 2007). Different technologies are developed to reduce these emissions, but post-combustion $CO_2$ capture by absorption remains a very attractive technology to treat the off-gases from already existing industrial sources. The technique consists in capturing $CO_2$ by reversible chemical reaction with an aqueous amine solution. The flue gases are injected into the absorber at 40 °C where $CO_2$ reacts with the amine to give carbamate and/or hydrogen carbonate and carbonate. The solution is then transferred to the stripper where the temperature is higher (about 120 °C) and the reverse reaction takes place, i.e. the regeneration of $CO_2$ and the amine itself. Various properties determine whether an amine is a "good" solvent. It should have high absorption capacity, fast kinetics. It should also be non-volatile, water soluble, cheap, and environmentally friendly. A final criterion is its chemical stability. Indeed, the degradation compounds can themselves be toxic and lead to solvent losses, corrosion, foaming, fouling, increase in viscosity, and thereby exclude themselves or generate additional costs (Kohl and Nielsen, 1997). MEA is so far the benchmark solvent for post-combustion $CO_2$ capture. However, its degradation can appear as an important limitation. In the process, solvents like MEA are subject to three types of degradation: thermal, carbamate polymerization, and oxidative (Goff and Rochelle, 2004). Thermal degradation (without or with $CO_2$) is more likely to take place in the stripper since the temperature can be above 140 °C while oxidative degradation may occur especially in the absorber because the amount of $O_2$ there is higher. Several authors have studied MEA degradation under these different conditions (Polderman et al., 1955; Strazisar et al., 2003; Goff, 2005). In fact, the objectives are two-fold. It is important to identify the degradation compounds in order to establish their effect on the process but it can also help to find new solvents for $CO_2$ capture. The companies are indeed more and more eager to replace MEA, for example Mitsubishi with KS-1 (Kishimoto et al., 2009) or Cansolv with DC-103 (Shaw, 2009).

In the same way, the stability of diethanolamine DEA (Meisen and Kennard, 1982; Hsu and Kim, 1985; Kennard and Meisen, 1985) and *N*-methyldiethanolamine MDEA (Chakma and Meisen, 1988; Chakma and Meisen, 1997; Critchfield and Jenkins, 1999) was also investigated in the literature. On the other hand, the use of 2-(methylamino)ethanol (MMEA) as a potential solvent for $CO_2$ removal has not been considered even if MMEA seems to have good properties for capturing $CO_2$. It has a structure very close to MEA and has faster kinetics. Recently, its degradation has been described and compared with MEA. It was shown that MMEA was more unstable than MEA at 140 °C with or without $CO_2$ (Lepaumier et al., 2009a). Regarding the oxidative degradation, the experiments were performed in close-batch but no significant difference was noticed between these two amines (Lepaumier et al., 2009b).

---

* Corresponding author. Tel.: +47 735 94100; fax: +47 735 94080.
*E-mail address:* hallvard.svendsen@chemeng.ntnu.no (H.F. Svendsen).

0009-2509/$ - see front matter
doi:10.1016/j.ces.2011.04.007

In this paper MMEA degradation is presented in more detail and compared with MEA. The chemical stability is described both at absorber and stripper conditions in order to show the impact, respectively, of air and $CO_2$ on degradation. New degradation compounds have been identified in comparison with previous works. Samples at regular time intervals have been taken and analyzed in order to evaluate the progress of amine degradation. Mechanisms are proposed and discussed.

## 2. Experimental section

### 2.1. Equipment and chemicals

2-(methylamino)ethanol (MMEA) was purchased from Aldrich with a 99% purity. Analytical-grade carbon dioxide was supplied by Aga ($CO_2$: 5.0) and air was produced in situ from the pure gas generator ($CO_2$ free).

### 2.2. Typical experimental run

*Thermal degradation without $CO_2$ loading.* A 30 wt% aqueous solution of MMEA was prepared using deionized water. After degassing with nitrogen for 15 min in order to strip any air or $CO_2$ contamination, the solution was introduced into 316 stainless steel cylinders: in half of them, 7 mL of the solution was directly introduced, and in the second half, 3.5 mL of solution was first filled into a glass tube before introducing into the cylinder. Later, the cylinders were put in an oven (Memmert GmBH, model 600) and heated for 5 weeks at 135 °C, a temperature representative of normal stripper conditions (around 120 °C for MEA). At regular intervals (every week), one cylinder was taken and analyzed by LC–MS and GC–MS under conditions described below. Potential leakages were checked by weight comparisons of each cylinder before and after experiment.

*Thermal degradation with $CO_2$ loading.* As previously, a 30 wt% amine solution was prepared with deionized water, degassed with $N_2$, and loaded with 0.5 mole of $CO_2$ per mole of amine. Afterwards, the same procedure as above was applied to the $CO_2$ loaded amine solution. One sample was taken each week and analyzed.

*Oxidative degradation.* A 30 wt% MMEA solution, previously loaded with $CO_2$ ($\alpha=0.4$), was introduced into an open-batch reactor. A gas blend of air with 5% $CO_2$ was sparged into the mixture and heated at 55 °C, a temperature representative of normal conditions in the absorber. Regularly, samples were taken from the liquid phase and analyzed by the following analytical procedures.

### 2.3. Analyses

*Liquid Chromatography–Mass Spectrometry (LC–MS).* Analyses of the degraded samples were carried out on an LC–MS/MS system, 6460 Triple Quadrupole Mass Spectrometer coupled with 1290 Infinity LC Chromatograph and Infinity Autosampler 1200 Series G4226A from the supplier Agilent Technologies. The molecules were converted to ions by an electrospray ionization source (ESI). The analytical column was an Ascentis® Express RP-Amide HPLC Column (15 cm · 4.6 mm, 2.7 μm, Cat#:53931-U, Supelco Analytical, Bellefonte, USA). The eluent was 25 mM formic acid in water, with a 0.6 ml/min flow rate.

For the quantification of the remaining amine, the samples were diluted to 1/10,000 in water before injection. A specific method (Selected Ion Monitoring) and addition of an internal standard, MEA-d4 ($HO–CD_2–CD_2–NH_2$) permitted a higher sensitivity and accuracy. For the detection of the degradation compounds (full Scan Mode), the initial sample was diluted in water before injection to 1/100 for the positive ions (M+H+) and 1/10 for the negative ions (M–H+).

**Table 1**
Specifications of the GC/MS system.

| | |
|---|---|
| Column | CP-SIL-8 CB-Amines |
| Length (m) | 30 |
| Internal diameter (μm) | 320 |
| Thickness (μm) | 1.0 |
| Initial temp. (°C) | 40 |
| Initial hold time (min) | 2 |
| Oven ramp (1) ($^\circ C\ min^{-1}$) | 5 |
| Intermediate temp. (°C) | 210 |
| Intermediate hold time (min) | 10 |
| Oven ramp (2) ($^\circ C\ min^{-1}$) | 6 |
| Final temp. (°C) | 300 |
| Final hold time (min) | 10 |
| Flow rate (constant) ($mL\ min^{-1}$) | 1.0 |
| Split ratio | 10 |
| Injector temp. (°C) | 275 |

*Gas Chromatography–Mass Spectrometry (GC–MS).* GC/MS analyses were carried out on a Gas Chromatograph 7890A equipped with an Autosampler 7693 and coupled with a mass spectrometer (inert XL EI/CI MSD with triple axis detector 5975C). The Mass Spectrometer allows having both Scan and SIM Mode and could be used in Electronic Impact (EI), Positive, and Negative Chemical Ionization (PCI and NCI). Helium was used as carrier gas and methane as reagent gas for chemical ionization (CI). The samples were first diluted in water 1/10 to 1/100 depending on the type of analyses and on the level of degradation. They were injected in Split mode to avoid contamination of the system and to have a higher sensitivity. Separation of the different analytes was performed on a CP-SIL-8 CB Amines column (Varian) from the method described in Table 1. The main degradation compounds were quantified in electronic impact (EI) in SIM mode, which means that the three main ions for each product were selectively chosen with the MS detector to enhance the sensitivity and confidence of the quantification. The calibration curves were obtained from commercial standards at different concentrations and performed before analysis of the degraded sample. When the degradation compound was not commercially available, quantification was estimated and based on a standard with a similar chemical structure.

## 3. Results and discussion

In order to determine the effect of the temperature and of the gases $CO_2$ and air, MMEA degradation was investigated in three different conditions: thermal degradation without $CO_2$ (MMEA/$H_2O$ system), thermal degradation with $CO_2$ (MMEA/$H_2O$/$CO_2$ system), and oxidative degradation (MMEA/$H_2O$/$CO_2$/$O_2$ system). In the MMEA/$H_2O$ system, the amine solution was heated at 135 °C for 5 weeks. In the MMEA/$H_2O$/$CO_2$ system, the amine solution was first loaded with $CO_2$ ($\alpha=0.5$) and then heated to 135 °C for 5 weeks. Finally, in the MMEA/$H_2O$/$CO_2$/$O_2$ system, the oxidative degradation was evaluated at 55 °C by sparging a gas blend of $CO_2$ and air into a $CO_2$ loaded amine solution.

At the end of the experiment, only the liquid phase was analyzed by LC–MS and GC–MS to determine, respectively, the percentage of amine loss and the percentage of formation of the different degradation compounds.

Identification was mainly performed by GC–MS by using a large library of mass spectra (NIST), which made easier the assessment of the product. Then, when a degradation product was assumed, its retention time was first compared with the pure standard (if commercially available), as well as their mass