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Chemical stability and biodegradability of new solvents for CO₂ capture

Ingvild Eide-Haugmo^a, H el ene Lepaumier^a, Aslak Einbu^b, Kai Vernstad^b, Eirik Falck da Silva^b, Hallvard F. Svendsen^{a*}

^a Norwegian University of Science and Technology, 7491 Trondheim, Norway

^b SINTEF Materials and Chemistry, 7465 Trondheim, Norway

Abstract

A study on thermal and chemical stability of amines has been performed for eleven chemicals, including ethanolamine (MEA), 2-amino-2-methylpropanol (AMP) and diethanolamine (DEA), trying to identify the impact of parameters such as amine function, alcohol group and steric hindrance. The chemicals were studied for 5 weeks at 135°C, both with and without the presence of CO₂ (0.5 mol/mol amine) and in contact with metal (316 SS) as well as in glass containers. In general, the presence of metal did not make an impact on the degree of degradation. As for thermal degradation without CO₂, most of the compounds were relatively stable. For thermal degradation in the presence of CO₂, the sterically hindered amine AMP had the highest stability, while the secondary amines had the lowest. Increasing chain length gave slightly higher stability. In comparison with biodegradation, most of the compounds showed higher thermal degradation in the presence of CO₂ than for biodegradation, and compounds stable at process conditions are likely also resilient with regards to biodegradation. None of the tested chemicals has the combined desired stability under process conditions while at the same time being sufficiently biodegradable.

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Keywords: Biodegradation; thermal degradation; amine degradation; solvent development; carbon dioxide; CO₂ capture

1. Introduction

In CO₂-capture absorption processes, degradation is a general problem which should be minimized. Partly because of amine loss and subsequent reduction in absorption capacity, but also due to the properties of the degradation products formed. These can promote corrosion as well as cause viscosity changes and foaming. The solvents should be thermally stable at the temperatures experienced in the stripper; around 118–120°C in the case of ethanolamine with surface temperatures up to 135–140°C. At these temperatures thermal degradation may already take place. The chemical stability in presence of carbon dioxide and oxygen is usually of even greater concern. On

* Corresponding author. Tel.: +47 73 59 41 00; fax: +47 73 59 40 80.
E-mail address: Hallvard.Svendsen@chemeng.ntnu.no

the other hand, while the solvents should have chemical and thermal stability in the process, they should preferably degrade when released to the environment.

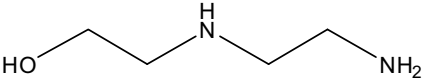
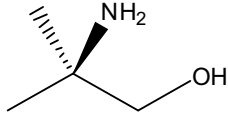
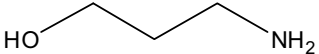
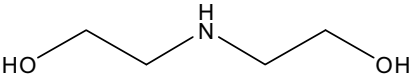
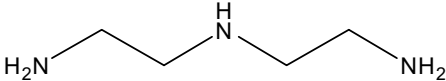
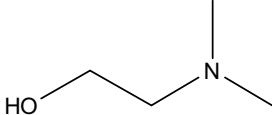
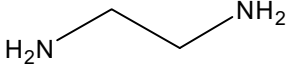
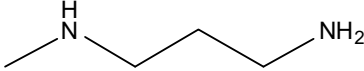
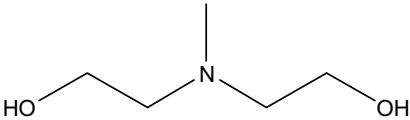
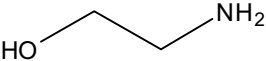
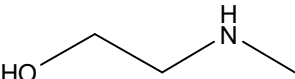
Emissions might occur through accidental spills or through the cleaned exhaust gas as volatile solvent or in the form of an aerosol. If the solvent is not naturally degradable, there might be a build up of the chemical in the environment. In order to identify the molecules which are both biodegradable and stable chemically under process conditions, the thermal degradation (with and without CO₂) is investigated and compared. One might initially assume that the readily biodegradable amines are less stable at process conditions. The compounds which have been studied in this work are presented in table 1, with abbreviations used, full name, CAS number and structure.

Previous work has established the biodegradability of a significant number of compounds (43) [1]. Other studies have been performed on wastewater treatment of ethanolamine (MEA)[2, 3] and methyldiethanolamine (MDEA)[4], finding that MEA was degradable under the right conditions, while MDEA was found to have no degradation. A study of the biodegradation of amines in seawater as well as freshwater was performed by Price *et al.*[5], finding that the rate of degradation in seawater was lower than in freshwater, even though the bacterial content in the tests was higher than that expected in the ocean. Diethylenetriamine (DETA) did not degrade, ethylenediamine (EDA) degraded in freshwater but not seawater, while diethanolamine (DEA) and triethanolamine (TEA) were degradable both in seawater and freshwater.

Several studies have been made investigating the thermal degradation of MEA with CO₂[6-8], identifying degradation compounds and mechanisms of degradation. In the study of Davis and Rochelle[8] it was shown that the degradation of MEA increased when increasing temperature and loading. Degradation of DEA was investigated by Kim and Sartori[9] as well as by Meisen and Kennard[10]. Several degradation compounds were identified in the presence of CO₂, whereas without CO₂ present, no significant degradation was found below 205°C. The degradation of MDEA was studied by Chakma and Meisen[11], who found that MDEA degraded in the presence of carbon dioxide. The pure thermal degradation of MDEA was in the same work found to be negligible up to temperatures of 240 °C. The degradation of several aqueous solutions of MDEA-DEA-AMP blends was studied by Reza and Trejo[12] in the presence of CO₂ and H₂S at about 200 °C. DEA was found to be the most degradable, while 2-amino-2-methylpropanol (AMP) was the most stable compound.

In a recent study Lepaumier et. al.[13] investigated the degradation mechanisms of several ethanolamines and ethylenediamines during thermal degradation, both with and without CO₂. The solutions had a concentration of 4 mol amine/kg, and were kept at 140 °C for 15 days in a batch reactor. For experiments with CO₂, the pressure was 2MPa. The thermal degradation without CO₂ was found to be insignificant, while adding CO₂ gave degradation. For the ethanolamines, the secondary amines were found to be the most degradable, while the tertiary amines were found to be the most stable, followed by the sterically hindered amine. MEA was found to have a degradation of approximately 40%. For the ethylenediamines, the overall trends were found to be the same as for ethanolamines. In the work of Davis[14], several amines including MEA, MDEA and AMP were screened for thermal degradation with CO₂. The solutions were at 7m alkalinity with a loading of 0.4 mol CO₂ /mol alkalinity and were kept at 135 °C for 4 weeks,. The secondary alkanolamine N-(2-hydroxyethyl)-ethylenediamine (AEEA) and the polyamine DETA were found to be the least resistant to degradation, while the cyclic amines without side chains were the most stable, followed by the sterically hindered amine AMP and the longer chained alkanolamines. MEA was found to have a degradation of 33%. Piperazine (PZ) was also studied by Freeman et al [15], confirming the stability of this compound compared to the other amines studied.

Table 1: Compounds tested for thermal degradation and degradation with CO₂.

Abbreviation	Full name	CAS	Structure
AEEA (HEEDA)	N-(2-hydroxyethyl)- ethylenediamine	111-41-1	
AMP	2-amino-2-methylpropanol	124-68-5	
AP (MPA)	3-aminopropanol	156-87-6	
DEA	Diethanolamine	111-42-2	
DETA	Diethylenetriamine	111-40-0	
DMMEA	N,N-dimethylethanolamine	108-01-0	
EDA	Ethylenediamine	107-15-3	
MAPA	3-amino-1- methylaminopropane	6291-84-5	
MDEA	N-methyldiethanolamine	105-59-9	
MEA	Ethanolamine	141-43-5	
MMEA	2-Methylaminoethanol	109-83-1	

2. Experimental

All absorbents were tested at the same concentration level (30 wt%) in deionised water and were degassed with nitrogen before the experiment started. For each compound a pure solution (30 wt%) was tested as well as one containing CO₂ at a level of 0.5 moles CO₂/mole amine. Closed metal cylinders (316 SS) with room for glass tubes were used. The unloaded and loaded solutions were tested both in contact with metal and without, using the glass tubes. The cylinders were stored at 135°C for 5 weeks. Each week, one cylinder was selected and analyzed to determine the amount of the starting amine. Samples were collected every week and metal cylinders opened for sampling were not returned for further testing. To check for leakage, the cylinders including solution were weighed before and after incubation. The degradation rate was determined by Liquid Chromatography-Mass Spectrometry (LC-MS).

Biodegradability was in previous work determined by a marine biodegradation test, conducted according to OECD guideline 306, “biodegradability in seawater” [1].

3. Results and discussion

The degree of degradation is presented as percentage loss of amine. The results from the thermal degradation without CO₂ are compared with the biodegradation results in Figure 1, while the results from thermal degradation in the presence of CO₂ are compared with biodegradation in Figure 2. The choice of container, whether metal or glass, did not seem to have an impact on the degree of degradation. One exception was MMEA for which the unloaded solution showed a significantly higher degradation rate in the presence of metal. This has not been investigated further in this work. With an exception for MMEA, only the results from the metal samples are presented.

Often, pure thermal degradation is considered negligible under process conditions. Still, AP and MMEA (metal sample) showed significant degradation at the chosen temperature, which should be representative of the steam coil surface temperature in a reboiler. For the compounds EDA, MAPA, DMMEA and DEA there was some degradation, while the rest of the tested amines showed no degradation. For degradation with CO₂ present, MMEA and DEA were completely degraded within 5 weeks, while AEEA had degradation above 60%, closely followed by MEA at 55%. When relating the structures of the amines to the degradation rate, the sterically hindered amine (AMP) showed the highest stability, while the secondary amines (DEA, MMEA and AEEA) showed the highest degradability. When comparing the tertiary amines with the primary amine MEA, both MDEA and DMMEA had higher stability. However, the primary amine AP showed less degradation which might suggest that longer carbon chains give higher stability. Comparing DETA with DEA and EDA with MEA, the alkanolamines seemed to have lower stability. However, the loading might play a significant role on the degree of degradation, so the results could change with higher loadings for the polyamines.

The work of Lepaumier et.al.[13] agree well with the results and structural trends in this work for the alkanolamine degradation with CO₂, with the exception of AMP and MDEA where their study showed higher and lower degradation respectively compared to this work. In the work presented by Davis [14], AMP showed comparable results to this study, and the trends with regards to amine functionality, chain length and steric hindrance are the same. However there is a difference for AEEA, EDA and DETA which have higher degradation in the Davis[14] study. This can be explained by the concentrations of CO₂, which were significantly different for these compounds when comparing the studies.

The biodegradation results presented in previous work showed large variation, especially for the primary and secondary amines. In general the sterically hindered, tertiary and cyclic amines tested showed low biodegradability. However, some exceptions were DMMEA and piperidine which were biodegradable – both of these are found in nature. For thermal degradation without CO₂, most of the compounds with no biodegradation were stable. The thermal degradation of AP was found to be higher than the biodegradation, while for the remaining compounds the biodegradation rates were higher. When comparing the biodegradation rates with the thermal degradation rates with CO₂ present, most of the amines showed similar or higher degradability at process conditions than obtained for biodegradation in seawater. The exceptions were the compounds with the highest biodegradability, DMMEA and MAPA. DMMEA still showed a thermal degradation of almost 30 wt%, while MAPA had 50%. The thermal and chemical stability of piperazine and morpholine was not studied in this work. However, Davis [14] found them to be

the most stable compounds screened in his study. The same is the case for biodegradation of the compounds. In general, compounds stable at process conditions are likely to also be resilient with regards to biodegradation; however natural compounds might be stable at process conditions while being biodegradable.

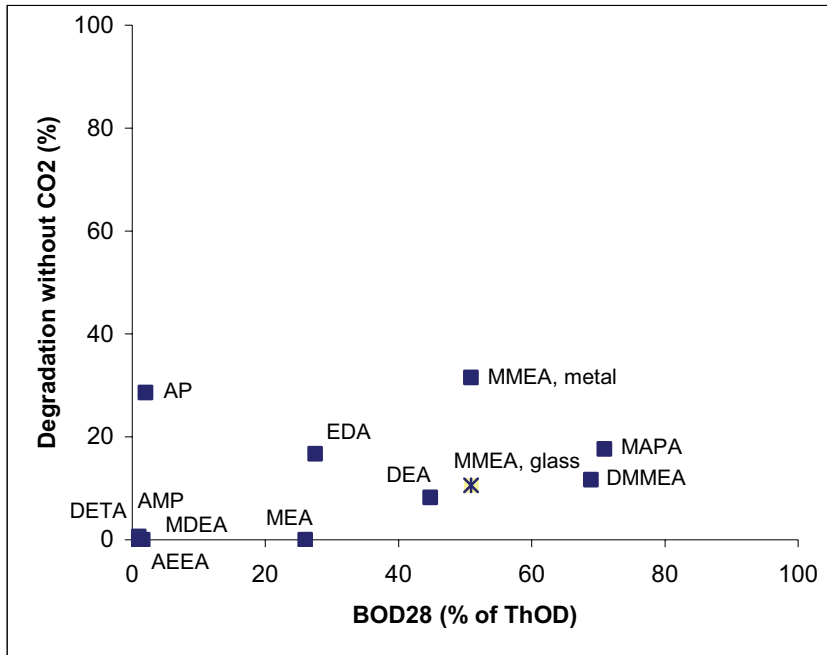


Figure 1: Comparison of thermal degradation without CO₂ with biodegradation.

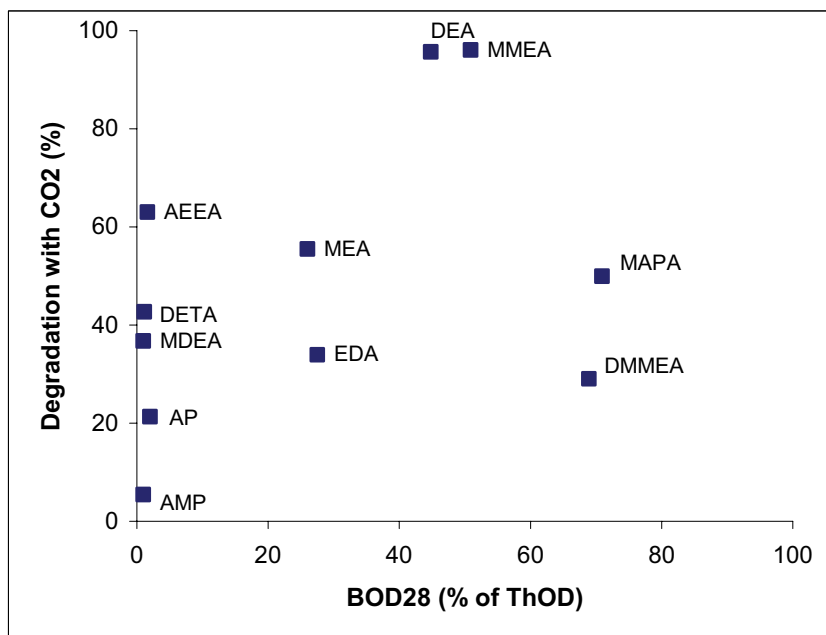


Figure 2: Comparison of thermal degradation with CO₂ with biodegradation.

4. Conclusion

A study on thermal and chemical stability of amines with and without the presence of CO₂ has been performed for eleven chemicals, including MEA, AMP and DEA. The chemicals were tested both in contact with metal (316 SS) and in glass containers. The presence of metal did not have any impact on the degree of degradation, with an exception for MMEA. MMEA and AP were susceptible to thermal degradation, while the rest of the compounds were relatively stable. For degradation in presence of CO₂, the sterically hindered amine (AMP) had the highest stability, while the secondary amines (DEA, MMEA and AEEA) had the lowest. Most of the compounds showed thermal degradation in the presence of CO₂ higher than the biodegradation. MAPA and DMMEA, which were the compounds with highest biodegradability of the amines tested for thermal degradation, were relatively stable without CO₂. However, in the presence of CO₂ the degradation of MAPA was 50%, while for DMMEA it was almost 30%. None of the tested chemicals have the desired combination of stability under process conditions while at the same time being sufficiently biodegradable.

Acknowledgement

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