



16th International Conference on Greenhouse Gas Control Technologies, GHGT-16

23rd -27th October 2022, Lyon, France

Identification of degradation compounds in a blend of 1-(2-hydroxyethyl)pyrrolidine and 3- amino-1-propanol

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Abstract

Aqueous amine solvents used for chemical absorption of CO₂ will form unwanted compounds, often called degradation compounds, in the capture plant. The degradation compounds have different functional groups and there are few general methods for analyzing these components, meaning that new analytical methods need to be developed for each system. In this work, identification of degradation compounds in a blend of 1-(2-hydroxyethyl)pyrrolidine (1-(2HE)PRLD and 3-amino-1-propanol (3A1P) has been done. This include both general and solvent specific degradation compounds, where the limitation for the solvent specific degradation compounds often are if these compounds are commercially available. The solvent specific degradation compounds were predicted by adapting the knowledge regarding other amine system such as monoethanolamide (MEA) to the molecular structure of e.g. 3A1P. This gave a comprehensive analytical program which included 42 compounds, both general and solvent specific degradation compounds. The pathways for several of the solvent specific degradation compounds (HPF, OZN, AP-urea, APAP, tHHPP, methyl-AP, HPAla, HPGly, HPAla & pyrrolidine) were also suggested. The degradation compounds contribute to closing the nitrogen balance over the solvent samples when the analytical uncertainties are taken into account, this indicate that still unknown compounds could be present in small amounts.

Keywords: CO₂ capture; amine blend; degradation; identification; LC-MS

1. Introduction

Chemical absorption of CO₂ using aqueous amine solvent is a mature technology. As other processes based on chemical reaction unwanted reactions are also observed. These reactions are in this case called degradation reactions and are occurring in the presence of CO₂, O₂, NO_x, other impurities, temperature, and dissolved metals. Additional simplification is also done separating this into thermal or oxidative degradation reactions. In the capture process the solvent is cycled between low and high temperature and all aspect around the chemical reactions occurring could not be represented by batch experiments for thermal or oxidative degradation studies. The thermal and oxidative degradation experiments are useful for characterization and identification of degradation compounds as well as in solvent screening phase. For a more realistic overview of the profile of degradation products a cycled set-ups that mimic the overall process is required. The degradation products formed contain various functional groups and usually advanced analytical instrumentation is required to analyze for the full specter of components. This work focuses on

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identification of degradation compounds in the blend of 1-(2-hydroxyethyl)pyrrolidine (1-(2HE)PRLD) and 3-amino-1-propanol (3A1P). This is a solvent previous developed in an EU project called HiPerCap [1-4] which has been further characterized in the ongoing EU project REALISE [5-7]. The REALISE project aim to demonstrate CO₂ capture technology based on advanced low-energy solvent at pilot scale, additionally emissions and solvent degradation will be quantified. Furthermore, the quality of the liquified CO₂ will be demonstrated when impurities from flue gases from an operating refinery are introduced to the pilot.

The samples used for identification of degradation compounds originates from a cycled degradation set-up called the solvent degradation rig (SDR) that has been presented elsewhere [8, 9]. This rig is often used to investigate the robustness of the solvent at stressed conditions such as higher desorber temperature or higher NO_x concentration. Despite of varying experimental conditions throughout the campaign the rig gives similar profile of degradation compounds for ethanolamine (MEA) that has been observed for larger pilots, e.g. MEA campaigns at the Technology Centre at Mongstad [10].

The degradation compounds identified in this work is based on reference materials of the degradation compounds provided by commercial suppliers. Overall, the analytical program for this blend included 42 compounds with various functional groups, where 30 of them where either observed in the solvent or in the condensate sample or in both. These 30 compounds could be divided in general and solvent specific components. For the solvents specific components, the following Liquid Chromatography – Mass Spectrometry (LC-MS) instrumentation was used for the analyses; Agilent Technologies 1290 Infinity LC coupled with Agilent Technologies 6495 Triple Quad MS detector.

Nomenclature

3A1P	3-amino-1-propanol (156-87-6)
1-(2HE)PRLD	1-(2-hydroxyethyl)pyrrolidine (2955-88-6)
3-Mpy	3-methyl-pyridine (123-75-1)
AMP	2-amino-2-methylpropanol (124-68-5)
APAP	3-[(3-aminopropyl)amino]-1-Propanol (40226-15-1)
AP-urea	N,N'-bis(3-hydroxypropyl)-urea (71466-11-0)
HEEDA	2-[(2-aminoethyl)amino]-ethanol (111-41-1)
HEF	N-(2-hydroxyethyl)-formamide (693-06-1)
HEIA	1-(2-hydroxyethyl)-2-imidazolidinone (3699-54-5)
HPAla	N-(3-hydroxypropyl)-β-Alanine (55937-35-4)
HPGly	N-(3-hydroxypropyl)-Glycine (100747-20-4)
HPF	N-(3-hydroxypropyl)-Formamide (49807-74-1)
LC-MS	Liquid Chromatography – Mass Spectrometry
MEA	ethanolamine (141-43-5)
MEA-urea	N,N'-bis(2-hydroxyethyl)-urea (15438-70-7)
Methyl-AP	3-(methylamino)-1-Propanol (42055-15-2)
Nitroso-N-methylAP	3-(methylnitrosoamino)-1-Propanol (70415-59-7)
NOXZN	tetrahydro-3-nitroso-2H-1,3-Oxazine (35627-29-3)
Pz	Piperazine (110-85-0)
OZD	2-oxazolidinone (497-25-6)
OZN	1,3-oxazinan-2-one (5259-97-2)
tHHPP	tetrahydro-1-(3-hydroxypropyl)-2(1H)-Pyrimidinone (670227-88-0)

2. Results/discussion

The REALISE solvent is an aqueous blend of two alkanolamines, one primary and one tertiary amine. To predict degradation compounds from the blend, degradation compounds from both of the single amines as well as the degradation compounds formed because of two amines present needs to be accounted for. The combination of

systematic degradation studies on various amines [11-14] and more in depth study of some amines such as ethanolamine (MEA) and piperazine (Pz) [9, 15-19] have given valuable insight into identification/quantification of degradation compounds and their formation pathway. For example, the systematic degradation studies have shown that there are typical degradation pathways that can be used to explain many of the degradation products formed from alkanolamines, ethylenediamine, polyamines with longer carbon chain between the amine functions and piperazine [11-15]. Furthermore, the mapping of degradation compounds of MEA has shown the full specter of which compounds to expect [9, 16-18].

The degradation compounds could be divided into primary and secondary degradation compounds, where primary is the degradation compounds formed by radical reactions and oxidation. This usually give compounds such as aldehydes, carboxylic acids, ammonia and alkylamines. The secondary degradation products are the larger compounds which either is a result of amine reacting with CO₂ (diamines, some cyclic structures, urea) or amine (both solvent amine and degradation products with amine functionality) reacting with primary degradation compounds. One example for the latter is carboxylic acid reacting with amine forming amides, e.g. HPF which is a results of formic acid reacting with 3A1P, see Figure 1. Intramolecular cyclisation and loss of water can then give 5,6-dihydro-2-methyl-4H-1,3-oxazine (5638-63-1) as proposed by Gouedard for 2-oxazoline (degradation products from MEA). As reference material for 5,6-dihydro-2-methyl-4H-1,3-oxazine was not commercially available this compound was not verified in this work.

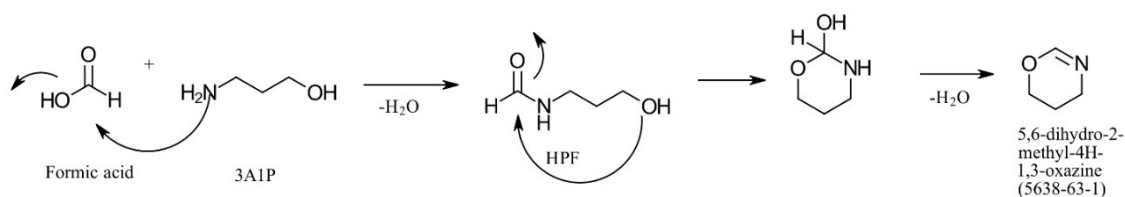


Figure 1 Pathway for formation of HPF and 5,6-dihydro-2-methyl-4H-1,3-oxazine (adapted from Gouedard [16])

3A1P has three carbons instead of two, like MEA has, between the amine and alcohol function. Similar degradation compounds are expected, but the extra carbon must be accounted for. When MEA reacts with CO₂, a cyclisation can occur resulting in a five membered ring called OZD (Figure 2). For 3A1P, the same reaction is expected to occur, but in this case, it will lead to formation of a six membered ring, which has been called OZN (Figure 2).

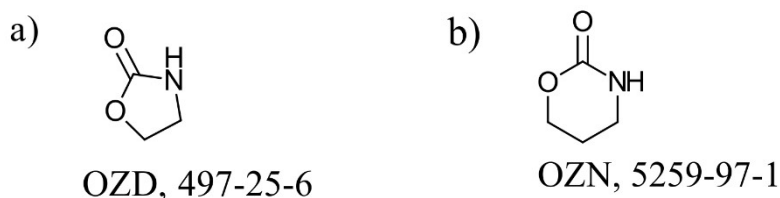


Figure 2 The molecular structure of OZD (picture a) and OZN (picture b).

The various products, often called thermal degradation compounds, expected for 3A1P is shown in Figure 3 (picture b). Additionally, the similar degradation compound from MEA is given in Figure 3 (picture a) as well. Several of these reactions consumes CO₂ and occur to large extent at higher temperature (e.g. stripper, reboiler) and is therefore often called thermal degradation reaction or carbamate polymerization reactions. Pathway for formation of these degradation compounds is available from Davis, Lepaumier et.al. and Eide-Haugmo [11, 13, 20, 21].

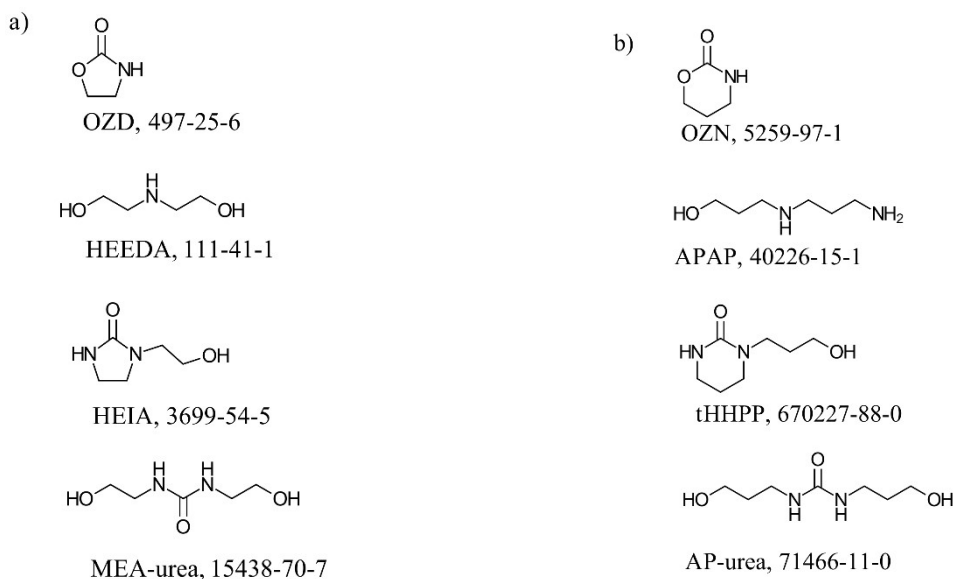


Figure 3 Typical thermal degradation compounds from MEA (picture a), and the degradation compound adapted to the molecular structure of 3A1P (picture b).

There are sometimes several pathways suggested for formation of certain degradation compounds. This is also the case for the diamine (HEEDA) [14, 20, 22] in MEA solvent. Overall, there are three different pathways suggested for HEEDA which could be adapted to APAP as shown by Vevelstad et al. [7].

One of the major degradation products for MEA, is the amino acid N-(2-hydroxyethyl)-glycine (HEGly, 5835-28-9). The pathways suggested for this compound require either glyoxylic acid [23] or glyoxal [16]. 3-oxo-propanoic acid (the glyoxylic acid compounds for 3A1P) could then give N-(3-hydroxypropyl)- β -Alanine (HPAla). Since this is a blend, there is a possibility that glyoxal or glyoxylic acid or both are formed as well. This means that another amino acid could be formed as well, N-(3-hydroxypropyl)-Glycine (HPGly). A more detailed explanation of the pathway could be found in Vevelstad et al. [7].

In the work by Lepaumier et al., methylation reactions occurred for several amines [13]. Methylation of 3A1P would give 3-(methylamino)-1-Propanol (Methyl-AP). There are at least two relevant pathways suggested for formation of methylated MEA which could be adapted to 3A1P. The first one is an Eschweiler-Clarke reaction from MEA and formaldehyde proposed by Lepaumier [24], the second one is a decarboxylation reaction of HEGly proposed by Gouedard [16].

The second component in the blend is a tertiary amine, tertiary amines are often more stable than primary and secondary amines. However, demethylation and dealkylation reaction can still occur which will result in secondary amines that can react further. Pyrrolidine was quantified in small amount in oxidative degradation experiment for 1-(2HE)PRLD (30 wt%) as described in Hartono et al. [1]. Pyrrolidine could react further using the pathways previously described, the difference in this case being that the concentration of pyrrolidine are much lower than 3A1P and 1-(2HE)PRLD which indicate that the resulting degradation compounds would be small. The initial reactions occurring in the absorber is not well described in this work, since the focus has been on identifying degradation compounds that build up to concentration levels that could be quantified analytically in the solvent mixture. More explanation of the radical reactions and which aldehydes, carboxylic acids and alkylamine to expect in this case could be found in Vevelstad et al. [7]. 3-methyl-pyridine is a degradation compound found for MEA, however since it is formed from formaldehyde and acetaldehyde [16] it could easily be present in more solvents and was therefore included in this work as well.

Analytical methods for the compounds with commercially available reference material (HPF, OZN, APAP, AP-urea, tHHPP, HPAla, HPGly, Methyl-AP and Pyrrolidine) were developed on LC-MS. As mentioned earlier, 5,6-

dihydro-2-methyl-4H-1,3-oxazine was not commercially available. Two solvent specific nitrosamines were also included, Nitroso-N-methylAP and NOXZN. Additionally, more general degradation compounds of compounds that requires monitoring were added for these samples as well, this includes carboxylic acids, ammonia, alkylamine, aldehydes, ketone, and nitrosamines. Overall, 25 of the 42 degradation compounds were found above the lower limit of quantification in the solvent samples. Additionally, 3 nitrosamines, one alkylamine and 3-methylpyridine were identified in the condensate, this is described elsewhere [7]. Identification of compounds is not enough to say that the solvent is characterized since the compound's contribution could be only at trace levels. Therefore, a nitrogen balance over the solvent samples is a useful tool to evaluate if the major degradation compounds are identified and quantified. Nitrogen balances for the lean samples from weeks 0, 3, 4 & 5 in this work are given in Figure 4 (picture a).

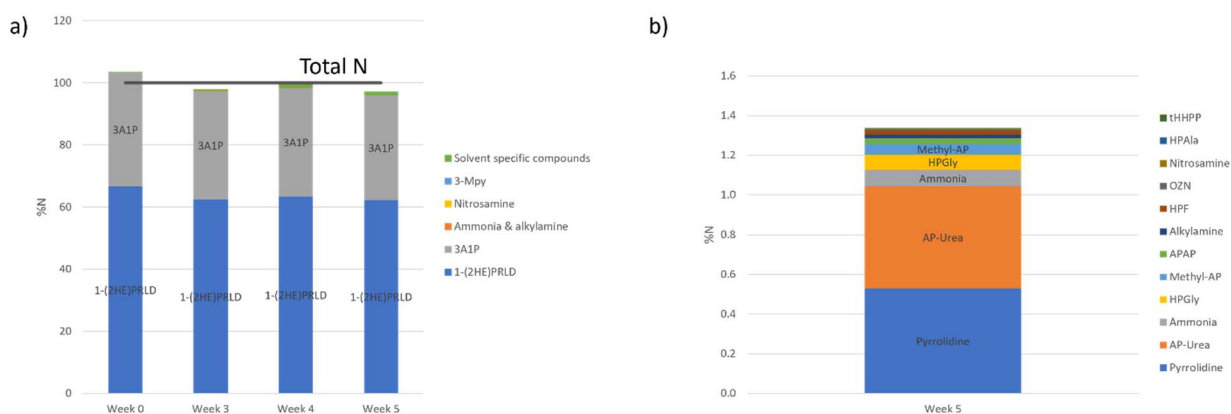


Figure 4 Overall nitrogen balance for solvent samples from weeks 0, 3, 4 & 5 are given in picture a. For picture b, the degradation compounds contribution to the nitrogen balance is shown for the solvent sample from week 5.

Naturally, the solvent amines are the main contributors to the nitrogen balance, and the overall nitrogen balance is relatively closed when considering the analytical uncertainties. Additionally, in picture b (Figure 4) it is shown how the various degradation compounds or groups contribute to the nitrogen balance (NOXZN was not observed above the lower limit of quantification).

3. Conclusion

The solvent samples from a cycled degradation set-up were used for identification of degradation compounds in a new blend of 3A1P and 1-(2HE)PRLD. All together the comprehensive analytical program, which is a result of general and solvent specific degradation compounds, included 42 compounds. In the solvent samples, 25 of 42 compounds, were found above the respective lower limit of quantification.

Degradation pathways described in literature for other amines is a useful tool for predicting degradation compounds in new amines and amine blends. When reference materials are commercially available, analytical methods for these degradation compounds could be developed and their presence verified. For this blend, the solvent specific degradation compounds commercially available were mainly from 3A1P except for pyrrolidine (from 1-(2HE)PRLD and HPGly (believed to be a result of the blend). More degradation compounds from 1-(2HE)PRLD would be expected, however, the degradation compounds quantified contributes to closing the nitrogen balance when the analytical uncertainties is taken into account. This should indicate that these not identified or quantified degradation compounds may only be present in small amounts.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 884266

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