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Thermal reclamation chemistry of common amine solvents

Vanja Buvik[a]*, Andreas Grimstvedt[a], Kai Vernstad[a], Merete Wiig[a], Ricardo R. Wanderley[b], Hanna K. Knuutila[c]

[a]*SINTEF Industry, NO-7465 Trondheim, Norway*
[b] *SLB Capturi, Okenøyveien 8, NO-1366 Lysaker, Norway*
[c]*Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway*

Abstract

Thermal reclaiming is a common solvent management technique to prolong problem-free operation of the CO_2 absorption process without having to replace the amine solvent. In this experimental study we look at the behaviour of one of the most common amine solvents for CO_2 capture, ethanolamine, to investigate how both the fresh solvent and a solvent after use for CO_2 capture from a refinery flue gas alter their chemical composition during thermal reclaiming. Laboratory tests with sampling throughout the experiments were designed and combined with powerful analytical methods for compound quantification. Three different pressures and temperatures were investigated for vacuum reclaiming of the used solvent, degraded 30wt% ethanolamine (MEA), and both the distillate and sludge were characterised. To compliment the simulated thermal reclaiming at reduced pressure, simple reclaiming chemistry tests were performed on laboratory scale to monitor the behaviour of ethanolamine degradation compounds when exposed to the thermal reclaiming conditions; high temperature and addition of sodium hydroxide. Alkaline hydrolysis of the contained amide species was successful in the simplified reclamation chemistry tests, but did not take place to the same extent during thermal distillation at reduced pressure. *N*-methylethanolamine was the most dominant degradation product in the reclaimed MEA solvent and was also seen to form during the simple alkaline hydrolysis tests.

Keywords: thermal degradation, oxidative degradation, MEA, reclaiming, solvent management

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1. Introduction

The consequences of solvent degradation in amine solvent-based post-combustion CO_2 capture (PCC) processes can be reduced and managed by implementing solvent management strategies. Thermal reclaiming is widely implemented as a means for regenerating degraded and contaminated solvents from the capture processes, and originally comes from other solvent-based industrial applications (Dumée et al., 2012; Kentish, 2016). Despite its wide-spread implementation, the solvent chemistry during the thermal reclaiming process has neither been fully investigated nor understood, and deepening this will help predict and mitigate any associated complications it may cause during long-term full-scale PCC, such as potential formation of problematic compounds, acceleration of any degradation reactions, or increases in amine or degradation product emissions. For establishing a methodology and gaining knowledge of the solvent chemistry during thermal reclaiming, ethanolamine (MEA, CAS: 141-43-5) reclamation has been studied in the laboratory, and changes in composition of an already degraded MEA solvent were

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* Corresponding author. Email address: vanja.buvik@sintef.no

followed during the reclaiming experiments. Volatile degradation compounds can be reclaimed or distilled with the solvent amine. This work aims to identify some of the chemical reactions taking place during the actual reclamation process and also how the solvent amine, MEA, behaves at the same conditions. Analysis of known degradation compounds in both the reclaimed solvent and sludge will give insights to whether any degradation compounds are prone to still remain after reclaiming, and how much additional degradation takes place due to the harsh conditions of the reclamation process.

Nomenclature

h	Hours
HSS	Heat Stable Salts
LC	Liquid Chromatography
MEA	Monoethanolamine
MS	Mass Spectrometry
PCC	Post-Combustion Capture
TN	Total Nitrogen
wt.	weight

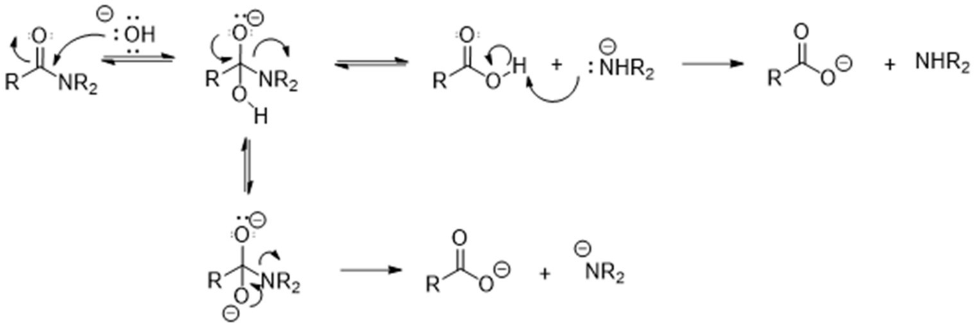
1.1. Solvent degradation and reclaiming

During degradation of amines in the CO_2 capture process, the solvent changes both its physical and chemical properties. If the flue gas contains impurities, these may also accumulate in the solvent and alter its properties. The change in chemical properties gives rise to catalytic effects, increase of the degradation rate, increase of corrosivity of the system, and changes in the CO_2 absorption kinetics (Kentish, 2016; Supap et al., 2011; Tanthapanichakoon et al., 2006). The changed physical properties impact the operation of the plant, as viscosity, density, volatility, and precipitation, may vary from the fresh solvent. Some of these issues can be circumvented by the operators, but to use the solvent in an economical and efficient manner, solvent reclamation is recommended and necessary (Kentish, 2016). Degradation creates a complex mixture of compounds with different chemical properties. If the amine reacts to form ionic compounds that are not CO_2 products (i.e., not carbonates, carbamates, etc.) these are often referred to as heat stable salts, or HSS. These mainly consist of small organic acids and their corresponding bases, such as formate and acetate. HSS can be removed by all reclamation methods – ion exchange, electrodialysis and thermal reclaiming (Kentish, 2016). Volatile degradation products are typically ammonia, small aldehydes, alkylamines, nitrosamines, and nitramines, and these need to be captured with emission mitigation technologies, such as acid or water wash columns on top of the absorber column, where the volatile components are likely to follow the cleaned flue gas (Reynolds et al., 2012). The remaining heterogenous group of compounds consists of all degradation products that are neither volatile nor ionic, which makes them unsuitable for removal by electrodialysis, or ion exchange, but possible to remove by distillation (thermal reclaiming). Many of the degradation compounds are amides, which may be hydrolysed as the first step of the thermal reclaiming process. This can lead to the recovery of the original amine by separating it from their ionic moieties. The ionic components remain in the non-volatile sludge after thermal reclamation. As ionic compounds in the reclaimer sludge are non-volatile, these will not boil off with the amine.

1.2. Amides

Amides are compounds with a nitrogen bound to a carbonyl group and a schematic of the alkaline amide hydrolysis mechanism is given in Scheme 1. Alkaline amide hydrolysis can take place by addition of a strong base, such as potassium- or sodium hydroxide (KOH or NaOH), where OH^- performs a nucleophilic attack on the acyl-group of the amide, forming a tetrahedral intermediate. The rate-limiting step of the alkaline hydrolysis then follows, as the anionic amide is a poor leaving group (Anslyn and Dougherty, 2006). These base-initiated reactions, therefore, often need elevated temperatures to take place (Robinson and Tester, 1990).

Scheme 1: Mechanism of base-initiated hydrolysis of amides, reproduced from Anslyn and Dougherty (2006).



One of the most studied amines for CO_2 capture is ethanolamine (MEA), for which more than 50 degradation compounds have been identified (Vevelstad et al., 2022). The abundance of known products and in-house analytical competence to quantify these, as well as MEA still being relevant in large-scale CO_2 capture processes, is the reason why this amine was chosen for this study. MEA reclamation temperatures can reach up to 145-160°C (Flø et al., 2017; Srivastava et al., 2021), but thermal degradation of CO_2-loaded MEA readily takes place at 135°C (Davis and Rochelle, 2009). Thus, the highest reclaiming temperature used in this work was 140°C.

1.3. Mimicking reclaiming chemistry

The goal of this study is to deepen the understanding of the solvent chemistry during thermal reclaiming. The main objective of this work is to show how vacuum distillation at three different pressures and temperatures impacts the purity of the distillate and sludge composition. The results are compared to simple reclaiming chemistry experiments, where alkaline hydrolysis is performed first at room temperature and then 140°C prior to characterising the solvent, as was presented by Buvik et al. (2023a). This work aims to identify some of the chemical reactions taking place during the actual reclamation process and also how the solvent amine, MEA, behaves under the same conditions. Analysis of known degradation compounds in both the reclaimed solvent and sludge will give insights into whether any degradation compounds are prone to still remain after reclaiming, where they end up (in the distillate or sludge), and how much additional degradation takes place due to the harsh conditions of the reclamation process.

2. Materials and Methods

2.1. Vacuum distillation experiments

The distillation experiments were performed using a Büchi Rotavapor® R-300. The equipment was kept in a ventilated fume cupboard for the entire duration of all experiments. For temperature control the heating bath was filled with an alcohol-ethoxylate based bath fluid (JULABO Thermal M) and cooling water was used for the built-in condenser. The minimum pressure for a stable vacuum was deemed to be 30 mbar, hence this was set as the minimum distillation pressure. The heating bath was always set to 30°C above the boiling point of pure MEA at the given pressure, giving the test matrix shown in Table 1. Approximately 200 mL of amine solution was used for each experiment. Approximately 1 g of 50 wt.% sodium hydroxide (NaOH, *aq*.) was added per 200 mL of amine solution, to hydrolyse the amides and recover covalently bound MEA and separate it from the HSS. The molar concentration of NaOH thereby slightly surpassed the total amide concentration in the start samples. At start-up of the experiment, the pressure is immediately reduced to the target pressure. The heating bath temperature was then carefully increased to the desired maximum distillation temperature to avoid shock boiling. After reaching the target temperature, the solution was left to distil for 2 h.

Table 1: Test conditions for the vacuum distillation experiments.

	Condition 1	Condition 2	Condition 3
Pressure (mbar)	30	65	100
Heating bath temperature (°C)	110	125	140

Both a fresh MEA solution (30wt%, *aq*.) and one previously used in a pilot campaign at a refinery were tested at the described conditions, and all but two tests (pilot-degraded MEA at 65 mbar and 100 mbar), were run in duplicates. The MEA solvent from pilot operations was the same as the one studied in Buvik et al. (2023b), where it was also fully characterised. Additionally, a fresh MEA solution was distilled at 100 mbar and 140°C without the addition of NaOH. The solvents used in the tests were analysed for their composition, and their total concentrations of MEA and degradation compounds are given in Figure 2.

Table 2: Composition of the MEA solvent samples prior to thermal reclaiming at reduced pressure.

MEA	***c* MEA**		***c* degradation compounds**	
	(mol/kg)	**(wt%)**	**(mmol/kg)**	**(wt%)**
Fresh	5.1	31%	0.52	0.02%
Pilot	3.8	23%	141	1.97%
SDR	5.6	34%	195	2.65%

2.2. Simple alkaline hydrolysis experiments

Following the procedure from Closmann et al. (2009) and Freeman and Rochelle (2012), samples of fresh or degraded ethanolamine (MEA) were mixed with 5 M NaOH in a 1:1 ratio. A 40 wt% MEA solution from a study in the SINTEF cyclic solvent degradation rig (SDR) was used for the test with degraded MEA (Grimstvedt et al., 2022). A sample was taken for analysis from each solution prior to the addition of NaOH, and another was taken after the mixture of amine and NaOH was allowed to react at room temperature for 24 h. The remaining solutions were then transferred to stainless steel cylinders, which were put in a heating cabinet at 140°C for 24 h. After cooling down the cylinders, they were opened, and a sample was taken for analysis.

Hence, three samples from each experiment were analysed for known degradation compounds, as well as MEA concentration. The compositions of the solutions were compared throughout the experiment to determine which factors of the thermal reclamation conditions impact the components in which way. The measured concentrations in the treated samples were multiplied with the dilution factor after NaOH addition, to facilitate the comparison of the different stages of the process.

2.3. Analyses

2.3.1. Liquid Chromatography coupled with Mass Spectrometry (LC-MS)

Degradation compounds and MEA were quantified in the solutions by liquid chromatography (LC) with triple quadrupole (QqQ) mass spectrometric (MS) detection. An overview of the studied compounds can be found in Tables 2 and 3. The samples are diluted and acidified prior to analysis. Carboxylates are therefore presented in their corresponding acidic form in this work.

Table 3: MEA degradation compounds quantified by LC-MS analysis.

Non-acidic degradation compounds of MEA		
Name	Abbreviation	CAS number
1-(2-hydroxyethyl)-2-piperazinone	1-HEPO	59702-23-7
N,*N*'-bis(2-hydroxyethyl)-ethanediamide	BHEOX	1871-89-2
Diethanolamine	DEA	111-42-2
N-(2-hydroxyethyl)-acetamide	HEA	142-26-7
2-[(2-aminoethyl)amino]-ethanol	HEEDA	111-41-1
N-(2-hydroxyethyl)-formamide	HEF	693-06-1
N-(2-hydroxyethyl)-glycine	HEGly	5835-28-9
N-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide	HEHEAA	144236-39-5

Non-acidic degradation compounds of MEA		
Name	Abbreviation	CAS number
1H-imidazole-1-ethanol	HEI	1615-14-1
1-(2-hydroxyethyl)-2-imidazolidinone	HEIA	3699-54-5
4-(2-hydroxyethyl)-2-piperazinone	HEPO	23936-04-1
2-hydroxy-*N*-(2-hydroxyethyl)-acetamide	HHEA	3586-25-2
N,*N*'-bis(2- hydroxyethyl) -urea	MEA-Urea	15438-70-7
N-methylethanolamine	MMEA	109-83-1
2-oxazolidinone	OZD	497-25-6

Table 4: Acidic degradation compounds quantified by LC-MS analysis.

Name	CAS number
Acetic Acid	64-19-7
Butyric Acid	107-92-6
Formic Acid	64-18-6
Glyoxylic Acid	298-12-4
Glycolic Acid	79-14-1
Isobutyric Acid	79-31-2
Lactic Acid	50-21-5
3-OH Propionic Acid	503-66-2
Propionic Acid	79-09-4

The uncertainty of the LCMS-methods is approximately 5%, meaning that small changes (i.e. the difference between two high concentrations) in the MEA concentration cannot be reliably determined in the fresh and degraded MEA solutions, as these already contain a very high concentration of MEA. However, in the aqueous solutions of degradation products used in the mixing experiments (see section 2.2), the formation of MEA through the hydrolysis reaction can be detected.

2.3.2. Total Nitrogen Analysis

Total Nitrogen was determined in the solutions by TOC analyser with also a total nitrogen module (Shimadzu TOC-L_{CPH} TNM-L). The nitrogen method is first an oxidative catalytic combustion followed by chemiluminescence detection. The relative uncertainty of this total nitrogen analysis is 10%.

3. Results

3.1. Vacuum distillation experiments

The main constituent of the sludge remaining after distillation was, in all cases, MEA, and the main component of the distillate of each experiment was water, followed by MEA. The obtained distillate is, in every case, clean, consisting only of small amounts of degradation compounds in the reclaimed MEA. Distillation of fresh 30 wt% MEA gave an MEA to known degradation compound ratio of 25.000-50.000, while distillation of used/degraded MEA gave a ratio of 250-500 (both by mass). Generally, the fresh MEA solution was easier to distil, in terms of MEA successfully reaching the distillate, compared to the MEA solvent from pilot operations, as shown in Figure 1. A high MEA recovery could, however, be obtained at the highest temperature and pressure used in these experiments. As fresh MEA could be more effectively distilled even at lower temperatures and higher pressures than the pilot solvent, it indicates that MEA distillation is less efficient for the more complex solvent matrix with various degradation compounds and impurities, than the fresh solvent.

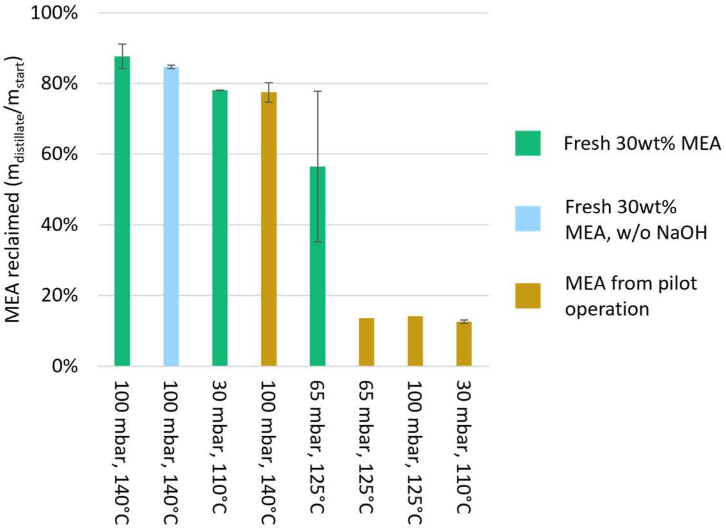


Figure 1: Percent of MEA effectively reclaimed during each experiment. Error bars represent the standard deviation between two parallel experiments. Two experiments (MEA from pilot operation at 65 and 100 mbar) were performed with only one parallel; hence, no error bars are displayed for these.

Table 5 shows the composition of each reclaimed MEA solvent sample in terms of MEA concentration and total known degradation product concentration. Despite the relatively low MEA recovery in some samples, the sum concentration of known degradation products is always low, below 0.04 wt%.

Table 5: Composition of the reclaimed MEA solvent samples.

MEA	Reps.	0.25 wt% NaOH	*T*	*p*	*c* MEA		*c* degradation compounds		$\frac{c_{MEA}}{c_{deg.cpds.}}$
			(°C)	(mbar)	(mol/kg)	(wt%)	(mmol/kg)	(wt%)	
fresh	2	no	140	100	4.76	29%	0.12	0.001%	34 960
	2	yes	140	100	4.71	29%	0.10	0.001%	41 169
	2	yes	125	65	3.24	20%	0.07	0.0008%	30 368
	2	yes	110	30	4.40	27%	0.06	0.0006%	69 361
Pilot	2	yes	140	140	3.24	20%	5.02	0.04%	560
	1	yes	125	100	0.74	5%	2.48	0.02%	228
	1	yes	125	65	0.71	4%	3.13	0.03%	337
	2	yes	110	30	0.69	4%	2.03	0.02%	234

The main constituent of the sludge remaining after distillation was, in all cases, MEA, as shown in Table 6, despite the distillation temperature theoretically surpassing the MEA boiling point at the given pressure in every experiment. In the pilot samples, MMEA was the most dominant degradation compound present in the reclaimed/distilled solvent, followed by HEF, HEHEAA, and BHEOX, as depicted in Figure 2. Figure 3 shows that trace amounts of HEF, MMEA, BHEOX, HEGly, and HEHEAA were also present in the distillate from the fresh solvent. Absolute amount of MMEA in the distillate of fresh MEA was even larger than that in the initial solvent sample prior to distillation, about 10 times higher, indicating that MMEA is formed during reclamation at 140°C. Despite seeing a formation of MMEA in the distillate of fresh MEA, something that was barely present in the solvent before distillation, MMEA generally disappeared from most of the systems during the reclamation process, likely due to evaporation into the vacuum pump as its boiling point is lower than that of MEA. The amount of HEF and HEHEAA generally increased during the reclamation process, but the amount of known degradation compounds that were consumed, or disappeared is even larger, as is evident in looking at Figure 4.

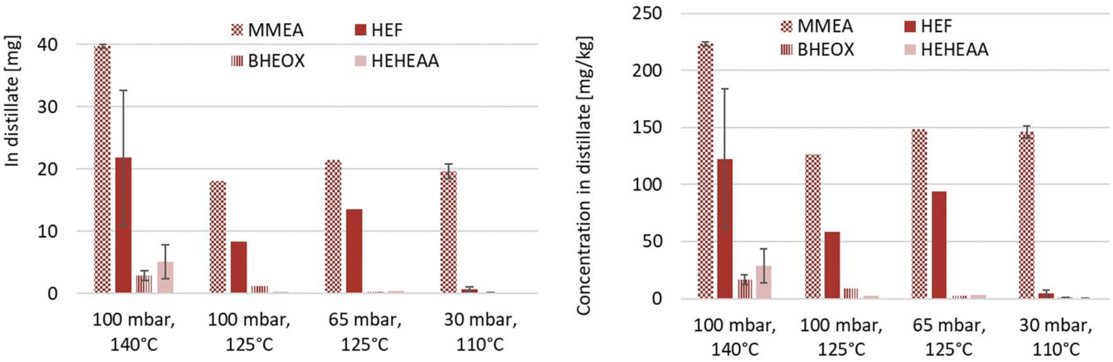


Figure 2: Absolute amounts (left) and relative concentrations (right) of the most dominant degradation products of MEA found in the reclaimed MEA solvent from pilot tests.

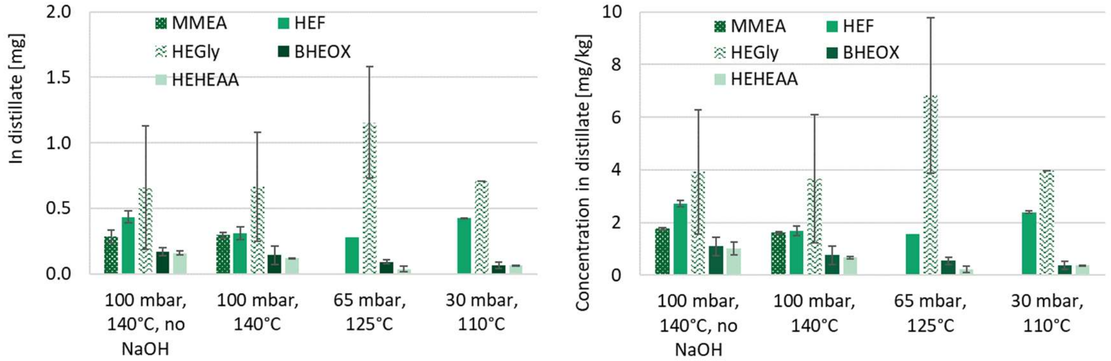


Figure 3: Absolute amounts (left) and relative concentrations (right) of the most dominant degradation products of MEA found in the distillate of fresh MEA solvent.

Table 6: Composition of the sludge after reclaiming the MEA solvent samples.

MEA	**Reps.**	**0.25 wt% NaOH**	***T***	***p***	***c* MEA**		***c* degradation compounds**	
			(°C)	**(mbar)**	**(mol/kg)**	**(wt%)**	**(mmol/kg)**	**(wt%)**
Fresh	2	no	140	100	15	93%	429	6%
	2	yes	140	100	14	86%	223	5%
	2	yes	125	65	17	101%	40	0%
	2	yes	110	30	16	100%	31	0%
Pilot	2	yes	140	100	7	45%	1974	26%
	1	yes	125	100	13	79%	630	8%
	1	yes	125	65	13	80%	660	8%
	2	yes	110	30	13	78%	573	8%

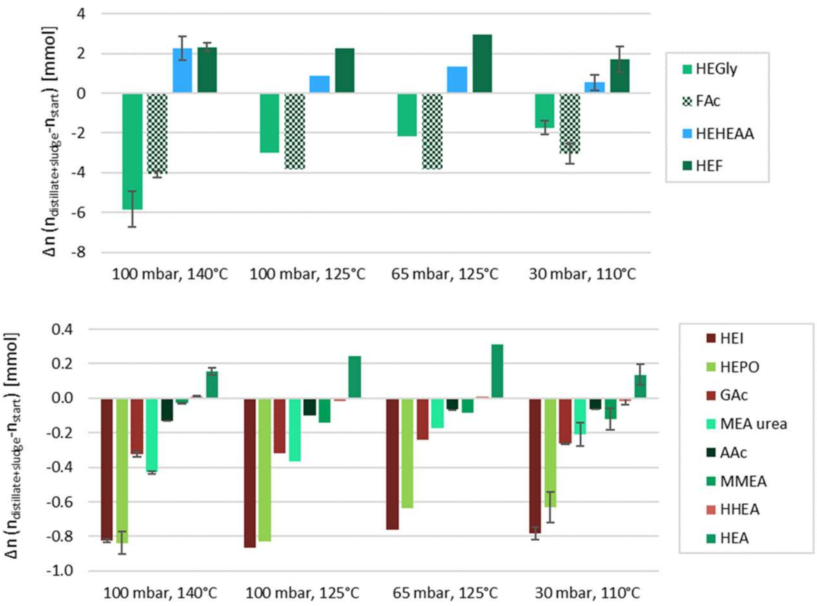


Figure 4: Change in total amount of MEA degradation products from start to after reclamation in the pilot-scale degraded solvent. The majority of these degradation compounds were found in the sludge.

From Figure 4 it becomes evident that the vacuum distillation process decomposes or removes more degradation products than those formed in the solvent from pilot-scale operations. Contrary to the findings presented later from the "simple" reclamation chemistry tests, the total formic acid (FAc) amount decreased during the thermal reclaiming experiments. It is expected that an increase of carboxylic acid concentrations should be observed as a result of alkaline hydrolysis in the solvent, but the only carboxylic acid that increases in total amount during the reclamation experiments is glycolic acid (GAc).

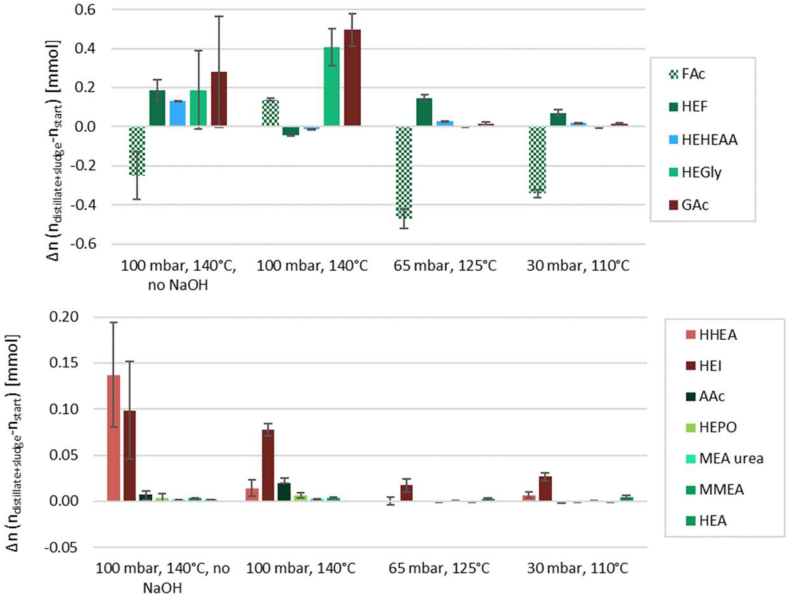


Figure 5: Change in total amount of MEA degradation products from start to after reclamation in the fresh MEA solvent. The majority of these degradation compounds were found in the sludge.

Looking at the change in degradation product amounts during reclaiming of the fresh MEA solvent in Figure 5, only FAc, which is so readily formed in MEA and is even present in the fresh solvent used here, is clearly removed or decomposed during the process. Small amounts of degradation products form during reclamation, primarily HEGly, HEI, HEHEAA, and HEF.

The sludge, or residue left after the distillation of the MEA solvent, consisted mainly of MEA, despite the temperature theoretically surpassing the boiling point of MEA and MEA with water, and no distillation could visibly be observed even long before the process was stopped. The sludge consisted not only of the degradation compounds that were present in the solvent at the start, prior to distillation, but also newly formed degradation compounds.

Table 7: Summary of the nitrogen balance in all distillation experiments. All concentrations are averages of the amounts in the parallels (Reps.).

MEA	**Reps.**	**0.25 wt% NaOH**	***T***	***p***	***n* MEA (mol)**			***n* N in degradation compounds (mmol)**			***n* total nitrogen (mol)**		
			(°C)	**(mbar)**	**Start**	**Distillate**	**Sludge**	**Start**	**Distillate**	**Sludge**	**Start**	**Distillate**	**Sludge**
Fresh	2	no	140	100	0.90	0.76	0.041	0.13	0.021	1.15	0.92	0.76	0.043
Fresh	2	yes	140	100	0.99	0.87	0.039	0.15	0.020	0.721	1.03	0.84	0.043
Fresh	2	yes	125	65	1.0	0.56	0.37	0.15	0.013	0.372	1.04	0.61	0.38
Fresh	2	yes	110	30	1.0	0.78	0.15	0.15	0.011	0.308	1.04	0.84	0.15
Pilot	2	yes	140	140	0.74	0.58	0.090	38	0.91	34	0.85	0.61	0.15
Pilot	1	yes	125	100	0.75	0.11	0.53	39	0.36	35	0.87	0.11	0.57
Pilot	1	yes	125	65	0.76	0.10	0.60	39	0.46	39	0.87	0.11	0.65
Pilot	2	yes	110	30	0.75	0.094	0.58	38	0.27	36	0.86	0.095	0.62

Table 7 gives the absolute amounts of MEA, the sum of nitrogen-containing degradation compounds (of those analysed in this work), and total nitrogen (TN) amount, calculated from the concentrations determined in the analyses and known masses of each sample. With the exception of one sample, the nitrogen balance is considered closed within the analytical uncertainty of the different methods.

Table 8: Summary of the nitrogen recovery in all distillation experiments.

MEA	**Reps.**	**0.25 wt% NaOH**	***T***	***p***	**Nitrogen balance**		
			(°C)	**(mbar)**	**Start**	**Distillate**	**Sludge**
Fresh	2	no	140	100	98%	100%	96%
Fresh	2	yes	140	100	97%	103%	92%
Fresh	2	yes	125	65	96%	92%	97%
Fresh	2	yes	110	30	96%	93%	103%
Pilot	2	yes	140	100	92%	94%	83%
Pilot	1	yes	125	100	92%	98%	98%
Pilot	1	yes	125	65	92%	97%	99%
Pilot	2	yes	110	30	92%	99%	99%

The nitrogen balance, which is calculated according to $N\ balance = \frac{n_{\mathrm{MEA}}+n_{\mathrm{N-containin\ \ deg.cpds.}}}{n_{\mathrm{TN}}}$, is presented in Table 8. n_{TN} represents the concentration of nitrogen measured by the total nitrogen analysis, while n_{MEA} is the amount of MEA quantified by LCMS, and $n_{\mathrm{N\ in\ deg.cpds.}}$ the sum of concentrations of each N containing degradation compound multiplied by number of N per molecule. In all the distillate samples, the nitrogen balance is 92-103%, and in the solvent samples at start, 96-98% in the fresh MEA, indicating that the nitrogen balance is "closed" with an inherent uncertainty of the TN analysis method of ±10%, or that all significant components are being quantified with the currently employed analytical methods. For the MEA sample from pilot operations, the nitrogen balance is only 87%, indicating that some nitrogen containing degradation products that are not accounted for with the 14 analysed in this work are present before distillation. In the sludge, after reclamation, the nitrogen recovery is 90-102% (±10%) after fresh MEA reclamation and 83-99% after reclamation of pilot-used MEA. The sludge samples from distillation of pilot-MEA at 140°C and 100 mbar stands out with its radically lower nitrogen recovery compared to all other samples.

It can be hypothesised that chemical reactions take place in the complex and degraded solvent sludge, forming new degradation compounds which are not included in the analytical methodology used in this work. Having the highest temperature of the tests, in combination with the pilot solvent being a much more chemically complex solution than fresh MEA may contribute to this observation. The high chemical complexity opens up for further thermal degradation pathways than in a solution containing nearly only MEA and water.

The fact that the nitrogen recovery is lower in the start solvent than in the sludge and distillate for the other reclamation experiments with MEA from pilot operations indicated that volatile degradation compounds were evaporated from the system during the experiment. These are likely mainly ammonia and alkylamines, which form during MEA degradation. The methodology used in this work did not include capturing and analysing those. The nitrogen balance for degraded MEA is generally considered closed with the nearly fifty known degradation compounds identified (Vevelstad et al., 2022).

3.2. Simple alkaline hydrolysis experiments

The tests showed that as well as successfully hydrolysing amides to form carboxylic acids (in the form of carboxylates), there were increases in concentrations of some secondary degradation products such as HEEDA (2-[(2-aminoethyl)amino]-ethanol, CAS 111-41-1), HEA (*N*-(2-hydroxyethyl)-acetamide, CAS 142-46-7), HEIA (1-(2-hydroxyethyl)-2-imidazolidinone, CAS 3699-54-5), DEA (diethanolamine, 111-42-2), and MMEA (*N*-methyl ethanolamine, CAS 109-83-1), with some of these compounds being characterised by relatively high volatility. Figure 6 shows the concentrations of specific degradation compounds in MEA during the tests.

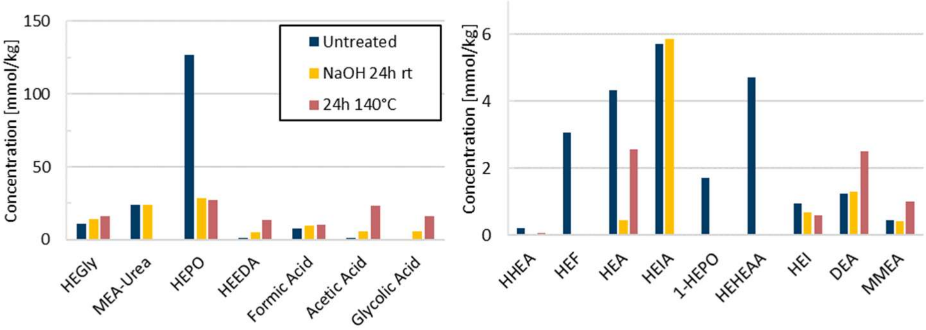


Figure 6: Degradation product concentrations during the thermal reclaiming tests with degraded 40wt% MEA (aq.) from the SINTEF SDR rig.

In Figure 7 it can be seen that, after alkaline hydrolysis at 140°C, fresh MEA undergoes some degradation, giving rise to the formation of acids and some secondary amines. The acids are present in the solution as their corresponding carboxylates and are therefore easy to remove with the distillation step of the thermal reclaiming process, where heat stable salts (HSS) such as these remain in the reclaimer sludge and can be disposed of. Secondary amines will, on the other hand, likely largely distil off with the solvent amine and remain in the solvent.

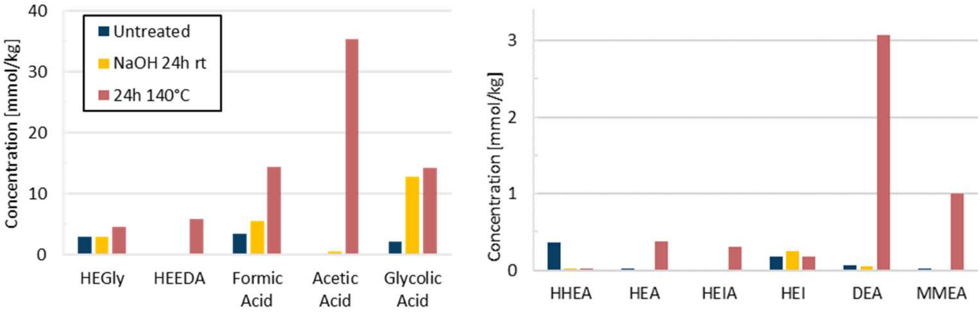


Figure 7: Degradation product concentrations during the thermal reclaiming tests with fresh MEA (aq.).

Discussion

The reclamation efficiencies presented for the different pressures, temperatures, and MEA solvents in this work do not quantitatively represent the efficiency that would be seen in a real thermal reclaimer, with a complex, optimized process design. The results, however, illustrate some important trends, such as the fact that a fresh MEA solvent was more efficiently distilled than a degraded MEA solvent at the same conditions.

Despite of many amides predictably decomposing or getting hydrolysed in the alkaline hydrolysis experiment, the same results are not observed during the vacuum distillation tests. The simple reclaiming tests show that HEA, HEF, HEIA, HEHEAA, and MEA urea should all decompose during thermal conditions and alkaline addition. Also, contrary to the simple tests, carboxylates (presented as acids in this work) are consumed rather than formed during distillation. HEPO is the only amide for which the concentration decreases during the distillation, as it does in the simple tests. The amino acid HEGly is consumed during the vacuum distillation but remains intact in the simple hydrolysis test.

The time of exposure to the elevated temperatures is much shorter in the distillation tests, which could of course impact the reactions taking place. Another radical difference is the concentration of NaOH, which was purposefully high in the alkaline hydrolysis experiments, to induce all the possible hydrolysis reactions. Increasing the pH by adding more NaOH than was used in the distillation tests in this work would likely favour a higher conversion of amides into MEA and carboxylates.

The additional degradation that takes place in the simple reclaiming tests shows that the time the solvent spends at high temperature should be limited as much as possible. This could also imply that reclamation needs to be performed at as low temperatures as possible. Looking at the results from distilling the pilot degraded MEA solvent at different pressures, there doesn’t seem to be that much benefit from operating at low temperature when it comes to the distillate composition, as the compositions of the different distillates are very similar.

The heating during reclamation seems to favour the formation of typical thermal degradation products, many of which are secondary amines like HEEDA, DEA, and MMEA. Secondary amines are known to form nitrosamines in the presence of nitrous oxides (Fostås et al., 2011), carcinogenic compounds. This implies an increased risk for operators and potentially the environment surrounding the plant (Reynolds et al., 2012). As many nitrosamines are volatile, the thermal reclamation process may increase the need for emission control technologies, to ensure that an increased concentration of volatile degradation compounds does not lead to unwanted emissions to the environment or impurities in the CO_2 product. It is, however, difficult to directly compare the formation rate of these secondary amines under these conditions to that in the presence of CO_2 and with more realistic NaOH concentrations. The evidence of MMEA being distilled with and ending up in the reclaimed solvent shows that secondary, nitrosamine forming amines may remain in the solvent. There is, however, no indication that diethanolamine is largely carried over to the distillate in this work. This is fortunate, as it can form nitrosodiethanolamine (NDELA). Other volatile amines were not studied in this work.

Conclusions

Alkaline hydrolysis of eight studied amide degradation products of MEA was successfully seen in simple reclaiming chemistry tests, where a strong base was added, and the sample was exposed to 140°C for one day. During distillation of a degraded MEA solvent at reduced pressure and the same temperature for two hours, the same was not observed. Only the amount of two of the amides, HEPO and MEA urea were seen to decrease during solvent reclaiming at elevated temperature and increased temperature.

Contrary to in the simple alkaline hydrolysis tests, the amount of some non-amide compounds decreased during reclaiming, such as the corresponding carboxylates of formic, acetic and glycolic acid, and the amino acid HEGly. Even the formation of new amide degradation compounds was observed during distillation of the MEA solvent at reduced pressure, where the amounts of HEF, HEHEAA and HEA increased, contrary to their decrease in the simple reclamation chemistry tests. It is probable that the lower pH during the thermal reclaiming compared to in the alkaline hydrolysis experiments does not suffice to hydrolyse most of the amides contained in the degraded solvent.

Despite of little alkaline hydrolysis taking place, a highly pure reclaimed MEA solvent was obtained, containing less than 0.04 wt% of known degradation products. Here MMEA was the main contaminant, being present in the concentration range of 2-3 mmol/kg solvent.

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