

Degradation rate and degradation kinetics of activated and non-activated aqueous *N*-Methyldiethanolamine (MDEA) absorption solutions

Benjamin Burfeind¹, Hendrik Multhaupt¹, Axel Brehm¹, Jörg Hofmann², Ute Mikow²

Abstract— This study focuses on the degradation rate and its kinetics of an aqueous *N*-Methyldiethanolamine (MDEA) solution containing different activators. Activated MDEA solutions are widely used as absorbent of acid gases. Piperazine (PZ), Morpholine (MP) and *N*-(2-Aminoethyl) ethanolamine (AEEA) were used as activators in this study. Hence, the following blended absorption solutions were availed in this research: non-activated MDEA, MDEA-PZ, MDEA-MP, and MDEA-AEEA. The influence of the temperature on the degradation rate was established and the difference in degradation behavior between carbon dioxide (CO₂) gassed and non-gassed aqueous alkanolamine solutions had been investigated. With increasing temperature, formation of a wider range of degradation products could be observed. While the degradation in non-gassed solutions seemed insignificant, increasing of the CO₂-concentration accelerates the aging process. Moreover, the addition of the above mentioned activators leads to a higher solubility of CO₂. This effect, which is particularly noticeable with MP in contrast to PZ, leads to higher and faster CO₂ initiated degradation. The range of the degradation product spectrum (determined by GC-FID and GC-MS) is also mainly influenced by an addition of the activators, as for instance the blended MDEA-AEEA solution had generated a narrow ranged degradation product spectrum in comparison to the other mixtures. Furthermore, a color change of the absorption solution from light yellow to dark brown had been observed while aging. In addition, in some aged alkanolamine solutions formation of turbid-oily filtrates had been perceived. In general, the degradation of the amines in absorption solutions is assumed to be one of the most important parameters regarding foam formation in biogas upgrading plants or similar gas processing plants.

Index Terms— Amine degradation, alkanolamine, absorption, biogas, kinetics, CO₂, foaming, acid gas, *N*-Methyldiethanolamine (MDEA), Piperazine (PZ), Morpholine (MP), GC-MS, GC-FID.

1 INTRODUCTION

Since many decades blended alkanolamine solutions are widely used for removal of acid gases from natural gas streams [1], [2]. Nowadays many biogas plant operators also use these chemical solutions to separate CO₂ from Methane (CH₄). Before upgrading, the raw biogas is produced by anaerobic fermentation of biomass in biogas plants. CH₄ and CO₂ are the main gas components formed. Moreover, the raw biogas contains a small amount of secondary constituents like hydrogen sulfide (H₂S), ammonia (NH₃), and saturated water vapor (H₂O_(g)) [3], [4], [5].

After the anaerobic digestion the raw biogas is upgraded. In this upgrading process the impurities H₂S, NH₃ and H₂O_(g) are firstly removed from the raw biogas by catalytic treatment or drying [6]. Following this, CH₄ and the CO₂ are separated from each other in a biogas washer column. This operation step is also known as amine scrubbing. At that stage the CO₂ is absorbed by an aqueous alkanolamine solution due to the chemical affinity of the absorption solution to the CO₂ [6].

Afterwards the CO₂-loaded aqueous amine solution leaves the column at the bottom and is added to a recirculation cycle, where the CO₂ is desorbed from the absorption solution under heat and pressure influence. After purifying, the aqueous amine solution is transported to the upper part of the biogas washer column. Simultaneously, the CO₂-loaded aqueous alkanolamine solution exits the column at the bottom; the CH₄ leaves the column at the top and is once again upgraded for its injection into the natural gas grid [6].

To ensure a far-reaching or in a best-case scenario a complete desorption of the CO₂ from the absorption solution, temperatures of 403 K and above and excess pressure are favorable in the recirculation cycle (17.6 % CO₂-desorption at 333 K, 86.6 % at 403 K, and 96.8 % at 433 K) [5].

This increased temperature which generates the phenomenon, commonly known as amine degradation, further results in a wide range of degradation products flowing through the entire process [7]. Apart from corrosion the amine degradation

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mentioned to be one of the main reasons of foam formation in aqueous amine solution including processes, as it is in several today's biogas treatment plants [7], [8], [11], [12]. In this, incipient foaming is described to be one of the most serious operational problems in alkanolamine-based gas absorption processes [13], [14]. Moreover, amine loss and further operational trouble such as corrosion, high solution viscosity, fouling, accumulations of non-regenerable contaminants, etc. are major problems caused by amine degradation [10], [15]. These difficulties necessitate a profound understanding of the amine degradation. Therefore, the first instance of this study was to investigate the influence of the CO₂ and the temperature on the degradation of MDEA and PZ. Furthermore, the degradation rate and its kinetics of a CO₂-loaded non-activated aqueous MDEA solution had been compared with a CO₂-loaded blended MDEA solution at a temperature of 453 K. Thus, PZ, which is widely used as main activator in alkanolamine blends [17] and in biogas upgrading processes respectively, had been added in different concentrations (3 % weight, 20 % weight, 40 % weight - in relation to the MDEA mass).

The main goal was to figure out a correlation between activator concentration and the degradation rate of the absorption solution. In addition MP and AEEA had been applied as alternative activators (20 % weight of MDEA mass each).

In order to identify the degradation products, thus the degradation rate, gas chromatography measurements (GC-FID and GC-MS) were used. Moreover, one filtrate of an aged alkanolamine absorption solution had been measured with the Simulated Distillation Method (SimDist) to observe the amount of high-boiling compounds. In contrast to the GC-MS method (boiling points up to 520 K measurable in our case) the SimDist Method offers the possibility to detect degradation products with boiling points up to 973 K [16].

2 EXPERIMENTAL

2.1 Materials

The chemicals which had been used for preparation of the samples are listed below.

- (a) N-Methyldiethanolamine, 98 % minimum purity, AppliChem (Germany)
- (b) Piperazine, 99 % purity - extra pure, Acros Organics (USA/Belgium)
- (c) Morpholine, 99+ % minimum purity - extra pure, Acros Organics (USA/Belgium)
- (d) N-(2-Aminoethyl) ethanolamine, 99 % purity, Alfa Aesar (Germany)

2.2 Preparation of samples

The initial aqueous MDEA solution (molarity 2.7 M), acting as a reference and source solution for the preparing of the blended absorption solutions, had been obtained from MDEA and de-ionized water under stirring in a single-neck 2000 ml

round-bottomed flask. Afterwards, the desired quantity of the relevant activator was added under stirring. The aqueous MDEA solution with a molarity of 2.7 M had been prepared by mass using a Sartorius BL3100 analytical balance with an accuracy of ± 0.1 g. The quantity of the activators had been weighed with a Sartorius CP323S analytical balance whose accuracy was ± 0.001 g.

To simulate real working conditions, the handling of a biogas upgrading plant operator respectively, neither the non-activated, nor the activated aqueous MDEA solutions had been further treated in order to remove potential impurities.

Analog to the initial aqueous absorption solution an aqueous MDEA solution with a higher MDEA concentration of 3.2 M had been prepared to faster figure out the degradation only caused by temperature influence (without CO₂-loading).

To obtain a CO₂-loaded solution the previously prepared aqueous absorption solution had been gassed with CO₂ in a stainless-steel autoclave with Teflon insert by a micro hose (88 g CO₂ / 1 liter of aqueous amine solution). After this loading step the sealed stainless-steel autoclaves had been heated in an oven at 403 K or 453 K for the desired period of time (one to 14 days).

2.3 Characterization of the degradation products

In order to identify the generated degradation products, gas chromatography (GC, with a flame ionization detector; FID) coupled with a mass spectrometer (MS) had been the method of choice.

The data of the FID and the MS are listed below.

- (a) FID- AGILENT 7820A with autosampler (gas chromatographic separation column - HP 5 MS UI (30 m x 0.25mm x 0.5 μ m))
- (b) MS- Varian 3800 coupled with Varian 2000GC-MS-MS (analog (a))

To analyse the filtrate and in comparison the corresponding alkanolamine solution the *Simulated Distillation Analysis (SimDist)* Method had been selected. This method ensures that the high boiling degradation products which had mainly been assumed in the filtrates had also been measured.

The instrument adjustment of the SimDist is listed below.

- (c) HP5890 Serie II (gas chromatographic separation column - WCOT ULTI METAL 10 m x 0.5 mm x 0.15 μ m; coating HAT simdist)

3 RESULTS AND DISCUSSION

For the following illustration of the degradation progress the peak areas of the respective compound peaks in the chromatograms of the aged solutions are displayed as percentages of those found for the fresh, unaged solutions. Afterwards, the identified and unidentified degradation products in different stages of aging are listed in tables.

3.1 Influence of CO₂ and temperature

The influence of CO₂ to the aging of MDEA and PZ is shown in figure 1 and 2, respectively. From these it appears that significant aging only takes place if CO₂ is present. After 4 days (96 h) at a temperature of 453 K and a loading of 88 g CO₂ / 1liter aqueous amine solution, the concentration of MDEA lowers to 92 % of the initial value, while PZ decreases even down to 10 %. It is therefore obvious that the activator PZ is subject to a much greater aging than the MDEA. Without the presence of CO₂ however even after 4 days at 433 K no degradation of MDEA or PZ could be observed.

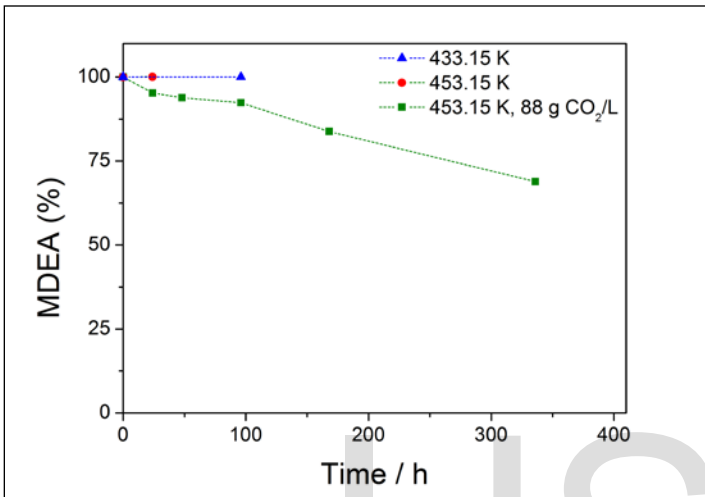


Figure 1: Aging of MDEA in a PZ (20 wt.-%) activated aqueous 2.7 M MDEA solution under the influence of CO₂ at temperatures of 433 K and 453 K.

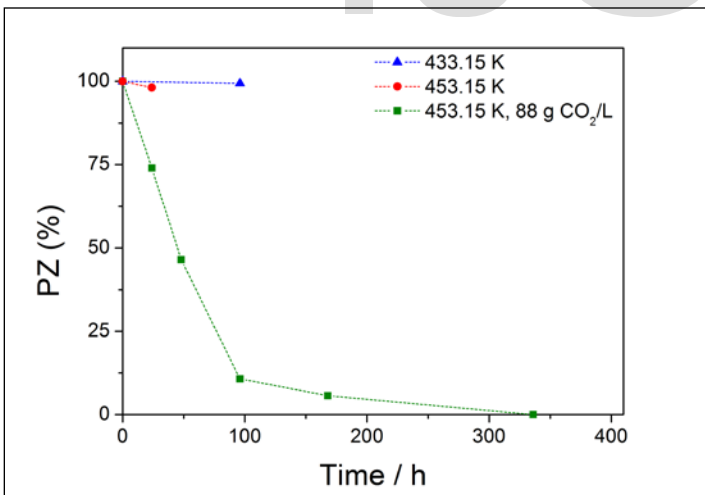


Figure 2: Aging of PZ in a PZ (20wt.-%) activated aqueous 2.7 M MDEA solution under the influence of CO₂ at temperatures of 433 K and 453 K.

In order to discuss the influence of the temperature on the aging of the CO₂ loaded solutions over time the respective residual amounts of MDEA and PZ are shown in figure 3 and 4, respectively. No significant degradation of the MDEA could be seen at 403 K up to a period of two weeks while a loss of 20 % is observed for PZ. At 453 K however both MDEA and

PZ show a noticeable degradation. In the solution containing 3 wt.-% PZ nearly no presence of the same (of PZ) could be found already after two days.

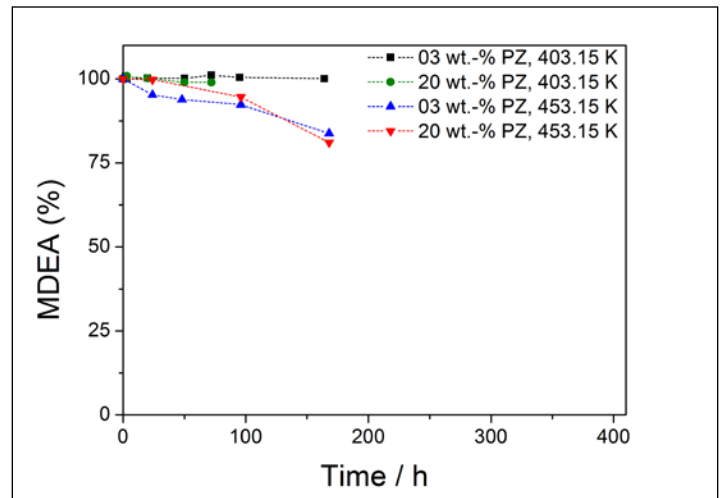


Figure 3: Influence of the temperature on the aging of MDEA in a PZ (3 wt.-% / 20 wt.-%) activated and CO₂-loaded (88 g/L amine at 453 K and 20 g/L amine at 403 K) aqueous 2.7 M MDEA solution.

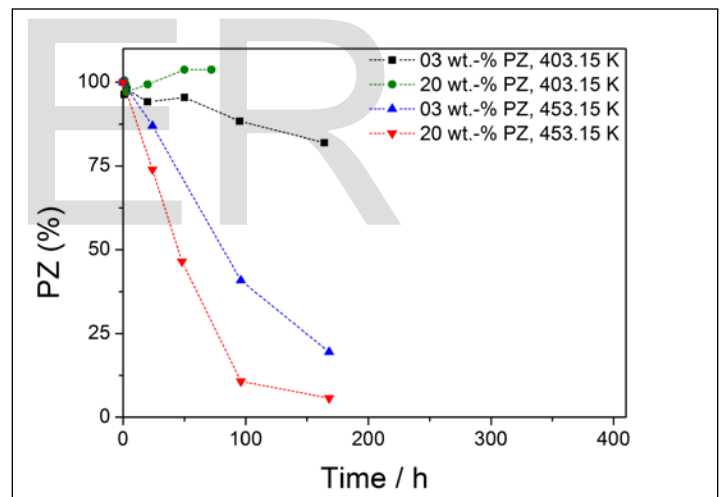


Figure 4: Influence of the temperature on the aging of PZ in a PZ (3 wt.-% / 20 wt.-%) activated and CO₂-loaded (88 g/L amine at 453 K and 20 g/L amine at 403 K) aqueous 2.7 M MDEA solution.

3.2 Influence of different activators

The effect of adding different activators on the aging of MDEA is shown in the figure 5 and 6, respectively. After 14 days at 453 K about 75 % of the initial MDEA amount is left in the CO₂-loaded solution if no activator is present. In contrast, by adding 3 or 20 wt.-% of PZ as an activator to the solution, the MDEA degrades down to 68 % of the starting value. When the concentration of piperazine in the solution is further increased to 40 wt.-% almost a doubling of the MDEA-degradation could be observed (residual amount MDEA: 35 %). The higher aging rate results from the increased CO₂-absorption in the solution caused by the activators.

Through the presence of large quantities of CO₂ degradation reactions can be initiated with more molecules leading to overall higher and faster degradation.

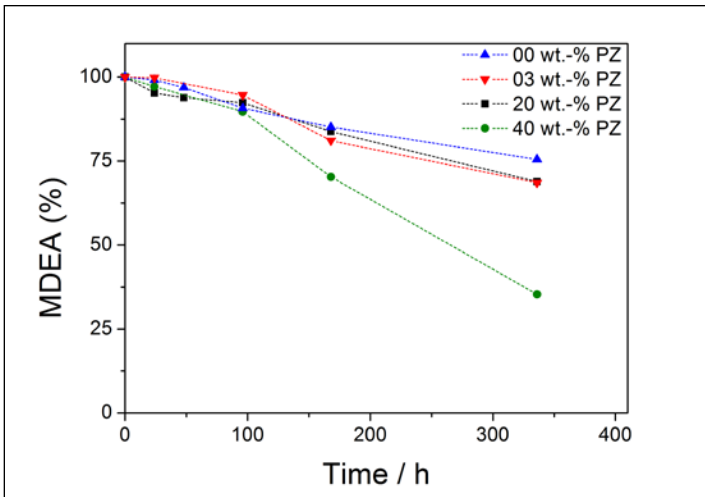


Figure 5: Influence of the PZ concentration (0, 3, 20, 40 wt.-%) on the aging of MDEA in an activated and CO₂-loaded aqueous 2.7 M MDEA solution at a temperature of 453 K.

The influence of the type of activator on the aging of MDEA is shown in figure 6. In aged solutions with 20 wt.-% AEEA the degradation of the MDEA and AEEA is considered together since the peaks for both compounds overlay in the relevant chromatograms.

After 14 days the highest residual amount of MDEA is present in the unactivated solution. By adding PZ a small increase to the degradation rate of the MDEA could be observed. The mixtures with AEEA showed the highest degradation rate in the first 4 days, which decreases until a certain degradation point is reached. The highest degradation could be found using morpholine as an activator for aqueous MDEA solutions.

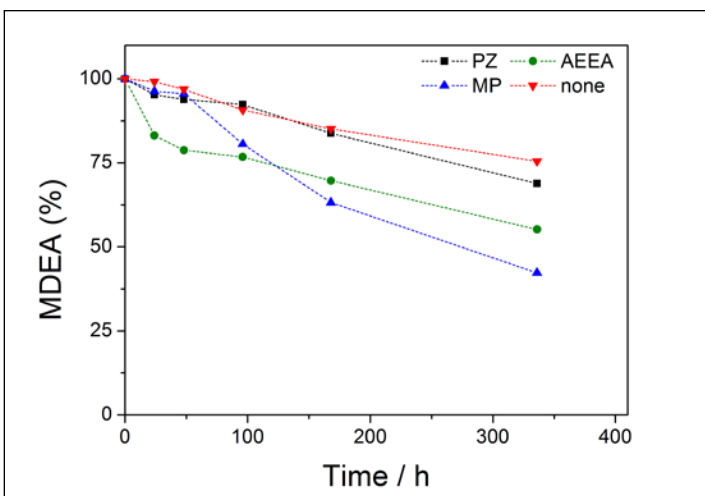


Figure 6: Influence of different activators (PZ, AEEA, MP) on the aging of MDEA in an activated (20 wt.-% each) and CO₂-loaded aqueous 2.7 M MDEA solution at a temperature of 453 K.

The aging of the various activators and the influence of their concentration were also studied and are shown in figure 7. The aging rate of PZ decreased with increased initial concentration in the solution. MP showed a smaller degradation rate which increases with time, until it reaches the same rate as PZ at around 100 h. An explanation could be the formation of intermediate products, which have a faster degradation rate, and can undergo further reactions with more morpholine. In all solutions with up to 20 wt.-% activator, none of those could be detected after 7 days and therefore degraded completely.

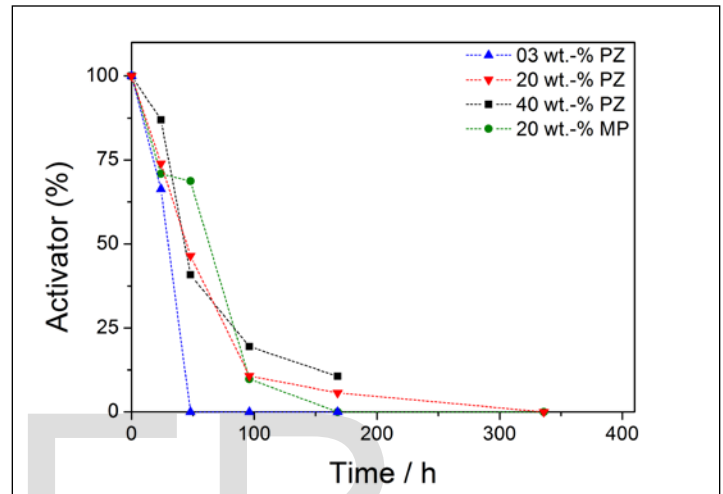


Figure 7: Influence of the activator concentration on their aging in an activated and CO₂-loaded aqueous 2.7 M MDEA solution at a temperature of 453 K.

3.3 Process of the reactant and product components by time

A high amount of degradation products could be found in all solutions, while mixtures with no activator or AEEA showed a minor product spectrum. Many products result from the degradation of the cyclic amines (PZ, MP). The formation of dimethylpiperazine from PZ or methylmorpholine from MP could be observed. In addition to the known main aging products after 2 to 4 days a wide variety of other aging substances had been seen, which weren't characterized further. With the progress of time up to 14 days some degradation products had been enriched significantly.

3.4 Degradation rate of activated and non-activated aqueous alkanolamine solutions

The aging of the selected solutions has been investigated (conditions see experimental part).

The wt.-% of the degradation products from an initial composition to a 14 day period in a non-activated 2.7 M MDEA solution is shown in table 1.

Table 1: Wt.-% of degradation products or retention times for a 14 day period in a non-activated 2.7 M MDEA solution.

compound or retention time	Time/ d					
	0	1	2	4	7	14
DMAE		0.86	1.96	3.85	6.09	9.38
MDEA	100.00	99.14	96.87	90.74	85.13	75.51
HEP						0.84
TEA				1.33	1.75	2.04
HEOD			1.17	3.15	5.57	9.44
BHEP						0.89
8.78				0.94	1.46	1.90

Obviously, the concentration of the MDEA decreased with time from an initial concentration of 100.00 wt.-% to 75.51 wt.-% (24.49 wt.-% MDEA loss, 24.49 % of the initial amine concentration respectively). Simultaneously, DMAE (Dimethylaminoethanol), HEP (1-(2-Hydroxyethyl) piperazine), TEA (Triethanolamine), HEOD (3-(2-Hydroxyethyl)-2-oxazolidinone) and BHEP (1, 4-Bis (2-hydroxyethyl) piperazine) were formed and identified. The unidentified aging product with its associated retention time of 8.78 min is listed in table 1. In the further course of this study the unidentified degradation products are listed with their corresponding retention times.

Exemplarily, the procentual MDEA degradation and the formation of the above-mentioned degradation products with time is shown in figure 8. The lowering of the amount % of MDEA (orange pillar) is noticeable. Moreover, the formation of DMAE (green pillar) or HEOD (red pillar) with time is clearly shown.

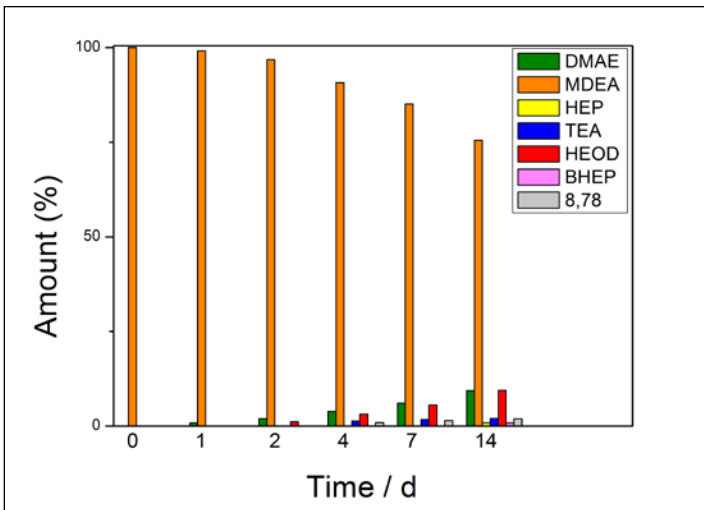


Figure 8: Behavior of the MDEA degradation and the formation of degradation products in a non-activated aqueous 2.7 M MDEA solution at a temperature of 453 K (unknown product listed with retention time).

The wt.-% of the degradation products from an initial composition to a 14 day period in a 2.7 M MDEA + 3 wt.-% PZ solution is shown in table 2. The concentration of the reagents

MDEA and PZ decreased with time. The PZ is fully degraded after 4 days of aging. The amount of MDEA lowers from 95.94 wt.-% to 65.74 wt.-% (31.48 % MDEA loss after 14 days). DMAE, DMPZ (1, 4-dimethylpiperazine), HEP, TEA, HEOD and BHEP were identified as degradation products formed. In comparison to the non-activated MDEA solution the MDEA loss is higher (31.48 % instead of 24.49 %). Furthermore, a significantly wider range of degradation products had been found out.

Table 2: Wt.-% of degradation products or retention times for a 14 day period in a 2.7 M MDEA + 3 wt.-% PZ solution.

compound or retention time	Time/ d				
	0	1	4	7	14
2.56					1.37
DMAE			2.52	6.45	9.55
DMPZ				0.96	1.36
PZ	4.06	2.69			
MDEA	95.94	95.73	90.81	77.80	65.74
HEP				2.31	4.35
TEA			1.15	2.64	2.72
HEOD			1.28	3.24	5.98
BHEP				2.01	4.11
8.01			2.02	1.41	1.13
8.78			0.88	2.15	2.35
9.36				1.02	1.35
10.82			1.35		

The wt.-% of the degradation products from an initial composition to a 14 day period in a 2.7 M MDEA + 20 wt.-% PZ solution is shown in table 3. The concentration of the reagents MDEA and PZ decreased with time. In comparison to the non-activated and the 3 wt.-% PZ activated solutions (table 1 and 2), a wider range of degradation products were formed. Even though in this degradation process the following aging products could be identified: DMAE, DMPZ, HEP, TEA and BHEP, there are still several unidentified aging products.

The PZ with an initial amount of 27.78 wt.-% had fully been degraded after 14 days of aging. The MDEA concentration decreased from 72.22 wt.-% to 49.72 wt.-% (31.50 % MDEA loss). The procentual degradation of MDEA is nearly the same in 3 wt.-% and 20 wt.-% PZ activated aqueous solutions.

Table 3: Wt.-% of degradation products or retention times for a 14 day period in a 2.7 M MDEA + 20 wt.-% PZ solution.

compound or retention time	Time / d					
	0	1	2	4	7	14
DMAE				2.00	2.67	4.79
DMPZ			1.19	4.38	5.57	9.36
PZ	27.78	20.54	12.90	2.98	1.58	
4.93						1.51
5.49						1.53
MDEA	72.22	68.81	67.78	66.69	60.51	49.72
HEP			1.78	3.05	6.79	
6.52		0.83	1.21	1.78	3.05	6.79
TEA					1.10	1.51
BHEP					1.26	2.65
8.01		1.06	3.37	7.86	7.83	7.14
8.08		7.06	7.79	2.42	1.06	
8.61				1.40	2.43	4.10
9.36					1.06	1.52
9.94					1.55	2.94
10.01			1.89			
10.11		1.69	2.57	2.20		
10.82		1.69	2.57	2.20		
11.41				1.65	2.19	2.14
12.00						1.38

In table 4 and 5 the degradation rates of the two chosen alternative activators (MP and AEEA) are shown.

Compared to the non-activated MDEA solution a similar range of degradation products were formed in the 2.7 M MDEA + 20 wt.-% MP solution (see table 4). In addition to the aging products formed in the non-activated 2.7 M MDEA solution, MMP (4-Methylmorpholine), DMPZ (a/m), HMP (4-(2-Hydroxyethyl) morpholine), AMP (4-Acetylmorpholine) and Bicin (*N,N*-Bis(2-hydroxyethyl)glycine) had been further identified as degradation products formed.

The MDEA loss, from 77.74 wt.-% to 32.87 wt.-% (57.72 % MDEA loss), is much higher compared to the non-activated (24.49 %) and the PZ activated (31.50 %) MDEA solutions. Moreover, the whole MP is completely lost after 7 days.

Table 4: Wt.-% of degradation products or retention times for a 14 day period in a 2.7 M MDEA + 20 wt.-% MP solution.

compound or retention time	Time / d					
	0	1	2	4	7	14
2.56					0.83	2.60
DMAE				1.84	4.43	7.52
MMP		2.93	3.80	7.42	8.28	9.81
MP	22.26	15.78	15.29	2.18		
DMPZ					0.82	2.44
MDEA	77.74	74.89	74.28	62.65	49.13	32.87
HMP				0.99	2.20	4.19
AMP				0.93	0.97	1.20
HEP					2.58	6.69
TEA				0.83	1.94	1.69
HEOD					1.08	1.81
BICIN		6.40	6.63	16.43	13.32	8.64

BHEP	0.75	2.89	5.95
8.12	1.88	2.72	3.04
8.78		0.91	0.74
9.36	3.22	1.11	0.81
9.54	0.87	1.17	0.76
9.72		1.62	2.41

As it is shown in table 5 the 2.7 M MDEA solution, activated to 20 wt.-% AEEA, exhibits a lower degradation rate and as a consequence a narrow range of aging products compared with PZ and MP as activator. Not more than three new unidentified degradation products were formed compared to the non-activated 2.7 M MDEA solution.

Since the MDEA and the AEEA peaks were very close to each other in the GC-MS spectrum, they were examined and evaluated together. The cumulative amine loss of MDEA and AEEA is merely 44.83 % after 14 days of aging; comparable solutions are MDEA-PZ 50.28 % loss, MDEA-MP 67.13 % loss. The cumulative loss of the minimally activated MDEA solution (3 wt.-% PZ) is 34.26 % loss. Without activation there is 24.49 % MDEA loss.

Table 5: Wt.-% of degradation products or retention times for a 14 day period in a 2.7 M MDEA + 20 wt.-% AEEA solution.

compound or retention time	Time / d					
	0	1	2	4	7	14
2.56						1.27
DMAE		1.04	1.76	2.28	4.26	7.63
MDEA/AEEA	98.99	82.31	77.98	75.96	68.97	54.61
HEP			1.24	1.77	3.11	6.23
TEA				1.23	1.46	2.12
HEOD	1.02	7.39	6.27	6.37	6.36	8.52
BHEP		5.02	7.12	7.61	10.59	14.98
8.78		3.09	3.15	3.45	3.32	2.71
8.83		1.16	1.26	1.11		
9.36					1.28	1.80

4 CONCLUSION

It was shown that aging of aqueous alkanolamine solutions takes place only in the simultaneous presence of CO₂. Another significant factor is the temperature, which must reach a sufficiently number, so that a CO₂-initiated degradation of the reactants can take place. Thus, at a temperature of 403 K and a pressure of 5 bars above atmospheric pressure, there will be no significant aging, whereas all solutions tested aged at 453 K. Furthermore, by adding an activator to the aqueous MDEA solution a stronger degradation of MDEA takes place, because more CO₂ is driven into the solution by the activator. This corresponds with the results of Daptardar *et al.* [12] contrary to those of Closmann *et al.* [17]. The results of the comparison of morpholine, which is discussed as a possible activator in the literature, and piperazine, however, contradict those of Daptardar *et al.* [12]. MP has the broader degradation product range, as Closmann *et al.* [17] also described. Thus, from the degradation rate perspective, Morpholine is not recommended for use in adsorption systems. Even when AEEA is used the MDEA ages faster, making the piperazine conventionally used

the best activator in terms of aging.

In addition, the course of the kinetics of the aging of the different solutions was studied, with a far broader range of products than previously discussed in the literature. With respect to the resulting aging products, the solutions activated with AEEA showed the minor substance spectrum. Thus, AEEA offers an interesting replacement for PZ in regard to possibly initiated aging product initiated foaming. Whether through a smaller number of formed aging products, the probability of the existence of products with foam-stabilizing effect has to be proven in further studies.

To clarify the question of foam formation in aged solutions, a study by means of a bubble column is already described in the literature by Thitakamol and Veawab [18]. In these, the aged solutions are gassed with CO₂ at different temperatures and the amount of incoming foaming is observed. From the comparison of the foaming behavior of the aged aqueous alkanolamines first signs of stabilizing foam degradation products can be obtained and in the ideal case compared to the product range. These could be added targetedly to fresh solutions, which could then be examined again with regard to the formation of foaming.

5 APPENDIX

The reagents used and all characterized degradation products are listed in their structural formulae in the following two tables.

Table 6: Reagent names and their corresponding structural formulae.

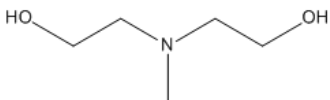
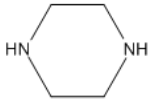
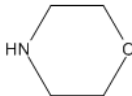
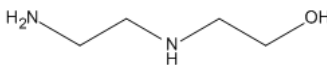
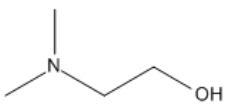
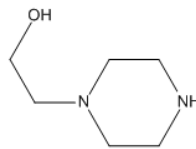
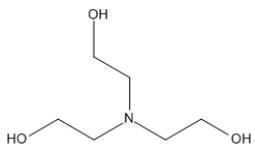
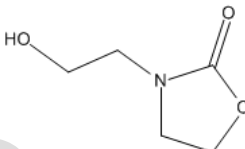
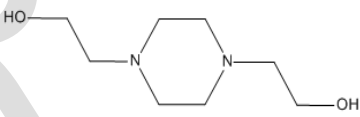
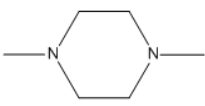
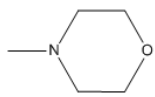
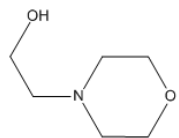
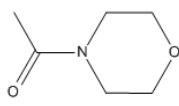
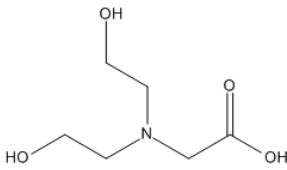
Reagent name	Structural formula
N-Methyldiethanolamine (MDEA)	
Piperazine (PZ)	
Morpholine (MP)	
N-(2-Aminoethyl) ethanolamine (AEEA)	

Table 7: Names of degradation products and their corresponding structural formulae.

Name of degradation product	Structural formula
Dimethylaminoethanol (DMAE)	
1-(2-Hydroxyethyl) piperazine (HEP)	
Triethanolamine (TEA)	
3-(2-Hydroxyethyl)-2-oxazolidinone (HEOD)	
1,4-Bis(2-hydroxyethyl) piperazine (BHEP)	
1,4-Dimethyl-piperazine (DMPZ)	
4-Methylmorpholine (MMP)	
4-(2-Hydroxyethyl) morpholine (HMP)	
4-Acetylmorpholine (AMP)	
N, N-Bis (2-hydroxyethyl) glycine (BICINE)	

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REFERENCES

- [1] A. Kohl, R. Nielsen, *Gas Purification*, 5th ed. Gulf Publishing Company, **1997**.
- [2] A.T. Zoghi, F. Feyzi, S. Zarrinpashneh, Experimental investigation on the effect of addition of amine activators to aqueous solutions of N-methyldiethanolamine on the rate of carbon dioxide absorption, *International Journal of Greenhouse Gas Control* **7**, **2012**, pp. 12-19.
- [3] Fachagentur Nachwachsende Rohstoffe e.V. (Hrsg.), Leitfaden Biogas - Von der Gewinnung zur Nutzung, Gülzow, **2010**, pp. 21, 30-31,
- [4] W. Urban, K. Girod, H. Lohmann, Technologien und Kosten der Biogasaufbereitung und Einspeisung in das Erdgasnetz - Ergebnisse der Markterhebung 2007-2008, *Fraunhofer UMSICHT*, Oberhausen, **2009**.
- [5] J. Hofmann, M. Wecks, U. Freier, Herstellung von Biomethan durch Aminwäsche, *LIAN-Kolloquium - Neue Verfahren und Materialien für Energie- und Umwelttechnik*, Zwickau, **2010**.
- [6] Biomethane - New perspectives for energy supply, *MT-BioMethan GmbH image Brochure*, Zeven, **2014**, pp. 21-23.
- [7] C.R. Pauley, R. Hashemi, Analysis of foaming mechanisms in amine plants, *Scientific & Technical Report*, Denver, **1988**.
- [8] X. Chen, S.A. Freeman, G.T. Rochelle, Foaming of aqueous piperazine and monoethanolamine for CO₂ capture, *International Journal of Greenhouse Gas Control* **5**, **2011**, pp. 381-386.
- [9] J. McCarthy, M.A. Trebble, An experimental investigation into the foaming tendency of diethanolamine gas sweetening solutions, *Chem. Eng. Commun.* **144**, **1996**, pp. 159-171.
- [10] I. Ratman, T.D. Kusworo, A.F. Ismail, Foam Behaviour of An Aqueous Solution of Piperazine- N-Methyldiethanolamine (MDEA) Blend as a Function of the Type of Impurities and Concentrations, *International Journal of Science and Engineering*, Vol. 1 (1), **2010**, pp. 7-14.
- [11] A. Chakma, A. Meisen, Corrosivity of Diethanolamine Solutions and Their Degradation Products, *Ind. Chem. Prod. Res. Dev.* **25**, **1986**, pp. 627-630.
- [12] S.D. Daptardar, V.V. Mahajani, S.J. Chopra, P.K. Sen, and S. Sridhar, On degradation of chemical solvents for bulk removal of CO₂, *Gas Separation & Purification*, Vol. 8 (2), **1994**, pp. 115-121.
- [13] B. Thitakamol, A. Veawab, Foaming behavior in CO₂ absorption process using aqueous solutions of single and blended alkanolamines, *Ind. Eng. Chem. Res.* **47**, **2008**, pp. 216-225.
- [14] C.R. Pauley, Face the facts about amine foaming, *Chem. Eng. Prog.* **87** (7), **1991**, pp. 33-38.
- [15] M.S. Islam, R. Yusoff, and B.S. Ali, Degradation studies of amines and alkanolamines during CO₂ absorption and stripping system, *Engineering e-Transaction (ISSN 1823-6379)* **2**, **2010**, pp. 97-109.
- [16] A.K. Vickers, Higher-Temperature Simulated Distillation with DB-HT Sim Dis Columns - Applications, *Agilent Technologies, Inc.*, **2002**, p. 6.
- [17] F. Closmann, T. Nguyen, G.T. Rochelle, MDEA/Piperazine as a solvent for CO₂ capture, *Energy Procedia* **1**, **2009**, pp. 1351-1357.
- [18] B. Thitakamol, A. Veawab, Foaming model for CO₂ absorption process using aqueous monoethanolamine solutions, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **349**, **2009**, pp. 125-136.