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Comparison of different solvents from the solvent degradation rig with real samples

Solrun Johanne Vevelstad[a*], Andreas Grimstvedt[a], Geir Haugen[a], René Kupfer[b], Nathan Brown[b], Aslak Einbu[a], Kai Vernstad[a] and Kolbjørn Zahlsen[a] *

[a]*SINTEF Materials and Chemistry, PB 4760 Sluppen, 7465 Trondheim, Norway*
[b]*ION Engineering, 3052 Sterling Circle, Boulder CO 80301, USA*

Abstract

A known drawback using chemical absorbents in post-combustion CO_2 capture is degradation of solvents, which increases the capture cost and produces unwanted compounds from a health and environmental perspective. Validation of lab results is necessary to determine how relevant data produced in a laboratory is to predict degradation in a real process environment. In this work, lean samples from SINTEF's SDR rig during two solvent campaigns (S1 and MEA) have been compared with samples from real pilots (comparison depends on available data from pilots). For S1, larger amounts of nitrosamines were observed in the real samples than from the SDR rig. The nitrosamine balance for the proprietary solvent in the SDR rig is closed while a deviation for the MEA solvent is observed. A thorough characterization of degradation compounds was also conducted for the MEA samples from the SDR rig, the evaluation involved 32 degradations compounds. Analytical methods for 31 of these compounds are available, however only 24 of these compounds were observed above the lower limit of quantification in the lean MEA samples. HEPO, HEGly and MEA urea were major degradation products in MEA samples. MEA samples from pilot and SDR rig show that nitrogen containing degradation compounds are well accounted for in the lean samples.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO_2 capture, Solvents, Degradation, Characterization, Balances, Lab and Pilot samples

* Corresponding author. Tel.: +47-40642608.
E-mail address: solrun.j.vevelstad@sintef.no

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1. Introduction

A known drawback using chemical absorbents in post combustion CO_2 capture is degradation of solvents. Degradation results in loss of solvent increasing the capture cost due to the need of solvent replacement, waste treatment and strategies to avoid emission of unwanted compounds [1, 2]. During the last 10-15 years several studies have been conducted to study degradation of different amines, this includes relative stability of specific solvents or more systematic studies [3-7]. Degradation studies have typically been conducted under oxidative or thermal degradation conditions. In addition, several laboratory rigs have been built to study solvent degradation under process conditions [8, 9]. Validation of lab results is necessary to determine how relevant data produced in a laboratory is for predicting degradation in a real process environment [10, 11]. In this work, solvents from two tests campaigns (one with MEA and one with novel solvent S1 supplied by ION Engineering) are investigated using SINTEF's Solvent degradation rig (SDR) and compared to real samples from actual power plants. The studies include nitrogen and nitrosamine balances. For the MEA solvent, characterization will take into account some of the new degradation compounds suggested in literature [12] as well as overall stability.

Nomenclature

DM Pyrazine	2,5-dimethylpyrazine, 2,6-dimethylpyrazine and 2,3-dimethylpyrazine
3-Mpy	3-methyl-pyridine
2-PO	2-piperazinone
2,3,5-TM-pyrazine	2,3,5-trimethylpyrazine
BHEOX	*N1*,*N2*-bis(2-hydroxyethyl)-ethanediamide
$C_{A,0}$	Initial amine concentration
$C_{A,i}$	Amine concentration at time i
$C_{NA,i}$	Nitrosamine concentration at time i
DiEA	Diethylamine
DMA	Dimethylamine
EA	Ethylamine
GC-NCD	Gas Chromatography – Nitrogen Chemiluminescence Detector
HEA	*N*-(2-hydroxyethyl)-acetamide
HEEDA	2-[(2-aminoethyl)amino]-ethanol
HEF	*N*-(2-hydroxyethyl)-formamide
HEGly	*N*-(2-hydroxyethyl)-glycine
HEHEAA	*N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide
HEI	1H-Imidazole-1-ethanol
HEIA	1-(2-hydroxyethyl)-2-imidazolidinone
HEPO	4-(2-hydroxyethyl)-2-piperazinone
HESucc	1-(2-hydroxyethyl)-2,5-pyrrolidinedione
LC-MS	Liquid Chromatography – Mass Spectrometry
MA	Methylamine
MEA	ethanolamine
MEA urea	*N*,*N'*-bis(2-hydroxyethyl)-urea
NDELA	Nitrosodiethanolamine
NDMA	*N*-Nitrosodimethylamine
N-HEGly	2-[(2-hydroxyethyl)nitrosoamino]-Acetic acid
NCCC	the National Carbon Capture Center, Wilsonville, Alabama, USA
NA	Nitrosamine
NA-S1	Nitrosamine of S1
OZD	2-oxazolidinone
S1	Novel solvent (ION Engineering)

SDR	Solvent degradation rig

2. Experimental set-up

The SDR, Fig. 1, is an advanced laboratory test rig designed to study solvent degradation in a continuous process at commercially relevant process conditions. The total solvent inventory in the SDR is roughly 5 liters. The solvent is circulating in a combined absorber and stripper setup where the temperature of the absorber and stripper are set at different levels (absorber: 25 - 80°C, stripper: 110-150°C). The flue gas is a synthetic mixture of different gases (e.g. N_2, CO_2, O_2, NOx, SOx) and the composition can be varied to represent several different types of combusted gasses, in addition to providing the ability to isolate, control and evaluate the impact of a specific gas or gas environment. Compared to separate setups for oxidative or thermal degradation, the SDR enables studies of the combined effect of different degradation mechanisms occurring in a process environment. More details about the rig are given by Einbu et. al. [5]. The water concentration in the solvent during this project was monitored every week by Karl Fisher titration.

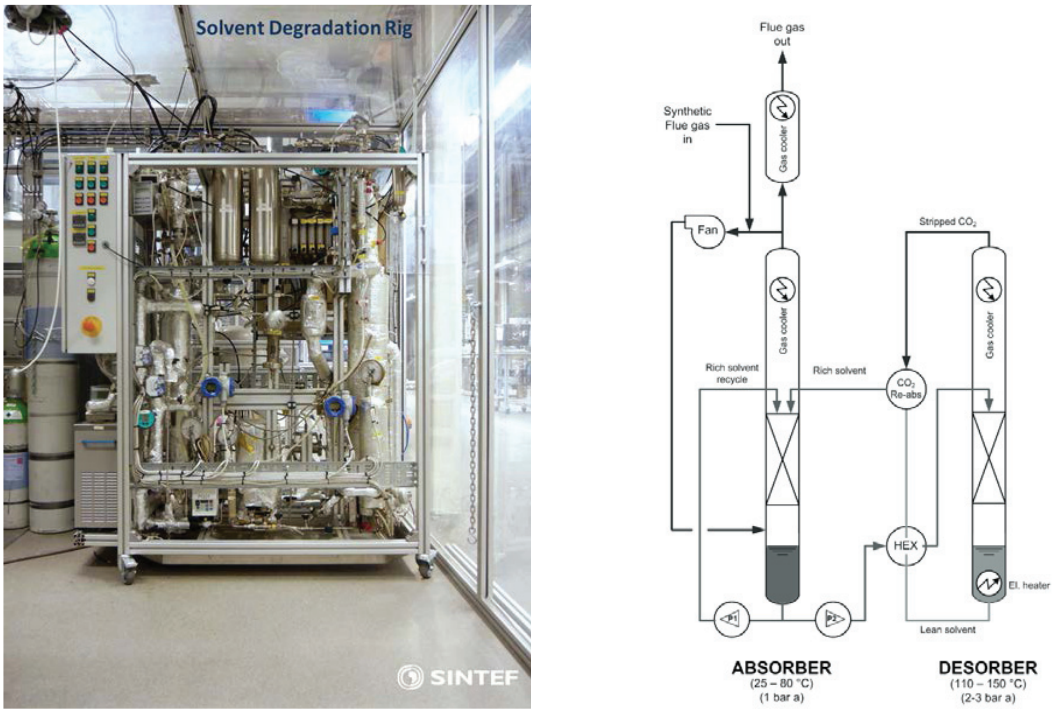

Fig. 1. Picture and simplified flow diagram of Solvent Degradation Rig (SDR) [8].

The test protocol used in this work is summarized in Table 1. The duration of the campaign was 5 weeks, for the first three weeks (week 1 to 3) it was operated at "standard" condition, while a higher stripper temperatures was used for the next week (week 4). For the last week (week 5) the stripper temperature was reverted back to the "standard" condition while increasing the NOx concentration tenfold to study nitrosamine formation.

ION Engineering's novel solvent was evaluated at the National Carbon Capture Center (NCCC) located in Wilsonville, Alabama, USA, which is a pre and post-combustion test facility that has been developed over the last 20 years. The Post-Combustion Carbon Capture Center (PC4) facility at NCCC was completed in 2011 and focuses specifically on testing and demonstration. Flue gas is supplied to the PC4 facilities by Plant Gaston, an 880 MW coal-

fired power plant operated by Southern Company. Flue gas processing at Plant Gaston includes particulate removal (bag filters and hot ESP), NOx removal (SCR) and desulphurization (wet-FGD) before diverting up to 13,600 kg/hr flue gas (3.0 MW eq.) to the PC4 facilities. The NCCC PC4 includes the 0.6 MW Pilot Solvent Test Unit (PSTU), two 1.0 MW pilot bays and four additional small pilot bays (0.1 MW). In the pilot bays developers can bring and test their process equipment while still benefiting from plant utilities and support services [13]. ION utilized the existing PSTU process with minimal modification for its test campaign (2015) [14].

Table 1: Test protocol for the SDR campaign.

Test protocol	Stripper T [°C]	Flue gas composition			Time [weeks]	Campaign period
		Oxygen content [Vol%]	CO_2 content [Vol%]	NOx content [ppmv]		
"Standard"	Standard	12	3	Low	3	Week 1-3
"High T"	High	12	3	Low	1	Week 4
"High NOx"	Standard	12	3	Moderate	1	Week 5

The operating parameters for the SDR rig at "standard conditions" are given in Table 2.

Table 2: Operating parameters for the SDR rig at "standard conditions"

Absorber temperature (°C)	50
Gas flow rate (m^3/hr)	3
Purge gas (L/min)	1
Absorber pressure (bar)	1
Stripper pressure (bar)	1.75

The solvent was loaded with CO_2 in the rig. During the campaign lean and rich solvent samples were taken on a weekly basis. The samples were analyzed using different analytical techniques depending on the analyte of interest. Specific amine, specific nitrosamine, alkylamines and ammonia were analyzed using Liquid Chromatography – Mass Spectrometry (LC-MS) while total nitrosamine was analyzed using Gas Chromatography (GC) with Nitrogen Chemiluminescence Detector (NCD) [8]. Total alkalinity was measured using titration with 0.1N H_2SO_4, CO_2 content using a TIC/TOC analyzer (Apollo 9000 TOC Combustion Analyzer from Teledyne Tekmar Co.) for total inorganic carbon, density using a Mettler-Toledo density meter (Mettler-Toledo CM40), organic nitrogen using Kjeldahl method [15] and water using a Karl Fisher titrator. For the MEA solvent several degradation compounds were analyzed using LC-MS, these compounds are given in Table 5.

3. Results/discussions

The total nitrosamine as well as nitrogen balance data were evaluated for solvent S1 (ION Engineering) from the SDR campaign. In addition a more detailed characterization is given for the MEA SDR campaign, here also quantification of several degradation compounds recently suggested in literature [12] are included.

3.1. Solvent S1 (ION Engineering)

The total organic nitrogen in lean samples from the SDR rig was measured using the Kjeldahl method [15] (see Table 3 for the nitrogen recovery (%) of these liquid samples). The nitrogen balance ("Recovery") for the lean samples are calculated as the ratio between the sum of nitrogen in quantified compounds and the total nitrogen. This balance tells how much nitrogen in the form of original components and degradation products is accounted for in the lean samples. For MEA, a large set of degradation products are available for quantification, and therefore the nitrogen recovery is usually high. Similar methods to predict degradation products and to develop analytical methods are used for other amines, however the nitrogen recovery is often lower than for MEA since MEA is the most characterized amine when it comes to degradation compounds.

Table 3: The nitrogen recovery for S1 for the experiment at the SDR rig based on Kjeldahl analysis.

Time [week]	Recovery N [%]	Test protocol
0	103	"Standard"
2	95.5	"Standard"
3	96.0	"Standard"
4	88.6	"High T"
5	89.6	"High NOx"

The nitrogen recovery is higher than 95% under standard conditions during the SDR campaign for S1 and drops to roughly 90% under highly stressed conditions.

The total nitrosamine (Total NA) and sum of specific nitrosamine(s) for the novel solvent (NA-novel solvent) were determined for selected samples from the SDR campaign. The results are plotted as $C_{NA,i}/C_{A,0}$ as a function of time (weeks) in Fig. 2.

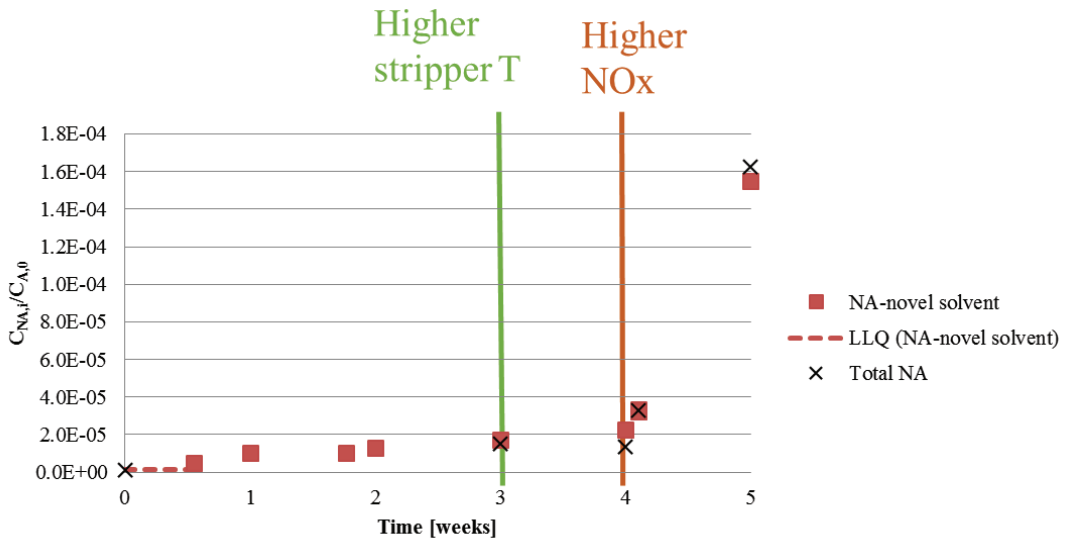

Fig. 2. The nitrosamine balance for selected samples, SDR campaign with solvent S1 (NA=nitrosamine, LLQ=Lower Limit of Quantification).

Overall, there is a good correlation between the NA-novel solvent (NA-S1) and total NA indicating that speciation with respect to nitrosation of the solvent is being accurately accounted for. NA-S1 was also measured in the NCCC samples (the National Carbon Capture Center, Wilsonville, Alabama, USA), a sample was taken from the NCCC campaign after 515 hrs (≈3 weeks), this was compared to the SDR campaign after 504 hrs (≈3 weeks, which is still under standard conditions). The results showed that the concentration in the NCCC sample was higher than in the SDR campaign at standard condition (week 0-3). The SDR is a lab rig, with fewer impurities present and also low NOx concentration added 5 ppmv at the standard conditions.

3.2. MEA solvent (30wt%)

The concentration of MEA (g/L, raw data, LC-MS) in lean solvent is plotted as a function of time (week) in Fig. 3.

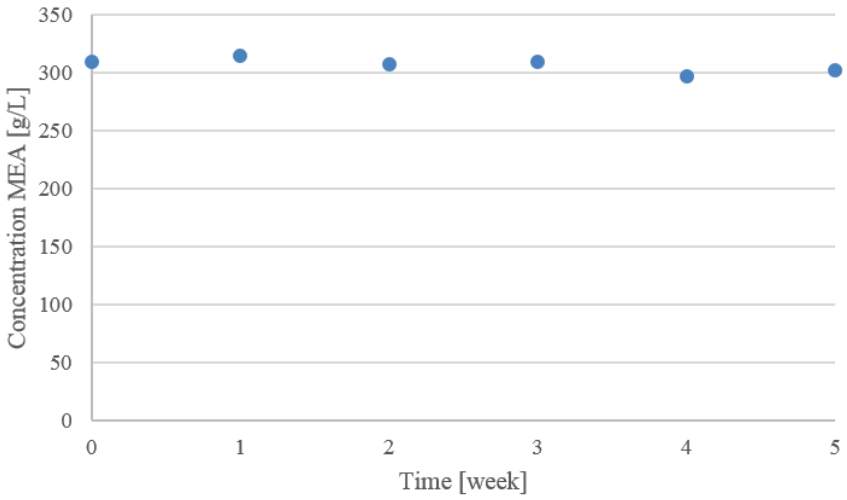

Fig. 3: The concentration (g/L) of MEA determined by LC-MS as a function of time (weeks) for the SDR campaign.

Fitting the raw concentrations of MEA versus time to a straight line (linear regression) yields a MEA loss of 2.5+/-1.1 g/Lweek for the overall campaign (standard and stressed conditions). This is slightly lower than the previous MEA campaign [8] using the same rig which resulted in a loss of MEA of 4.1+/-1.8 g/Lweek (standard conditions for 5 weeks), however the uncertainty is relatively high.

The organic nitrogen content in the lean sample from the SDR rig was measured using Kjeldahl method [15], see Table 4 for the nitrogen recovery (%) in these lean samples.

Table 4: The nitrogen recovery for MEA experiment at SDR rig based on the Kjeldahl analysis.

Week	Recovery N [%]
0	104.6
2	104.0
3	103.7
4	104.8
5	102.2

The table shows that the nitrogen is well accounted for in the initial sample, the analytical error together with experimental and sampling error could explain the deviation from 100%. For comparison, da Silva showed that 99.7% of the nitrogen was accounted for in a MEA campaign at the Tiller pilot [11, 16] with fewer degradation compounds than are quantified in this work.

In this work, N-HEGly was the only nitrosamine investigated. N-HEGly has been shown to be present at higher concentrations than several of the other specific nitrosamines e.g. NDELA [8, 17] in MEA solvent samples. From this work, the results for total nitrosamine and N-HEGly showed that N-HEGly only accounted for 10% of the total nitrosamine in the solvent. The deviation observed could partly be an effect of high uncertainty connected with the total nitrosamine method [17], as well as other nitrosamines present than N-HEGly. In the work by Einbu et al. [8], N-HEGly accounted for 56% of the total nitrosamine during a MEA campaign in the SDR. In the same work by Einbu et al., the concentration of HEGly, under the same conditions after 3 weeks, was 2/3 higher than in this work.

3.2.1. Degradation compounds of the MEA solvent

For this campaign, 32 standards for degradation products were available in the laboratory (Table 5), 28 of them could be quantified. 2-PO was not separated from MEA in the current method and data for this compound is therefore not available. 2,5-dimethylpyrazin, 2,6-dimethylpyrazin and 2,3-dimethylpyrazine were not separated in the current analytical method and they are reported together as DM-Pyrazine. The only nitrosamine analyzed in this work was N-HEGly. From earlier work [8] using the same set-up, N-HEGly has been found to be several magnitudes higher than other known nitrosamines which are commercial available (such as NDELA and NDMA).

Table 5: Cas numbers and name for secondary compounds analyzed on LC-MS.

CAS	Name	Abbreviation
497-25-6	2-oxazolidinone	OZD
1871-89-2	*N1*,*N2*-bis(2-hydroxyethyl)-ethanediamide	BHEOX
142-26-7	*N*-(2-hydroxyethyl)-acetamide	HEA
5835-28-9	*N*-(2-hydroxyethyl)-glycine	HeGly
23936-04-1	4-(2-hydroxyethyl)-2-piperazinone	HEPO
693-06-1	*N*-(2-hydroxyethyl)-formamide	HEF
1615-14-1	1H-Imidazole-1-ethanol	HEI
144236-39-5	*N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide	HEHEAA
111-41-1	2-[(2-aminoethyl)amino]-ethanol	HEEDA
3699-54-5	1-(2-hydroxyethyl)-2-imidazolidinone	HEIA
5625-67-2[a]	2-piperazinone[a]	2-PO[a]
108-99-6	3-methyl-pyridine	3-Mpy
504-77-8	4,5-dihydro-oxazole	2-oxazoline
18190-44-8	1-(2-hydroxyethyl)-2,5-pyrrolidinedione	HESucc
15438-70-7	*N*,*N'*-bis(2-hydroxyethyl)-urea	MEA urea
290-37-9	Pyrazine	
109-08-0	2-methylpyrazine	
123-32-0	2,5-dimethylpyrazine	
108-50-9	2,6-dimethylpyrazine	
5910-89-4	2,3-dimethylpyrazine	
13925-00-3	2-ethylpyrazine	
14667-55-1	2,3,5-trimethylpyrazine	2,3,5-TM-pyrazine
15707-23-0	2-ethyl-3-methylpyrazine	
7664-41-7	Ammonia	
74-89-5	Methylamine	MA
75-04-7	Ethylamine	EA
124-40-3	Dimethylamine	DMA
109-89-7	Diethylamine	DiEA
624-78-2	Ethylmethylamine	
142-84-7	Dipropylamine	
107-10-8	Propylamine	
80556-89-4	2-[(2-hydroxyethyl)nitrosoamino]-Acetic acid	N-HEGly

[a]A method could not be developed on LC-MS since 2-PO was overlapping with MEA.

The concentration [mg/L] of degradation compounds determined by LC-MS is given in Appendix A. The concentration (mg/L) of detected degradation products observed above the lower limit of quantification (LLQ) as a function of time (week) is shown in Fig. 4. HESucc, DiEA, diproylamine, propylamine, 2-ethylpyrazine, 2,3,5-TM-pyrazine and 2-ethyl-3-methylpyrazine were not observed above the LLQ in the lean samples.

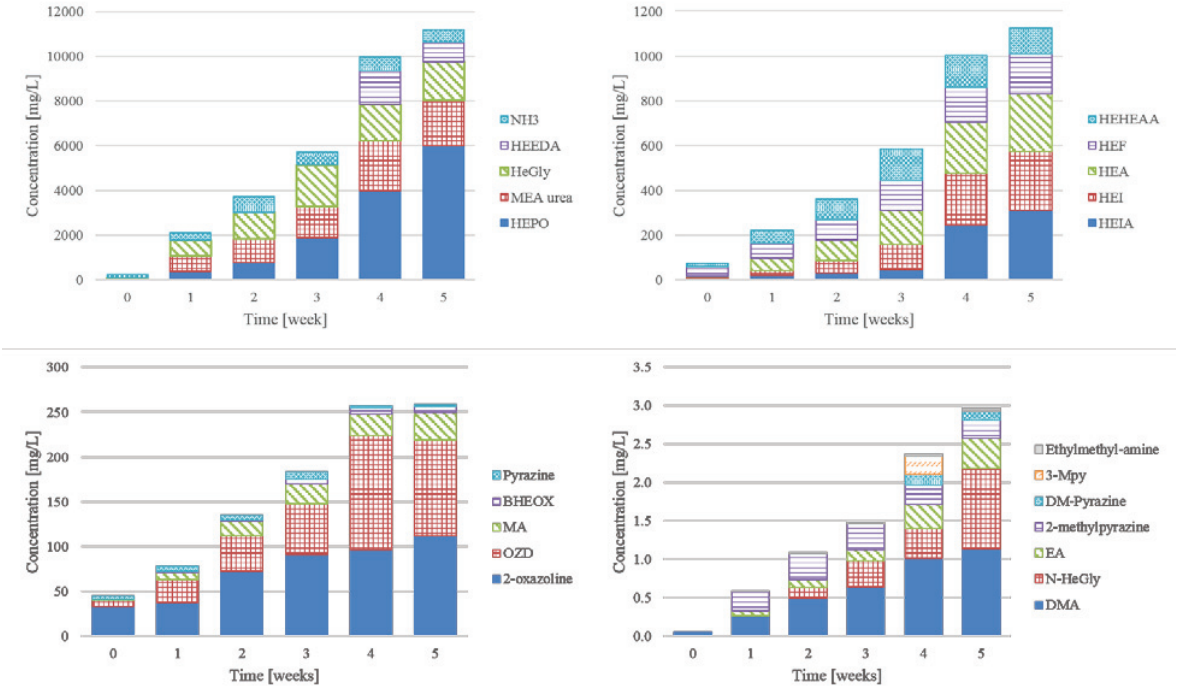

Fig. 4: The concentration of determined degradation compounds in lean samples from the SDR rig analyzed by LC-MS [mg/L] plotted against time [weeks].

Fig. 4 shows that BHEOX, HEA, HEF, HEI, HEIA, 2-oxazoline and HEPO increase over 5 weeks, while OZD, HEHEAA, HEEDA, 3-Mpy and MEA urea have a maximum at week 4. HEGly has a maximum at week 3. In the campaign the conditions were changed 2 times. The starting conditions were held for 3 weeks (week 1-3), then higher desorber temperature for one week (week 4) before reverting to normal desorber temperature and higher NOx concentration (week 5). The higher desorber temperature from week 4 explains several of the maximums observed in week 4 since most of these compounds are carbamate polymerization products (OZD, HEEDA and MEA urea) that are favored at high temperature and high CO_2 concentration. From thermal degradation studies with CO_2, several mechanisms have been suggested for formation of OZD, MEA urea, HEEDA and HEIA. According to the mechanism by Davis [18] OZD is precursor for both MEA urea and HEEDA which makes them competing reactions, while HEIA is formed from HEEDA. Based on those results, it was concluded that both HEIA and MEA urea were stable once formed. Earlier suggestions for mechanism changes the order of precursors, according to Polderman et al. HEEDA is formed from HEIA which again is formed from OZD [19] while Yazvikova et al. suggest that HEIA is formed from MEA urea which again is formed from OZD [20].

HEPO, HEGly and MEA-urea are generally the major degradation products quantified in the solvent samples, but HEPO increases significantly compared to HEGly and MEA-urea after week 3. One of the major degradation products has also been HEPO in pilot campaigns [11]. HEPO has a steep formation rate under the whole campaign. A logarithmic plot of HEPO seems to nearly give a linear line over the whole time period, this suggests that its formation is directly dependent on its own concentration (first order reaction) and close to independent of external factors as

temperature and NOx. A similar trend could be observed for HEF and HEA. In the last years, several mechanisms have been suggested for formation of HEPO [11, 12], where either secondary degradation compounds such as HEEDA, HEGly or HEGly/OZD is one of the intermediates. All three of these compounds are present at all time, which may suggest that the degradation reaction producing HEPO is not complete or that this reaction is slower than the formation of each of them. From week four to five 14 mmol/L HEPO was formed, the reduction of HEEDA was 6 mmol/L. A loss of 0.2 mmol/L was observed for OZD while HEGly increased by 0.76 mmol/L in the same time period. All of those compounds are formed as well as consumed in the process and their relationship to HEPO can therefore not be established. Some variation of degradation products between the two SDR campaigns (this work and the work by Einbu et al.) is observed [8]. For example, the HEGly, HEA, HEF and HEI concentrations are higher in the work by Einbu (comparison between the lean sample after 3 weeks at standard conditions in both campaigns) than in this work.

At the end of the five week SDR campaign, water condensate from the absorber gas was collected using a cooling trap. This condensate was analyzed with the same methods as the lean solvent samples to identify degradation products in the effluent gas. The SDR is designed as a closed system with only a small purge gas flow rate. Thus, volatile compounds in the SDR unit will to a much lesser extent be emitted to the surrounding air relative to a real plant. Consequently, the concentration of volatile compounds will be higher in the laboratory SDR samples relative to an industrial plant. Nevertheless, analysis results from the SDR condensate will give a qualitative measure of expected degradation products emitted to air. Several of those compounds were not observed above their respective LLQ's, such as BHEOX, HEHEAA, HEEDA, HEIA, 2-oxazoline, HESucc and dipropylamine. The concentration of degradation compounds observed in the condensate, except ammonia, is shown in Fig. 5. The major compound in the condensate was ammonia with a concentration of 1363 mg/L. Methylamine and pyrazine were the second and third significant compound in the condensate.

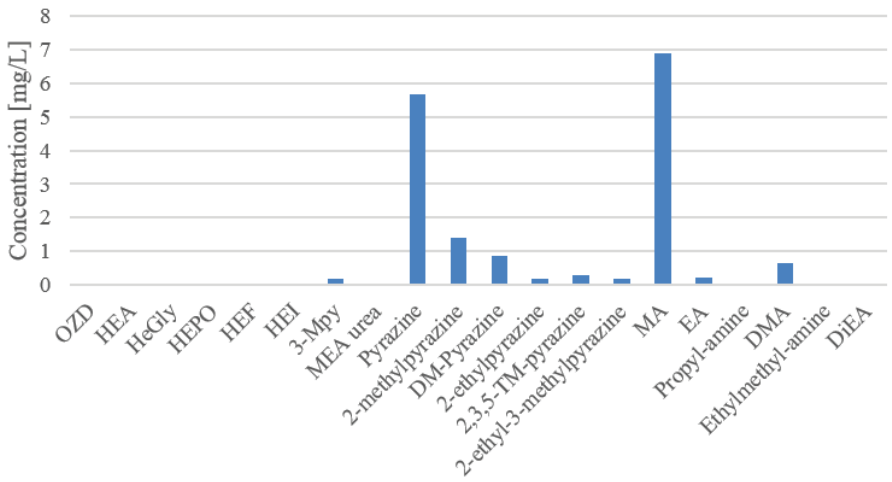

Fig. 5: Concentration [mg/L] of compounds except NH_3 (1363 mg/L) quantified in the condensate during the MEA SDR campaign. DM pyrazine are 2,5-dimethylpyrazine, 2,6-dimethylpyrazine and 2,3-dimethylpyrazine).

The purge gas is low in the SDR rig, the volatile compounds in the condensate are therefore artificially high compared to a real plant, thus the data is only qualitative.

4. Conclusion

Samples from SINTEF's SDR rig have been compared with samples from real pilot plants. For S1, larger amounts of nitrosamines were observed in the real samples than from the SDR rig. This is expected as synthetic flue gas provides much less opportunity for side reactions to occur than real flue gas, which contains many (reactive) trace compounds. The nitrogen recovery for lean MEA samples from SDR rig and real samples is comparable and the balance is closed when the uncertainty is taken into account. Different conditions and focus between lab and pilot experiments results in lack of data for comparison.

The nitrosamine balance for the proprietary solvent in the SDR rig is closed while a large deviation for the MEA solvent is observed.

The SDR campaign with MEA includes quantitative results for a set of new degradation compounds, overall 32 compounds were evaluated, analytical methods are available for 31 of these compounds. For the lean MEA samples 24 compounds were observed over the lower limit of quantification. HEPO and HEGly, as previously observed in pilot samples and previous SDR campaigns were major degradation compounds. Quantification of MEA urea showed that this compound is also a major decomposition product together with HEPO and HEGly.

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Appendix A. Raw data MEA campaign

The raw data for the MEA campaign is given in Table A1-A5.

Table A1: Results of wet chemical analysis, CO_2 and nitrogen (wt%N, Kjeldahl analysis) and MEA (LC-MS) for the Solvent samples (*na* = not analyzed).

Sample id	Week	Days	Total Amine [amine eq/kg]	CO_2 (TIC) [mol CO2/kg]	ρ [g/ml]	H_2O [wt%]	Total HSS [eq/kg]	MEA [mol/L]	wt% N
Unused	0		4.88	*na*	1.01	70.62		5.10	6.75
Lean Week 0 unloaded	0		4.79	<0.025	1.01	71.15		5.00	*na*
LEAN Week 0	0	0	4.66	1.03	1.06	67.61		5.07	*na*
LEAN Week 1	1	7	4.67	0.99	1.06	67.51		5.15	*na*
Rich Week 1	1	7	4.42	2.16	1.11	63.79		5.03	*na*
LEAN Week 2	2	14	4.63	0.99	1.06	68.18		5.03	6.52
Rich Week 2	2	14	4.38	2.06	1.11	65.08		5.06	*na*
LEAN Week 3	3	22	4.64	1.03	1.06	65.80		5.07	6.59
Rich Week 3	3	22	4.44	2.13	1.11	62.63		5.03	*na*
LEAN Week 4	4	29	4.60	0.96	1.06	66.56		4.87	6.38
Rich Week 4	4	29	4.38	2.09	1.11	63.04		4.95	*na*
LEAN backup (Extra 2)	5	35	4.64	1.02	*na*	*na*		4.98	*na*
LEAN Week 5	5	36	4.60	0.99	1.06	65.82		4.95	6.66
Rich Week 5	5	36	4.39	2.11	1.11	62.55		4.92	*na*
LEAN bulk (Extra3)	5	36	4.53	*na*	1.08	65.38		*na*	*na*

Concentration of degradation compounds in the SDR rig is given in Table A2-A4. In addition several degradation compounds was not observed over the lower limit of quantification (LLQ), these compounds were HESucc (<1 mg/L), DiEA (<1E-02 mg/L), Propylamine (<1E-02 mg/L), 2,3,5-trimethylpyrazine (<0.1 mg/L), 2-ethylpyrazine (<0.1 mg/L), 2-ethyl-3-methylpyrazine (<0.1 mg/L) and dipropylamine (<1E-02 mg/L).

Table A2: Determined degradation compounds by LC-MS part 1, concentration given in mg/L.

Time [week]	HEPO	MEA urea	HEGly	HEEDA	NH3	HEIA	HEI	HEA
0	8	53	45	< 1	136	0	14	3
1	394	683	703	6	322	21	23	54
2	768	1068	1189	7	691	32	56	91
3	1917	1379	1853	8	576	46	113	154
4	4001	2215	1623	1538	575	247	231	226
4.9	5677	1684	1711	685	655	303	258	257
5	5998	2036	1714	889	546	314	260	257

Table A3: Determined degradation compounds by LC-MS part 2, concentration given in mg/L.

Time [week]	HEF	HEHEAA	2-oxazoline	OZD	MA	BHEOX	Pyrazine	DMA
0	45	13	33	7	1	< 1	4.2	0.05
1	66	58	38	25	8	2	4.9	0.26
2	92	89	73	39	15	1	5.6	0.49
3	134	141	91	57	22	5	7.5	0.65
4	157	141	96	128	24	7	1.8	1.00
4.9	179	115	98	104	32	7	2.2	1.10
5	177	117	112	107	31	7	1.7	1.13

Table A4: Determined degradation compounds by LC-MS part 3, concentration given in mg/L.

Time [week]	N-HEGly	EA	2-methylpyrazine	DM-Pyrazine	3-Mpy	Ethylmethyl-amine
0	<0.1	<1E-02	< 0.1	< 0.1	< 0.1	<1E-02
1	<0.1	0.07	0.25	< 0.1	< 0.1	1.2E-02
2	0.15	0.10	0.34	< 0.1	< 0.1	2.0E-02
3	0.33	0.14	0.34	< 0.1	< 0.1	2.2E-02
4	0.40	0.31	0.26	0.13	2.3E-01	3.4E-02
4.9	0.95	0.41	0.28	0.11	< 0.1	3.5E-02
5	1.06	0.39	0.23	0.12	< 0.1	3.7E-02

The determined degradation compounds in condensate is given in Table A5. BHEOX (<1), N-HEGly (<0.1), 2-oxazoline (<1E-02), HESucc (<1E-03), dipropylamine (<1E-04), HEEDA (<1E-04), HEHEAA (<1E-04) and HEIA (<1E-04) were not observed over the lower limit of quantification (LLQ).

Table A5: Determined degradation compounds by LC-MS, concentration given in mg/L.

Compounds	Condensate week 5
NH3	1363
MA	6.9
Pyrazine	5.7
2-methylpyrazine	1.4
DM-Pyrazine	0.87
DMA	0.65
2,3,5-TM-pyrazine	0.29
EA	0.20
2-ethylpyrazine	0.18
3-Mpy	0.18
2-ethyl-3-methylpyrazine	0.17
Ethylmethyl-amine	3.0E-02
DiEA	9.3E-03
HEF	7.2E-03
Propyl-amine	4.3E-03
HEA	3.4E-03
OZD	1.5E-03
HeGly	1.3E-03
HEPO	3.0E-04
HEI	2.0E-04
MEA urea	1.1E-04

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Appendix B. Required Disclaimer