Extensive dataset for oxidative degradation of ethanolamine at 55-75 °C and oxygen concentrations from 6-98%.

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Abstract

Post combustion CO_2 capture using amines as chemical absorbents is a relatively mature technology. Rate of reaction and desorption energy demand are normally prime criteria for evaluation of new solvents while degradation and corrosion studies are often postponed. However, degradation and corrosion are in many cases showstoppers and should be considered at an early stage. In this work, a systematic study has been conducted on oxidative degradation of 30 wt% ethanolamine (MEA) for oxygen concentrations: 6, 21, 49 and 98% and temperatures: 55, 65 and 75 °C. The formation of ten primary degradation compounds (acids, ammonia and alkyl amines) and seven secondary degradation compounds (HEGly, OZD, HEPO, HEF, HEA, HEI and BHEOX was monitored as function of time over a period of 3 – 6 weeks. The full comprehensive data set is available in the supplementary information for development of models describing the degradation behavior. Suggested mechanisms for formation of seven secondary degradation compounds; HEGly, HEPO, OZD, HEF, HEA, BHEOX and HEI from literature were compiled and discussed in view of the experimental results to suggest pathways which are more likely than others.

The rate of MEA degradation increases with increasing temperature and oxygen concentration. The overall nitrogen balances were closed within 83-97%; the higher deviations observed at the highest temperature, 75 °C. HEF, HEI and ammonia were the degradation compounds that most significantly contributed to the nitrogen balance in most experiments. However, at 6% O_2 content, HEGly was the major nitrogen containing degradation compound identified. Formate was found to be the major anionic compound in all experiments.

HEGly formation was found to be independent on O_2 partial pressure, but this may not be true for the further reaction of HEGly. The results suggests OZD formation to be oxygen dependent. However, only one mechanism is so far suggested for an oxygen dependent pathway. Both OZD and HEPO concentrations increase with oxygen concentration. Separate laboratory experiments at constant temperature (55-75 °C) do not capture the HEPO formation seen in pilot plant samples indicating that higher temperatures and/or temperature cycles are necessary.

The results clearly show that performing accelerated degradation tests with 98% oxygen cannot easily be extrapolated to what happens at 6% oxygen, and therefore may not be representative for the situation in an industrial plant both with regard to rates of formation and products formed.

Keywords: MEA, oxidative degradation, temperature, oxygen concentration, degradation compounds, nitrogen balance

AMP	2-amino-2-methyl-1-propanol
BHEOX	*N,N'*-Bis(2-hydroxyethyl)-ethandiamide
DETA	Diethylene-triamine
DiEA	Diethylamine
DMA	Dimethylamine
EDA	Ethylene diamine
EA	Ethylamine
HEA	*N*-(2-hydroxyethyl)-acetamide
HEEDA	*N*-(2-hydroxyethyl)ethylenediamine
HEF	*N*-(2-hydroxyethyl)-formamide
HEGly	*N*-(2-hydroxyethyl)-glycine
HEHEAA	*N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide
HEIA	*N*-(2-hydroxyethyl) imidazolidone
HEI	*N*-(2-hydroxyethyl)-imidazole
HEPO	4-(2-hydroxyethyl)-2-piperazinone (4HEPO)
1HEPO	1-(2-hydroxyethyl)-2-piperazinone (1HEPO)
IC	Ion Chromatography
LC-MS	Liquid Chromatography – Mass Spectrometry
MA	Methylamine
MEA	Ethanolamine
MMEA	2-(Methylamino)ethanol
NDBA	*N*-Nitroso-n-dibutylamine
NDELA	*N*-Nitrosodiethanolamine
NDMA	Nitrosodimethylamine
NDPA	Nitrosodi-*N*-propylamine
NHEGly	Nitroso-(2-hydroxyethyl)-glycine
NMEA	Nitroso-*N*-methylethylamine
NMOR	Nitrosomorpholine
NPIP	Nitrosopiperidine
NPYR	Nitrosopyrrolidine
OZD	2-Oxazolidinone

1 Introduction

Post combustion CO_2 capture using amines as chemical absorbents is a relatively mature technology. For tertiary amines the energy requirement for stripping of CO_2 can be lower than for secondary and primary amines because of lower heat of reaction, but may have a lower equilibrium temperature sensitivity increasing the demand for stripping steam, see (Svendsen et al. 2011) and the absorption rate is also normally significant lower. An ideal amine system combines high absorption rate and cyclic capacity with low energy requirement for stripping and low degradation and corrosions. However, for many of these properties there will be a tradeoff.

When developing a new solvent system, rate of reaction and the desorption energy demand is normally prime criteria for evaluation and degradation and corrosion studies may be postponed till later in the process. Degradation and corrosion, however, in many cases turn out to be showstoppers, e.g. for ethylene diamine (EDA) and diethylene-triamine (DETA) corrosion was shown to be a major issue. It is therefore important to consider these issues at early stage. Lately there have been several systematic degradation studies conducted to review how molecular structure influences different types of degradation (Lepaumier et al. 2009a, 2009b, 2010; Eide-Haugmo 2011; Vevelstad et al. 2013a).

In the post combustion absorption plants conditions vary significantly, both with regard to temperature and oxygen exposure. This gives rise to different types of degradation. Oxidative degradation takes place in presence of oxygen at both low and high temperature, implying that most of the formation will be associated with the absorber. However, some oxygen will be present in the rich solution leaving the absorber and can therefore give oxidative degradation in other parts of the plant, e.g. heat exchanger and desorber, then at higher temperature. Carbamate polymerization (thermal degradation with CO_2) and chemical reaction between amine and CO_2, usually occur at higher temperatures, and is therefore more pronounced under stripper conditions. Degradation as a result of temperature only occurs at very high temperatures. Lepaumier observed little degradation at 140 °C in the absence of CO_2 (Lepaumier et al. 2009a). Formation of certain degradation compounds in the high temperature parts of the process could also contribute to formation of other degradation compounds in the absorber section acting as intermediates. This complicates the mapping of degradation compounds and the understanding of the formation mechanisms. There is thus a need for conducting well-controlled degradation experiment in the laboratory at specific conditions to understand the formation of many of these compounds. Such earlier experiments have resulted in improved understanding of the formation mechanism of several of the compounds formed, especially the carbamate polymerization products (Lepaumier et al. 2009a). The formation mechanisms for the oxidative degradation compounds are more difficult to reveal since the starting point is normally thought to be a radical mechanism, and since no studies has been performed to verify whether a hydrogen or electron abstraction mechanism dominates. However, both of the mechanisms give aldehydes and imines as products, which then react further with amine. Several of the imines that can form are not stable and would directly react further, while for the aldehydes, oxidation or further reaction could occur. Aldehydes, imines and acids can be defined as primary degradation compounds, while amides, imidazoles, piperazinones, oxazolidinones can be defined as secondary degradation compounds. These secondary degradation compounds depend on intermediate degradation compounds (primary degradation compounds) and amine or other secondary degradation compounds. The primary degradation compounds usually take part in the

formation of several secondary products and in some cases there are several mechanisms suggested in the literature for the same degradation compounds, e.g. HEPO (Strazisar et al. 2003; da Silva et al. 2012; Gouedard 2014) and HEGly (Gouedard 2014; Vevelstad et al. 2014a).

In this work, a systematic study has been conducted on MEA degradation under absorber conditions where the oxygen concentration and temperature were varied. The formation of formate, oxalate, nitrate and nitrite, ammonia (primary compounds) and HEGly, OZD, HEPO, HEF, HEA, HEI and BHEOX (secondary compounds) were monitored as function of time for the oxygen concentrations: 6, 21, 49 and 98 % and temperatures: 55, 65 and 75 °C. In addition, nitroso-HEGly was analyzed for in some of the experiments. This data set is the first available that is comprehensive enough to enable the development degradation model over a relative large range of oxygen content and temperature. In addition, there are only few data available for degradation at lower oxygen concentration.

2 Experimental section

The results reported in this paper comprise data from earlier work, reported in (Vevelstad et al. 2013b; Vevelstad et al. 2014b) and new data (primary degradation compounds and overall nitrogen balance), all experiments using the same open experimental setup and procedures. The complete data set for MEA degradation from this set-up is discussed taking all results into account and with a thorough investigation of the degradation compound formation. An overview of the complete set of experiments is given in Table 1, where the experiments are split into letters A, B or C denoting the temperature and numbers 1-4 indicating the oxygen concentration. Roman numerals indicate repeated experiments.

Table 1: Overview of the full data set.

O_2 (%)/Temperature (°C)	55 (A)	65 (B)	75 (C)
6 (1)	A1[b]	B1[b]	C1[b]
21 (2)	A2-I[a]	B2-I[b]	C2[a]
	A2-II[a]	B2-II[b]	
	A2-III[b]		
49 (3)	A3[a]	B3[b]	C3[b]
98 (4)	A4[a]	B4[b]	C4[b]

[a] Reported by Vevelstad (Vevelstad et al. 2013b). [b] Minor parts reported by (Vevelstad et al. 2014b)

An evaluation of the first order reaction rate constant for MEA disappearance, the relative rate of formation of the various secondary degradation compounds (group LC-MS mix in Table 2), weighted based on nitrogen content, and the organic nitrogen balance for the liquid phase end samples are described in (Vevelstad et al. 2014b). The experimental setup (Figure 1) was reported in detail by (Lepaumier et al. 2011b; Vevelstad et al. 2013b) and is only briefly described here.

2.1 Set-up and analytical methodology

A preloaded MEA solution (30wt%, α=0.4 mol CO_2 per mol MEA) was introduced into a glass reactor (6) (1L). A recycle gas stream [50L/min] was bubbled through the reactor (6) maintained by a fan (5) and feed gas (oxygen+nitrogen [0.35 L/min], CO_2 [7.5 mL/min] pre-saturated with water in reactor (4)) was fed to this recycle via mass flow controllers (3). The temperature in the pre-saturation chamber (4) was maintained the same as in the condensers (7/8). The dry feed gas

compositions were: a) 98% O_2/0% N_2/2% CO_2 b) 49% O_2/49% N_2/2%, c) 21% O_2/77% N_2/2% CO_2 or d) 6% O_2/92% N_2/2% CO_2. All experiments were run at atmospheric pressure. Excess gas was emitted through two condensers (7 and 8) and one or two gas bubble flasks (10 and 11) with different medium (water or sulfuric acid). The gas bubble flasks were added to absorb volatile basic degradation products. In most of the experiments the reactor solution was spiked with sodium sulphate (sulphate 35 – 2000 mg/kg), as internal standard to check the water balance, see Table 4.

The oxygen levels are given for feed gas and thus represent dry gas levels. The throughput of gas (0.35 L/min) was in all experiments so high that the consumption of oxygen in the degradation reactions was negligible compared to the oxygen feed rate. However, the water vapor pressure in the reactor is significant and in Table 2 the actual oxygen and water vapor pressures in the reactor are given for all experiments. The calculations are based on the e-NRTL model, see (Hessen et al. 2010, Aronu et al. 2011). In the figures and tables the nominal feed dry oxygen levels are used. As MEA is degraded in the experiments the amount of bound CO_2 also reduces. As the feed gas CO_2 content was kept constant during an experiment the loading (mol CO_2/mol MEA) would also be expected to remain reasonably constant.

Table 2: The actual oxygen pressure (kPa) and vapor pressure (kPa) in the reactor.

|	Corrected Oxygen Pressure, kPa		
	55 °C (A)	65 °C (B)	75 °C (C)
Water kPa(e-NRTL)	14-15.3	22.3-24.3	34.3-37.4
6% O_2 (1)	5.16-5.1	4.66-4.54	3.94-3.76
21% O_2 (2)	18.1-17.8	16.3-15.9	13.8-13.1
49% O_2 (3)	42.1-41.5	38.2-37.1	32.2-30.7
98% O_2 (4)	84.3-83.0	76.3-74.2	64.4-61.3
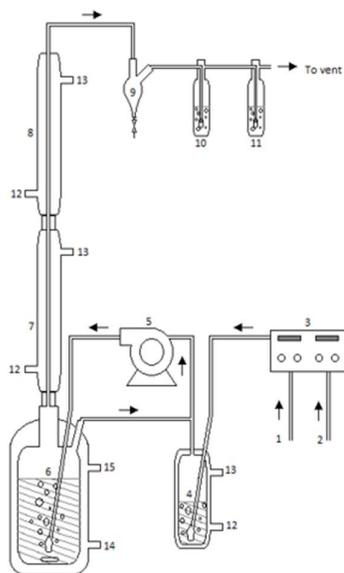
Figure 1: Flow sheet for the open batch experiment.

Sampling was conducted throughout the experiments with regular intervals. The total experimental time varied from 3 – 6 weeks depending on temperature and oxygen concentration.

For 21% O_2, a significant loss of MEA was seen already after 3 weeks whereas longer duration was needed for lower oxygen concentration. The mass and water balances were controlled by weighing the solution in and out of the system. Samples were analyzed using different analytical techniques. Liquid Chromatography – Mass Spectrometry (LC-MS) was used for MEA, DEA, the LC-MS mix (group LC-MS mix in Table 3), ammonia, the alkyl amines (group AA in Table 3) and nitrosamine (group NA in Table 3). Ion Chromatography (IC-anion) was used for the anions. Titration with acid (0.1 M H_2SO_4) was used for total alkalinity by a standard method (Kim et al. 2008). CO_2 concentration was determined by the $BaCl_2$ method (Ma'mun et al. 2007) and total organic nitrogen was analyzed using the Kjeldahl method (Kjeldahl 1883). Analyses of the anions (acids, nitrate, and nitrite) were conducted on mass basis while MEA and degradation compounds analyzed using LC-MS were analyzed volumetrically. Densities were measured for the initial and end samples for each experiment. The density was assumed to be a linear function of time. On this basis all concentration data were converted to volume basis.

The system used for LC-MS analyses was a LC-MS-MS 6460 Triple Quadrupole Mass Spectrometer coupled with a 1290 Infinity LC Chromatograph and Infinity Auto sampler 1200 Series G4226A from the supplier Agilent Technologies. The molecules were converted to ions using electrospray ionization (MEA, LC-MS mix, alkyl amine and ammonia) or atmospheric-pressure chemical ionization (nitrosamine). Mobile phases and columns used are described by (Lepaumier et al. 2011a,b; da Silva et al. 2012; Vevelstad et al. 2013b; Vevelstad et al. 2014a). The system used for analyses of anions was an ICS-5000 Dual RFIC Ion Chromatography Dionex System. The system was equipped with an AS Auto sampler, DP Analytical Gradient, a CD Conductivity Detector with an Integrated Cell, ASRS300 suppressor (2mm), a carbonate removal device (CRD-200, 2mm), a continuously regenerated anion trap column (CR-ATC) and a EG eluent Generator Module with potassium hydroxide eluent generator cartridge. Two columns were used for separation of analytes; IonPac AG15 guard column (2*50 mm)/AS15 analytical column (2*250 mm) and IonPac AG11HC guard column (2*50 mm)/AS11HC analytical column (2*250 mm) (Vevelstad et al. 2013b). An overview of analyses performed for the different experiments is given in Table 3.

Table 3: Abbreviations and full names of degradation compounds analyzed

Abbreviation	Compound	CAS	Structure	Group
	Ammonia	7664-41-7	NH_3	AA
BHEOX	N,N'-Bis(2-hydroxyethyethan-diamide	1871-89-2		LC-MS mix
DiEA	Diethylamine	109-89-7		AA
DMA	Dimethylamine	124-40-3		AA
EA	Ethylamine	75-04-7		AA
HEA	N-(2-hydroxyethyl)-acetamide	142-26-7		LC-MS mix
HEF	N-(2-hydroxyethyl)-formamide	693-06-1		LC-MS mix
HEGly	N-(2-hydroxyethyl)-glycine	5835-28-9		LC-MS mix
HEI	N-(2-hydroxyethyl)-imidazole	1615-14-1		LC-MS mix
HEPO	4-(2-hydroxyethyl)-2-piperazinone (4HEPO)	23936-04-1		LC-MS mix
MA	Methylamine	74-89-5		AA
NDBA	N-Nitroso-n-dibutylamine	924-16-3		NA
NDELA	N-Nitrosodiethanolamine	1116-54-7		NA
NDMA	Nitrosodimethylamine	62-75-9		NA
NDPA	Nitrosodi-N-propylamine	621-64-7		NA
NHEGly	Nitroso-(2-hydroxyethyl)-glycine	80556-89-4		NA

Abbreviation	Compound	CAS	Structure	Group
NMEA	Nitroso-*N*-methylethylamine	10595-95-6		NA
NMOR	Nitrosomorpholine	59-89-2		NA
NPIP	Nitrosopiperidine	100-75-4		NA
NPYR	Nitrosopyrrolidine	930-55-2		NA
OZD	2-Oxazolidinone	497-25-6		LC-MS mix
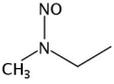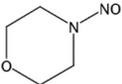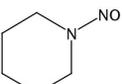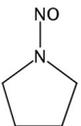
Table 4: **Overview of compounds analyzed for in liquid phase for each experiment.**

	Experiment	MEA	DEA	Anion IC	LC-MS mix	Alkyl-amine	NH$_3$	Kjeldahl (N)	CO2 and alkalinity	Nitros-amine
55 °C (A)	6% O$_2$ (1)	x	x	x		x	x	x	x	
	21% O$_2$ (2-I)	x	x	x^a				x	x	x^c
	21% O$_2$ (2-II)	x		x		x	x	x	x	
	21% O$_2$ (2-III)	x	x	x			x	x	x	x^e
	49% O$_2$ (3)	x		x		x	x	x	x	x^d
	98% O$_2$ (4)	x	x	x	x	x	x	x	x	x^d
65 °C (B)	6% O$_2$ (1)	x	x	x	x	x	x	x	x	
	21% O$_2$ (2-I)	x		x	x			x	x	x^e
	21% O$_2$ (2-II)	x		x	x		x	x	x	x^e
	49% O$_2$ (3)	x	x	x^a	x	x	x	x	x	
	98% O$_2$ (4)	x	x	x	x		x	x	x	x^e
75 °C (C)	6% O$_2$ (1)	x	x	x	x	x	x	x	x	
	21% O$_2$ (2)	x	x	x	x	x	x	x	x	x^c
	49% O$_2$ (3)	x	x	x^a	x^b	x	x	x	x	
	98% O$_2$ (4)	x	x	x	x	x	x	x	x	

^{a}Not SO$_4^{2-}$
^{b}Not the last sample
^{c} 9 nitrosamines: NDELA, NPIP, NDBA, NDMA, NMEA, NMOR, NDPA and NPYR.
^{d}1 nitrosamine: NDELA
^{e}2 nitrosamines: NDELA and NHEGly

2.2 Evaluation and validation of experimental methods

There are several issues to be considered when evaluating the experimental results, related both to the experimental set-up and procedure. All experiments were conducted in a similar manner. However, operational conditions could vary slightly, e.g. level of water in the feed gas pre-saturator influencing the water balance and fluctuations in the cooling water temperature.

2.2.1 Mass/water balance

An open system using pre-saturated gas was used for the experiments. A major issue in the experiments was to maintain the water balance since both evaporation or build-up of water could occur. Evaporation of water is likely a combination of the effect of the continuous flow of gas (less because of saturated gas) and the not fully effective condensers. A build-up can result from the pre-saturation of the gas, which was conducted by passing through a jacketed vessel with pure water kept at the condenser temperature as the water vapor pressure over pure water is slightly higher than above the reaction mixture. The water level in the reactor was measured manually by reading the liquid level off a calibrated scale. It was observed that the level of water in the saturation vessel influenced the reactor water balance slightly, but a systematic study of this was not performed. An overview of the mass balances for all experiments is given in Table 5.

Table 5: Mass balance for each experiment (in, out and the difference Δ) for total mass and for CO_2 free mass.

Experiment		Total mass			CO_2 free mass		
		In	Out	%Δ	In	Out	%Δ
55 °C (A)	6% O_2 (1)	1037	1081	-4.2	957	1009	-5.4
	21% O_2 (2-I)	1081	1119	-3.5	995	1040	-4.5
	21% O_2 (2-II)	1088	1092	-0.4	1005	1004	0.1
	21% O_2 (2-III)	1055	1020	3.3	972	956	1.6
	49% O_2 (3)	1079	1100	-1.9	997	1029	-3.2
	98% O_2 (4)	1118	1136	-1.6	1032	1069	-3.6
65 °C (B)	6% O_2 (1)	1028	1037	-0.9	948	971	-2.4
	21% O_2 (2-I)	1044	882	15.5	962	813	15.5
	21% O_2 (2-II)	1016	982	3.4	937	868	7.4
	49% O_2 (3)	1020	1001	1.9	940	971	-3.2
	98% O_2 (4)	1053	1002	4.9	972	976	-0.4
75 °C (C)	6% O_2 (1)	1039	1101	-6.0	958	1051	-9.8
	21% O_2 (2)	1081	1153	-6.7	996	1133	-13.8
	49% O_2 (3)	1025	1015	1.0	946	1005	-6.2
	98% O_2 (4)	1041	1021	1.9	959	1015	-5.8

For experiments, C1-C4 (75 °C - 6-98% O_2), high mass balance deviations were observed based on both CO_2 free mass and total mass, highest deviations observed for the lowest oxygen concentrations (6 and 21% O_2). Deviations lower than 5-6% were considered acceptable. B2-I (65 °C - 21% O_2 run 1) was repeated because of the high mass balance deviation and is disregarded in the following discussion.

For most of the experiments, small amounts of sodium sulphate were added as internal standard for the water balance and analyzed by IC. It was not expected that sulphate significantly would influence the degradation of MEA. Unfortunately the accuracy of the IC analyses was not good enough for this method to give additional valuable information, but the results are included in the supplementary information (Table S16).

2.2.2. MEA (titration and LC-MS)

Both titration for alkalinity and MEA analyses using LC-MS were used. In addition, the initial and end samples were analyzed for CO_2 concentration and density. The raw data are given in supplementary information part A, Table S1-S15, for all systems given in Table 1. No corrections are made to these data. MEA analyses on all initial samples using LC-MS were compared with titration results and the differences were, apart from a few cases, below 5%. The LC-MS method gave systematically slightly higher MEA concentration values than titration. Validation of the titration method versus weighed in concentration values compared within <1%. All data are given in supplementary information (supplementary information, Table S17 and S18).

2.2.3 Analytical quantitative data

For MEA, alkyl amine, ammonia and most of the nitrosamines an internal standard was used to correct for drift in the instrument and effects from the sample matrix. The uncertainty for quantification for these compounds is therefore expected to be ±5%. For the rest of the compounds the analytical uncertainty is higher. The uncertainty was not investigated systematically but is estimated to be ±10%. To reduce the uncertainty the time series samples from one experiment were analyzed together. The absolute values of the degradation compound concentrations are less important than their development over time.

3 Results

3.1 MEA degradation

There were small variations in the initial MEA concentrations used in the different experiments. Using CO_2 free solution basis the initial concentrations varied from 4.66 − 4.98 mol/kg total amine (titration). Because of these variations, concentrations normalized against the initial value are used for comparison between the experiments. Since degradation potentially can form other amines, which would be included when using titration, concentrations measured by LC-MS are used to evaluate the MEA loss with time. In Figure 2 the normalized concentrations for CO_2 free solutions as a function of time [days] are given for the four oxygen concentrations. CO_2 was only measured for the initial and end samples for experiment A2-I to II (55 °C - 21% O_2 run 1 and 2), C2 (75 °C - 21% O_2), A3 (55 °C - 49% O_2) and A4 (55 °C - 98% O_2).
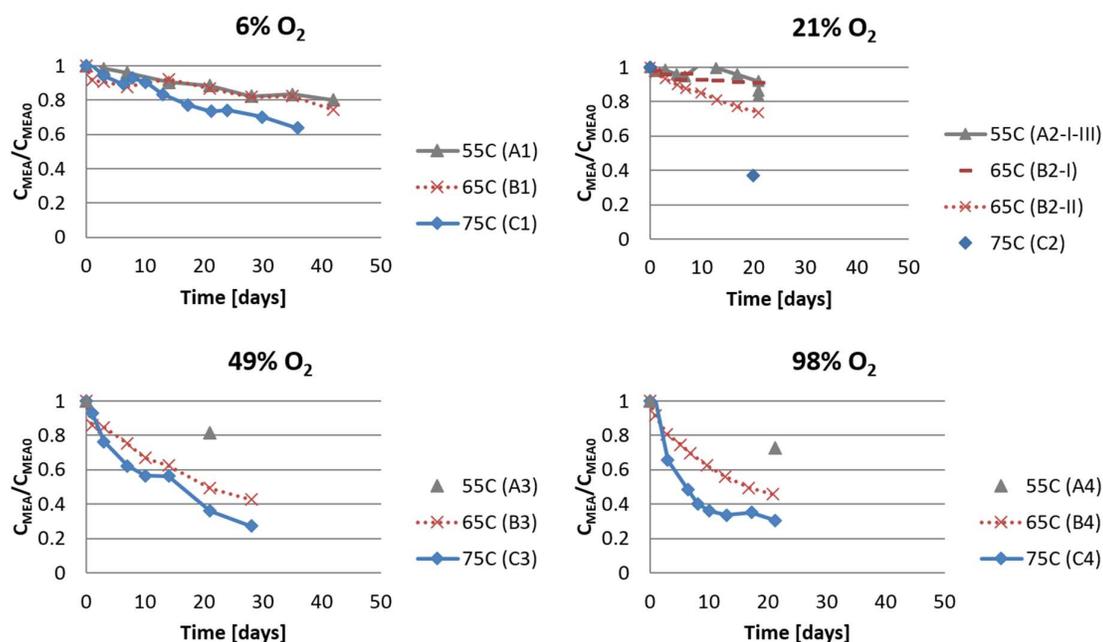
Figure 2: The normalized concentration for CO_2 free solution as a function of time [days] are given for all oxygen concentrations (1-4: 6-98% O_2) and temperatures (A-C: 55-75 °C).

For all oxygen concentrations (1 to 4, 6-98% O_2), an increase in degradation rate with temperature (A to C, 55-75 °C) is observed. For the lowest oxygen concentration, the difference is small between 55 °C (A) and 65 °C (B), which is likely an effect of low degradation rate and therefore more influence by the variation in water balance. For the lowest two oxygen concentrations (1 and 2, 6 and 21% O_2), the curves seem to be close to linear, while at the higher oxygen concentrations (3 and 4, 49 and 98% O_2) the reaction rate is higher in the beginning and also the dependence on temperature is more visible. The variation in behavior between the different oxygen concentrations indicate that running so-called "accelerated" experiments at high oxygen content may not represent well industrial conditions with oxygen concentrations of 3-11%.

At the highest temperatures, 65 (A) and 75 °C (B), the two highest oxygen concentrations seem to follow each other or end up at a similar degradation loss after 20 days. One may notice that experiment C2 (75 °C - 21% O_2) shows similar concentration as for C3 (75 °C - 49% O_2) and C4 (75 °C - 98% O_2) after around 20 days, however this experiment had a high water loss which gives an artificial high MEA concentration because of less water present. None of the curves is smooth which may be an indication of analytical uncertainty and that the variation in water balance can influence the curves.

The variation in water balance for the experiments is in most cases lower than 5% and it is not believed that this small variation in water content will significantly influence the MEA concentration profiles. From Supap et al. (Supap et al. 2009), increasing the concentration of MEA from 5 kmol/m^3 to 7 gave a small increase in MEA degradation rate, however the difference was small and insignificant compared to other uncertainties.

3.1.1 Total alkalinity

Alkalinity and CO_2 concentration are important factors to consider when studying the degradation behavior. In thermal degradation CO_2 is a building block in several of the compounds formed (e.g. *N*-(2-hydroxyethyl) imidazolidone (HEIA) and OZD) (Davis and Rochelle 2009; Eide-Haugmo et al. 2011; Lepaumier et al. 2011a). OZD is also formed under oxidative degradation conditions. All end samples were analyzed for alkalinity by titration. In un-degraded solutions this compares well with MEA content as already shown, but for degraded samples other alkaline and acidic components will influence the result. In Figure 2, the alkalinity losses in the end samples are given based on three ways of interpreting the titration results. In the first method, blue (filled), the measured alkalinities in the initial and end samples were compared directly with no correction. In the second method, the initial and final alkalinities were corrected for the amounts of CO_2 present by referring to CO_2 free solutions (red, diagonal lines). In the third method, the alkalinities were weighted with the total initial and final masses (green, horizontal lines).
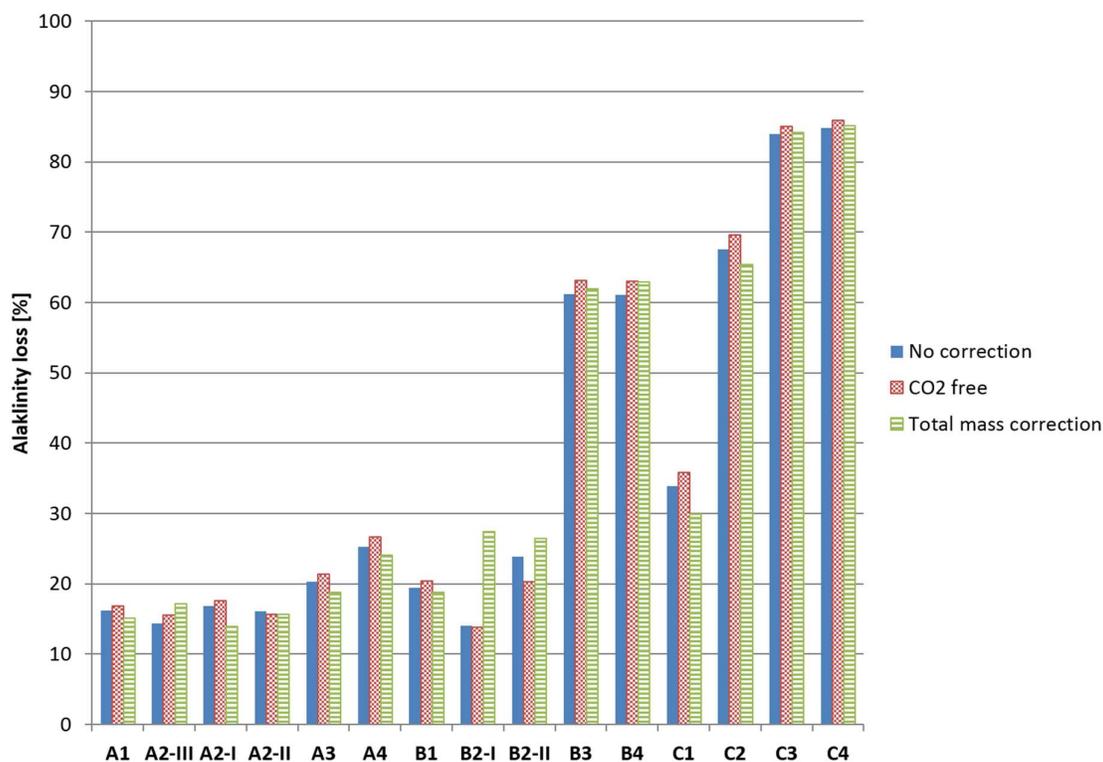
Figure 3: Loss [%] of alkalinity depending on which correction method was used, no correction (blue, filled), correction based on CO_2 free mass (red, diagonal lines) and correction based on total mass (green, horizontal lines).

As seen from Figure 3 the three methods mostly compare well and deviate up to about 5% from each other. The data show a main trend that loss of alkalinity and CO_2 increases with increasing oxygen concentration (1 to 4, 6-98% O_2) as well as with increasing temperature (A to C, 55-75 °C). Temperature seems to have a stronger effect than oxygen concentration. At 55 °C (A), changing the oxygen level from 6 (1) to 21% (2) seems to have little effect whereas at 75 °C (C) the effect of oxygen level is strong. The low alkalinity loss observed for experiment B2-I (65 °C - 21% O_2 run 1) is not only explained by high water loss for this experiment, resulting in increased concentrations for all components in the solution.

3.1.2 Amine loss

For thermal degradation experiments with CO_2 a deviation between the specific amine and total alkalinity analysis is normally observed and explained by formation of other amines such as *N*-(2-hydroxyethyl)-ethylene diamine (HEEDA/111-41-1) (Eide-Haugmo 2011). It is therefore also of interest to compare the loss of MEA, based on LC-MS, and loss of alkalinity (titration) to get an indication if there are other amines formed from degradation of MEA. The loss of MEA [mol/kg] and loss of alkalinity [mol/kg] are given in Table 6.

Table 6: The loss of MEA and of total alkalinity [mol/kg].

Ex	55 °C (A) Δ (Initial - End) -mol/kg		65 °C (B) Δ (Initial - End) -mol/kg		75 °C (C) Δ (Initial - End) -mol/kg	
	MEA	Alkalinity	MEA	Alkalinity	MEA	Alkalinity
6% O_2 (1)	1.10	0.82	1.36	1.01	1.83	1.75
21% O_2 (2-I)	0.82	0.86	0.46	0.69	3.05	3.37
21% O_2 (2-II)	0.64	0.75	1.21	1.31		
21% O_2 (2-III)	0.43	0.37				
49% O_2 (3)	0.88	1.03	2.97	3.06	3.89	4.12
98% O_2 (4)	1.29	1.27	2.56	3.09	3.14	4.18

The difference between loss of MEA and loss of total alkalinity varies with both temperature and oxygen level. A higher loss may be expected for MEA than for alkalinity, but in contrast to thermal degradation amine dimers are not expected and the formation of acids will also influence the alkalinity. At the highest temperatures and oxygen concentrations the alkalinity loss is higher than the MEA loss. One may imagine this attributed to formation of acid, but in the end sample of C4 (98% O_2 – 75 °C) the MEA concentration is about 1.5mol/kg whereas the formate concentration is about 100mmol/kg and thus cannot explain the difference. Another explanation could be the difference in analytical techniques. Alkalinity titration is a robust method whereas LC-MS may be more sensitive to matrix variations. For the details around individual degradation compounds this may be important, but for the larger picture these relatively small differences are insignificant. Based on these data conclusions regarding possible formation of other amines, e.g. *N*-(2-hydroxyethyl)ethylene diamine (HEEDA) which is formed in thermal degradation experiment with CO_2 (Davis and Rochelle 2009; Eide-Haugmo et al. 2011; Lepaumier et al. 2011a), cannot be drawn. Nevertheless, if formation of other amines is occurring the amount is low in the present experiments compared to the cited thermal degradation experiments with CO_2.

3.2 CO_2 concentration

The experiments were run with a preloaded solution of CO_2 and a gas flow of air and 2 vol% CO_2 was continuously fed to the reactor throughout the experiment. The purpose of the CO_2 flow is to maintain a CO_2 loading in the solution. The initial and end samples were all analyzed for CO_2 and the contents and differences in loading (α=mol CO_2/mol MEA) between the initial and end samples are given in Figure 4 and in Table 7. It should be noted that alkalinity is used as a measure of MEA concentration.

Table 7: CO$_2$ concentration (mol/kg) of the initial and the end samples as well as the loss for all experiments.

Ex	55 °C (A)			65 °C (B)			75 °C (C)		
	Initial	End	Δ	Initial	End	Δ	Initial	End	Δ
6% O$_2$ (1)	1.76	1.60	0.16	1.76	1.49	0.27	1.77	1.06	0.71
21% O$_2$ (2-I)	1.81	1.65	0.16	1.78	1.83	<0.01	1.79	0.39	1.40
21% O$_2$ (2-II)	1.72	1.82	-0.10	1.76	1.39	0.37			
21% O$_2$ (2-III)	1.79	1.46	0.33						
49% O$_2$ (3)	1.73	1.49	0.24	1.78	0.68	1.10	1.76	0.21	1.55
98% O$_2$ (4)	1.75	1.37	0.38	1.76	0.59	1.17	1.78	0.11	1.67
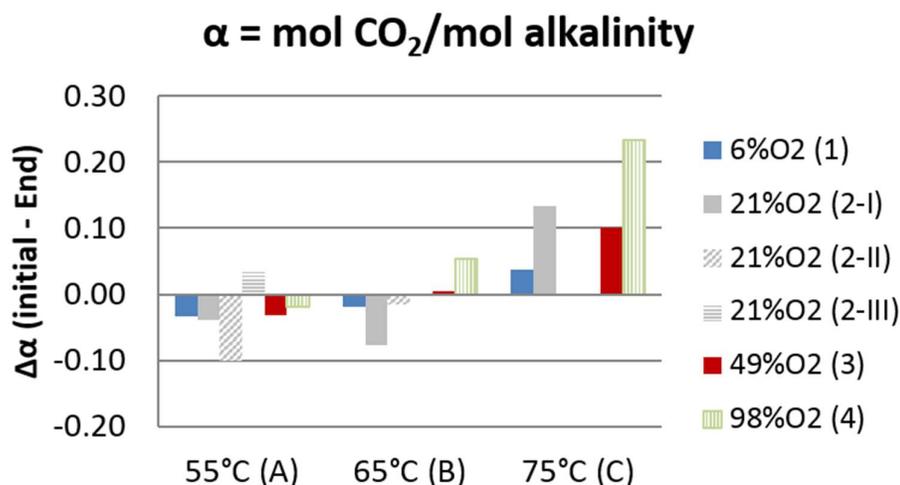
Figure 4: Δα (Initial – End) for the experiments at different temperatures (A-C, 55-75 °C) and oxygen concentrations (1-4, 6-98% O$_2$).

For 55 and 65 °C, A and B, the start and end loadings are relatively similar with less than +/- 0.05 in loading between the initial and end sample. This does not imply that the CO$_2$ concentrations are the same, as seen from Table 7. The MEA concentration decreases over time and thus at a given loading the CO$_2$ content will also decrease. For 75 °C, C, the CO$_2$ content is drastically reduced with increasing oxygen concentration. This is because the degradation rates increases and the remaining MEA decreases. It is also seen, Figure 4, that the loading seems to be reduced with increasing oxygen concentration. A high water balance loss was observed for C2 (75 °C - 21% O$_2$) which does not explain the deviation. The reduction of CO$_2$ loading may be explained by CO$_2$ being incorporated in the degradation compounds at high oxygen contents at this highest temperature as experienced for thermal degradation. The generally lower CO$_2$ levels are explained by the higher temperature.

3.3 Nitrogen balance

During several of the experiments, the outlet gas was bubbled through gas absorption flasks containing acid to obtain an indication on the amount of ammonia and MEA leaving the system. Based on these data an overall nitrogen balance for the system could be established. In the liquid phase the inorganic nitrogen is nitrite and nitrate while organic nitrogen, including ammonia, can be determined by a Kjeldahl analysis. Ammonia and MEA were also analyzed in the gas absorption flask liquid and were taken to represent the nitrogen emitted from the system. For the total nitrogen

balance of the system several contributions have to be considered, as total nitrogen in end sample (organic and inorganic), MEA/alkalinity for samples taken out during the experiment and nitrogen emitted from the reactor (MEA and NH$_3$). The procedure used for the nitrogen balance is described in detail in the supplementary information part B (B.3). In Table 8 the results are given and show a 3-10% deviation, apart from 6% O$_2$, 75 °C (C1), between titrated initial solution and sum of contributions from end solution, samples and emitted nitrogen which is deemed satisfactory. As expected the data show increasing emitted losses with increasing temperature, but what may seem more surprising, the emissions tend to increase with oxygen content. This may be explained by increased formation of volatile degradation products as ammonia.

Table 8: Total nitrogen balance for experiment at 6% O$_2$ (A1-C1: 55-75 °C), 49% O$_2$ (B3 &C3: 65 and 75 °C) and 98% O$_2$ (C4: 75 °C)

Experiment	Liquid			Emitted	Total
	Titration (Alkalinity)	Samples (alkalinity)	Kjeldahl (org) + IC (inorg)	MEA+NH$_3$ (C)	**Sum N end (A+B+C)**
	Initial	Middle (A)	End (B)		
A1 (55°C – 6% O$_2$)	**4.65**	0.15	4.18	0.18	**4.51**
B1 (65°C – 6% O$_2$)	**4.66**	0.15	3.98	0.29	**4.41**
C1 (75°C – 6% O$_2$)	**4.68**	0.19	3.31	0.40	**3.90**
B3 (65°C – 49% O$_2$)	**4.56**	0.10	3.68	0.60a	**4.38**
C3 (75°C – 49% O$_2$)	**4.59**	0.09	3.31	0.74a	**4.14**
C4 (75°C – 98% O$_2$)	**4.68**	0.07	3.54	0.75a	**4.36**

apH in the gas bubble flask was basic indicating that not enough acid was used

In (Vevelstad et al. 2014b) the organic nitrogen balance for the end samples was given from Kjeldahl analysis. These data showed that MEA is the main contributor and its contribution decreases with increasing oxygen concentration. At 6% O$_2$ (1), HEGly is the main degradation compound contributing to the nitrogen in the end sample and HEF and HEI are other degradation compounds that significantly contribute. The HEGly contribution is less significant at increasing oxygen concentrations, while HEI and HEF's positions are strengthened at increasing oxygen concentration.

3.4 Degradation compounds

3.4.1 Primary degradation compounds

Primary degradation compounds comprise the degradation compounds formed initially through radical reactions and oxidation reactions. These primary compounds are aldehydes, ammonia, alkyl amine, imine (usually unstable), acids, nitrite and nitrate.

The anionic components quantified in this study were formic, acetic, nitric, nitrous and sulfuric acid, and ammonia and alkyl amines (methylamine, dimethylamine, ethylamine and diethyl amine). The results for the individual component as a function of time is given in Figure 5 - Figure 10.

3.4.1.1 Anionic compounds

As seen from Figure 5 - Figure 8, formic acid, converted to formate, is a major anionic contributor in all experiments. Oxalate is more important at higher temperatures. Nitrite has generally a higher contribution than nitrate. Suphate is present because of the addition of sodium sulphate to the initial solution as described in chapter 2. The general trend is that the acid concentration increase with both temperature and oxygen concentration.

The concentration of formate [mmol/kg] as a function of time [days] for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2) is presented in Figure 5.
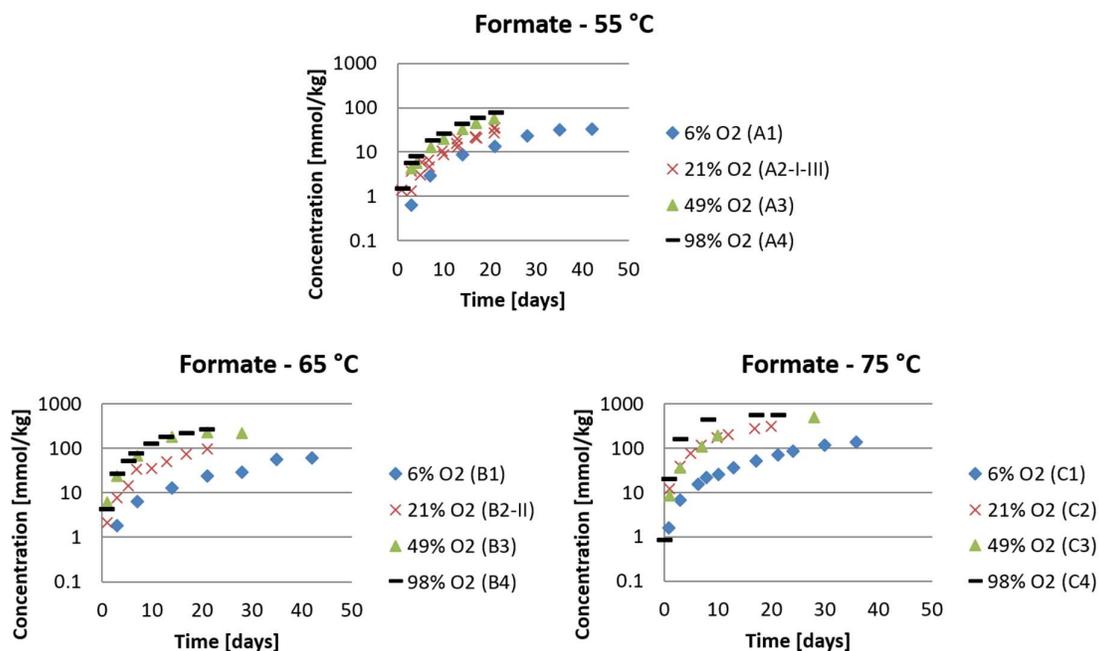
Figure 5: Formate concentration [mmol/kg] as a function of time [days] for all oxygen concentrations (1 to 4, 6- 98% O_2) and temperatures (A to C, 55-75 °C).

For all oxygen levels the concentration of formate increases with temperatures. (Vevelstad et al. 2013b) showed that the formate formation rate increased with increasing oxygen concentration (21-98 %) at 55 °C. The same behavior is observed for the other temperatures although experiments B3 (65 °C - 49% O_2) and B4 (65 °C - 98% O_2) and experiments C2 (75 °C - 21% O_2) and C3 (75 °C - 49% O_2) are similar. For C2 (75 °C - 21% O_2) and C3 (75 °C - 49% O_2) part of the explanation could be the higher loss of water in C2 which would give artificially high concentrations of all degradation compounds because of less water in the experiment, but the correction for water loss do not seem to impact the concentrations significantly. Formation of formate is likely a function of both splitting of the amine molecule as well as an oxidation reaction. Both of these routes are radical reactions that are favored by higher oxygen concentrations and temperatures. In experiment C4 (75 °C - 98% O_2) it is seen that the formate concentration increases rapidly in the beginning and then slows off after about 10 days. This might be a consequence of secondary reactions taking place where formate is an intermediate, but also of the MEA degradation itself slowing down because of reduced MEA concentration, see Figure 2.

The concentrations of oxalate [mmol/kg] as a function of time [days] for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2) are given in Figure 6.
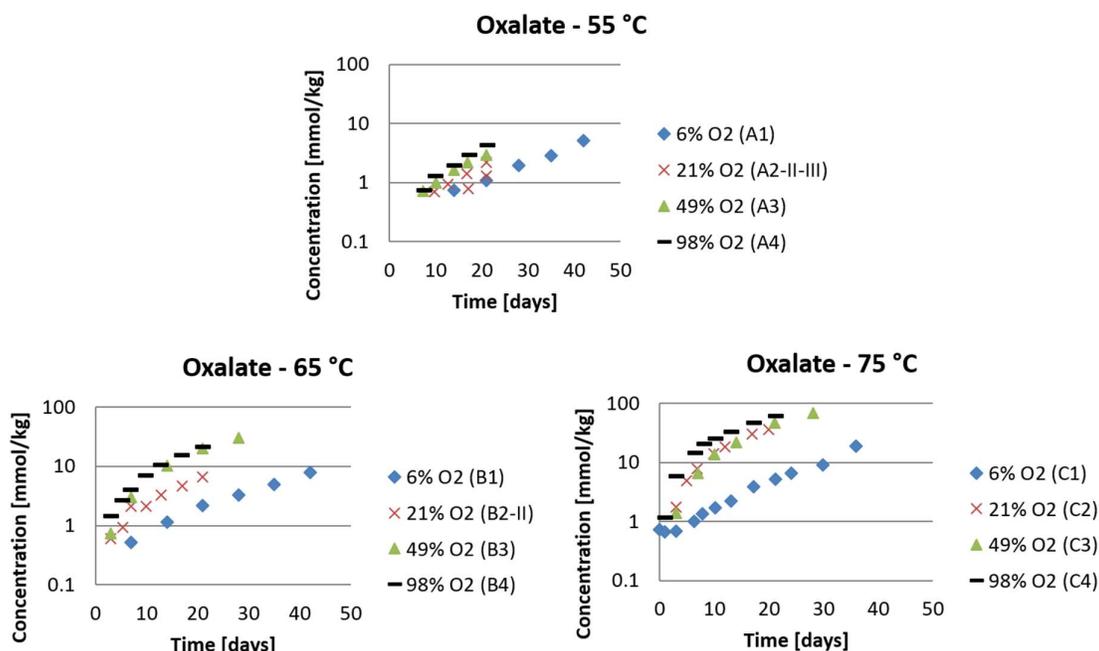

Figure 6: Oxalate concentration [mmol/kg] as a function of time [days] for all oxygen concentrations (1 to 4, 6-98% O_2) and temperatures (A to C, 55-75 °C).

An increase in oxalate rate of formation with temperature and oxygen concentration is observed as for formate. As also mentioned for formate, C2 (75 °C - 21% O_2) and C3 (75 °C - 49% O_2) show very similar concentration levels. Compared to formate, it takes longer for oxalate to form and the concentrations are much lower. Oxalate is believed to be formed in more steps than formate (Rooney et al. 1998), and the route toward oxalate might also be less favorable. Rooney and coworkers investigated oxygen solubility in water and several alkanolamine solutions (including 20wt% MEA) between 15 – 80 °C (Rooney and Daniels 1998). In this temperature range (for MEA/H_2O and H_2O) the oxygen solubility decreased with increasing absorber temperature. In addition it was observed that increasing concentration of salts decreased the O_2 solubility in water dramatically. All the anionic degradation compound concentrations are small compared to the total CO_2 present in the solvent. The total CO_2 concentration in the solvent decreased with increasing temperature (see Table 7), and the salting out effect which decreases O_2 solubility is therefore expected to be less pronounced for the experiments at higher temperatures. The experiments seem to indicate that temperature (in this range) has less impact on oxygen solubility than the concentration of salt.

The concentrations of nitrate [mmol/kg] as a function of time [days] for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2) are given in Figure 7.
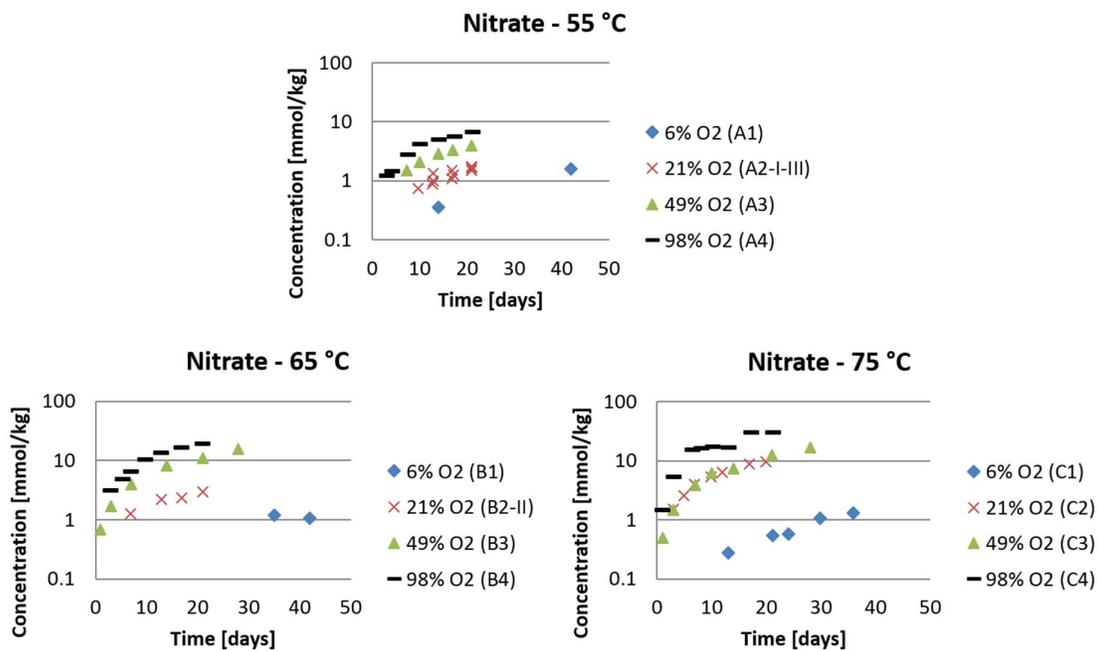
Figure 7: Nitrate concentration [mmol/kg] as a function of time [days] for all oxygen concentrations (1 to 4, 6-98% O_2) and temperatures (A to C, 55-75 °C).

The nitrate rate of formation increases with temperature and oxygen concentration. As for formate and oxalate, the nitrate concentration curves for C2 (75 °C - 21% O_2) and C3 (75 °C - 49% O_2) are very similar. Small amounts of nitrate are formed at 6% O_2 (1), and these concentrations are so low that trends could not be discussed.

The concentration of nitrite [mmol/kg] as a function of time [days] for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2) is given in Figure 8.
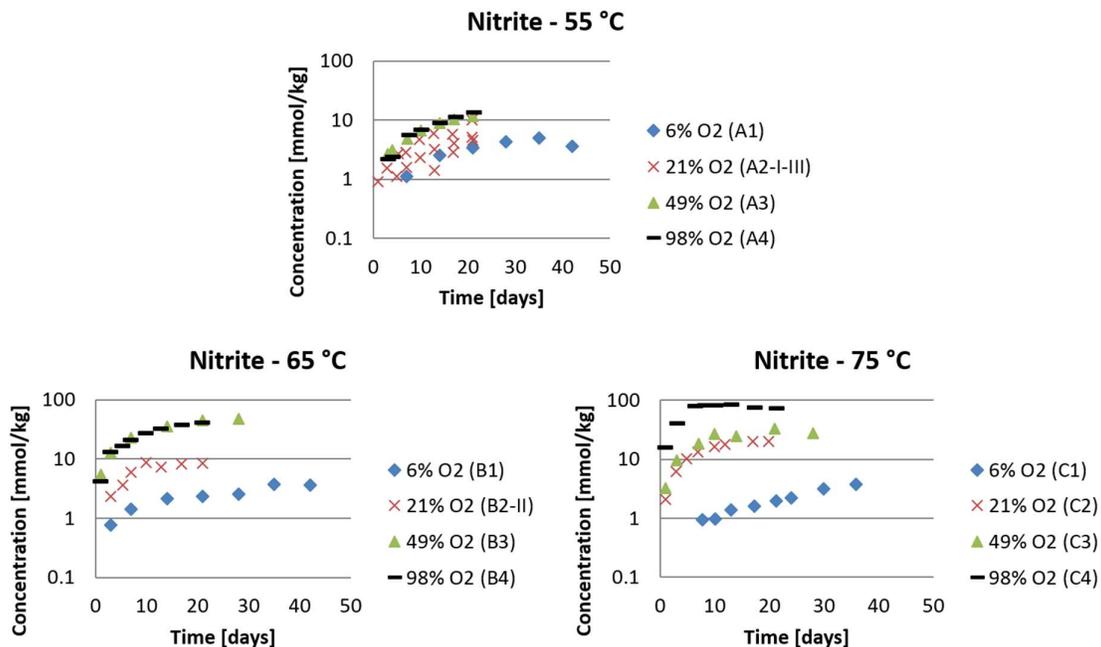
Figure 8: Nitrite concentration [mmol/kg] as a function of time [days] for all oxygen concentrations (6-98% O₂) and temperatures (55-75 °C).

The development of nitrite shows a more complex picture than the other anions. Both temperature and oxygen level influence rate of formation, but a generalization is difficult. For 6% O_2, there is little effect of temperature, but the data indicate that the nitrite formation rate decreases with increasing temperature. At 21% O_2 (2), an increase in nitrite formation with temperature is observed, with an approximate doubling every 10 °C. At 75 °C (C) the concentration seems to reach a plateau after about 12 days indicating that there are mechanisms for both production and destruction/consumption of nitrite. At 49 (3) and 98% O_2 (4) the development of nitrite concentration follow each other for the two lowest temperatures, but the formation rate is higher at 65 °C (B). At 75 °C (C) there is a rapid increase in nitrite concentration for 98% O_2 (4), leveling off after 10 days and thereafter going down after 14 days. Both production and destruction of nitrite is probably dependent on liquid phase oxygen level. This level increases with gas phase O_2 pressure and decreases with temperature. At the lowest oxygen level the access to O_2 seems to be rate determining, giving a small, or negative, temperature effect as the solubility decreases with temperature. At 21% O_2 (2) there seems to be a mixed O_2 and temperature control in the production term, whereas destruction still is of minor importance. At 49 % (3) and 98% O_2 (4), there is still mixed control and for 55 °C (A) and 65 °C (B) it seems the decrease in O_2 solubility just compensates the temperature effect on rate. At 75 °C (C) it seems that destruction is playing a significant role reducing the nitrate build-up at 49% O_2 (3) and creating a maximum at 98% O_2 (4). As will be seen, similar trends are observed for BHEOX and OZD.

For all of these anions, including nitrite, comparable amounts was observed for C2 (75 °C - 21% O_2) and C3 (75 °C - 49% O_2), the variation in water balance did not significantly impact the concentrations in these experiments.

3.4.1.2 Ammonia and alkyl amines

The concentrations of ammonia [mmol/L] in the liquid phase as a function of time [days] for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2) are given in Figure 9.
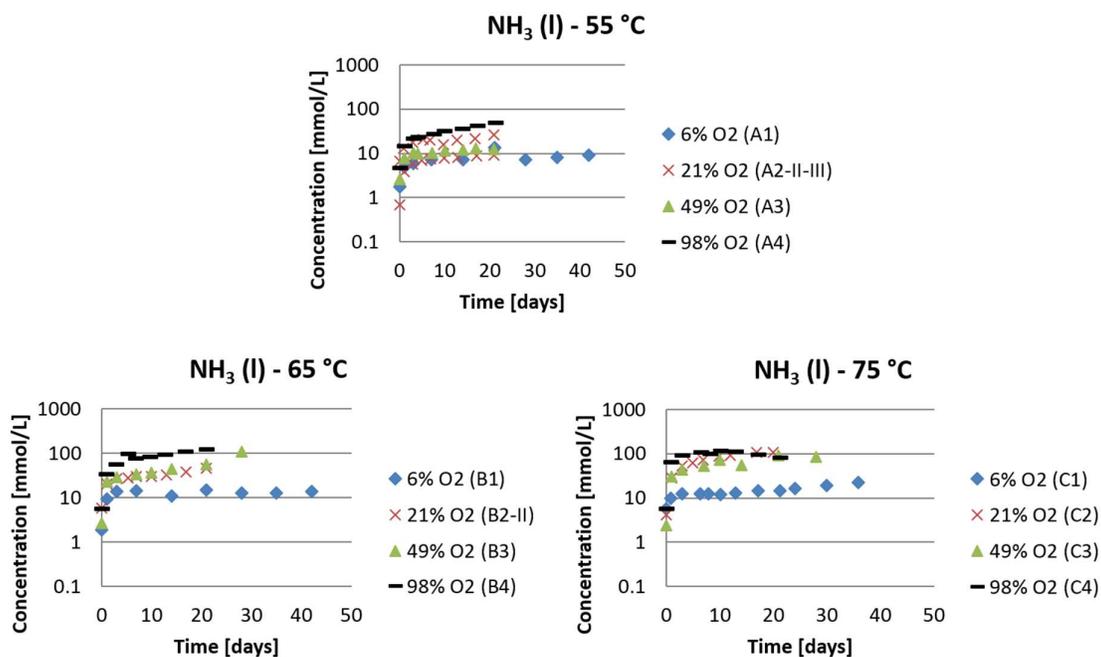

Figure 9: Ammonia concentration [mmol/L] in liquid phase as a function of time [days] for all oxygen concentrations (1 to 4, 6-98% O_2) and temperatures (A to C, 55-75 °C).

The behavior of ammonia in the experiments is complicated since it is volatile. Therefore more factors than formation of, and reactions using ammonia as intermediate need to be considered, in particular the amount emitted. The general trend is that ammonia formation increases with temperature and oxygen concentration. However, little effect of the O_2 level increase from 21 (2) to 49% (3) is observed. The gas-liquid phase equilibrium is important and may be the explanation for the similarity between the 98% O_2 (4) curves at 65 (B) and 75 °C (C). At 75 °C (C) and 98% O_2 (4) it is also observed that the build-up of ammonia goes through a maximum. The reason for this may be a combination of the production rate going down because of less MEA left, the use of ammonia as intermediate and the removal of ammonia through the continuous gas flow.

Formation of alkyl amines, methylamine (MA), dimethylamine (DMA), ethylamine (EA) and diethyl amine (DiEA) was also observed. The concentrations were low, but the general trend is an increase in formation rate with both O_2 pressure and temperature.

Methylamine is the major compound and its concentrations [µmol/L] as a function of time [days] at different temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2) are shown in Figure 10.
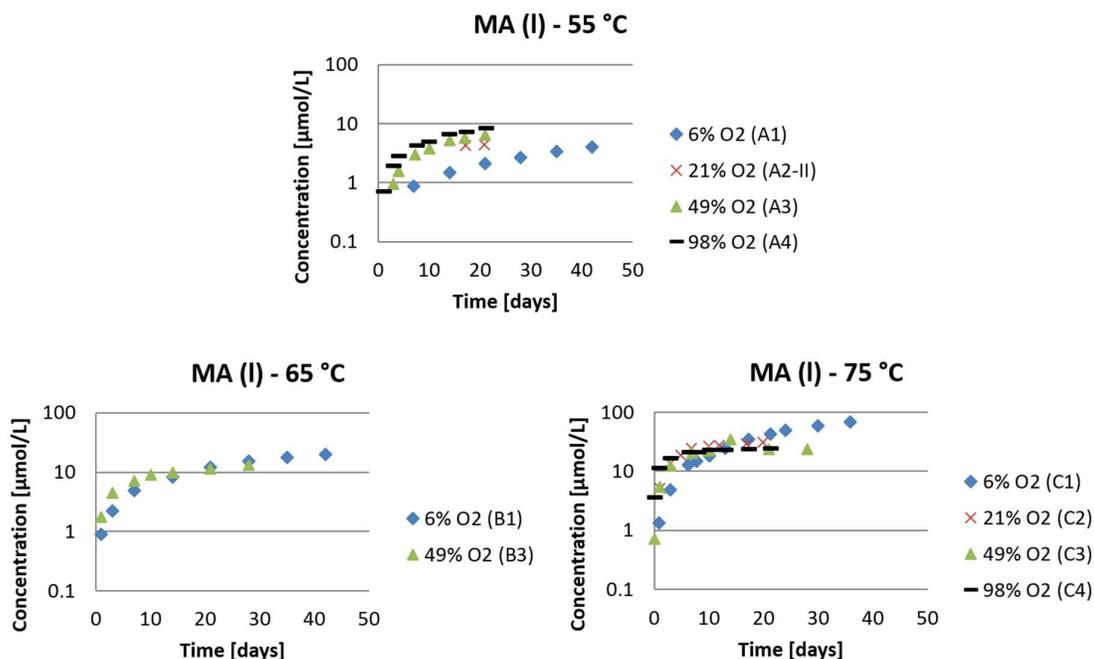

Figure 10: MA concentration [µmol/L] in liquid phase as a function of time [days] for oxygen concentrations (1 to 4, 6-98% O_2) and temperatures (A to C, 55-75 °C).

At 55 (A) and 65 °C (B) the mentioned general trend is observed whereas at 75 °C (C) a leveling off after about 14 days is seen, and the effect of O_2 pressure is reversed for the three highest levels. The reasons for this behavior may be similar to those mentioned for ammonia.

Similar trends are observed for the other alkyl amines, DMA, EA and DiEA (see supplementary information part B, B.4). The alkyl amine concentrations are generally low, and for several of them the concentrations are close to the lower quantification limit, which could result in trends being misinterpreted. In addition, all of them are volatile and their liquid phase concentration levels are both a result of degradation and gas phase losses.

3.4.2 Secondary degradation compounds

Secondary degradation products are formed from primary degradation compounds and MEA or other secondary degradation compounds. Seven secondary degradation products; HEGly, HEPO, OZD, HEF, HEA, BHEOX and HEI, were quantified in this work and all the raw data are given in supplementary information (Part A). In addition, a range of nitrosamines were quantified. A limited data set based on percent formation relative to nitrogen is also given in (Vevelstad et al. 2014b). In

the following, the formation of degradation products as function of time is given and discussed based on suggested reaction mechanisms and the individual component's role as end product or intermediate. At the end the nitrosamine formation results are discussed.

3.4.2.1 HEGly, HEPO & OZD

HEGly and HEPO are major degradation compounds found in pilot samples (da Silva et al. 2012). OZD is an important degradation product during thermal degradation with CO_2 and is also an intermediate for several other secondary degradation compounds. The formation of HEPO and HEGly has earlier been compared based on the suggestion that HEPO could be formed from HEGly in a two-step mechanism (da Silva et al. 2012). The first step is formation of *N*-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]-acetamide (HEHEAA) (da Silva et al. 2012) and the second step cyclisation of HEHEAA with loss of water (Strazisar et al. 2003; da Silva et al. 2012). Recently several new mechanisms have been suggested for the formation of both HEGly and the two isomers of HEPO (1HEPO - 1-(2-hydroxyethyl)-2-piperazinone/59702-23-7 & 4HEPO - 4-(2-hydroxyethyl)-2-piperazinone/ 23936-04-1 (Gouedard 2014; Vevelstad et al. 2014a)). For one of the mechanism OZD plays an important role together with HEGly for the formation of HEPO. It has also been suggested that HEGly is an intermediate in other reactions and Gouedard has shown several new compounds suspected to be formed from HEGly (Gouedard 2014). The reaction scheme in Figure 11 shows all suggested mechanisms for the formation of HEGly and the two isomers of HEPO as well as the formation of other products from HEGly. F1 means that the reaction pathway is suggested by (Gouedard 2014), F2 by (da Silva et al. 2012), F3 by (Strazisar et al. 2003) and F4 by (Vevelstad et al. 2014a).
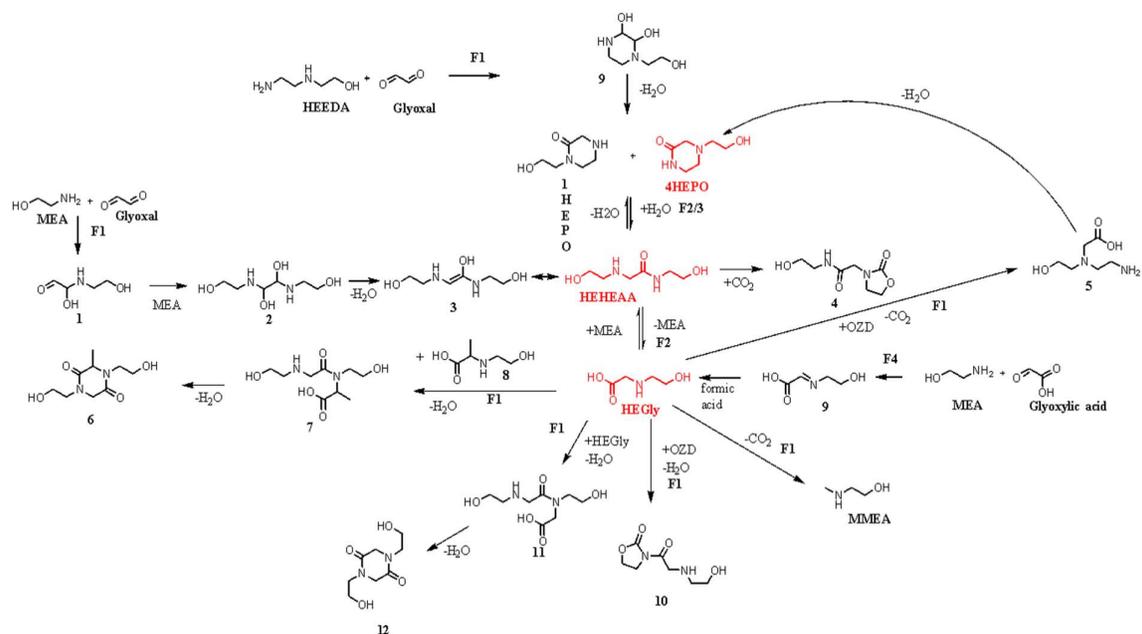
To summarize, two formation reactions are suggested for HEGly and 6 reactions consuming HEGly. For 1HEPO there are two formation reactions and for 4HEPO there are 3 formation reactions. HEPO is considered to be an end product. Another formation reaction was also suggested by Gouedard (Gouedard 2014) where HEGly is formed from HEHEAA and not the other way around as earlier suggested and supported by mixing experiments (da Silva et al. 2012; Vevelstad et al. 2014a). It is likely that several of these mechanisms occur in a plant, and which ones are the more favorable could be supported using molecular modelling (Gupta et al. 2014).

The further discussion on formation of HEGly, HEPO and OZD is based on the suggested mechanisms as shown in Figure 11. HEGly and OZD are both intermediates for the formation of HEPO in the mechanism by Gouedard (Gouedard 2014) and it is of interest to see which of these two is formed in largest quantity as function of time. The concentration profile of HEGly at different oxygen concentrations (1 to 4, 6-98% O_2) and temperatures (A to C, 55-75 °C) is given in Figure 12.
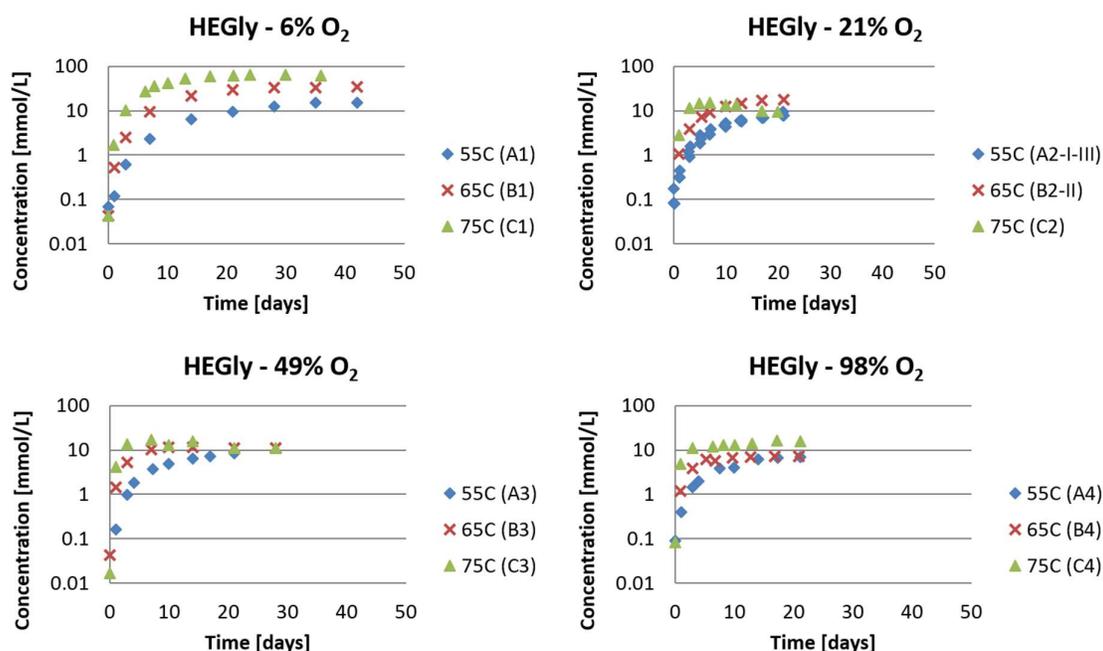

Figure 12: The concentration of HEGly (mmol/L) as a function of time (days) for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O_2).

Studying the build-up of HEGly, some clear trends are visible. At 6% (1) oxygen content the formation rate of HEGly shows a strong temperature dependency. After one day the amount formed at 75 °C (C) is about 20 times higher than at 55 °C (A). The formation reaction thus has very high activation energy and is not restricted by oxygen supply as diffusional processes do not show such temperature dependency. This may indicate a reaction that does not involve oxygen as a direct

reactant. At all temperatures the concentration levels of HEGly are highest at the lowest oxygen content and decrease at 21% (2) oxygen and then remain about constant or go slightly down with further increasing oxygen content. This may indicate that a reaction with HEGly as reactant, and dependent on oxygen consumes HEGly.

The OZD concentration levels are low at 6% (1) oxygen and lower concentrations are seen with increasing temperature, see Figure 13. Again, this is probably a result of competing formation and consumption reactions. In Figure 11, HEGly is suggested to react with OZD giving compound 5 or 10. At high levels of HEGly and low formation rates of OZD this reaction may explain the low levels of OZD and also the reverse temperature dependency. At higher oxygen contents the levels of OZD increase and the temperature dependency is opposite of at 6% (1) oxygen. Possibly the formation reaction(s), apparently demanding oxygen then produce enough OZD to maintain the seen level and also react with HEGly, causing a decrease in the HEGly levels as seen. The interplay between HEGly and OZD is also illustrated in Figure 14 where the ratios ($HEGly/OZD = C_{HEGly}/C_{OZD}$) are given.
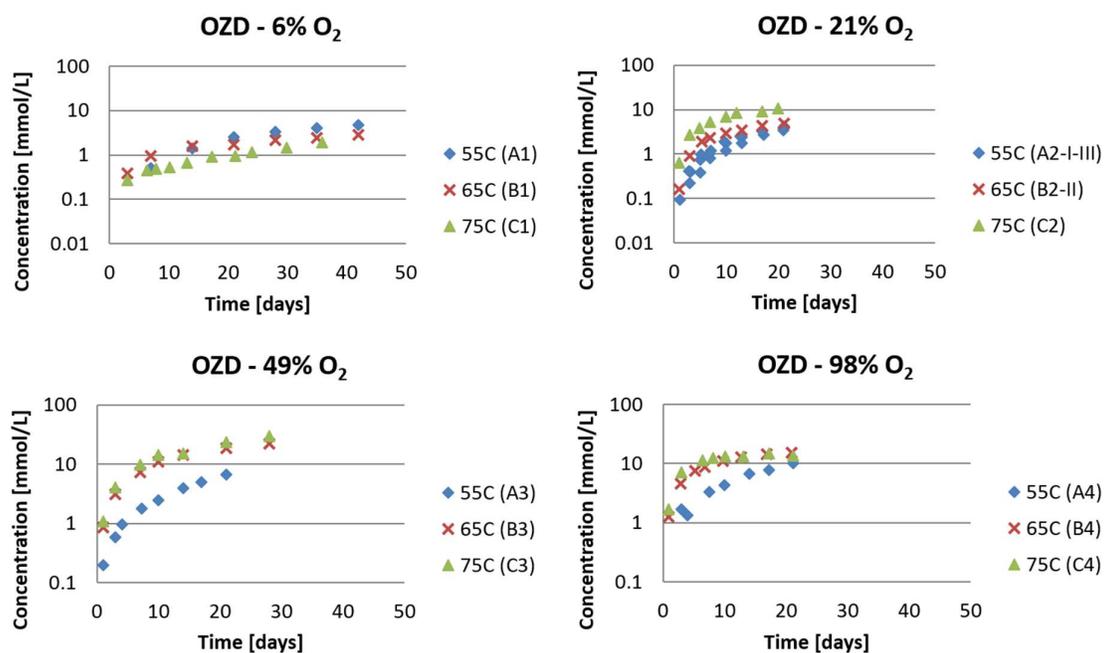

Figure 13: The concentration of OZD (mmol/L) as a function of time (days) for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O₂).
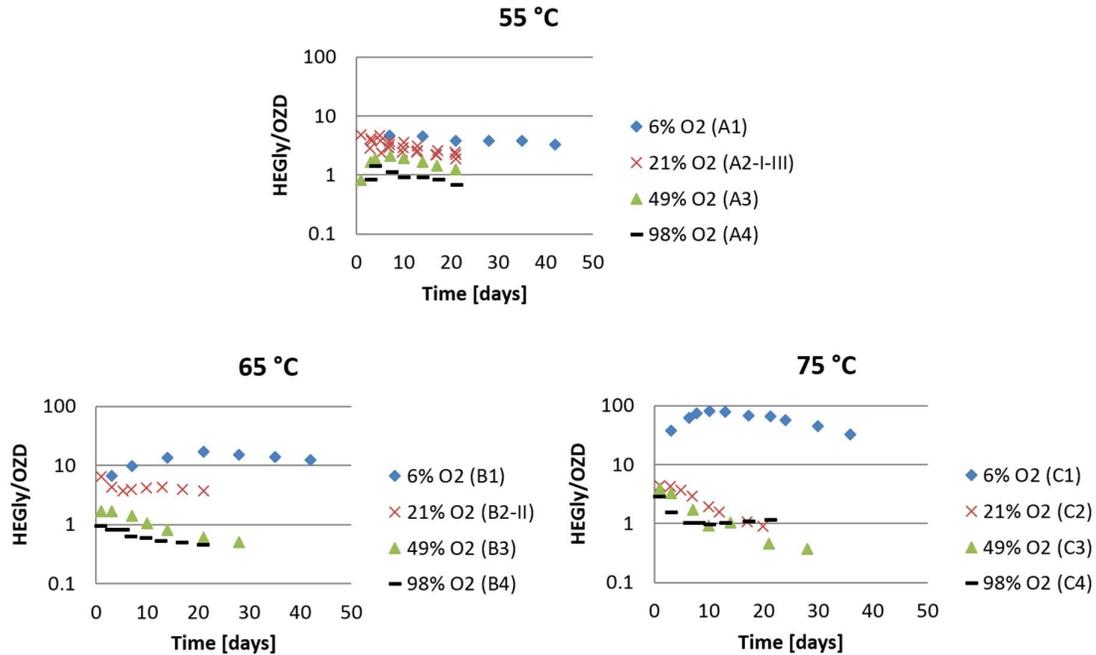
Figure 14: Ratio of concentration of HEGly to OZD for all oxygen concentrations (1 to 4, 6-98% O_2) and temperatures (A to C, 55-75 °C).

At 55 °C (A) the ratio decreases with increasing oxygen content. Initially, at the two highest oxygen levels, OZD is favored, then HEGly builds up, the ratio goes through a maximum, and falls off again. The maximum seems to be reached faster the higher the oxygen level and the higher the temperature. This may imply that the formation of OZD is more oxygen dependent than HEGly. At the higher O_2 levels OZD forms rapidly, giving a low HEGly/OZD ratio at the beginning. From thermal degradation experiments indications are that OZD can form by direct reaction between MEA and CO_2 (Davis and Rochelle 2009; da Silva et al. 2012). The oxidative degradation results indicate that this reaction may not be so important at lower temperatures and that there must be another oxygen dependent route to OZD, discussed also in (Vevelstad et al. 2013b).

According to the suggested mechanisms in Figure 11, HEGly should react in equilibrium reactions to HEHEAA and further to HEPO. The HEPO formation curves (Figure 15) show that the HEPO concentrations are very roughly ten times smaller than the HEGly concentrations. At 75 °C (C) we see from Figure 12 that the HEGly concentration is very high at 6% (1) oxygen but lower and approximately the same for the higher oxygen levels.
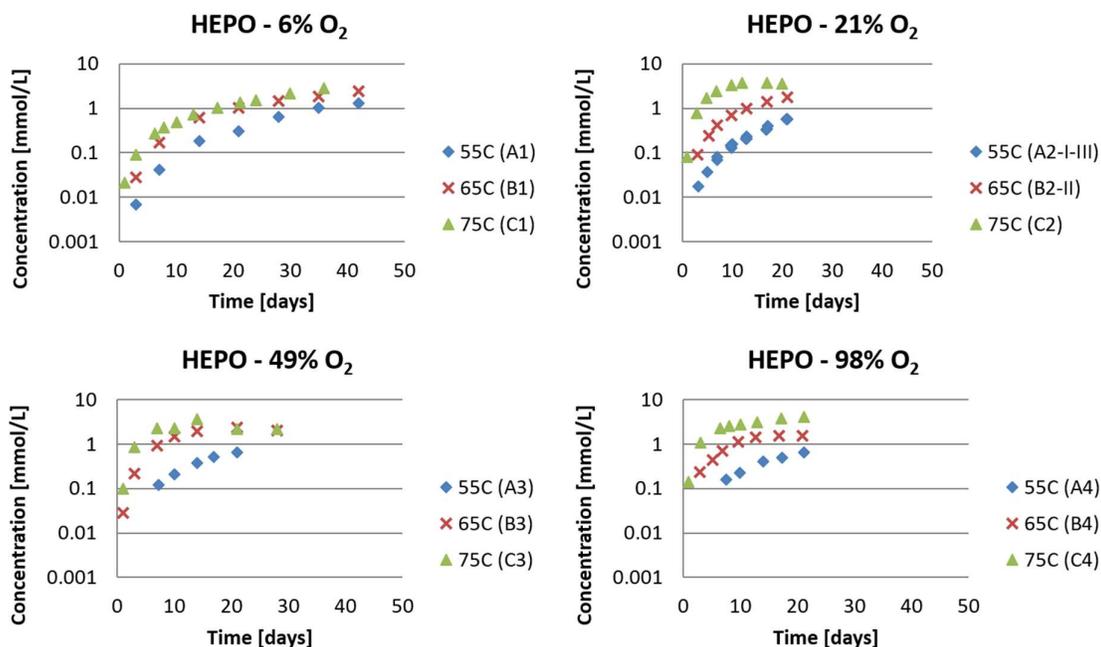
Figure 15: The concentration of HEPO (mmol/L) as a function of time (days) for all temperatures (A to C, 55-75 °C) and oxygen concentrations (1 to 4, 6-98% O$_2$).

For HEPO we see, at 75 °C (C), that the lowest concentration occur at 6% (1) oxygen and then the curves are very similar for the other oxygen levels, see Figure 15. This becomes very clear in Figure 16 where the ratios are given. As the postulated equilibrium in Figure 11 should not be affected by oxygen level, these results are in apparent contradiction to the suggested pathway where HEPO is formed from HEGly through HEHEAA (F2). In (Vevelstad et al. 2014a) is given a figure showing that, at 75 °C (C) and 21% (1) oxygen, the HEHEAA concentration goes through a marked maximum after about 5 days. It is clearly rapidly formed, but reacts further. The concentration goes up to about 5 mmol/L and drops after 20 days to about 1 mmol/L. If an equilibrium between HEHEAA and HEPO existed, and this was the main mechanism, one might expect a similar trend in the HEPO concentration. This is not the case. This may indicate that this pathway between HEGly and HEPO (suggested by F2) does not exist or that the equilibrium is shifted strongly toward HEGly.

Another suggested route to HEPO, F1, goes via HEEDA reacting with glyoxal. HEEDA can be formed from OZD and MEA. At 6% (1) oxygen the OZD concentrations are low, particularly at 75 °C (C). This can explain the low rate of formation of HEPO at these conditions. As the oxygen level increases the OZD concentrations also rise and the same is seen for HEPO.
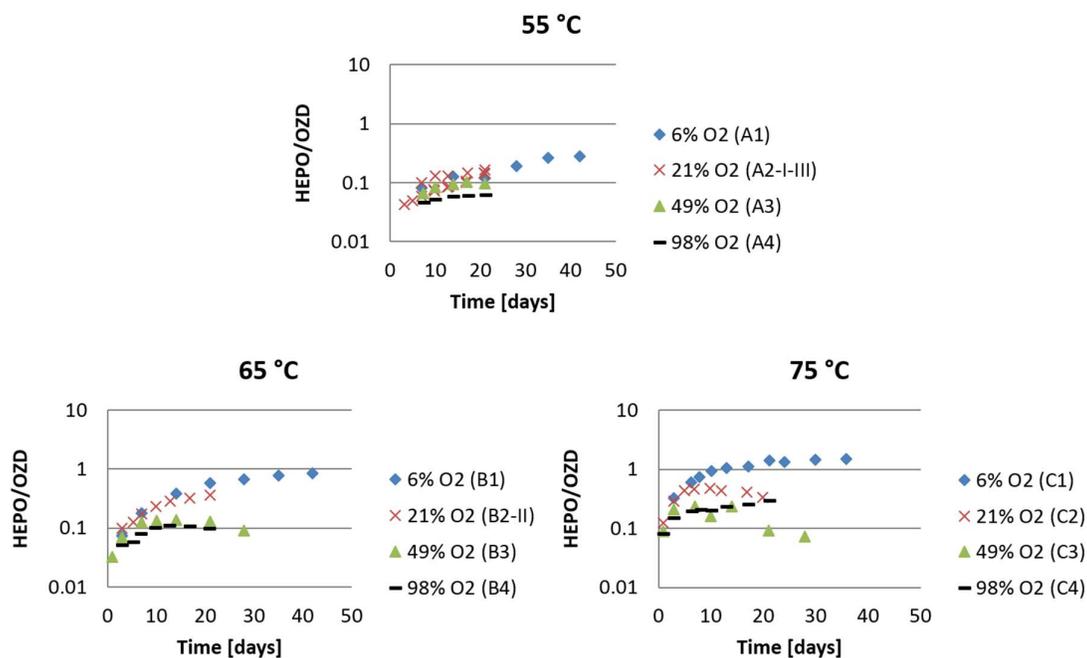
Figure 16: Relation between HEPO and OZD for all oxygen concentrations (1 to 4, 6-98% O₂) and temperatures (A to C, 55-75 °C).

From Figure 16 we see that the effect of oxygen level on the HEPO/OZD ratio becomes stronger with increasing temperature. Based on the formation mechanism via OZD and MEA forming HEEDA which then reacts with glyoxal to HEPO one may imagine that at 55 °C (A) the reaction(s) forming HEPO from HEEDA are slow and that the lowering of the HEPO/OZD ration is a result of increased OZD concentration because of more oxygen. This is consistent with the concentration curves in Figure 13. At the higher temperatures it seems that the actual concentration of HEPO goes over a top and then decreases with time. OZD still increases as reflected in the HEPO/OZD ratio also showing a maximum. The exception at 75 °C (C) and 98% (4) oxygen may be due to experimental variations but this is not certain.

In the shown experiments the OZD concentrations are comparable to HEGly, apart from at 6% (1) oxygen. In pilot samples it has been found that OZD is one of the degradation compounds with small concentration (da Silva et al. 2012). This is in line with the results at 6% (1) oxygen, which are closer to the pilot plant conditions with oxygen content even lower than 6%.

Another reason for the small amounts of OZD in pilot samples could be higher amounts of typical thermal degradation compounds as HEEDA and HEIA as these compounds can be formed from OZD (Lepaumier et al. 2011). In all our experiments the HEPO formation is low compared to what is found in pilot samples, being generally low compared to other secondary degradation compounds as HEGly, OZD, HEF and HEI. Thus this indicates that these systematic experiments are not able to capture HEPO's behavior in pilots where HEPO is one of the major compounds. This is probably due to HEPO mainly being formed at high temperatures.

3.4.2.2 Amides like HEF/HEA/BHEOX

HEF, HEA and BHEOX are amides which are suggested to be formed from MEA and different acids (Lepaumier et al. 2011a; Supap et al. 2011). Rivera et al. supported this suggestion in a synthesis study on the formation of 2-hydroxy-*N*-(2'-hydroxyethyl)-acetamide (HHEA) from glycolic acid and MEA (Rivera et al. 1999). HEF, HEA and BHEOX formation from MEA and their respectively acids was confirmed by lab experiments (Supap et al. 2011; Vevelstad et al. 2014a). HHEA formation experiments conducted by Rivera (Rivera et al. 1999) were done in absence of solvent (water) and with equal amounts of glycolic acid and MEA. HEF, HEA and BHEOX are expected formed with similar mechanisms as HHEA but low concentrations were observed in the lab mixing experiments with water present, conducted by Vevelstad et al. (Vevelstad et al. 2014a). This difference may be caused by the water content in the latter experiments. Recently also the formation of different analogues of 2-oxazoline (see Figure 17) from amides observed in pilot plant studies has been suggested (Gouedard et al. 2014).

R=H
R=CH$_3$
R=CH$_2$OH
R=COOH

Oxazoline
R=H: 2-oxazoline
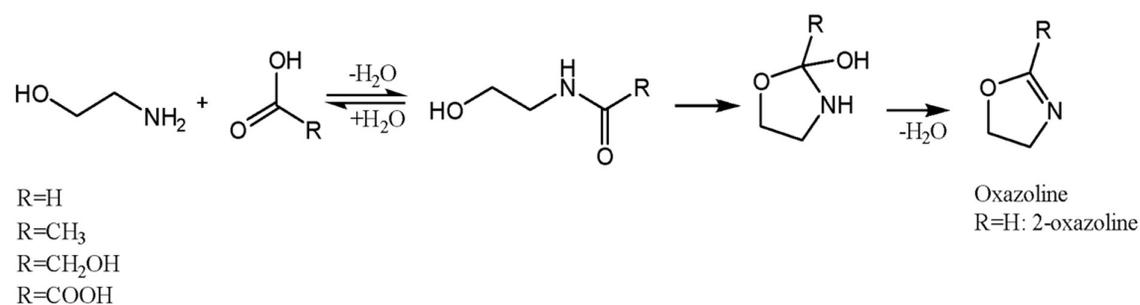
Figure 17: Formation of different amides and 2-oxazoline.

The amino and the alcohol group in the amino alcohol have to be on neighboring carbon atoms like in for example MEA (Frump 1971). The reaction is more favored if the carbon to the amino group is completely substituted as for 2-amino-2-methyl-1-propanol (AMP). Oxazoline can then react further with several of the compounds present in degraded solutions, e.g. amines, aldehydes, acids. Examples are given by Frump (Frump 1971).

The formation of HEF is believed to take place via a reaction between formic acid and MEA (Lepaumier et al. 2011a). The ratios between HEF and formate as a function of time [days] for the different experiments are given in Figure 18 (the concentration profiles for HEF are given in supplementary information part B, B.5, and for formate see Figure 5).
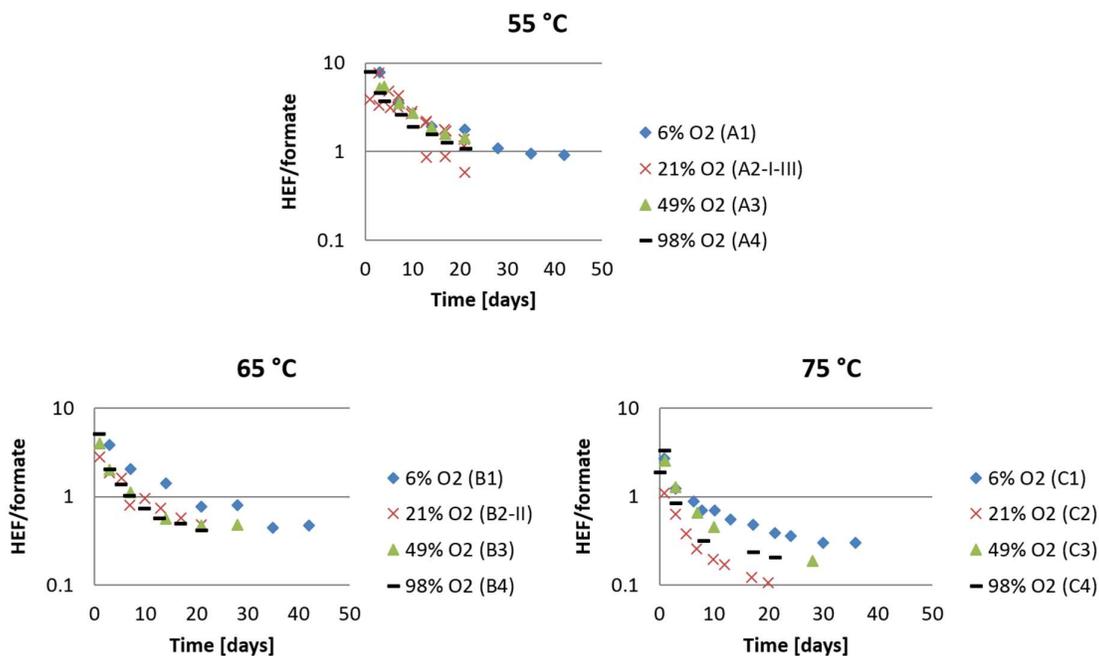
Figure 18: HEF/formate ratio as a function of time [days] for all oxygen concentrations (1 to 4, 6-98% O₂) and temperatures (A to C, 55-75 °C).

The general trend in Figure 18 is that HEF is formed rapidly and has higher concentrations than formate in the beginning of the experiments. If the main mechanism is a suggested in Figure 17, this indicates a rapid transformation of formic acid to HEF. At 55 °C (A) the HEF/formate ratio is seen to be almost independent of oxygen level whereas both HEF and formate increase in formation rate with increasing oxygen level. This may possibly indicate an equilibrium reaction. With time the ratio decreases by a factor about 10, which is much more than the decrease in MEA concentration. This trend is caused by the HEF concentrations levelling off whereas the formate concentration continues to rise. This seems to contradict the equilibrium hypothesis. At 65 °C (B) similar trends are seen, but the decrease in HEF/formate ration is more rapid. Also at this temperature the ratio decrease is much larger that the lowering of MEA concentration over time. At 75 °C (C) similar trends are seen, but here a significant effect of oxygen pressure is seen. In particular 21% (2) oxygen sticks out giving the lowest HEF/formate ratios. This may be caused by the particularly rapid MEA degradation in this experiment, as seen from Figure 2, and may be an outlier experiment because of this. However it still shows that MEA concentration has an impact on HEF formation.

HEA is believed to be formed in a similar mechanism as HEF but with acetic acid instead of formic acid. It is formed in low amounts in these experiments, approximately at 10% of HEF. Acetic acid, which is believed to be the intermediate, was analyzed for but not observed. This is rather surprising since the lab mixing experiment with acetic acid and MEA showed that the conversion to HEA was not 100% (Vevelstad et al. 2014a), which would imply that acetic acid should still be present in the solvent mixture. HEA development over time is similar to most other degradation compounds as it generally increases with oxygen concentration and temperature. Details are given by (Vevelstad et al. 2014b) and the concentration profiles for HEA are given in supplementary information part B,

B6). Both BHEOX and oxalic acid are formed after several reaction steps, which explain why small amounts, if any, are observed in the beginning of the experiments. The oxalic acid concentrations increase with time over the whole testing period for all experiments, whereas BHEOX goes through a maximum at 75 °C (C) and oxygen concentrations from 21% (2) and up (3 to 4). The BHEOX/oxalate ratios as function of time [days] for all experiments are given in Figure 19.
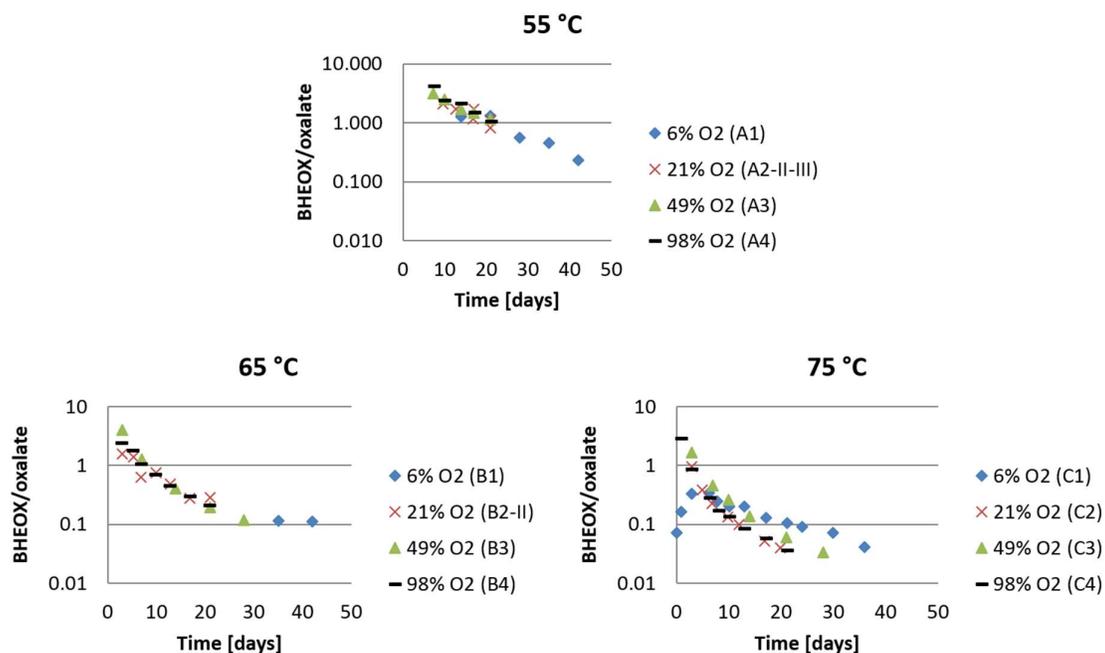

Figure 19: BHEOX/oxalate ratio as a function of time (days) for all oxygen concentrations (1 to 4, 6-98% O$_2$) and temperatures (A to C, 55-75 °C).

The BHEOX concentration is generally low and increase with increasing oxygen concentration (the concentration profiles for BHEOX are given in supplementary information part B, B7). At 6% (1) oxygen content the highest concentrations are found at 55 °C (A) and at the other oxygen levels the concentrations at 65 (B) and 75 °C (C) seem to go through maxima after 3-15 days. The maximum comes earlier at the higher oxygen content. This might be explained by BHEOX decomposing at higher temperature. At 135 °C all the BHEOX and most of the oxalate decomposed during one week in thermal degradation experiments (Vevelstad et al. 2013c). BHEOX is not a major degradation compounds, it is also clear that BHEOX and oxalate will likely decompose under stripper conditions increasing the concentration of e.g. formate.

3.4.2.3 HEI

HEI is an imidazole, and is the only compound of this group quantified in the degradation mixture. Several other imidazole's have been suggested formed, such as e.g. 1-(2-hydroxyethyl)-2-methylimidazole (Vevelstad et al. 2013b; Gouedard 2014). Except for the MEA base structure, all the other compounds necessary for HEI formation are primary degradation compounds and different

aldehydes and ammonia. HEI forms in quantities at about the same level as HEGly and is thus an important degradation product. The formation is believed to be from ammonia reacting with formaldehyde and MEA and is favored by high temperature and oxygen concentration. The ratio between HEI and ammonia as a function of time [days] is given in Figure 20. The concentration profiles for HEI are given in supplementary information part B, B8, and for ammonia see Figure 9.
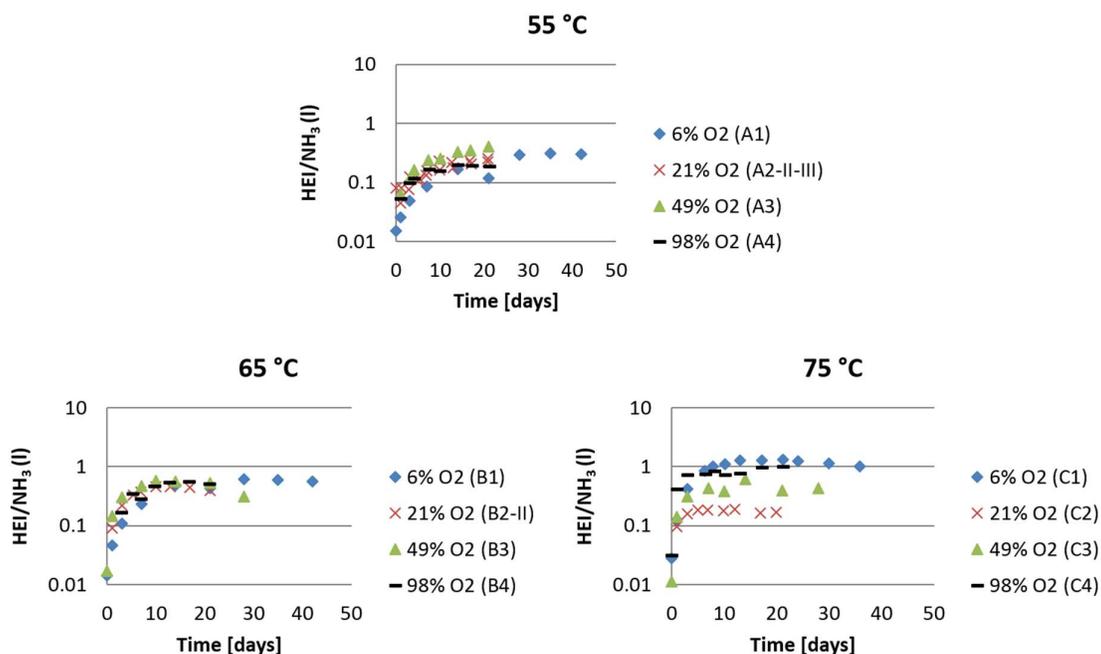

Figure 20: HEI concentration compared against ammonia concentration for experiment with temperature 55- 75 °C (A-C) and oxygen concentration from 6 – 98% (1-4).

With the exception of experiment 75°C - 6% O_2 (C1), ammonia is present in higher amounts in the liquid phase than HEI. Ammonia is formed in the first step of the degradation process while minimum two MEA molecules have to participate in the formation of HEI. Higher ammonia formation is therefore reasonable. The complete picture of the role of ammonia in HEI formation is complex, and cannot be deduced from the ration between HEI and ammonia alone since ammonia is volatile and in significant quantities will leave the reactor with the gas flow and believed to participate in several secondary degradation compounds. However, the general picture that ammonia is present in excess compared to HEI indicates that ammonia is not a limiting factor for formation of HEI. Either some of the other intermediates necessary for formation of HEI are the limiting factor or the reaction itself is not very favorable under these conditions. As mentioned, the HEI concentrations are significantly higher at high oxygen concentration and temperature and this is consistent with thermal degradation experiments where HEI from oxidative degraded solutions were introduced into closed cylinders and heated at 135 °C. This gave a rapid increase in HEI concentration the first week (Vevelstad et al. 2013c), which is similar as observed in this work. One of the major differences between these experiments is that in this work intermediates for HEI formation are still formed while for the cylinders the system is closed and a limited amount of intermediates were present in solution. The combination of temperature (Vevelstad et al. 2013c) and closed environment

(Vevelstad et al. 2014a) seems to be favorable for HEI formation. The cylinders also showed that after the first week the concentration of HEI is reduced (Vevelstad et al. 2013c) which might indicate that the imidazole decomposes at 135 °C or that imidazole reacts further under these conditions. This has to be considered if thermal reclaiming is conducted.

3.4.2.4 Nitrosamines

Nitrosamine formation has been observed for amine solvents, in particular for secondary amines. For degraded MEA *N*-nitrosodiethanolamine (NDELA), *N*-nitrosomorpholine (NMOR) and Nitrosodimethylamine (NDMA) were observed in both pilot samples and in samples from lab experiments (Fostås et al. 2011; da Silva et al. 2012). Formation of nitroso-(2-hydroxyethyl)-glycine (NHEGly) was also observed (Einbu et al. 2013). NHEGly was a major contributor to the total nitrosamines observed in MEA samples from a tailored solvent degradation rig (SDR) (Einbu et al. 2013), while NDELA was only observed in small amounts. The experiments presented in this work were conducted in campaigns spread over several years during which significant improvement in analytical techniques took place. This means that several degradation compounds could be analyzed in later experiments that were below detection limit in earlier experiments. The first experiments conducted, A2-I (55 °C - 21% O_2 run 1) and C2 (75 °C - 21% O_2) were analyzed for nine nitrosamines; NDELA, NDMA, NDEA, NPIP, NMEA, NPYR, NMOR, NDPA and NDBA while A3 (55 °C - 49% O_2) and A4 (55 °C - 98% O_2) were only analyzed for NDELA. For A2-I (55 °C - 21% O_2 run1), none of the nitrosamines were detected in amounts above the quantification limit at the time. Quantifiable amounts of NDELA were, however, observed in both C2 (75 °C - 21% O_2) and A3 (55 °C - 49% O_2). Some of the newer experiments, B4 (65 °C - 98% O_2), B2-I (65 °C - 21% O_2, run1), B2-II (65 °C - 21% O_2 run2) and A2-III (55 °C - 21% O_2, run3), were analyzed for NDELA and NHEGly. NHEGly was observed in higher amounts than NDELA, which is consistent with findings of Einbu et al. (Einbu et al. 2013). The concentrations of NDELA and NHEGly (µmol/L) as function of time (days) for experiment A2-III (55 °C - 21% O_2 run 3), B2-II (65 °C - 21% O_2 run 2) and B4 (65 °C - 98% O_2) are shown in Figure 21.
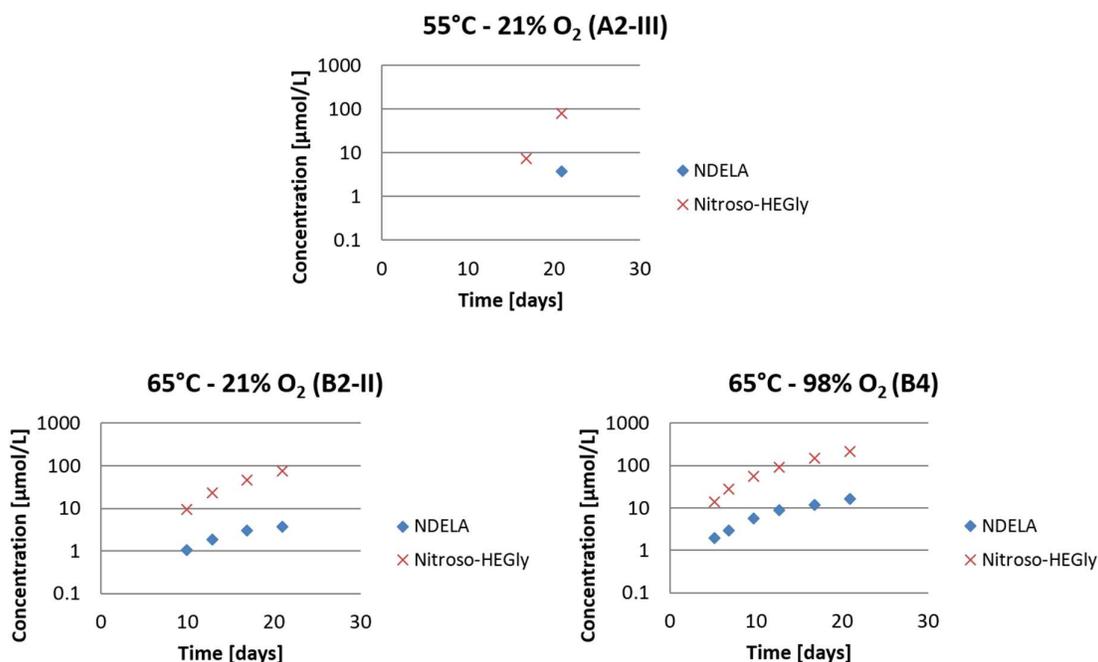
Figure 21: NDELA and NHEGly concentration (µmol/L) as a function of time (days) for experiment B4, B2-II and A2-III.

The highest concentrations of NHEGly and NDELA were observed for B4 (65 °C - 98% O_2), while comparable amounts of NHEGly and NDELA were observed for B2-II (65 °C - 21% O_2 run2) and A2-III (55 °C - 21% O_2 run3) after 21 days. As can be seen, NHEGly starts to form in appreciable amounts only after some time and as in B4 (65 °C - 98% O_2), the concentration becomes higher with time. This is reasonable, as the concentration of HEGly itself needs to become appreciable before NHEGly can form.

4 Conclusions

In this work, a systematic study has been conducted on oxidative degradation of 30 wt% ethanolamine (MEA) for oxygen concentrations: 6, 21, 49 and 98% (1 to 4) and temperatures: 55, 65 and 75 °C (A to C). The formation of ten primary degradation compounds (acids, ammonia and alkyl amines) and seven secondary degradation compounds (HEGly, OZD, HEPO, HEF, HEA, HEI and BHEOX was monitored as function of time over a period of 3 – 6 weeks. The full comprehensive data set is available in the supplementary information for development of models describing the degradation behavior.

One main uncertainty with an open experimental set-up is maintaining the water balance throughout the experiment. The deviation in water balance at 55 °C was less than 5% for all experiments, but slightly higher deviations were observed at higher temperatures. MEA concentration and alkalinity decreased more rapidly with increasing temperature and oxygen concentration. Temperature was found to have a higher impact than oxygen concentration. A total

nitrogen balance was conducted summarizing total nitrogen in the end solution together with ammonia and MEA collected in the exit gas. The balances were closed within 83-97% and the higher deviations were observed at the highest temperature. HEF, HEI and ammonia were the degradation compounds that most significantly contributed to the nitrogen balance in most experiments. However, at 6% O_2 content, HEGly was the major nitrogen containing degradation compound identified. The HEGly contribution was less significant at increasing oxygen concentrations, while HEI's and HEF's positions were strengthened.

Formate is the major anionic compound in all experiments. Formate, oxalate, nitrate, ammonia (liquid phase) concentrations generally increase with temperature and oxygen concentration but some exceptions were observed. The exceptions observed for ammonia could be related to the gas-liquid phase equilibrium, and subsequent loss of ammonia, instead of degradation chemistry. Nitrite shows a more complicated picture than the other anions and generalization is difficult. Formation of alkyl amines; methylamine (MA), dimethylamine (DMA), ethylamine (EA) and diethyl amine (DiEA) was very low.

Suggested mechanisms for the formation of seven secondary degradation compounds; HEGly, HEPO, OZD, HEF, HEA, BHEOX and HEI from literature were compiled and the results discussed in light of these mechanisms. The present data set have shown that some of the suggested pathways e.g. for formation of HEPO and consumption of HEGly are likely more important than the other pathways. Based on the data it seems like HEGly formation is not dependent on O_2, while the opposite might be true for the HEGly consumption reaction. It was also found that at least one of OZD formation reactions is likely oxygen dependent, one mechanism has been suggested (Vevelstad et al. 2013b). OZD concentration increases with oxygen concentration and the same is also seen for HEPO. The experiment at 6% O_2, where HEGly was the major degradation compound while OZD was a minor one, is consistent with analytical results from pilot samples (da Silva et al. 2012). However HEPO, as a major compound in pilot samples, is only formed in small amounts at all oxygen concentrations and temperatures in the these experiments.

One formation pathway for the amides HEF, BHEOX and HEA is from MEA and their corresponding acid. Tailored mixing experiment verified that this could occur. Generally, HEF/formate ratios are initially high, change over time and stabilize at HEF/formate ratios 1-3, increasing with temperature. The BHEOX/oxalate ratios behave similarly both indicating a sequence of reactions. HEA was formed in low amounts in all experiments and the levels generally increase with oxygen concentration and temperature.

HEI is the only quantified imidazole up to this point. Formation is dependent on several volatile compounds e.g. ammonia. Ammonia in liquid phase is generally present in higher amount than HEI and ammonia are therefore not expected to be a limiting factor for formation of HEI. High oxygen concentration and high temperature as well as closed system seem to favor HEI formation.

The results in this work clearly show that performing accelerated degradation tests with 98% oxygen cannot easily be extrapolated to what happens at 6% oxygen, and therefore may not be representative for the situation in an industrial plant both with regard to rates of formation and products formed.

To generalize the data in this work a preliminary model is established considering also mass transport to the gas phase, see (Pinto et al. 2014)). This work will be further improved and published.

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