Degradation of amine-based solvents in CO_2 capture process by chemical absorption

F. Vega[1, 2], A. Sanna[2], B. Navarrete[1], M.M. Maroto-Valer[2], V. Cortés[1]

[1]Chemical and Environmental Engineering Department, School of Engineering, University of Seville, C/ Camino de los Descubrimientos s/n 41092 Sevilla, Spain, Phone: 954481397, fvega1@etsi.us.es

[2]Centre for Innovation in Carbon Capture and Storage (CICCS), School of Engineering and Physical Sciences, Heriot-Watt University, EH14 4AS, Edinburgh, UK

ABSTRACT

Carbon dioxide capture and storage (CCS) technologies have been proposed as promising alternative to reduce CO_2 emissions from fossil-fuel power plants with post-combustion capture. Absorption by aqueous amine-solutions is considered the most mature and industrially developed technology for post-combustion capture. One of the most significant issues hindering a large deployment of this technology is potential amine degradation. Amines degrade in presence of O_2, CO_2, NO_x, SO_2 and heat resulting in solvent loss, equipment corrosion and generation of volatile degradation compounds. Two types of degradation have been identified in the literature, namely oxidative and thermal degradation. A review of the amine-based solvents, its main degradation products, the apparatus and analytical methods most widely used, as well as the mechanism proposed and kinetic studies are presented and discussed here. Moreover, amines emissions from CO_2 capture units can react in the atmosphere via photo-oxidation and also via NO_X reactions to give nitrosamines and nitramines, which are potentially harmful to the human health and the environment. A discussion of the recent works on atmospheric degradation of amine solvents is also included in this review.

1. - INTRODUCTION

Global energy demand is expected to increase up to 30% in the next 22 years, with fossil fuels continuing as the primary energy source.[1] Carbon dioxide capture and storage (CCS) technologies have been proposed as promising alternative to reduce CO_2 emissions from fossil-fuel power plants. Post-combustion capture using chemical absorption by aqueous amine-solutions is the most mature and industrially developed technology. The amine-based chemical absorption process has been used for CO_2 and H_2S removal from gas-treating plants for decades.[2] Monoethanolamine (MEA) is considered as a benchmark sorbent due to its high cyclic capacity, significant absorption-stripping kinetic rates at low CO_2 concentration and high water solubility.[2] Some other amine-based absorbents have also been studied, such as diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), N-methyldiethanolamine (MDEA), piperazine (PZ), 2-amino-2-methyl-1-propanol (AMD) and N-(2-aminoethyl)piperazine (AEP).

A typical chemical absorption scheme is shown in Fig.1. A low CO_2 concentration flue gas, typically between 12-15%, is introduced in the absorber in countercurrent with lean absorbent from the stripper at 50 - 55ºC and ambient pressure.[3] As CO_2 is absorbed, rich amine from the absorber bottom is fed into a cross-exchanger with lean amine before it is introduced into the stripper. The stripping temperature varies between 120ºC -150ºC and the operating pressure reaches up to 5 bar. A water saturated CO_2 stream is released from the top and is subsequently ready for transport and storage, while lean amine leaving the stripper is introduced into the absorber.[2,4]

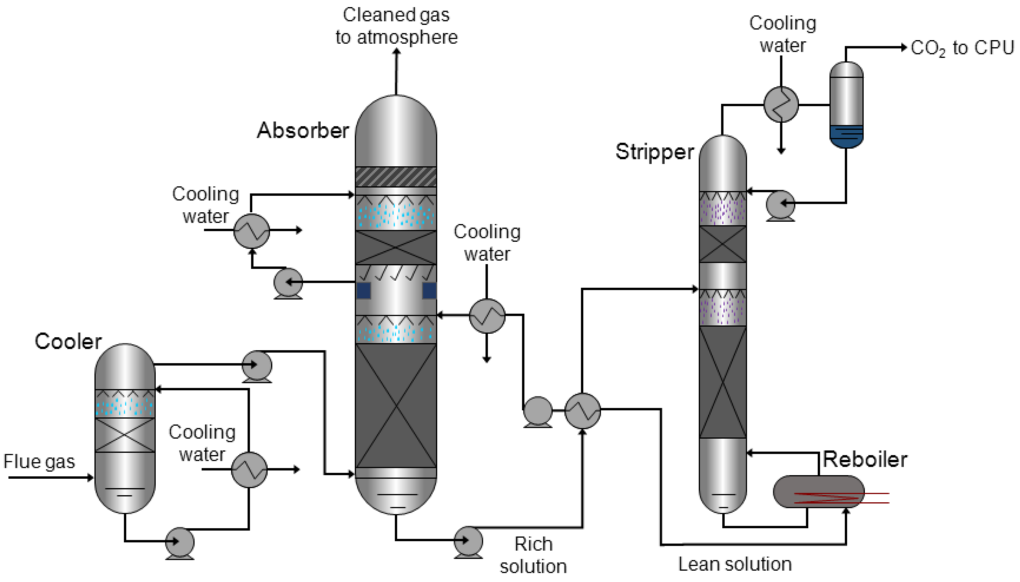

Figure. 1. Diagram of a conventional CO_2 capture process using amine-based chemical absorption [2]

However, the high energy penalty related to amines regeneration and solvent degradation is hindering a large deployment of this technology. Solvent regeneration is a high-intensive energy process due to the stripper operating conditions and solvent used. New solvents and blends have been proposed to reduce the reboiler duty in comparison with MEA. Moreover, the operating costs related to amine degradation have been estimated to be around 10% of the total CO_2 capture cost.[5] Solvent degradation can lead to operational issues, such as fouling, foaming, increase of corrosion rates and environmental issues due to waste disposal and generation of volatile degradation compounds, which have been identified as potentially harmful to the human health and the environment.[6-8] In recent years, the use of more resistant amines, blends and inhibitors has been proposed to reduce the solvent loss and operational cost.[4] CO_2 chemical absorption can be optimized by using more resistant solvents, reducing economical losses (solvent make-up) and the environmental impact of the degradation products. Moreover, CO_2 capture operational costs can be minimized by using higher operating conditions (temperature and pressure) in the stripper, and treating flue gases with low level of SO_2 and NOx, since this would decrease the degradation of the solvent.[4]

Degradation studies have been required to identify potential environmental and operational issues related to amine degradation compounds. Two main types of amine degradation have been identified, namely oxidative and thermal degradation. Oxidative degradation occurs in the presence of O_2 from the flue gas into the absorber and the cross-exchanger. Thermal degradation mainly occurs in the stripper in the presence of CO_2 at temperatures between 100 and 150ºC. Moreover, recent studies have identified that volatile amine and degradation products from cleaned gas at the absorber and stripper top degrade in the atmosphere by photo-oxidation.[8,9] Higher temperature and pressure conditions increase degradation rates.[4] The presence of cations from corrosion products catalyzes the process, speeding up the degradation rates.[10-12] Finally, solvents degrade in the presence of traces of SO_2 and NO_x present in the flue gas.[13-15]

This review summarizes the recent growing body of literature in amine degradation. The development of further advanced analytical methods in the last decade has provided the identification of new degradation products. Therefore, novel degradation mechanisms have been proposed to address the formation of new compounds. Moreover, amine-based solvent degradation studies have provided novel degradation kinetic models for piperazine, N-methyletanolamine or 2-amino-2-methyl-1-propanol. Several studies have analyzed samples taken from long-term operated pilot plants, taking into account both oxidative and thermal degradation during operation,[16-20] whereas other authors have focused on one of the types of degradation at lab scale plants: oxidative,[21-24] thermal,[15,25-27] thermal oxidative,[28,29] atmospheric degradation.[8,30] The effect of NO_x, SO_2, cations and the development of anti-foam products and inhibitors has also been studied.[7,12,14,31] Since solvent degradation rates are slow, the use of cations and higher temperature and pressure conditions are required in order to speed up the degradation process in laboratory tests and minimize experimental time.[4,11]

Recently published reviews have either focused on one of the degradation mechanism, oxidative,[32] thermal[4] or atmospheric degradation,[33] or a combination of thermal and oxidative degradation.[3] A global overview of the entire degradation phenomena is crucial to understand the operating conditions, parameters and configurations more suitable to implement and design post-combustion capture based on CO_2 chemical absorption at industrial scale in mid-term. In this review we are addressing all types of degradation for different amine solvents used in chemical absorption and the apparatus and analytical techniques used in the degradation studies. A critical survey and discussion of all the recent works on this topic is presented, including atmospheric and process-based degradation, studied solvents, main degradation products and mechanisms proposed. Finally, the knowledge gaps and areas of further interest are identified and critically discussed.

2. – OXIDATIVE DEGRADATION

2.1. - Background

Oxidative degradation is caused by presence of oxygen in the gas stream. This type of degradation has become a key issue for the separation of CO_2 from flue gas, where the O_2 concentration varies typically between 3 and 5%. Oxidative degradation occurs mainly in the absorber, at 40-70ºC, and in the rich solvent at the cross-exchanger outlet, at 100-145ºC.[4]

The first studies about amine-based solvent degradation were carried out by the U.S Army during the 1950s and 1960s and were applied to submarine atmosphere purification systems.[23] More than forty amine-based solvents and blends were investigated. The behavior of these compounds under oxidative conditions was studied using chlorine oxide as oxidant. Solvent loss and degradation compounds were determined and several mechanisms were proposed.[34-39] In the following years, other amine degradation products and mechanisms were identified, thanks to the development of new advanced analytical methods and techniques.[40-43]

The most relevant amine-based solvent degradation studies are summarized in Table 1 and the main findings are discussed on the following sections.

2.2. - Apparatus and lab-scale plants

Most of the studies referenced in Table 1 have been carried out using batch and semi-batch reactors at laboratory scale. For semi-batch reactors, low gas flow apparatus has been used.[10,12,44,52,53] The experiments consisted of introducing 100 mL/min of a pre-saturated mixed gases CO_2 (2%)/O_2 (98%) in a 600 mL stirred and jacketed reactor, where solvents were previously added. The temperature was maintained at 55ºC (absorber operating conditions) and the experiments were run at ambient pressure.[10-12,31,44,60] Other works were carried out by Rochelle's group using a high gas flow apparatus, where the gas flow was set between 0.5 to 7.5 L/min. Pre-saturated CO_2(2%)/O_2(15%)/N_2(83%) mixed gases was bubbled into a 1000 mL reactor to increase O_2 mass-transfer.[10,23,52,53] Batch reactors have been used in many degradation studies.[14,16,22,24,28,45,46,48,50,61] Stainless steel or glass vessels were used depending on the operating pressure. The volume of the reactors varied between 100 mL[48] and 600 mL.[24,50] Batch reactors allow a more precise control of the experimental conditions (e.g. pressure), and are more appropriate if only one type of degradation is studied. In general, the experimental procedure was the same for all the cited references. About 60%-70% of the vessel volume was loaded with the solution and the reactor was sealed to ensure any gas-leak. Then, the solution was stirred between 200 and 500 rpm and heated at the desired temperature.[14,24,50] When the temperature was reached, gas with different compositions, from 6% O_2 to pure O_2,[14,22,61] was introduced in the reactor and the pressure was set at the required level, from 2.5 bar O_2 partial pressure[24,50,73] up to 3.7 bar O_2 (20 bar air).[48] Oxygen was sparged into the solution and since a small amount of O_2 was initially dissolved, an extra volume of O_2 was added to compensate for the pressure drop and the pressure loss produced during the sampling process.[22] A close batch reactor, where solvents were pumped continuously in a structured packed column at absorption operating condition, has also been used.[74,75]

New designs have been proposed to study solvent degradation during CO_2 capture by chemical absorption process. For example, a system called Integrated Solvent Degradation Apparatus (ISDA) has been reported to study both oxidative and thermal degradation cycles during CO_2 capture.[29,76] Absorber/stripper configurations have been integrated in a single experimental apparatus in order to observe and identify secondary effects produced by CO_2 capture. The oxidative degradation reactor consists of a 750-mL jacketed and stirred glass vessel. The oxidative section consist of 400-mL vessel where the solution is exposed to a specific gas composition, typically defined as CO_2 (2%)/O_2 (98%). The bottom of the oxidative reactor, a 330-mL vessel, simulates the absorber sump. Rich amine is pumped from the bottom section to a single-pass tube-in-tube cross-exchanger, where is heated at the thermal reactor temperature, typically 120ºC. The effect of dissolved and entrained O_2 in the degradation process is studied in this exchanger. Finally, the thermal section consists of a 1200 mL stainless steel tube-in-tube heat exchanger, operating a 120ºC and 5 bar.

High Temperature Cycling System (HTCS) has been used to analyze oxidative degradation cycles at higher temperature by ammonia quantification in the exhaust gas.

HTCS consists of an oxidative reactor operating at 35-45ºC where amine solvents were contacted with 0.5% CO_2 in air. The solution was pumped from the oxidative reactor to a plate-and-frame cross-exchanger following by a plate-and-frame trim heater where solvents were exposed to higher pressure (20 bar) and temperature (150ºC).[76]

Oxidative degradation is a very slow process, where a typical laboratory test lasts between 4 and 8 weeks.[10,25,29,44,50] In some cases, the experiments have been prolonged for 30 weeks.[44] Extreme experimental conditions are required to obtain results in a relative short-term, which means less than 2 weeks.[46,48] Pressures above 1 bar,[14,61,73] high O_2 concentration in the gas,[10,22,44], high temperature[50,61,77] and addition of Fe, V, Cu, Cr/Ni cations[11,12,23,31] are used to speed up the degradation rates without changes in the degradation products and their formation mechanism. The same degradation products have been identified at pilot plant test running typical CO_2 chemical absorption-stripping conditions.

2.3. - Analytical Methods

The analytical methods and equipment used to identify amine degradation products are summarized in this section.

2.3.1. - Gas Chromatography (GC)

GC is employed to separate the degradation products from the solvents liquid samplings through the use of polar and non-polar columns.[16,24,48,60] GC is combined with different detectors to identify and quantify the main degradation products and the amine remaining in the solution, with the most widely used Flame Ionization Detector (FID).[60,61] GC combined with Atomic emission detection (AED) has been used to determine the elemental ratios of carbon, hydrogen, nitrogen and oxygen.[47] Mass Spectrometry (MS) and Fourier Transform Infrared Spectroscopy (FTIR) have also been used in amine degradation studies.[16,24,28,45,47,48,50,61,74,75]

GC-MS is the technique chosen for degradation product identification and quantification of new solvents.[16,24,28,29,45,61,78]

2.3.2. - Ion Chromatography (IC)

IC has been used to study amine degradation compounds. Anion chromatography was used to identify heat stable salts (HSS), such as carboxylates, nitrate and nitrite. It is the most common method used to determine negatively charged compounds.[10,11,23,31,44,45,52,53,60,61,74,76] Cation chromatography was used to quantify the amine loss in the solution.[11,23,24,44,45,52,53,61,76] However, this technique is not able to detect amine in samples with degradation rates less than 0.3 mM/h.[10] This technique was also used to determine the positively charged degradation products and species exhibiting amine functionality (alkalinity).[10,29,44]

2.3.3. - Liquid Chromatography (LC)

LC combined with electrochemical detection (ED) has been used for amino acid detection and combined with MS, to quantify amine concentration remained in the solution.[16,28,29,74,75,76,78] It has been reported that LC-MS showed is motre accurate in the determination of amine concentration (2%) than GC-MS. For this reason, lately, LC-MS has been adopted by other authors for amine loss determinations.[674,75,78]

2.3.4. - High Performance Liquid Chromatography (HPLC)

HPLC has been widely applied in amine degradation studies. Amine concentration in the solution was quantified using HPLC combined with MS.[29] or with refractive index detection (RID).[14,22,46,73] Supap et al. compared different analytical methods for amine degradation studies, such as GC-MS, HPLC-RID and CE-DAD (capillary electrophoresis-diode array detection), confirming HPLC-RID as the best analytical method to carry out simultaneous analysis of MEA concentration and degradation products.[22] HPLC-MS was used for the determination of N-(2-hydroxyethyl) formamide (HEF) and N-(2-hydroxyethyl) imidazole (HEI), as main degradation products of MEA (Table 2). Other combination such as HPLC with evaporative light scattering detection (ELSD) and HPLC with electrochemical detection (ED) were used for the identification of non-anionic degradation compounds and the determination of the total glycine in the solution, respectively.[10,11,31] A method for detecting aldehydes is reported by Nielsen et al.,[79] where 2,4-dinitrophenylhydrazine (DNPH) reacted selectively with aldehydes to produce aldehyde-DNPH. This complex was separated with reverse-phase chromatography and detected by UV which was used to HEF determinations.[52,53] HPLC was also recommended for the evaluation of all the material balances, because it did not alter the chemistry of samples during the analysis.[10]

Other analytical methods have been used for more specific determinations. FTIR was used to analyze the gas samples and to identify the amine volatile compounds;[10-12,23,31,52,53,60,61] Ultraviolet-Vis Spectrophotometry (UV-Vis) was used for 2,4-lutidine identification in AMP studies.[12,24,60] Finally, Nuclear Magnetic Resonance (NMR) was used to identify degradation compounds.[48.60]

2.4. - Degradation products and formation mechanism

The main oxidative degradation products identified in the literature are listed by increasing molecular weight in Table 2 and their formation mechanisms are discussed in the following sections.

Two main mechanisms, namely electron abstraction and hydrogen abstraction, have been proposed as formation pathways of the degradation compounds summarized in Table 2. According to several authors,[32,35-39] the electron abstraction mechanism is based on the extraction of an electron from the nitrogen in the amine group by a reactive free radical (most likely a metal ion from corrosion phenomenon), which is considered the rate-limiting step.[11,12] The radical formed from the amine, aminium cation radical, reacts to produce imine radical, which then loses a free radical to produce imine.

The second mechanism is hydrogen abstraction that consists of an amine cyclic formation by hydrogen bonds, in which amine radical is transferred internally through the ring structure formed, resulting in ammonia, aldehydes and aldehydes radicals as main degradation products.[11,12,32,43] The hydrogen is likely extracted from the α-carbon.[23,37] Bedell[21,64] proposed hydroxyl radical and organo-peroxy radical as potential pathways to produce the hydrogen abstraction and form the organic radical (Figure 2).

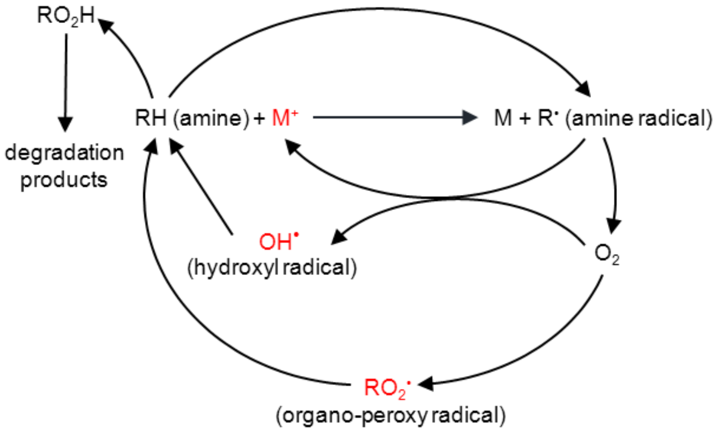

Figure. 2. Potential precursors for hydrogen abstraction adapted from Bedell.[21,64]

Carboxylic acids are the most common degradation compounds in amine-based solvents, as shown in Table 2. Aldehydes are auto-oxidized in the presence of oxygen to form carboxylic acids by peroxy acid.[11,80] Carboxylic acids can be dissociated in pH-basic solution to form heat stable salts (HSS) with the amines.

More than forty degradation compounds have been identified with unknown pathways .[3] Many works have proposed specific mechanisms to explain some degradation product formation. Lepaumier et al.[48] studied twelve ethanolamines and ethylendiamines and found the main reactions that lead to their degradation compounds. For secondary and tertiary ethanolamines, the proposed reactions were demethylation, methylation, dealkylation, addition, ring closure and hydroxethyl substitution. For the primary ethanolamines, dealkylation, addition and piperazinones formation were the most common reactions. In the case of ethylenediamines, piperazinones were the main degradation product, except for TMEDA.

According to Lepaumier et al.,[48] tertiary amines are more stable than MEA due to steric hindrance, which prevents dealkylation, and due to reduction of volatile compound formation. The latter is related to the formation of one radical on the R-position of the nitrogen atom. It is important to notice that steric hindrance in AMP does not inhibit alkylation reaction, since oxazolidone was observed as degradation product.[45]

MEA is the solvent which has received the most extensive investigations because it is the most widely used as CO_2 capture solvent. MEA degrades by electron abstraction mechanism to form aldehyde compounds and ammonia from the imine. Two main routes have been identified (Figure 3): 1) hydrolysis[35] and 2) amino-peroxide radical route.[82,83]

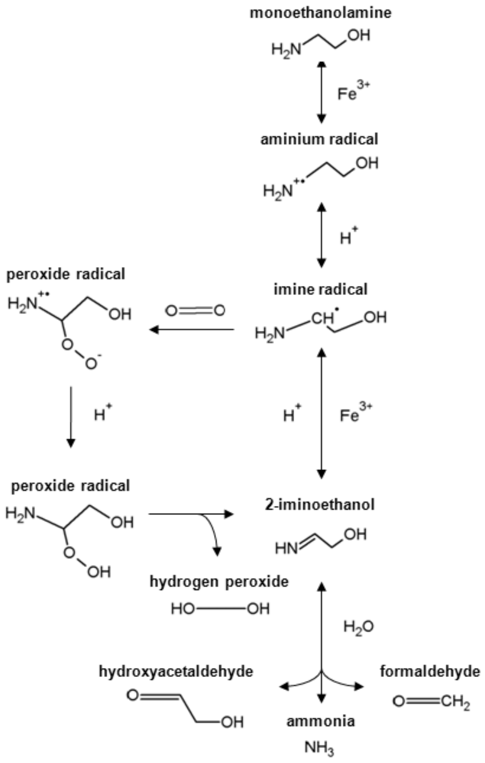

Figure. 3. Routes for the MEA degradation pathways by electron abstraction adapted from Chi and Rochelle.[82,83]

Strazisar et al.[47] and Rooney et al.[51] have proposed two different pathways to describe carboxylic acids formation by hydrogen abstraction, in which 2-hydroxyethylamino-N-hydroxyethyl acetamide and hydroxyethyl-formamide are identified as the main produced organic acid when MEA reacts with carboxylic acids and respective aldehydes. Both pathways lead to the same degradation products.

Specific mechanisms to describe the formation of MEA degradation products have been proposed (Table 2). Formic and acetic acids formation mechanisms have been identified by Supap et al.[84] OZD is produced by carbamate ring closure reaction.[16] MEA reacts with acid formic to form HEF.[10,16] HEPO is formed by dehydration of HEHEAA[47] and HEI mechanism is proposed by Sexton et al.[10] and Arduengo et al.[85] Other authors have leaded efforts to other solvents, such as MMEA[16] and AMP.[24,45]

2.5. – O_2 mass-transfer considerations

Based on mass transfer with chemical reaction theory, oxidative degradation of amine solvents with O_2 must take into account two types of interactions. First, O_2 must reach liquid bulk by dissolution into amine solution and then reacts with solvents to be degraded. Therefore, oxidative degradation rate depends on both O_2 absorption rates from flue gas into aqueous amine solutions (mass transfer), as well as kinetic behavior of the O_2-solvent reactions.[80]

Goff and Rochelle studied NH_3 formation rates during oxidative degradation experiments of MEA to evaluate O_2 mass transfer effects. NH_3 formation rates were increased by faster stirring the solution and a linear dependence of O_2 concentration was observed.[10,80] Goff concluded that MEA degradation rates are O_2 mass transfer limited under certain conditions. Therefore, O_2 mass transfer plays an important role in oxidative degradation. Presence of cations such as Fe, Mn and Cu in moderate concentrations lead to mass transfer controlled regime whereas, a reaction rates and kinetic controlled degradation was the result of presence of low concentrations and inhibitors. Mn showed higher oxidative rates in MEA degradation studies than Cu.[52,53] MEA concentration showed the same effect: mass transfer controlled at low concentrations and kinetic controlled at high concentration. Values between 2m and 7m provided intermediate mass transfer-kinetic effects.[12,80] Sexton et al.[10,11] showed that V cations produced opposite effects compared to that observed in Fe and Cu experiments. Sexton also concluded that products which increase ionic strength of the solution and lower CO_2 loading of the solvent, decrease O_2 mass transfer and thus result in lower degradation rates.[11] Voice et al.[52,53] indicated that the presence of CO_2 increase NH_3 formation until CO_2 loading equal to 0.3.

Other amines showed similar behavior than MEA. O_2 mass transfer limitations were observed in presence of high concentration of cations for PZ aqueous solutions[60] and studies conducted by Wang[45] indicated that AMP is partially controlled by O_2 mass transfer. CO_2 loading and O_2 concentration were considered the key parameters to determine oxidative degradation rates for this solvent.[45]

Low degradation rates obtained from industrial-scale plants suggests oxidative degradation in real plants is probably controlled by O_2 absorption rate in the liquid solution[80] and it occurs in the CO_2 absorption section.[4]

2.5. - Kinetic studies

According to Goff and Rochelle[80], previous studies on kinetic of degradation process reported lower degradation rates and apparent mass transfer coefficient. Results showed O_2 absorptions rates instead of kinetic rates due to O_2 mass transfer effects were not considered. Later studies on kinetics were carried out at higher stirring and O_2 concentration to avoid O_2 mass transfer interactions. In those cases, kinetic phenomena were evaluated appropriately during degradation experiments.

A few kinetic models for describing oxidative degradation process can be found in the literature and are presented in Table 3. The predictions obtained fit fairly well with the experimental results, showing 25% of average absolute deviation in some cases, indicating that these models must be improved in order to increase the prediction accuracy on degradation rates and product speciation.[14] Bedell[21,64] summarized the constant rates for the amine reactions with radicals. The highest rate constant was shown by hydroxyl radical (OH•), between 10^8 – 10^{11} L/mols. Other radicals, such as HO_2 and and $O_2^{\bullet -}$ showed rate constants lower than 100 L/mols. According to Sexton et al.,[11] MEA degradation rates below 7 mM/h indicate kinetic-controlled reactions, whereas higher values represent O_2-mass transfer as the rate-limiting step.

2.6. - Inhibitors

Inhibitors have been proposed to reduce oxidative solvent degradation, performing as oxidative species scavengers and chelating agents for radicals. Sulphite and thiosulphate have been used as OH radical scavengers.[86] Ethylenediaminetetraacetic acid (EDTA) is the most used inhibitor, being an excellent chelator for Cu and Fe cations, avoiding their exposure to O_2 and subsequent oxidative degradation of the solvent.[11,12,23,31,46] A potential new inhibitor, identified as inhibitor A in the literature, has been developed which can be used with MEA, PZ or MEA/PZ blends in CO_2 absorption conditions and at temperatures below 90ºC.[11,29,31,44] Voice et al.[23] verified a reduction in NH_3 formation in MEA solutions through a change in the formation mechanism in presence the inhibitor A. Other inhibitors have been used tested, such as sodium sulphite, formaldehyde, formate[31], hydroquinone, manganese, ascorbic acid, stable salts[12], and radical scavengers as p-benzoquinone and 2,2,6,6-tetramethyl -4-piperidinol.[87]

Supap et al.[46] optimized the operation of four inhibitors and their blends in MEA solutions operating with flue gas at high levels of SO_2 (up to 196 ppm) and 120ºC. Sodium sulphite was used as an O_2/SO_2 scavenger, whereas potassium sodium tartrate tetrahydrate, EDTA and hydroxylamine were used as radical scavengers. This research identified the concentration of the inhibitor as key parameter for its efficacy. Table 4 shows the averaged degradation rate of MEA for each inhibitor tested. As can be seen, inhibitor concentrations above the optimal value increase the degradation rate and made inhibitors ineffective (Table 4). Sodium sulphite 0.05 M and potassium sodium tartrate tetrahydrate blend 0.01 M were identified as the most effective inhibitor either in the presence or absence of CO_2. EDTA 0.0025 M and hydroxylamine 0.025 M showed were less effective as oxidative degradation inhibitors, showing higher averaged degradation rates.

Several authors noticed operational issues related to the use of inhibitors either for reduction of corrosion or degradation. Corrosion inhibitors as $NaVO_3$ are potential degradation catalyst.[73] EDTA showed degradation issues, promoted Fe formation and acted as catalyst for activating intermediate peroxide and hydroxyl radical formations.[21]

3. – THERMAL DEGRADATION

3.1. - Background

Thermal degradation occurs in the stripping column at the operating temperature, typically 120ºC, being catalyzed by the presence of CO_2.[2,88] A summary of the main thermal degradation studies of amine-based solvents is shown in Table 1. Degradation products decrease the cyclic capacity of the amine-based sorbent as well as increase the viscosity and the foaming formation. Corrosion issues also have been associated with these compounds.[62,77] First studies of thermal degradation were carried out by Polderman et al.,[89,] where MEA degraded in the presence of CO_2. HEED was identified as the main degradation product and a mechanism was proposed to produce this compound from carbamate ion. Other published works focused on DEA in which BHEP,[90] THEED,[91] TEA[92,93] and a high molecular weight polymer[94] were identified as main degradation products and an adapted mechanism from MEA was proposed. DIPA,[95] DGA[96,97] and MDEA[98,99] were also studied.

Temperature has been reported as key parameter to control the extent of the degradation process in chemical absorption. Operation at low temperature during solvent regeneration can lead to further reductions of the degradation rate and minimization of solvent make-up.[4,90,100] However, the specific energy requirement related to the solvent regeneration in the stripper is minimized at higher temperature, typically between 120-

150ºC.[4] Therefore, a careful balance between solvent make-up and overall solvent regeneration costs must be conducted to optimize CO_2 stripping process.[4] CO_2 loading in the lean amine and the presence of CO_2 in the gas phase have been identified to influence thermal degradation and they must be taken into account to optimize the CO_2 capture process by chemical absorption.[88] Experiments using MEA oxidative degraded has showed lower thermal degradation rates than MEA make-up due to decomposition of the main oxidative degradation compounds at higher temperature.[54]

3.2. - Apparatus and lab-scale plants

Thermal degradation studies have been carried out in batch operation mode. Two different experimental procedures have been reported. Batch reactors and autoclaves were filled with amine solution, being purged with either N_2 or CO_2 to strip the dissolved O_2. Afterwards, the solution was heated at the desire temperature and the pressure was set up through a blanket of either N_2, to study only temperature effects on thermal degradation,[16,24,28,68,69] or on CO_2 .[48,69,70,77] Other mixed gases such as 75% molar CO_2 concentration have also been used.[77] Reactor volumes varied between 100 and 1000 mL,[45,48] being 600 mL the most commonly used.[68-70,72] Other thermal degradation experiments have been carried out using a large amount of small cylindrical vessels with a volume between 4 and 10 mL,[15,16,25,27,28,44,54-57,65,66] The amine solution was degassed before being introduced in the vessels. Then, the multiple vessels were placed in convection ovens and heated at the desired temperature and then withdrawn at regular intervals to be analyzed. The number of vessels used depended on the regular intervals assumed and the total time required for each experiment.[16,25,27,,28,44,54-57,65,66,101] Thermal degradation experiments in the presence of O_2 have been carried out using an Integrated Solvent Degradation Apparatus (ISDA).[29] Solvents were alternatively exposed to oxidative and thermal degradation with O_2 entrainment into the crossexchange and the stripper. The thermal reactor consisted of a 1.2 L stainless steel tube-in-tube heat exchanger. Stainless steel has been widely used in thermal degradation reactors. However, several authors have worked with glass vessels to avoid the presence of cations from the steel corrosion during the experiments.[28,45]

Thermal degradation experiments were carried out at temperatures from 100ºC[24,25,44,65,66,69] up to 200ºC[66,69], with 135ºC and 140ºC as the most common temperature used.[16,24,28,48,77] High pressure has been used to speed up the degradation process, reaching up to 137 bar,[71] typically close to 20 bar.[69,102]

3.3. - Analytical Methods

A literature review of the analytical methods used in thermal degradation studies is summarized here.

3.3.1. - Gas Chromatography (GC)

GC-MS is the most used analytical technique in thermal degradation studies, being applied to identify and quantify degradation compounds,[16,26,28,68-70,77,101-103] non-ionic degradation compounds[45] and to determinate the remaining solvent concentration in the solution.[48,101] Electron Impact (EI) and Chemical Ionization (CI) using methane as an agent gas were used to carry out GC-MS analysis.[45,48,69,70] Other techniques such as thermal conductivity detection (TCD) and flame ionization detection (FID) have been used in thermal degradation.[72] In several oxidative degradation studies, GC-MS was the preferred method to identify and quantify degradation products[16,26,28,67,101] and to be applied to new solvents degradation studies[45,77] due to its comprehensive compounds libraries.[78]

3.3.2. - Ion Chromatography (IC)

IC has been used to determine ionic species.[15,25,54-56,64] For oxidative degradation, anion chromatography was used to identify the heat stable salts (HSS)[103] and anionic degradation species,[27,44,65] while cation chromatography was used to quantify the amine loss in the solution.[25,27,44,45,55,56,65,66,103] This technique has also been used to determine the positive charged degradation products and species exhibiting amine functionality (alkalinity).[25,27,44,55,56,65,66,103]

3.3.3. - Liquid Chromatography (LC)

LC combined with MS is cited as an optimal technique to determine amine concentration.[16,26,28,54,67] LC combined with ED has been used to quantify the amine acids formed during thermal degradation.[103] Despite many authors used GC-MS to determine amine concentration, both LC and IC method showed less uncertainty and they were preferred to quantify amine losses and degradation product concentrations.[16,25-28,45,67] Several references showed that the uncertainty varied from 1% for IC methods to 10% for GC methods.[45]

3.3.4. - High Performance Liquid Chromatography (HPLC)

HPLC combined with both MS and ELSD has been used to determine amine degradation compounds.[25,64,103] In particular, HPLC-ELSD has been applied in MEA-urea and HEIA determinations.[25,64] HPLC was preferred to identify new degradation compounds instead of typical GC-MS method.

3.3.5. - Other methods

Total Inorganic Carbon (TIC) described by Hillard et al.[104] was used to determine the CO_2 loading in the amine solution, defined as mole CO_2 per mol amine.[15,27,44,65] Titration method described by Mámun et al.[105] was also used. Wang[45] instead employed Total Organic Carbon (TOC).[101] Finally, high resolution mass spectrometry technique (FT-ICR/MS) with electrospray ionization (ESI) has been used to identify the highest molecular weight degradation compounds.[48]

3.4. - Degradation products and formation mechanism

Table 5 summarizes the main thermal degradation products identified in the literature by increasing molecular weight.

Thermal degradation studies without the presence of CO_2 have resulted in no measurable amine loss, showing values below 1.7% and extremely low degradation rates.[25,45,48] Many authors have focused on thermal degradation studies in presence of CO_2 in which the prevalent formation mechanism related to ethanolamines is carbamate polymerization. Therefore, presence of CO_2 is crucial to degrade amines by thermal mechanisms.[4,15,25,45,66,102] A general pathway for ethanolamine degradation is shown in Fig. 4:

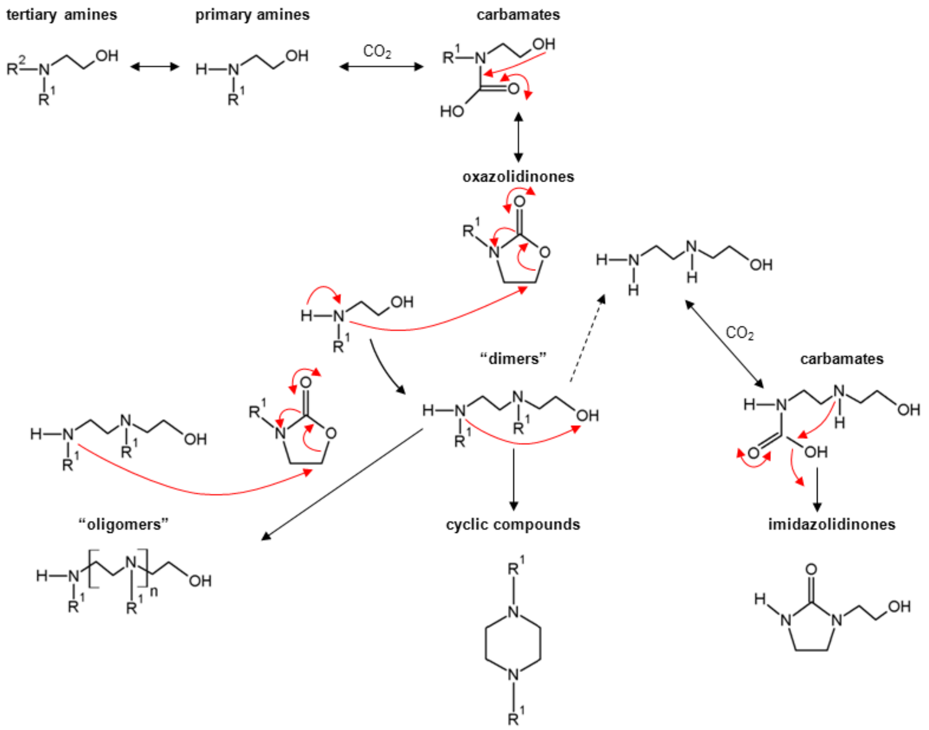

Figure. 4. General pathways scheme of thermal degradation in ethanolamines adapted from Lepaumier et al.[102]

The first step is carbamate formation, where primary and secondary ethanolamines react with CO_2 to form carbamate. Under stripping temperature conditions, carbamate ring closure reaction occurs and oxazolidinones are formed as a degradation product. This compound is highly reactive and leads to dimers of the previous amines by oxazolidinone ring opening, reacting with amines.[48] Dimers can lead to further heavy weight compounds (oligomers). In particular, MEA degrades in OZD from MEA carbamate by a cyclic reaction. OZD can react with another molecule of MEA to give imidazolidones such as HEEDA, HEIA, urea derivates and polymerization products.[4,15,16,25,66] HEEDA has been found as an intermediate compound to form HEIA.[66] DEA[63,68,69] and MMEA[28] also degrade following the same mechanism. Temperature, CO_2 loading and amine concentration have been identified as the most important parameters to affect the degradation rate.[66]

It is known that tertiary amines do not form carbamate from CO_2 reactions. In this case, CO_2 is absorbed by carbonate-bicarbonate equilibrium. Firstly, tertiary amines are involved in demethylation/methylation reactions that lead to either primary or secondary amines, as shown in Fig. 4.[102] These reactions are catalyzed either by CO_2 or acid presence.[4] Elimination reactions of tertiary amines can lead to more secondary amines, being further degraded by carbamate polymerization. For this reason, MDEA can degrade at 119-129°C.[4]

An identical mechanism has been used to explain the thermal degradation of sterically hindrance amines, such as AMP. DMOZD is formed from ring closure AMP carbamate. DMOZD is less reactive than OZD, as main MEA thermal degradation product, due to the steric hindrance and slow down thermal degradation in comparison with MEA. DMOZD can react following the same pathways explained before to form addition products such as AMPAMP by ring opening, followed by DBHTMI formation from AMP ring closure reaction.[45]

Ethylenediamines follow similar degradation pathways to ethanolamines (Fig.5). The main difference lies in the imidazolidinones formation instead of oxazolidinone, being more stables and will be accumulated in the solution.[48] Elimination mechanism by either amines or neighboring group participation has been identified to be the most common way to produce intermolecular nucleophilic substitutions, giving polymeric degradation products such as dimer and trimer species from ethylenediamines.[102]

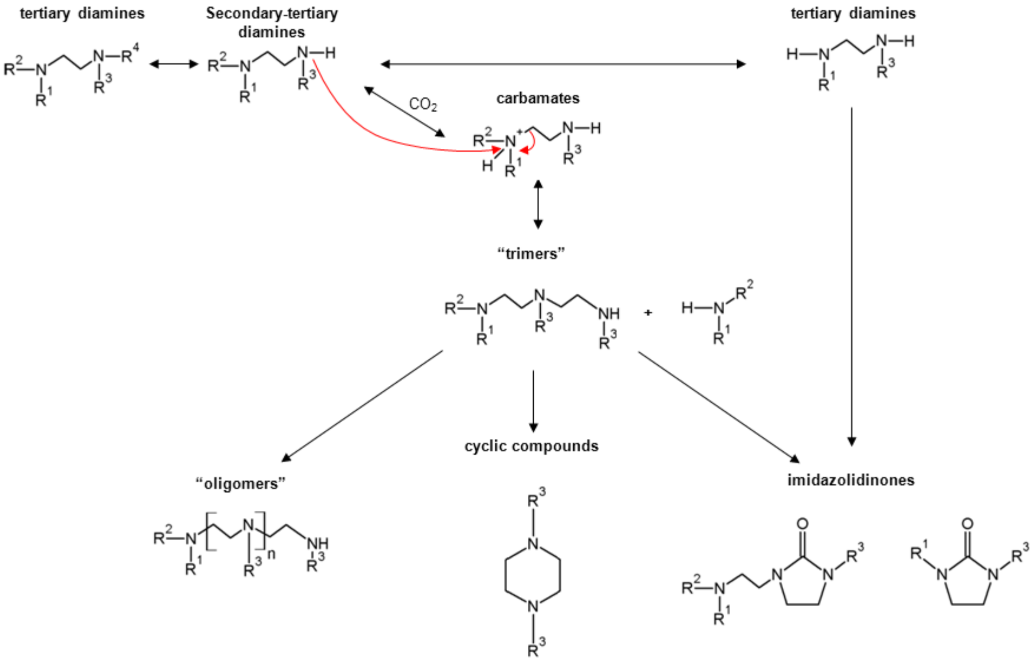

Figure. 5. General pathways scheme of thermal degradation in ethylenediamines adapted from Lepaumier et al.[102]

In the case of PZ, secondary S_N2 substitution has been proposed as the main degradation mechanism as PZ and its degradation products are considered strong nucleophilic compounds.[4,15,65] S_N2 reactions are based on that protonated PZ is attacked at the α-carbon by PZ to form AEAEPZ following this mechanism. AEAEPZ can react with CO_2 to give urea derivate products. AEAEPZ, PZ and urea derivate products can lead to further degradation by PZ nucleophilic attacks, producing AEP, PEP and EDA. These products react by elimination reactions to produce further degradation compounds. Urea can be produced by EDA carbamate ring closure. Finally, formate have been identified as a degradation products in PZ studies and its formation mechanism has been unknown yet.[65] PZ degrade in higher rate in MEA/PZ blends due to the fast reaction with OZD (main MEA degradation compound) to give AEP.[25] In

PZ/AEP blends, the presence of both compounds has no effect on the PZ degradation rates but AEP degrades in lower levels than concentrated AEP. Competition of PZ for H^+ produces less protonated AEP which is a precursor of AEP degradation compounds and the presence of PZ can inhibit AEP degradation.[57] Recent studies of PZ/diamines blends have shown that the presence of diamines has no effects on PZ degradation rates.[55,56]

Other mechanism have been proposed to analyzed amine degradation in the presence of another compounds as CS_2[68] and acidic gases such as Na_2SO_3, SO_2, H_2SO_4, and HNO_3.[15]

3.5. - Kinetic studies

The kinetic models found in the literature consist of first order rate law based on Arrhenius law. A summary of the most relevant models is presented in Table 6.

A kinetic model for MDEA thermal degradation was developed by Chakma and Meisen.[69] The model took into account thirteen equations including the most relevant degradation products. The apparently first order constants showed a slight deviation from linear behavior at higher temperature. The model was in good agreement with the experimental results, being the predictions of BHEP and EG not as good as the rest of degradation compounds. Similarly, Davis[25] developed a kinetic model to predict MEA degradation. Six equations were used in this model, which were in agreement with the experimental results. Several models have been proposed for other amines, such as PZ and AMP based on a pseudo-first order model.[44,45] This model has been applied to evaluate apparent kinetic constant of PZ in PZ/AEP[57] and PZ/diamines blends.[55,56] For AMP, it is not clear if the degradation mechanism is first or second order.Wang[45] reported the rate constants from several works and the results showed higher AMP rate constants than MDEA rates. Moreover, the results highlighted that AMP and PZ have higher resistance to thermal degradation (up to seven times) in comparison with MEA.

4. – NO_x RECTIONS AND ATMOSPHERIC DEGRADATION. NITROSAMINES AND NITRAMINES GENERATION

4.1. - Background

Amine emissions are one of the main concerns associated with the integration of CO_2 capture by chemical absorption process in fossil-fuel power plants. It is known that certain amine-sorbents and degradation compounds can be present in flue gas emissions from absorption and stripping columns gas outlet due to the high volatility of these compounds.[106-108] Absorbers using MEA release up to 0.8 and 0.03 kg MEA per tonne CO_2 captured in the gas exhaust without and with wash-water treatment, respectively.[109] Amines and degraded compounds react under atmospheric conditions by photo-oxidation to form several compounds called nitrosamines, nitramines, nitramides and amides, which have been identified as carcinogenic and highly hazardous for human health and the environment.[9,13,110-113] Those compounds can also be produced by NO_x-derivate reactions with amines in the absorber.[19,114] All amines are potential nitrosamine precursors.[3] However, primary amines produce unstable nitrosamines and they are considered minor precursors for nitrosamines formation. Nitrosamines are formed from reactions between NO compounds with secondary amines or degradation products from tertiary amines. Avoiding primary amines reactions to form secondary amines is required to reduce nitrosamine formation from primary amines. Both pathways have been summarized in this paper.

Several alternatives have been proposed to mitigate amine and derivates emissions from CO_2 chemical absorption units. Washing treatment with both water and acid aqueous solutions and UV radiation are the most common techniques. They can reduce those emissions up to 90%. Recent studies carried out by Fine et al.[115-117] and Knuutila et al.[118] showed that thermal decomposition of nitro-compounds is a promising technique to reduce nitrosamines and nitramines levels in the exhaust gas. A pseudo-first order was proposed to determine the decomposition rate of the main nitro-compounds produced from PZ and MEA.[115-117]

Many works about nitrosamine and nitramine chemistry reactions have been developed in the last decades[30,119-121] but studies on the generation of those compounds in chemical absorption units for CO_2 capture are relatively scarce. MEA is the most studied sorbent[9,13,122] and AMP, MDEA, PZ and aliphatic amines are also theoretically studied.[123]

4.2. - Apparatus and lab-scale plants

Specific equipment has been designed to analyze nitrosamine and nitramine reactions from amine solvents under typical post-combustion capture conditions. The solvent degradation rig (SDR) was described as a continuous lab-scale plant consisting of an absorption column, operated at 25 – 80ºC, and a stripping column, operated at 110 – 150ºC. CO_2 loading was maintained at 0.45 and 0.2 mol CO_2 per mol MEA for rich amine and lean amine, respectively, although not being constant along the cycle. A mixed gas with N_2, O_2, CO_2, H_2O and NO_x was used. NO_x concentration varied between 5 – 50 ppmv, whereas, O_2 concentration was either 12 or 18%. Four operation modes were set up for 14 weeks with temperature, O_2 and NO_x concentration as variables. Liquid and gas samples were analyzed in several points along the SDR in order to determine the amine loss and the nitro-compounds production.[122] Other facilities, such as Amino^{TX}, were based on one absorption column combined with a high temperature bench scale autoclave where further thermal degradation was produced. The absorber was a random packed column where typical flue gases with different O_2 and NO_x

composition were used. NO_x was introduced in a range of 5 – 45 ppmv, with a NO/NO_2 ratio of 9/1, and O_2 varied between 0 – 14%. The absorber and stripper temperature were 40ºC and 120ºC, respectively. The experiment was run for 100 hours in the absorber, plus 24 hours in the high temperature autoclave. In this case, only O_2 and NO_x were varied.[13] Batch reactors[115-117] and cylindrical steel tubes[114] were used to evaluate thermal degradation nitro-compounds at 120-150ºC and stripper pressure

The European photochemical reactor (EUPHORE) has been design to investigate the photo-oxidation of MEA at atmospheric conditions in the presence of NO_X. This equipment consists of two hemispherical outdoor reactors built in PTEF.[9] In this study, NO_x concentration varied between 0.005 and 1.5 ppmv.

4.3. - Analytical methods

There are only a few studies where nitrosamines and nitramines compounds have been analyzed. Liquid samplers were analyzed by LC-MS using triple quadrupole detector[60,122] to determine amine concentration and nitrosamine production. GC combined with Nitrogen Chemiluminescence Detection (NCD) is instead used to identify total nitrosamine concentration.[122] Fine et al.[115-117] and Goldman et al.[114] used reverse-phase HPLC-UV detector to determinate nitrite and nitrosamines. Other analytical techniques such as IC, GC-MS and LC-MS are used to identify nitrosamine and nitramine compounds.[13] On-line method for amine volatile emissions at pilot plants has been developed by Fujita et al.[124] In atmospheric photo-oxidation studies, nitrosamines and nitramines are analysed off-line by using different adsorbent tubes to collect samples. The analyses were performed using HPLC combined with either high resolution mass spectrometry (HRMS) using $^{13}C_2$–labeled N-nitrosodimethylamine and D10-labeled N-nitrosodiethylamine as internal standards or diode array detector (DAD-

UV).[7,9,125] Gas samples are analyzed using FT-IR to determine volatile compounds such as MEA, ammonia, formamide and nitro-compound derivates.[9,13,125]

4.4. - Degradation products

The main degradation products referenced in the literature have been summarized in Table 7. Two types of degradation phenomena are considered, nitro-compounds formation during CO_2 capture operation and MEA photo-oxidation in atmospheric conditions under different NO_x concentrations. NO_x reacts directly with amines given nitro-compounds such as nitrosdiethanolamine, nitrosomorpholine and nitrosodimethylamine in CO_2 capture process,[13] while OH radicals attacks MEA by α-carbon giving more than 80% of the degradation compound as formamide and formaldehyde.[9] Amides and polyacrylonitrile-like compounds are the main degradation product theoretically proposed from MDEA.[122] In PZ case, the main route is considered OH radicals attacks to form amines, nitrosamines and nitramines derived from PZ.[122]

4.5. – Mechanisms and kinetic studies

4.5.1.- Amine degradation in presence of NO-compounds

Primary amines react with nitrosating agents to produce unstable nitrosamines. Therefore, nitrosamines are given from secondary amines by diazonium cation. A mechanism for nitrosamines during CO_2 capture process was proposed by Fostas et al.[13] DEA reacts in presence of NO to from nitrosamine as it is shown in Fig. 6. Other nitrosamines such as NDMA and NMOR are produced through DMA and MOR reactions with NO. NPZ was expected to be formed but it was not detected.[13]

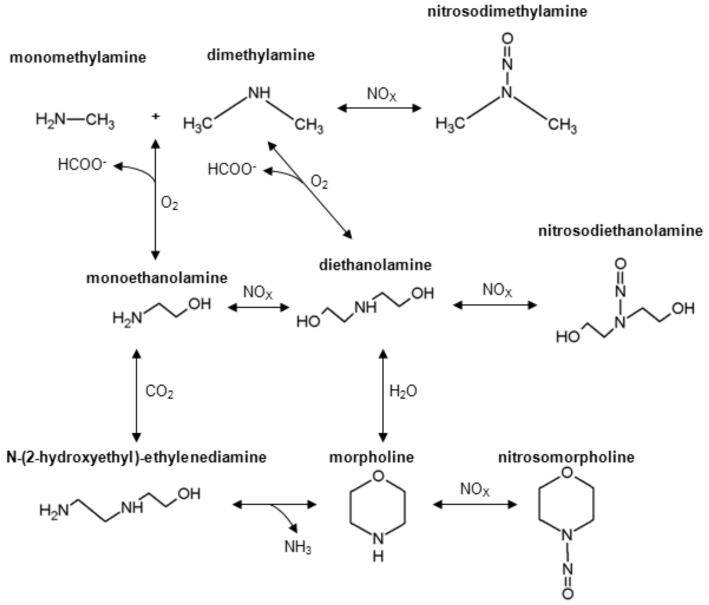

Figure. 6. Mechanism proposed for nitrosamine formation from MEA in CO_2 capture process adapted from Fostas et al.[13]

Goldman et al studied N-nitrosopiperazine formation from PZ by NO_2^- reactions. An acid-base equilibrium followed by a nucleophilic attack, carbonyl group reformation and N-nitrosamine bond formation were proposed as mechanism. Reaction follows an Arhenius model with a first order in nitrite, piperazine carbamate and hydronium ion concentration. Activation energy was 84 kJ/mol and constant rate was $8.5 * 10^3$ dm^6/mol^2s.[114]

4.5.2.- Atmospheric degradation

The main degradation products through atmospheric photo-oxidation are explained by H abstraction by OH radical.[9,110,111,122] Degradation products from MEA such as formamide, formaldehyde, acetylenediol, methanimine and 2-oxo acetamide are formed by $-CH_2$ group attack. H extraction from $–CH_2OH$ gives 2-hydroxy acetamide and formamide and rarely produces nitrosamines and nitramines.[9,122] 2-imine ethanol is produced via $–NH_2$ group attack. Nitramines react with OH radicals to form N-nitramine hydroxyl acetamide.

H extractions from $-CH_2$ and $–CH_3$ in AMP solvent lead to acetone, acetamide and hydroxyacetone. Nitramines will be formed by $–NH_2$ group attacks. Amides and polyacrylonitrile-like compounds are produced by $-CH_2OH$ and $-CH_3$ group attack in MDEA and nitrosamines are formed from N-radicals produced by thermal decomposition reactions. OH radicals cause also main degradation products from PZ.[122]

Nitrosamines undergo further photo-oxidation under atmospheric conditions. Lifetime of those compound in the atmosphere is less than 30 minutes and thus direct emissions from CO_2 capture units are considered the main source of nitrosamines. Nitramines are mainly produced under atmospheric conditions. They do not undergo photo-oxidation, showing higher lifetime under atmospheric conditions.[122]

Amine contribute to produce aerosols and submicrons particles that can lead to rainfall droplets. Amines has high solubility in water and surfactant properties and thus the presence of amine in the atmosphere can contribute to form new particles and droplets from smaller aerosols. Mechanism related to aerosol and particles formation has also been proposed in the literature.[107,122]

5. - FUTURE DIRECTIONS

Amine degradation involves a large amount of reactions and degradation compounds. Many authors have suggested that the current knowledge about degradation compounds of major amine-based solvents is not enough to complete the mass balance during degradation. About 50% to 75% of the carbon mass balance is known when using MEA as sorbent,[11,25] while only one third of the nitrogen mass balance has been determined.[28] Although the main degradation products have been identified, many degradation compounds are still unknown. Further research must be focused on the degradation products identification in order to close the nitrogen and carbon mass balance during the experimental tests.

The analytical methods used in amine loss determination and degradation products identification have experienced a great development in recent years. LC-MS and IC-MS provide uncertainty less than 1% in amine concentration measures, and have been preferred to GC-MS analysis. However, in the case of products identification, authors still prefer GC-MS methods because of their superior identification tools.

Although several oxidative and thermal degradation studies have been carried out, a comparison between thermal and oxidative degradation is not straight forward for several reasons. Firstly, degradation studies were carried out at extreme operation conditions, such as temperatures higher than 120ºC, pressure up to 2MPa, using high purity CO_2 and O_2 and addition of cations in the solution in order to speed up the degradation rates obtained at real operating conditions and to reduce experimental time from months to weeks. Moreover, degradation studies carried out at both pilot plants and thermal-oxidative cycling units, i.e. ISDA unit, provided a global degradation overview and did not discuss each degradation process individually.

Experimental tests have been set up in different operation modes for each type of degradation. Most of thermal degradation studies were run in batch reactors, while gas streams with different levels of O_2 were pumped through the solution in oxidative degradation studies in semi-batch reactors. Only few works have provided a comparison between both oxidative and thermal degradation running the experiments at 140ºC and 2MPa in batch reactors,[16,28,45,48,79,102], where thermal degradation without CO_2 was considered negligible in comparison with the presence of CO_2 and O_2.[44,48,102] The degradation with CO_2 was higher than in the presence of O_2 (21%) in all the cases. The results showed that 42% of MEA was lost in 15 days in the presence of CO_2, while 21% was lost with O_2,[48,102] AMP degraded 21% and 8.6% at the same conditions, respectively.[45]

In general, degradation rates in oxidative degradation experiments were higher than thermal degradation rates, even more in the presence of cations such as Fe^{+2} and Cu^{+2}.[16,28,44,45] At 55°C, PZ and MEA degraded 8% and 44%, respectively, in presence of 1mM Fe^{+2} for 450 hours. Their degradation increased to 28% and 73%, respectively, in presence of Cu^{+2} for 200 hours. Thermal degradation of PZ at 150ºC required 30 weeks to reach comparative degradation rates.[44]

Finally, several studies have shown amines as precursors of nitrosamines, nitramines and nitramides compounds by both NO_X reactions and atmospheric photo-oxidation. Only a few apparatus have been designed to study nitro-compounds reactions under CO_2 chemical absorption conditions and atmospheric degradation, including SDR and EUPHORE, respectively. MEA is the only solvent which has been studied and its products and mechanism are well known. Extensions to other solvents and blends are required to evaluate the potential capacity to form nitro-derivate compounds. Studies of degradation of amines in presence of other radicals in the atmosphere such as Cl^-, O_3 and NO_3^- are required to identify new potential harmful degradation products under atmospheric conditions.[122]

6. – CONCLUSIONS

A review of recent works on degradation of amine-based solvents used in CO_2 capture by chemical absorption has been summarized, including over 25 solvents and blends.

In general, batch reactors have been typically used at temperatures between 120-200ºC and pressures up to 25 bar due to low degradation rates showed by amine solvents. New cyclic systems and apparatus have been designed, such as ISDA and HTCS, to reproduce the real operating conditions in chemical absorption units, while only a few pilot plant studies on amine degradation have been reported in the literature.

The main analytical methods used in amine degradation studies have been summarized in this review. LC-MS and IC-MS have been selected to be applied to amine loss determination while IC-MS and HPLC have been used to amine degradation products quantification. GC-MS is still the preferred method to identify degradation products.

Several formation mechanisms have been proposed for amine degradation. Electron abstraction and hydrogen abstraction are reported as the main mechanisms for oxidative degradation, while carbamate polymerization is the prevalent mechanism for thermal degradation. Therefore, presence of CO_2 is crucial to produce thermal degradation in amine solvents. Carbamate polymerization affects primary, secondary and also tertiary amines, which are involved in methylation/demethylation reactions previous thermal degradation. Many degradation products have been identified but their mechanism is still unknown. A few kinetic models have been proposed and reviewed here, which fit fairly well with the reported experimental data.

Oxidative degradation studies have shown higher degradation rates than those reported for thermal degradation. Several studies carried out using pilot plants found that the degradation products were very close to typical oxidative degradation products. Therefore, oxidative degradation is considered the dominant mechanism in real CO_2 absorption process.

Concerns about nitrosamine and nitramines formation during CO_2 capture process using amine-based solvents has grown in recent years. It has been shown that MEA has potential capacity to react with NO_x from flue gas to form nitro-compounds which are potentially harmful to the human health and the environment. Further studies are required to identify other potential nitro-compounds and main formation mechanism in presence of NO_x via photo-reduction and to extent to other amine-based solvents.

Acknowledgments

The authors thank the financial support provided by the Centre for Innovation in Carbon Capture and Storage (EPRSC grant EP/F012098/02).

REFERENCES

1. International Energy Agency: World Energy Outlook 2013. IEA, London, United Kingdom (2013) pp. 38.

2. Kohl A and Nielsen R, *Gas Purification*, 5th Edn, Gulf Publishing Company, Houston (1997) pp. 41-48.

3. Gouedard C, Picq D, Launay F and Carrette PL. Amine degradation in CO_2 capture. I. A review. *Int J Greenh Gas Con* **10:**244–270 (2012).

4. Rochelle GT. Thermal degradation of amines for CO_2 capture. *Curr Opin Chem Eng* **1:**183–190 (2012).

5. Rao AB and Rubin ES. A Technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environ Sci Technol* **36:**4467-4475 (2002).

6. Karl M, *Atmospheric degradation of amines (ADA): Amines in aerosol - A review.* Climit Project No 201604. Report OR 60/2010. Norwegian Institute for Air Research (NILU), Kjeller, Norway (2010).

7. Thitakamol B, Veawab A and Aroonwilas A. Foaming in amine-based CO_2 capture process: experiment, modeling and simulation. *Enrgy Proced* **1:**1381-1386 (2009).

8. Dye C, Schmidbauer N and Martin Schlabach M, *Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air Phase I – CO_2 and amine screening study for environmental risk.* Project No 108068. Norwegian Institute for Air Research (NILU), Kjeller, Norway (2010).

9. Nielsen CJ, Anna BD, Dye C, Graus M, Karl M, King S et al. Atmospheric chemistry of 2-aminoethanol (MEA). *Enrgy Proced* **4:**2245-2252 (2011).

10. Sexton AJ and Rochelle GT. Reaction Products from the Oxidative Degradation of Monoethanolamine. *Ind Eng Chem Res* **50:**667–673 (2011).

11. Sexton AJ. Amine degradation in CO_2 capture process. Thesis. University of Texas, Austin, USA (2008).

12. Goff GS. Oxidative Degradation of Aqueous Monoethanolamine in CO_2 Capture Processes: Iron and Copper Catalysis, Inhibition, and O_2 Mass Transfer. Thesis. University of Texas, Austin, USA (2005).

13. Fostås B, Gangstad A, Nenseter B, Pedersen S, Sjøvoll M and Sørensen AL. Effects of NO_x in the Flue Gas Degradation of MEA. *Enrgy Proced* **4:**1566-1573 (2011).

14. Supap T, Idem R, Tontiwachwuthikul P and Saiwan C. Kinetics of sulfur dioxide- and oxygen-induced degradation of aqueous monoethanolamine solution during CO_2 absorption from power plant flue gas streams. *Int J Greenh Gas Con* **3:**133-142 (2009).

15. Zhou S, Wang S and Chen C. Thermal degradation of monoethanolamine in CO_2 capture with acidic impurities in flue gas. *Ind Eng Chem Res* **51:**2539-2547 (2012).

16. Lepaumier H, Da Silva EF, Einbu A, Grimstvedt A, Knudsen JN, Zahlsen K et al. Comparison of MEA degradation in pilot-scale with lab-scale experiments. *Enrgy Proced* **4:**1652-1659 (2011).

17. Gao J, Wang S, Zhou S, Zhao B and Chen C. Corrosion and degradation performance of novel absorbent for CO_2 capture in pilot-scale. *Enrgy Proced* **4:**1534-1541 (2011).

18. Mertens J, Knudsen J, Thielens ML and Andersen J. On-line monitoring and controlling emissions in amine post combustion carbon capture: A field test. *Int J Greenh Gas Con* **6:**2-11 (2012).

19. Moser P, Schmidt S, Sieder G, Garcia H and Stoffregen T. Performance of MEA in a long-term test at the post-combustion capture pilot plant in Niederaussem. *Int J Greenh Gas Con* **5:**620-627 (2011).

20. Strazisar BR, Anderson RR and White CM. Degradation of monoethanolamine used in CO_2 capture from flue gas of a coal-fired electric power generating station. *Journal of Energy Environmental Research* **1:**32–39 (2001).

21. Bedel SA. Oxidative degradation mechanisms for amines in flue gas capture. *Enrgy Proced* **1:**771-778 (2009).

22. Supap T, Idem R, Tontiwachwuthikul P and Saiwan C. Analysis of monoethanolamine and its oxidative degradation products during CO_2 absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations. *Ind Eng Chem Res* **45:**2437-2451 (2006).

23. Voice AK and Rochelle GT. Oxidation of amines at absorber conditions for CO_2 capture from flue gas. *Enrgy Proced* **4:**171-178 (2011).

24. Wang T and Jens KJ. Oxidative degradation of aqueous 2-Amino-2-methyl-1-propanol solvent for postcombustion CO_2 capture. *Ind Eng Chem Res* **51:**6529−6536 (2012)

25. Davis J and Rochelle GT. Thermal degradation of monoethanolamine at stripper conditions. *Enrgy Proced* **1:**327-323 (2009).

26. Eide-Haugmo I, Lepaumier H, Da Silva EF, Einbu A, Vernstad K, Svendsen HF. A study of thermal degradation of different amines and their resulting degradation products. 1st Post Combustion Capture Conference, IEA Greenhouse Gas R&D Programme, Abu Dhabi, United Arab Emirates (2011).

27. Freeman SA and Rochelle GT. Thermal degradation of aqueous piperazine for CO_2 capture. 1. Effect of process conditions and comparison of thermal stability of CO_2 capture amines. *Ind Eng Chem Res* **51:**7719−7725 (2012).

28. Lepaumier H, Grimstvedt A, Vernstad K, Zahlsen K and Svendsen HF. Degradation of MMEA at absorber and stripper conditions. *Chem Eng Sci* **66:**3491–3498 (2011).

29. Closmann F and Rochelle GT. Degradation of aqueous methyldiethanolamine by temperature and oxygen cycling. *Enrgy Proced* **4:**23-28 (2011).

30. Kemper J, Walse SS and Mitch WA. Quaternary amines as nitrosamine precursors: A role for consumer products?. *Environ Sci Technol* **44:**1224-1231 (2010).

31. Sexton AJ and Rochelle GT. Catalysts and inhibitors for MEA oxidation. *Enrgy Proced* **1:**1179-1185 (2009).

32. Fredriksen SB and Jens KJ. Oxidative degradation of aqueous amine solutions of MEA, AMP, MDEA, PZ: A review. *Enrgy Proced* **37:**1170-1177 (2013).

33. Da Silva EF, Hoff KA and Booth A. Emissions from CO_2 capture plants; an overview. *Enrgy Proced* **37:**784-790 (2013).

34. Atwood K, *Amines for the removal of carbon dioxide from gas streams: suppliers and physical properties*. Report No T2.20-22-2. Navy Department Bureau of Ships, Washington, USA (1950).

35. Dennis WH, Hull LA and Rosenblatt DH. Oxidations of amines. IV. oxidative fragmentation. *J Org Chem* **32:**3783–3787 (1967).

36. Hull LA, Davis GT, Rosenblatt DH and Mann CK. Oxidations of mines. VII. Chemical and electrochemical correlations. *J Phys Chem* **73:**2142-2146 (1969).

37. Hull LA, Davis GT, Rosenblatt DH, Williams HKR and Weglein RC. Oxidations of amines. III. Duality of mechanism in the reaction of amines with chlorine dioxide. *J Am Chem Soc* **89:**1163–1170 (1967).

38. Kindrick RC, Atwood K and Arnold MR. *The relative resistance to oxidation of commercially available amines.* Report No T2.15-1-3. Navy Department Bureau of Ships, Washington, USA (1950).

39. Rosenblatt DH, Hull LA, De Luca DC, Davis GT, Weglein RC and Williams HKR. Oxidations of amines. II. Substituent effects in chlorine dioxide oxidations. *J Ame Chem Soc* **89(5):**1158-1163 (1967).

40. Hsu CS and Kim CJ. Diethanolamine (DEA) degradation under gas treating conditions. *Ind Eng Chem Prod Res Dev* **24:**630–635 (1985).

41. Lindsay S and Masheder D. Amine oxidation. Part 13. Electrochemical oxidation of some substituted tertiary alkylamines. *J Chem Soc, Perkin Trans 2* 1732–1736 (1977).

42. Lindsay S and Mead LAV. Amine oxidation. Part VII. The effect of structure on the reactivity of alkyl tertiary amines towards alkaline potassium hexacyanoferrate (III). *J Chem Soc, Perkin Trans 2* 206–210 (1973).

43. Petryaev EP, Pavlov AV and Shadyro OI. Homolytic deamination of amino alcohols. *Russ J Org Chem of the USSR* **20:**25–29 (1984).

44. Freeman SA, Davis J and Rochelle GT. Degradation of aqueous piperazine in carbon dioxide capture. *Int J Greenh Gas Con* **4:**756-761 (2010).

45. Wang T. Degradation of Aqueous 2-Amino-2-methyl-1-propanol for Carbon Dioxide Capture. Thesis. Telemark University College, Faculty of Technology, Porsgrunn, Norway (2012).

46. Supap T. Kinetic Study of oxidative degradation in gas treating unit using aqueous monoethanolamine. Thesis. University of Regina, Regina, Saskatchewan, Canada (1999).

47. Strazisar BR, Anderson RR and White CM. Degradation pathways for monoethanolamine in a CO_2 capture facility. *Energy Fuels* **17:**1034-1039 (2003).

48. Lepaumier H, Picq D and Carrette PL. New amines for CO_2 capture. II. Oxidative degradation mechanisms. *Ind Eng Chem Res* **48:**9068–9075 (2009).

49. Lepaumier H. Étude des mecanismes de dégradation des amines utiliseespour le captage du CO_2 dans les fumées. Sciences Pour l'Ingénieur, Savoie. Thesis. University of University of Savoie, Savoie, France (2008).

50. Lawal O, Bello A and Idem R. The Role of Methyl Diethanolamine (MDEA) in Preventing the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous Monoethanolamine (MEA)-MDEA Blends during CO_2 Absorption from Flue Gases. *Ind Eng Chem Res* **44**:1874-1896 (2005).

51. Rooney PC, Dupart MS and Bacon TR. Oxygen's role in alkanolamine degradation. *Hydrocarbon Process* **77:**109–113 (1998).

52. Voice AK and Rochelle GT. Products and process variables in oxidation of monoethanolamine for CO_2 capture. *Int J Greenh Gas Con* **12:**472-477 (2013).

53. Voice AK. Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing. Thesis. University of Texas, Austin, USA (2013).

54. Vevelstad SJ, Grimstvedt A, Knuutila H, Svendsen HF. Thermal degradation on already oxidatively degraded solutions. *Enrgy Proced* **37:**2109-2117 (2013).

55. Namjoshi O, Li L, Du Y and Rochelle GT. Thermal degradation of piperazine blends with diamines. *Enrgy Proced* **37:**1904-1911 (2013).

56. Li L, Voice AK, Li H, Namjoshi O, Nguyena T, Du Y and Rochelle GT. Amine blends using concentrated piperazine. *Enrgy Proced* **37:**353-369 (2013).

57. Du Y, Li L, Namjoshi O, Voice AK, Fine NA and Rochelle GT. Aqueous piperazine/N-(2-aminoethyl) piperazine for CO_2 capture. *Enrgy Proced* **37:**1621-1638 (2013).

58. Freeman SA and Rochelle GT. Thermal degradation of aqueous piperazine for CO_2 Capture: 2: Product types and generation rates. *Ind Eng Chem Res* 51:7726–7735 (2012).

59. Freeman SA, Closmann FB and Rochelle GT. Oxidation of Aqueous Piperazine: Oxidation Rates, Products, and High-Temperature Oxidation. In: *Recent Advances in Post-Combustion CO_2 Capture Chemistry*. Pags. 219-237 (2012).

60. Alawode AO. Oxidative Degradation of Piperazine in the Absorption of Carbon Dioxide. Thesis. University of Texas, Austin, USA (2005).

61. Wang T and Jens KJ. Oxidative Degradation of 2-Amino-2-Methyl-1-Propanol. 1st Post Combustion Capture Conference, IEA Greenhouse Gas R&D Programme, Abu Dhabi, United Arab Emirates (2011).

62. Kennard ML and Meisen A. Mechanisms and kinetics of diethanolamine degradation. *Ind Eng Chem Fundam* **24:**129–140 (1985).

63. Kennard ML. Degradation of Diethanolamine (DEA) Solutions. Thesis. The University of British Columbia, Vancouver, Canada (1983).

64. Bedell SA. Amine autoxidation in flue gas CO_2 capture - Mechanistic lessons learned from other gas treating processes. *Int J Greenh Gas Con* **5:**1-6 (2011).

65. Freeman SA. Thermal degradation and oxidation of aqueous piperazine for carbon dioxide capture. Thesis. University of Texas, Austin, USA (2011).

66. Davis J. Thermal Degradation of Aqueous Amines Used for Carbon Dioxide Capture. Thesis. University of Texas, Austin, USA (2009).

67. Eide-Haugmo I, Lepaumier H, Einbu A, Vernstad K, Da Silva EF and Svendsen HF. Chemical stability and biodegradability of new solvents for CO_2 capture. *Enrgy Proced* **4:**23–28 (2011).

68. Dawodu OF and Meisen A. Degradation of aqueous diethanolamine solutions by carbon disulfide. *Gas Sep Purif* **10:**1–11 (1996).

69. Chakma A and Meisen A. Methyl-diethanolamine degradation – mechanism and kinetics. *Can J Chem Eng* **75:**861–871 (1997).

70. Chakma A and Meisen A. Identification of methyl diethanolamine degradation products by gas-chromatography and gas-chromatography mass-spectrometry. *J Chromatogr* **457:**287–297 (1988).

71. Dupart MS, Rooney PC and Bacon TR. Comparing laboratory and plant data for MDEA/DEA blends. *Hydrocarbon Process* **78:**81–86 (1999).

72. Reza J and Trejo A. Degradation of aqueous solutions of alkanolamine blends at high temperature, under the presence of CO_2 and H_2S. *Chem Eng Commun* **193(1):**129-138 (2006).

73. Uyanga IT and Idem RO. Studies of SO_2- and O_2-induced degradation of aqueous MEA during CO_2 capture from power plant flue gas streams. *Ind Eng Chem Res* **46:**2558-2566 (2007).

74. Vevelstad SJ, Grimstvedt A, Einbu A, Knuutila H, Da Silva EF and Svendsen HF. Oxidative degradation of amines using a closed batch system. *Int J Greenh Gas Con* **18:**1-14 (2013).

75. Vevelstad SJ, Grimstvedt A, Elnan J, Da Silva EF and Svendsena HF. Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation. *Int J Greenh Gas Con* **18:**88-100 (2013).

76. Voice AK, Closmann F and Rochelle GT. Oxidative degradation of amines with high-temperature cycling. *Enrgy Proced* **37:**2118-2132 (2013).

77. Martin S, Lepaumier H, Picq D, Kittel J, De Bruin T, Faraj A et al. New amines for CO_2 capture. IV. Degradation, corrosion, and quantitative structure property relationship model. *Ind Eng Chem Res* **51:**6283−6289 (2011).

78. Da Silva EF, Lepaumier H, Grimstvedt A, Vevelstad SJ, Einbu A, Vernstad K et al. Understanding 2‑ethanolamine degradation in postcombustion CO_2 capture. *Ind Eng Chem Res* **51:**13329−13338 (2012).

79. Nielsen PT, Li L and Rochelle GT. Piperazine degradation in pilot plants. *Enrgy Proced* **37:**1912-1923 (2013).

80. Goff GS and Rochelle GT. Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. *Ind Eng Chem Res* **43:**6400-6408 (2004).

81. Fessenden R J and Fessenden J S. *Organic Chemistry*. Brooks/Cole Publishing Company, Pacific Grove, California, pp.   (1994).

82. Chi S and Rochelle G.T. Oxidative degradation of monoethanolamine. *Ind Eng Chem Res* **41:**4178–4186 (2002).

83. Chi S. Oxidative degradation of MEA. Thesis. University of Texas, Austin, USA (2008).

84. Supap T, Idem R and Tontiwachwuthikul P. Mechanism of formation of heat stable salts (HSSs) and their roles in further degradation of monoethanolamine during CO_2 capture from flue gas streams. *Enrgy Proced* **4:**591-598 (2011).

85. Arduengo AJ, Gentry FP, Taverkere PK and Simmons H, Process for manufacture of imidazoles. US Patent No. 6177575 B1 (2001).

86. Hakka LE and Ouimet MA, Method for recovery of CO_2 from gas streams. US Patent No. 7056482 (2006).

87. Delfort B, Carrette PL and Bonnard L. MEA 40% with improved oxidative stability for CO_2 capture in post-combustion. *Enrgy Proced* **4:**9-14 (2011).

88. Kim CJ and Sartori G. Kinetics and mechanism of diethanolamine degradation in aqueous solutions containing carbon dioxide. *Int J Chem Kinet* **16:**1257–1266 (1984).

89. Polderman LD, Dillon CP and Steele AB. Why monoethanolamine solution breaks down in gas-treating service. *Oil Gas J* **53:**180–183 (1955).

90. Polderman LD and Steele AB. Degradation of diethanolamine in gas treating service. *Oil Gas J* **54:**49–56 (1956).

91. Hakka LE, Singh KP, Bata GL, Testart AC and Andrejchyshyn WN. Some aspects of diethanolamine degradation in gas sweetening. *The Canadian Natural Gas Processing Association* **61(1):**32-37 (1968).

92. Smith RF and Younger AH. Tips on DEA treatment. *Hydrocarbon Process* **51(7):**98-100 (1972).

93. Smith RF and Younger AH. Operating Experiences of Canadian Diethanolamine Plants. Gas Conditioning Conference, University of Oklahoma, Norman, Oklahoma, USA (1972).

94. Hsu CS and Kim CJ. Diethanolamine (DEA) degradation under gas treating conditions. *Ind Eng Chem Prod Res Dev* **24:**630–635 (1985).

95. Kim CJ. Degradation of alkanolamines in gas-treating solutions: kinetics of di-2-propanolamine degradation in aqueous solutions containing carbon dioxide. *Ind Eng Chem Res* **27(1):**1-3 (1988).

96. Kenney T J, Khan AR, Holub PE and Street DE. DGA agent shows promise for trace sulfur compound removal from hydrocarbon streams. Sulfur Recovery Conference, Gas Research Institute, Austin, Texas, USA (1994).

97. Dingman JC. Gas sweetening with diglycolamine agent. Third Iranian Congress of Chemical Engineering, Department of Chemical Engineering, School of Engineering, Shiraz University, Shiraz, Iran (1977).

98. Blanc C, Grall M and Demarais G. The part played by degradation products in the corrosion gas sweeting plantas using DEA and MDEA. Gas Conditioning Conference, University of Oklahoma, Norman, Oklahoma, USA (1982).

99. Blanc C, Elgue J and Lallemand F. MDEA Process Selects H_2S. *Hydrocarbon Process* **60(8):**111-116 (1981).

100. Meisen A and Kennard ML. DEA degradation mechanism. *Hydrocarbon Process* **61(10):**105-108 (1982).

101. Zoannou KS, Sapsford DJ and Griffiths AJ. Thermal degradation of monoethanolamine and its effect on CO_2 capture capacity. *Int J Greenh Gas Con* **17:**423-430 (2013).

102. Lepaumier H, Picq D and Carrette PL. New amines for CO_2 capture. I. Mechanisms of amine degradation in the presence of CO_2. *Ind Eng Chem Res* **48:**9061–9067 (2009).

103. Closmann F. Oxidation and thermal degradation of methyldiethanolamine/ piperazine in CO_2 capture. Thesis. University of Texas, Austin, USA (2011).

104. Hilliard M. A Predictive Thermodynamic Model for an Aqueous Blend of Potassium Carbonate, Piperazine, and Monoethanolamine for Carbon Dioxide Capture from Flue Gas. Thesis. University of Texas, Austin, USA (2008).

105. Ma´mun S. Selection and Characterization of New Absorbents for Carbon Dioxide Capture. Thesis. Norwegian University of Science and Technology, Trondheim, Norway (2005).

106. Ge X, Wexler AS and Clegg SL. Atmospheric amines e Part I. A review. *Atmos Environ* **45:**524-546 (2011).

107. Shao RJ and Stangeland A. Amines Used in CO_2 Capture e Health and Environmental Impacts. Report. The Bellona Fundation, Oslo, Norway (2009).

108. Karl M, Wright RF, Berglen TF and Denby B. Worst case scenario study to assess the environmental impact of amine emissions from a CO_2 capture plant. *Int J Greenh Gas Con* **5:**439-447 (2011).

109. Thitakamol B, Veawab A and Aroonwilas A. Environmental impacts of absorption-based CO_2 capture unit for post-combustion treatment of flue gas from coal-fired power plant. *Int J Greenh Gas Con* **1:**318-342 (2007).

110. National Toxicology Program, *Report on Carcinogens 12th Edn.* U.S. Department of Health and Human Services, Public Health Service, Washington, D.C, USA (2011).

111. Knudsen S, Karl M and Randall S. *Summary report: Amine emissions to air during carbon capture. Phase I: CO2 and amines screening study for effects to the environment.* Report TR 04/2009, Norwegian Institute for Air Research (NILU), Kjeller, Norway (2009).

112. Reh BD, DeBord DG, Butler MA, Reid TM, Mueller C and Fajen JM. O6-methylguanine DNA adducts associated with occupational nitrosamine exposure. Carcinogenesis **21(1):**29–33 (2000).

113. Pitts JN, Grosjean D, Vanmcauwenberghe K, Schmidt JP and Fitz DR. Photooxidation of aliphatic amines under simulated atmospheric conditions: Formation of nitrosamines, nitramines, amides, and photochemical oxidant. *Environ Sci Technol* **12:**946 (1978).

114. Goldman MJ, Fine NA and Rochelle GT. Kinetic of N-nitrosopiperazine formation from nitrate and piperazine in CO2 capture. *Environ Sci Technol* **47:**3528-3534 (2013).

115. Fine NA and Rochelle GT. Thermal decomposition of n-nitrosopiperazine. *Enrgy Proced* **37:**1678-1686 (2013).

116. Fine NA, Goldman MJ, Nielsen PT and Rochelle GT. Managing n-nitrosopiperazine and dinitrosopiperazine. *Enrgy Proced* **37:**273-284 (2013).

117. Fine NA, Nielsen PT and Rochelle GT. Decomposition of secondary nitrosamines in amine scrubbing. *Environ Sci Technol* DOI: 10.1021/es404949v (2014)

118. Knuutila H, Asif N, Vevelstad SJ and Svendsen HF. Formation and destruction of NDELA in 30wt% MEA (monoethanolamine) and 50wt% DEA (diethanolamine) solutions. *Oil Gas Sci Technol* DOI: http://dx.doi.org/10.2516/ogst/2013168 (2013)

119. Challis BC and Challis JC. The chemistry of functional groups, the chemistry of amino, nitroso and nitro compounds and their derivates, Supplement F, Part 2. In: Pataï (Ed.), N-nitrosamines and N-nitrosoimines. Wiley (1982). pp. 1151–1223.

120. Hanst PL, Spence JW and Miller M. Atmospheric chemistry of N-nitroso dimethylamine. *Environ Sci Technol* **11:**403-405 (1977).

121. Fiddler W, Pensabene JW, Doerr RC and Wasserman AE. Formation of N-nitrosodimethylamine from naturally occurring quaternary ammonium compounds and tertiary amines. *Nature* **236:**307 (1972).

122. Einbu A, DaSilva E, Haugen G, Grimstvedt A, Lauritsen KG and Zahlsen K et al. A new test rig for studies of degradation of CO_2 absorption solvents at process conditions; comparison of test rig results and pilot plant data for degradation of MEA. *Enrgy Proced* **37:**717-726 (2013).

124. Bråten HB, Bunkan AJ, Bache-Andreassen L, Solimannejad M and Nielsen CJ, *Final Report on a Theoretical Study on the Atmospheric Degradation of Selected Amines*. Report OR 77/2008. Norwegian Institute for Air Research (NILU), Kjeller, Norway (2008).

124. Fujita K, Muraoka D, Ogawa T, Kitamura H, Suzuki K and Saito S. Evaluation of amine emissions from the post-combustion CO_2 capture pilot plant. *Enrgy Proced* **37:**717-726 (2013).

125. Nielsen CJ, D’Anna B, Dye C, George C, Graus M and Hansel A, *Atmospheric degradation of amines (ADA) summary report: Gas phase photo-oxidation of 2-aminoethanol (MEA).* Climit Project No 193438. Report OR 8/2010. Norwegian Institute for Air Research (NILU), Kjeller,, Norway (2010).

Table 1. Summary of oxidative and thermal degradation studies

Abb	**Name**	**Chemical Formula**	**MW**	**BP (ºC)**	**Oxidative Degradation**	**Thermal Degradation**
EDA	Ethylenediamine	$NH_2C_2H_4NH_2$	60	117	11,23,44	25,26,44,65,66
MEA	Monoethanolamine	$NH_2C_2H_4OH$	61	171	10-12,14,16,22,23,31,44-54	15,16,25,26,44,45,101
DAP	1,2-diamino-propane	$CH_3CHNH_2CH_2NH_2$	74	120	23	-
MPA	3-aminopropanol	$NH_2C_2H_4OH$	75	185	-	25,67
MIPA	1-amino-2-propanol	$CH_3CH(OH)CH_2NH_2$	75	160	-	26
MMEA	N-methylethanolamine	$CH_3NHC_2H_4OH$	75	160	28,48,49	25,28,48,67
PZ	Piperazine	$C_2H_4NHC_2H_4NH$	86	140	23,44,45,55-60	27,44,45,5-59,65
MAPA	3-methylamino-1-propylamine	$NH_2C_3H_6NHCH_3$	88	140	23	25,67
N,N-diMEDA	N,N-dimethylethylenediamine	$(CH_3)_2NC_2H_4NH_2$	88	105	48,49	48
N,N'-diMEDA	N,N'-dimethylethylenediamine	$CH_3NHC_2H_4NHCH_3$	88	119	48,49	48
AMP	2-amino-2-methyl-1-propanol	$HOCH_2C(NH_2)(CH_3)_2$	89	165	11,23,24,44,45,47-49	25,26,44,45 48,67
DMAE	N,N-dimethylethanolamine	$(CH_3)_2NC_2H_4OH$	89	135	48,49	48,67
NMPZ	N-methyl-piperazine	$C_2H_4(CH_3)NC_2H_4NH$	100	138	23	65
N,N,N-triMEDA	N,N,N'-trimethylethilenediamine	$(CH_3)_2NC_2H_4NHCH_3$	102	140	48,49	48
DETA	diethylenetriamine	$NH_2C_2H_4NHC_2H_4NH_2$	103	207	44	25,44,67

HEEDA	N-(2-hydroxyethyl)ethylenediamine	$NH_2C_2H_4NHC_2H_4OH$	104	239	48,49	25,48,67
AMPD	2-amino-2-methylpropane-1,3-diol	$(HOCH_2)_2C(NH_2)CH_3$	105	151	-	26
DGA	Diglycolamine	$NH_2C_2H_4OC_2H_4OH$	105	221	11,44,51	25,44
DEA	Diethanolamine	$(C_2H_4OH)_2NH$	105	269	11,21,48,49,51,62,63	48,64,67,92
GLY	potassium glycinate	$KCOOCH_2NH_2$	113	241	11,23	-
DMP	N,N'-dimethylpiperazine	$C_2H_4(CH_3)NC_2H_4N(CH_3)$	114	132	48,49	48
2-PM	2-piperidinemethanol	$C_2H_4NHCH(CH_2OH)C_2H_4$	115	101	-	25
HMDA	Hexamethylenediamine	$NH_2C_6H_{12}NH_2$	116	205	-	65
TMEDA	N,N,N',N'-tetramethylethylenediamine	$(CH_3)_2NC_2H_4N(CH_3)_2$	116	121	48,49	48
MDEA	Methyldiethanolamine	$CH_3N(C_2H_4OH)_2$	119	247	21,29,48-51,64	25,29,48,67 69,70
2-PE	2-piperidineethanol	$C_2H_4NHCH(C_2H_4OH)C_2H_4$	129	234	-	65
AEP	N-(2-aminoethyl)piperazine	$C_2H_4(C_2H_4NH_2)NC_2H_4NH$	129	220	-	25
HEP	N-(2-hydroxyethyl)piperazine	$C_2H_4(C_2H_4OH)NC_2H_4NH$	130	246	44	25,44
TAU	potassium taurinate	$KSO_3CH_2NH_2$	149	-	23	-
MEA-DGA	Blends	-	-	-	-	25
MEA-MDEA	Blends	-	-	-	50	50,70
MEA-PZ	Blends	-	-	-	44	25,45
MEA-AMP	Blends	-	-	-	11,44	25,45
AMP-PZ	Blends	-	-	-	44	45,65
DIAMINES-PZ	Blends	-	-	-	-	55,56
AEP-PZ	Blends	-	-	-	-	57
MDEA-PZ	Blends	-	-	-	23	-
PZ-MPZ	Blends	-	-	-	-	65
MDEA-DEA	Blends	-	-	-	-	71
MDEA-DEA-AMP	Blends	-	-	-	-	71
PZ-DMPZ-MPZ	Blends	-	-	-	-	65

Table 2. Summary of the amine solvents studied in the literature and its main degradation products

Solvent	Main Degradation Product	Abbreviation	MW
MEA	Ammonia	-	17
	Formic Acid	-	46
	Acetic Acid	-	60
	2-oxazolidone	OZD	87
	N-(2-hydroxyethyl)formamide	HEF	89
	N-(2-hydroxyethyl)imidazole	HEI	112
	N-(2-hydroxyethyl)piperazin-3-one	HEPO	144
	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	HEHEAA	162
	N,N’-Bis (2-hydroxyethyl)oxamide	BHEOX	176
DEA	Formic Acid	-	46
	Acetic Acid	-	60
	Monoethanolamine	MEA	61
	Glycolic Acid	-	76
	N-methyldiethanolamine	MDEA	119
	N-(carboxymethyl)diethanolamine	BICINE	163
	N,N -bis(2-hydroxyethyl)piperazine	BHEP	174
	N,N,N -tris(2-hydroxyethyl)ethylenediamine	THEED	192
MDEA	Methylamine	-	31
	Ethylene Oxide	EO	44
	Dimethylamine	-	45
	Formic Acid	-	46
	Acetic Acid	-	60
	N-methylethanolamine	MAE	75
	Glycolic Acid	-	76
	N,N-(dimethyl)ethanolamine	DMAE	89
	Oxalic Acida	-	90
	Diethanolamine	DEA	105
	N-methylmorpholin-2-one	-	115
	N-methylmorpholin-2,6-dione	-	129
	2-[Methyl(2-hydroxyethyl)amino] Acetic Acid	-	133
	N,N,N -trimethyl-N -(2-hydroxyethyl)ethylenediamine	-	146
	triethanolamine	TEA	149
	N-(carboxymethyl)diethanolamine	BICINE	163

PZ	Formic Acid	-	46
	Nitrous Acid	-	47
	Acetic Acid	-	60
	Nitric Acid	-	63
	Ethylenediamine	EDA	75
	Glycolic Acid	-	76
	Oxalic Acida	-	90
	2-oxopiperazine	OPZ	100
	Formylpiperazine	FPZ	114
	1-mononitrosopiperazine	MNPZ	115
AMP	Ammonia	-	17
	Formic Acid	-	46
	Nitrous Acid	-	47
	Acetic Acid	-	60
	Nitric Acid	-	63
	Glycolic Acid	-	76
	Oxalic Acida	-	90
	2,4-Lutidine	-	107
	4,4-dimethyl oxazolidinone	DMOZD	115
MMEA	Formic Acid	-	46
	Acetic Acid	-	60
	Monoethanolamine	MEA	61
	ethylenglycol	EG	62
	Glycolic Acid	-	76
	1-methylimidazole	MI	82
	2.dimethylamino ethanol	DMAE	89
	1,x-dimethylimidazole	DMI	96
	N-methyloxazolidinone	MOZD	101
	N-(2-hydroxyethyl)-N-methylformamide	HEMF	103
	1-(2-hydroxyethyl)imidazole	HEI	112
	N,N -dimethyl-N -(2-hydroxyethyl)ethylenediamine	-	132
DMAE	Formic Acid	-	46
	Acetic Acid	-	60
	N-methylethanolamine	MMEA	75
	Glycolic Acid	-	76
	Oxalic Acid	-	90
	N,N -dimethyl-N -(2-hydroxyethyl)ethylenediamine	-	132
	N,N,N -trimethyl-N -(2-hydroxyethyl)ethylenediamine		146
HEEDA	Monoethanolamine	MEA	61
	Ethylenediamine	EDA	75
	N-(2-hydroxyethyl)piperazin-3-one	HEPO	144
	N,N-bis(2-hydroxyethyl)ethanodiamine	-	148
DMP	Formic Acid	-	46
	N,N'-dimethylethylenediamine	N,N´-diMEDA	88
	N-methylpiperazine	MPZ	100
	N,N-dimethylpiperazin-3-one	-	128
	N,N-dimethyl-2-methylpiperazin-3-one	-	141
TMEDA	Glycolic Acid	-	76
	N,N,N'-trimethylethilenediamine	N,N,N´-triMEDA	102
	N,N -dimethylpiperazine	DMP	114
	N,N-dimethylpiperazin-3-one	-	128
	N,N,N',N'',N''-pentamethyldiethilenetriamine	-	173
N,N´-diMEDA	Formic Acid	-	46
	N-methylethilenediamine	MEDA	89
	N,N,N'-trimethylethilenediamine	N,N,N´-triMEDA	102
	N,N-dimethylpiperazin-3-one	-	128
	N,N-dimethyl-2-methylpiperazin-3-one	-	141
N,N-diMEDA	Formic Acid	-	46
	Glycolic Acid	-	76
	N,N-dimethylethylenediamine	N,N-diMEDA	88
	N,N,N',N'-tetramethylethylenediamine	N,N,N´,N´-tetraMEDA	116
	N,N-dimethylpiperazin-3-one	-	128
	N,N-dimethyl-2-methylpiperazin-3-one	-	141

Table 3. Kinetic model for oxidative degradation

Reference	Description	Equation	Parameters	Value		
				Formate	DEA	Bicine
29	MDEA degradation model developed to allow preditions of three degradation products	$S=\frac{\Delta[\mathrm{Pr}]}{\Delta[O_2]}$ $\Delta[\mathrm{Pr}]=S*P_{O_2}*Q*t*\frac{1-e^{-\left(\frac{k*V_{TR}}{Q}\right)}}{H_{O_2}*V_{total}}$	K_0 (1/h)	2.42	0.06	$3.388*10^{-3}$
			E_a (J/mol)	107000	85054	85010
			S	0.1	16.7	4848.2
14	Model for MEA degradation in presence of SO_2, O_2 and CO_2 It is supposed that MEA only reacts with O_2 dissolved	$-r_{\mathrm{MEA}}=\frac{k_0\,\mathrm{e}^{-E_a/RT}[\mathrm{MEA}]^a([\mathrm{O_2}]^b+[\mathrm{SO_2}]^c)}{1+k[\mathrm{CO_2}]^d}$	K_0 *	$6.74*10^9$		
			E_a (J/mol)	29403		
			a	0.015		
			b	2.91		
			c	3.58		
			d	1.18		
73	Linealizable Power Law, Model for MEA degradation in presence of SO_2, O_2 and CO_2 It is supposed that MEA only reacts with O_2 dissolved	$-r_{\mathrm{MEA}}=k[\mathrm{MEA}]^n[\mathrm{SO_2}]^m[\mathrm{CO_2}]^p[\mathrm{O_2}]^s$	K_0 *	0.7189		
			E_a (J/mol)	20752		
			n	1.359		
			p	-0,033		
			m	0.02945		
			s	2.004		
73	NonLinealizable Rate Model, Model for MEA degradation in presence of SO_2, O_2 and CO_2 It is supposed that MEA only reacts with O_2 dissolved	$-r_{\mathrm{MEA}}=k_0\exp\left(-\frac{E}{RT}\right)[\mathrm{MEA}]^n[\mathrm{CO_2}]^m\{[\mathrm{SO_2}]^p+[\mathrm{O_2}]^s\}$	K_0 *	0.00745		
			E_a (J/mol)	45285		
			n	1.91		
			p	0,33		
			m	3.42		
			s	2.78		

Table 4. Averaged MEA degradation rate (kmol/m^{3}h*10^{-5}) obtained for each inhibitor tested. Operating conditions: 5 m MEA, 6% O_2 and 6 ppm SO_2 and 393 K. * Na_2SO_3 was investigated without the presence of SO_2 .[46]

Inhibitor	**Concentration (mol/m^3)**											
	0	1.25	2.5	5	10	25	50	60	100	300	500	1000
Na_2SO_3*	47.4	-	-	-	-	-	4	-	65.6	128	-	-
$KNaC_4H_4O_6{\cdot}4H_2O$		-	-	57.1	2.6	-	-	10.2	8.04	18.8	-	-
EDTA		34.1	14.4	52.9	-	-	-	-	148	-	-	-
NH_2OH		-	-	-	-	5.96	-	-	-	-	37.6	21.4

Table 5. Summary of the amine solvents studied in the literature and its main thermal degradation products

Solvent	Main Degradation Product	Abb.	MW
MEA	1-amino-2-propanol	-	75
	2-oxazolidone	OZD	87
	2-Methylpiperazine	-	100
	2-methyl-3-oxazolidine	-	101
	4-methylmorpholine	-	101
	N-(2-hidroxyethyl)-ethylenediamine	HEEDA	104
	1-(2-hydroxyethyl)-2-imidazolidone	HEIA	130
	1-piperazineethanol	-	130
	N,N`-bis(2-hidroxyethyl)urea	UREA	148
	N-(2-aminoethyl)-N’-(2-hydroxyethyl)imidazolidinone	AEHEIA	173
	N,N´-bis(2-hydroxyethyl)imidazolidin-2-one	BHEI	174
	N,N,N -tris(2-hydroxyethyl)ethylenediamine	THEED	192
DEA	Monoethanolamine	MEA	61
	N-(2-hydroxyethyl)aziridine	HEM	87
	N-(2-hydroxyethyl)oxazolidin-2-one	HEOD	131
	N,N-bis(2-hydroxyethyl)ethylenediamine	-	148
	Triethanolamine	TEA	149
	N,N -bis(2-hydroxyethyl)piperazine	BHEP	174
	N,N,N -tris(2-hydroxyethyl)ethylenediamine	THEED	192
	Bis-(2-(2-hydroxyethylamino)ethyl)ether	BHEAE	192
	N-(2-hydroxyethyl)-N -(2-(2- hydroxyethylamino)ethyl)piperazine	HEAEHEP	217
	N-2-[bis(2-hydroxyethyl)-amino]ethylpiperazine	HEAEP	217
	N-2-[bis(2-hydroxyethyl)-amino]ethyloxazolidin-2-one	HAO	218
	N,N,N ,N -tetrakis(2-hydroxyethyl)urea	TEHEU	236
	N,N,N ,N -tetrakis(2-hydroxyethyl)ethylenediamine	THEED	236
	N-2-[bis(2-hydroxyethyl)-amino]ethyl-N -(2-hydroxyethyl)piperazine	HAP	261
	N,N,N ,N -tetrakis(2-hydroxyethyl)diethylenetriamine	TEHEDT	279
	N,N,N ,N -tetrakis(2-hydroxyethyl)diethylenetriamine	i-THEDT	279
MDEA	Methanol	-	32
	Ethylene oxide	EO	44
	Formamide	-	45
	Formic Acid	-	46
	Trimethylamine	TMA	59
	Ethyleneglycol	EG	62

	N,N-dimethylethylamine	DMEA	73
	N-methylethanolamine	MMEA	75
	2 - dimethylamino etanol	DMAE	89
	Diethanolamine	DEA	105
	1,4-dimethylpiperazine	DMP	114
	3-(hydroxyethyl)-2-oxazolidone	HEOD	131
	1-(2-hydroxyethyl)-4-methylpiperazine	HPM	144
	Triethanolamine	TEA	149
	N-(carboxymethyl)diethanolamine	BICINE	163
	N,N-bis-(2-hydroxyethyl)-piperazine	BHEP	174
	N,N,N -tris(2-hydroxyethyl)ethylenediamine	THEED	192
PZ	Ammonia	-	17
	Ethylenediamine	EDA	75
	Formic Acid	-	46
	N-methylpiperazine	MPZ	100
	N-formylpiperazine	FPZ	114
	N,N –dimethylpiperazine	DMP	114
	N-ethylpiperazine	EZP	114
	1-(2-aminoethyl)piperazine	AEP	129
	N-(hydroxyethyl)piperazine	HEP	130
	1,4-di(2-aminoethyl)piperazine	DAEP	172
AMP	N,2,2-trimethylethanolamine	-	103
	4,4-Dimethyloxazolidin-2-one	DMOZD	115
	N,4,4-Trimethyloxazolini-2-one	-	129
	4,4-Dimethyl-1-hydroxytertiobutylimidazolidin-2-one	DMHTBI	186
	2-[(2-amino-2-methylpropyl)amino]-2-methyl-1-propanol	AMPAMP	
MMEA	N-methyloxazolidinone	MOZD	101
	N,N –dimethylpiperazine	DMP	114
	N,N´-dimethyl imidazolidinone	DMIDZ	114
	N,N´-dimethyl-N`-(2-hidroxyethyl)ethylenediamine	DMHEED	132
	N-(-hydroxyethyl)-N´-methylpiperazine	HMP	144
	N,N´,N´´-trimethyl-N´´-(2-hydroxyethyl)diethylene triamine	trimer	189
	N,N´,N´´,N´´-tetramethyl-N´´´´-(2-hydroxyethyl) triethylenetetramine	tetramer	246
AEP	1-[2-[(2-aminoethyl)amino]ethyl]piperazine	-	170
	1,4-piperazinediethanamine	-	172
DMAE	Ethyleneglycol	EG	62
	N-methylethanolamine	MMEA	75
	N-methyloxazolidinone	MOZD	101
	N,N -dimethyl-N -(2-hydroxyethyl)ethylenediamine	-	132
HEEDA	Monoethanolamine	MEA	61
	2-oxazolidone	OZD	87
	N-(2-hydroxyethyl)piperazin-3-one	HEPO	144
	N,N-bis(2-hydroxyethyl)ethanodiamine	-	148
DMP	N-methylpiperazine	MPZ	100
	N,N´-bis(2-methyl)imidazolidin-2-one	-	114
	N,N-dimethylpiperazin-3-one	-	128
	N,N-dimethyl-2-methylpiperazin-3-one	-	141
TMEDA	N-methyloxazolidinone	MOZD	101
	N,N,N'-trimethylethilenediamine	N,N,N´-triMEDA	102
	N,N –dimethylpiperazine	DMP	114
	N,N,N',N",N"-pentamethyldiethilenetriamine	-	173
N,N´-diMEDA	N,N´-bis(2-methyl)imidazolidin-2-one	-	114
	N,N –dimethylpiperazine	DMP	114
	N,N',N"-trimethyldiethilenetriamine	-	145
N,N-diMEDA	Monoethanolamine	MEA	61
	N-methylethilenediamine	MEDA	89
	N-[2-[(N,N-dimethyl)amino] ethyl]imidazolidin-2-one	-	113
	1-methyl-2-imidazolidone	-	130

Table 6. Summary of thermal degradation kinetic models in the literature.

Reference	Description	Equation	Parameters	Value
69	MDEA degradation first order kinetic model based on Arrhenious law. CO_2 absorption is not mass transfer limited	$-\frac{dC_{PZ}}{dt} = k_1 C_{PZ}$ $k_i = Ae^{\frac{E_A}{RT}}$	A (1/s)	$2{,}34*10^{4}$
			E_a (J/mol)	57400
25	MEA degradation kinetic model based on Arrhenious law	$\frac{\partial[MEA]}{\partial t} = A + B + C$ $A = -2k_1[MEA][CO_2]$ B= $-k_2[HEEDA][CO_2]$ C= $-k_3[Trimer][CO_2]$ $lnk_i = lnA - \frac{E_A}{RT}$	A_1 (L/mols)	$1{,}22*10^{11}$
			E_{a1} (J/mol)	143792
			A_2 (L/mols)	$2{,}49*10^{11}$
			E_{a2} (J/mol)	139194
			A_3 (L/mols)	$0{,}37*10^{11}$
			E_{a3} (J/mol)	131670
44	PZ (8 m) pseudo-first order degradation kinetic model based on Arrhenious law at different temperatures (α = 0.3)	$-\frac{dC_{PZ}}{dt} = k_1 C_{PZ}$ $lnk_1 = lnA - \frac{E_A}{RT}$	k_1 (1/s) at 135ºC	$1{,}16*10^{-9}$
			k_1 (1/s) at 150ºC	$6{,}12*10^{-9}$
			k_1 (1/s) at 175ºC	$1{,}40*10^{-7}$
			E_a (J/mol)	184000
55-57	PZ/AMP and PZ/DIAMINES blends pseudo-first order degradation kinetic model based on Arrhenious law (α = 0.3-0.4 and T=175ºC)	$-\frac{dC_{PZ}}{dt} = k_1 C_{PZ}$ $lnk_1 = lnA - \frac{E_A}{RT}$	k_1 (1/s) PZ in PZ/AEP	$1{,}6*10^{-7}$
			k_1 (1/s) PZ in PZ/BAE	$1{,}3*10^{-7}$
			k_1 (1/s) PZ in PZ/DAB	$1{,}6*10^{-7}$
			E_a (J/mol)	180000
45	AMP (4,75 M) degradation kinetic	$-\frac{dC_{AMP}}{dt} = k_1 C_{AMP}$	k_1 (1/s) at α = 0,15	$13{,}1*10^{-9}$

	model at different CO_2 loadings at 135ºC	$lnk_1 = lnA - \frac{E_A}{RT}$	k_1 (1/s) at α = 0,3	$18{,}9*10^{-9}$

Table 7. Summary of the main nitrosamines and nitramine products formed from MEA referenced in atmospheric and NO_X degradation studies.

Degradation study	Solvent	Main Degradation Product	Abb.	MW	References
CO_2 capture in presence of NO_x	MEA	nitrosodimethylamine	NDMA	74	13,122
		nitrosomorpholine	NMOR	116	13
		nitrosodiethanolamine	NDELA	134	13,83,122
		nitroso-(2-hydroxyethyl)-glycine	NHEGly	148	122
	PZ	N-nitrosopiperazine	MNPZ		115-117
		dinitrosopiperazine	DNPZ		
Photo-oxidation of solvent emitted to air in presence of NOx	MEA	methanimine	-	28	122
		formaldehyde	-	30	9, 122
		formamide	-	45	9, 122
		acetylenediol	-	58	122
		amine acetaldehyde	-	59	122
		2 imine ethanol	-	59	9
		2-oxo acetamide	-	73	9
		2-hydroxy acetamide	-	75	122
		2-nitroamine ethanol	-	106	9
	AMP	Acetone	-	58	122
		Acetamide	-	59	
		Hydroxyacetone	-	74	
		Hydroxylacetamide	-	75	
		N-nitroso formamide	-	88	
		N-nitro formamide	-	104	
	MDEA	N-methyl formamide	-	59	122
		N-hydroxymethylformamide	-	75	
		N-methyl, N-methanol formamide	-	89	
		N-nitroso N-methyl ethanolamine	-	90	
		N- methyl, N-ethanol formamide	-	103	
		N,N-dimethanol-formamide	-	105	
		N-nitroso diethanolamine	-	106	
		N-methanol, N-ethanol formamide	-	119	
		N,N-diethanol formamide	-	133	
	PZ	2-Piperazinone	-	100	122
		N-(N’-nitroso ethanamine) acetamide	-	131	
		N-(N’-nitro ethanamine) acetamide	-	147	
		N,N'-1,2-ethanediylbis-formamide	-	174	