Université Pierre et Marie Curie

ED397

Laboratoire / Equipe de recherche

Novel degradation products of ethanolamine (MEA) in CO_2 capture conditions: identification, mechanisms proposal and transposition to other amines

Par Camille GOUEDARD

Thèse de doctorat de chimie

Dirigée par Franck Launay

Présentée et soutenue publiquement le 30 septembre 2014

Devant un jury composé de :

MM. Antoine GEDEON, Professeur Président du Jury
Thierry BILLARD, Directeur de recherche au CNRS Rapporteur
Klaus-Joachim JENS, Professeur Rapporteur
Earl GOETHEER, Docteur-ingénieur à TNO
Dominique PICQ, Chercheur CNRS
Pierre-Louis CARRETTE, Docteur-ingénieur à IFPEN
Franck LAUNAY, Professeur, directeur de thèse

Except where otherwise noted, this work is licensed under
http://creativecommons.org/licenses/by-nc-nd/3.0/

A mes grands-parents, Francine et René

Remerciements

Cette thèse a été effectuée au sein d'IFPEN dans le département séparation de la direction catalyse. Je tiens à remercier vivement M. Alain Methivier, chef du département, et M. Denis Guillaume, directeur de la direction pour leur accueil.

J'adresse mes plus sincères remerciements à M. Franck Launay pour m'avoir encadrée malgré les 500 kms de distance, pour ses conseils avisés, les discussions enrichissantes et les nombreuses corrections qui ont contribué à parfaire ce document.

Je voudrais remercier chaleureusement mes encadrants de tous les jours, M. Pierre-Louis Carrette et M. Dominique Picq, pour leur présence, leur investissement, leur enthousiasme et les nombreux conseils (scientifiques ou non) qu'ils m'ont donnés. Vous avez su me guider et m'épauler tout au long de ces trois années. Je vous remercie pour tous les bons moments qui ont parsemé ces trois ans et qui vont me manquer.

I'm grateful to Pr. Klaus J. Jens and Dr. Thierry Billard for the time that they have past to evaluate my work. I would like to thank Pr. Antoine Gedeon and Dr. Earl Goeether for their interest in this study and their participation to my committee.

Sans la contribution des partenaires DALMATIEN, cette thèse n'aurait pu être ce qu'elle est. Je remercie donc CETHRA (Lisa et Nathalie), EDF (Fabrice et Domitille) et le LRS (Myriam, Siham et Jae dong). J'adresse un remerciement particulier à toute l'équipe de l'ESPCI, Aurélien, Mélanie, Julien, Vincent, Lorena, Audrey et Emeric, qui ont supporté mes questions de novice, mes demandes de dernières minutes et qui ont partagé tous leurs résultats avec moi. Merci aussi à José et Jérôme pour avoir relu ma partie analytique et y avoir apporté de précieux commentaires. Ce fut un réel plaisir de travailler avec vous tous et de vous voir tous les six mois pour nos fameuses réunions.

Je tiens à remercier Paul pour m'avoir permis de suivre le projet OCTAVIUS.

Je tiens à remercier Bruno pour avoir partagé ses connaissances et avoir planché sur les mécanismes avec nous.

Cette thèse n'aurait pu se faire sans la précieuse collaboration de la direction analytique de l'IFPEN, je tiens à remercier tout particulièrement l'équipe de l'ICP, Fréderic, Catherine et Nathalie et l'équipe de la chromatographie ionique, Naima et Hanane, pour leur patience et leur disponibilité. Bien sûr je ne peux pas oublier Fred, Nadège, Lyes, et Jérémie qui en plus de me former à la GC/MS ont dû supporter mes ajouts d'échantillons imprévus et mes longues journées d'exploitation dans leur bureau. Merci pour votre accueil, votre bonne

humeur générale et surtout pour votre disponibilité. Merci Jérémie d'avoir cru en moi et pour ton soutien. Merci aussi à Ludovic pour m'avoir fait confiance.

Je tiens à remercier aussi tout le département R062 pour la RMN, le prêt de matériel, les différents conseils que vous m'avez donné.

Merci Olivia pour toutes nos pauses café, ta bonne humeur, ton soutien infaillible et quotidien lors de cette thèse et de m'avoir fait rencontrer ta petite famille avec qui j'ai passé des moments mémorables. Merci Stéphane pour y avoir contribué en partageant avec moi ta passion de la chimie lors de grandes discussions sous la véranda. Et bien sûr je remercie mes trois petits bonhommes pour leur pep's, leurs câlins et tous les bons moments que j'ai pu passer en les gardant.

J'aimerais remercier mes collègues du département séparation pour leur accueil. Gardez cette bonne humeur générale qui y règne. Ça a été un réel plaisir de travailler avec vous tous. Je n'oublierai pas les pauses café avec les grands discours et les fous rires. Merci de m'avoir supporté même quand je râlais (ou rigolais !!) et d'être toujours disponible pour aider un thésard en détresse. Ces 3 années parmi vous resterons pour moi un très bon souvenir. Merci à Antoine, Catherine, Christine, David, Emmanuelle, Fabrice, Patrick, Javier, Jean-Pierre C., Julien, Karine, Marc J., Michel, Philibert, Thierry et Arnaud. Je tiens à remercier Laetitia, Morgane, Alexandre, Anthony, Monique, Laurent, Aurèlie avec qui j'ai partagé de nombreuses discussions le midi et que j'ai adoré embêter (surtout toi Alex). Merci aussi à toi Elsa qui m'a permis de grandir et de prendre du recul. Merci Sophie pour ta patience, ta présence et ta disponibilité. Merci au bureau d'en face pour les boum boums, les éclats de rires et votre bonne humeur. Merci Jean-Pierre, pour ton sourire et nos discussions «cultes», merci Danielle pour ton franc parlé, ton oreille attentive et tes nombreux conseils. Merci Sonia pour ton sourire et ta bonne humeur de tous les jours, tu es un exemple à suivre.

Ma petite Leslie qu'aurais je fais sans toi pendant cette thèse ? Tu m'as accueillie dans ton bureau à mon arrivée, tu m'as formée au labo tu as râlé et tu râleras encore je le sais pour mes petits oublis de rangements, mais tu as toujours été disponible pour m'aider, m'écouter. Je te remercie de la confiance que tu m'as accordée en me laissant la T045 quelques mois mais merci surtout pour tous les fous rires et autres bons moments qu'on a pu passer ensemble. J'ai beaucoup appris à tes côtés, merci de m'avoir prise et gardée sous ton aile.

Sandra, je suis heureuse d'avoir appris à te connaitre et d'avoir partagé surtout cette dernière année avec toi. Merci pour tous les services que tu as pu me rendre. Je ne compte plus le nombre de fois où tu m'as vu débarquer dans ton bureau aussi bien surexcitée que

dépitée et tu as toujours été là pour m'écouter et me conseiller, voir même me secouer. Sans toi cette dernière année m'aurait paru beaucoup plus longue. Merci pour tout.

Je tiens à remercier les secrétaires Nathalie et Sandrine pour votre aide, votre bonne humeur et surtout pour votre disponibilité.

J'aimerai adresser mes remerciements aux autres thésards et post-doc. D'abord aux anciens qui m'ont donné des conseils précieux pour aborder et finir la thèse. Merci Laure et Vincent L. Merci Thibaut et Vincent G. pour m'avoir fait tourner la tête de nombreuses fois (à la salsa bien sûr). Merci à toi Caro pour tes conseils avisés. Merci Mathias pour m'avoir ravi les papilles plus d'une fois. Merci à Jérémy pour les bons moments et pour tes tacles légendaires. Merci Gaby, pour ta gentillesse et ton partage. Merci Alex pour les tant attendues images du vendredi qui ont manqué cette dernière année, merci aussi pour tes conseils. Merci à Lilia, pour m'avoir redonné le gout à la salsa, pour tous les moments partagés sur la piste et en voiture.

Merci aux thésards de la promo 2014 avec qui j'ai partagé les joies de l'ADIFP et de la thèse. Merci Yoldes et Taha. Merci Manu pour avoir essayé de sauver mon DD. Merci Régis pour la pause de 17h. Merci Camille, the Secrétaire, pour les nombreux souvenirs et les bons moments partagés. Merci Agnès pour m'avoir divertit lors de nos covoiturages et tes soirées de folies.

Je tiens à remercier aussi ceux qui continuent encore, Hugo, Benjamin, Mathieu, Nadia, Clément doudou et Robin.

Je souhaite dire un grand merci à mon Pierrot qui a partagé mon bureau après son excursion hollandaise. Merci de m'avoir accueillie à Amsterdam et fait découvrir la ville, d'avoir supporté mes bavardages, mes éclats de rires, les longues discussions avec Pierre-Louis et tout le reste. Merci pour les croissants du matin… Et n'oublie pas « duo rime avec Bureau ».

Florine, je ne pouvais pas t'oublier dans ces remerciements. Merci d'avoir toujours été là, d'avoir supporté mes excès de joies et de ras le bol. Pour tes conseils et tes câlins. Merci de m'avoir fait confiance. Merci pour la soirée du 28/09/2013. Tu as été le catalyseur d'une alchimie. Je te souhaite bon courage pour ta dernière ligne droite.

Ma debo, sans toi mon audition se serait mieux portée mais ces trois années auraient été bien tristes. Merci d'avoir toujours été dispo pour m'écouter, me secouer, me changer les idées. Merci pour ton brin de folie qui apporte une bouffée d'air frais, pour tous les bons

moments (et y en a eu beaucoup et j'espère qu'il y en aura beaucoup encore), pour les soirées à deux, à trois ou en famille !

Je finis ces remerciements thésard par mon covoitureur-viking, le plus grand pour la fin. Alban, déjà merci pour avoir commencé mon éveil musical, parce que c'était mal parti. Merci pour avoir supporté mon passage dans ton bureau 15 fois par jours et mes coups de fil à répétition !! Pour nos soirées bières, ta tartiflette, même si elle a un gout de trop peu, pour m'avoir dépannée quand j'en avais besoin, m'avoir écoutée, soutenue, pour ton fameux débat avec deb «chimie ou pas» qui me fait toujours tant sourire. Merci aussi d'avoir bien voulu partagé Olivia aux pauses !

Je souhaite remercier mes amis qui ont suivi de plus ou moins loin cette thèse mais qui ont toujours été là pour moi malgré la distance, le manque de temps. Merci Aurélie, Delphine, Marion R., Marion T., Sophie & juju, Anne-Laure, Zhilin et Zelie.

Merci Celia d'avoir toujours trouvé du temps et d'avoir pris des nouvelles de moi malgré la distance qui nous sépare, merci pour la Thaïlande et la visite de Singapour, qui m'ont permis de souffler pour finir la thèse sur les chapeaux de roues.

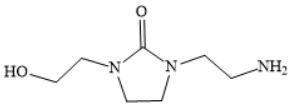
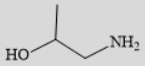
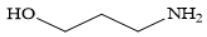
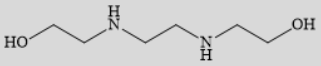
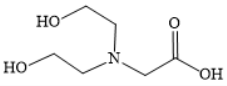
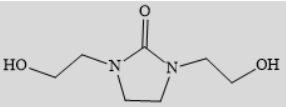
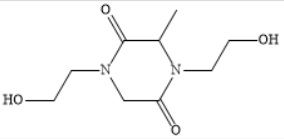
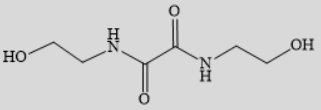
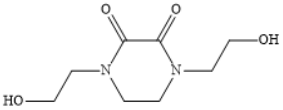
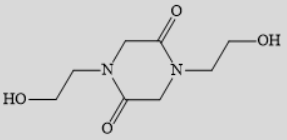
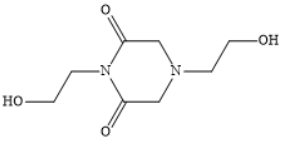
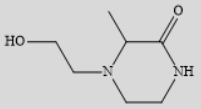
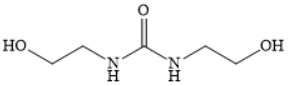
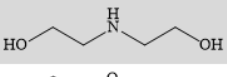
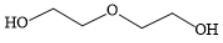
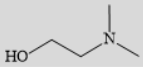
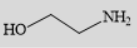
Merci à Seb et Nico, pour m'avoir encouragée depuis des années et m'avoir soutenue.

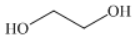
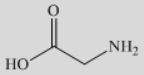
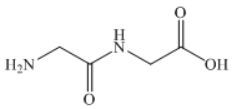
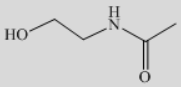
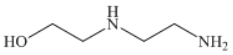
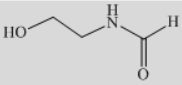
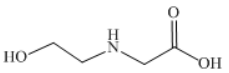
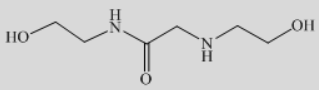
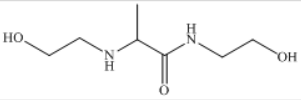
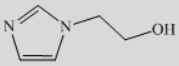
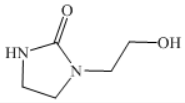
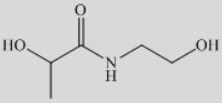
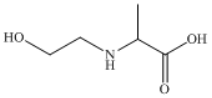
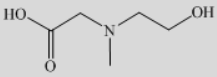
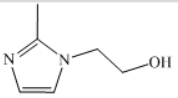
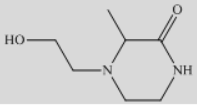
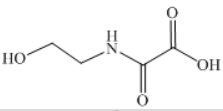
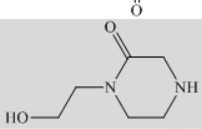
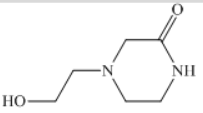
Merci Cindy pour m'avoir soutenue en prépa, pour avoir continué en école d'ingé pour avoir été là dans les bons moments comme dans les mauvais. Merci de rester là avec la distance.

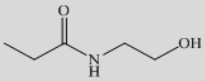
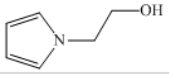
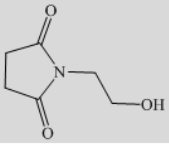
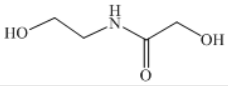
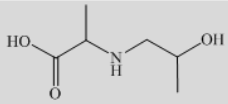
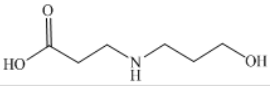
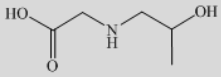
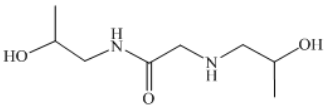
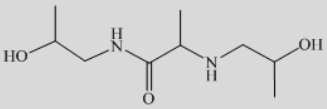
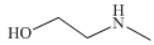
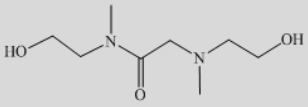
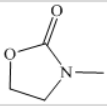
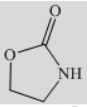
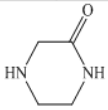
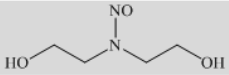
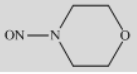
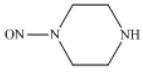
Je souhaite remercier ma famille. Merci à mes oncles, tantes, cousins et cousines qui m'ont toujours soutenue et encouragée. Je tiens aussi à remercier ma sœur Cathy, pour ses encouragements toujours aux moments cruciaux. Merci à mes parents, mes grands-parents pour leur soutien indéfectible qui m`a permis d'aller jusqu'au bout de mes études.

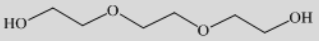
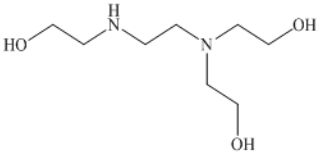
Et pour finir merci Quentin, sans ton soutien pendant cette dernière année de rédaction, je n'y serais pas arrivée avec autant d'aisance, tu as toujours cru en moi et su être présent au bon moment pour me remotiver ou me secouer. Merci pour ta patience lors de ces derniers mois et merci de toujours me donner le sourire.

Abbreviations of chemicals compounds (to be printed alone)

Abbreviations	Identification	Chemical structure	M g/mol
AEHEIA	N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidin-2-one		173
1AP2	1-Aminopropan-2-ol		75
3AP1	3-Aminopropan-1-ol		75
BHEEDA	N,N'-bis(2-hydroxyethyl)ethylenediamine		148
Bicine	N,N-bis(2-hydroxyethyl)glycine		163
BHEI	N,N'-bis(hydroxyethyl)imidazolidin-2-one		174
3-MBHEPDO2,5	1,4-bis(2-hydroxyethyl)-3-methylpiperazin-2,5-dione		216
BHEOX	N,N'-bis(2-hydroxyethyl)oxalamide		176
BHEPDO2,3	N,N'-bis(2-hydroxyethyl)piperazin-2,3-dione		202
BHEPDO2,5	N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione		202
BHEPDO2,6	N,N'-bis(2-hydroxyethyl)piperazin-2,6-dione		202
BHEPO	1,4-bis(2-hydroxyethyl)piperazin-2-one		188
BHEU	N,N'-bis(2-hydroxyethyl)urea		148
DEA	Diethanolamine		105
DEG	Diethyleneglycol		106
DMAE	Dimethylaminoethanol		89
DMPO	1,4-dimethylpiperazin-2-one		
MEA	Ethanolamine		61

Abbreviations	Identification	Chemical structure	M g/mol
EG	Ethyleneglycol		62
Gly	Glycine		75
Glygly	N-Glycylglycine		132
HEA	N-(2-hydroxyethyl)acetamide		103
HEEDA	N-(2-hydroxyethyl)ethylenediamine		104
HEF	N-(2-hydroxyethyl)formamide		89
HEGly	N-(2-hydroxyethyl)glycine		119
HEHEAA	N-(2-hydroxyethyl)-2-((2-hydroxyethyl)amino)acetamide		162
2-MHEHEAA	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)propanamide		176
HEI	N-(2-hydroxyethyl)imidazole		112
HEIA	N-(2-hydroxyethyl)imidazolidin-2-one		130
HEL	N-(2-hydroxyethyl)lactamide		133
HEMGly	N-(2-hydroxyethyl)-2-methylglycine		133
N-MHEGly	N-(2-hydroxyethyl)-N-methylglycine		133
HEMI	N-(2-hydroxyethyl)-2-methylimidazole		126
3-M-4HEPO	4-(2-hydroxyethyl)-3-methyl-piperazin-2-one		158
HEOX	N-(2-hydroxyethyl)oxamic acid		133
1HEPO	1-(2-hydroxyethyl)piperazin-2-one		144
4HEPO	4-(2-hydroxyethyl)piperazin-2-one		144

Abbreviations	Identification	Chemical structure	M g/mol
HEPr	N-(2-hydroxyethyl)propanamide		117
HEPyr	N-(2-hydroxyethyl)pyrrole		111
HESucc	N-(2-hydroxyethyl)succinimide		143
HHEA	2-Hydroxy-N-(2-hydroxyethyl)acetamide		119
HPAla	N-(2-hydroxypropyl)alanine		147
HPβala	N-(3-hydroxypropyl)-β-alanine		147
HPGly	N-(2-hydroxypropyl)glycine		133
HPHPAA	N-(2-hydroxypropyl)-2-(2-hydroxypropylamino)acetamide		190
HPHPPA	N-(2-hydroxypropyl)-2-(2-hydroxypropylamino)propanamide		204
MAE	(2-Methylamino)ethanol		75
MHEAHEMAA	2-[methyl-(2-hydroxyethyl)]amino-N-(2-hydroxyethyl)-N-methylacetamide		190
MOZD	N-methyloxazolidinone		101
OZD	Oxazolidin-2-one		87
PO	Piperazin-2-one		100
NDELA	N-nitrosodiethanolamine		134
NDMA	N-Nitrosodimethylamine		75
NMOR	N-nitrosomorpholine		116
NPZ	N-nitrosopiperazine		115

Abbreviations	Identification	Chemical structure	M g/mol
TEG	Triethyleneglycol		150
THEED	N,N,N'-tris(2-hydroxyethyl)ethylenediamine		192

Contents

Abbreviations 15

1. Introduction 17

1.1. General context 17

1.2. Carbon capture and storage 18

1.3. Objectives 20

2. Literature review 21

2.1. Thermal degradation 21

2.2. Oxidative degradation 25

2.3. Effect of SO_x and NO_x 41

2.4. Conclusion 43

3. Analytical methods 44

3.1. Liquid phase analyses 46

3.1.1. Ion chromatography 46

3.1.2. GC/FID 46

3.1.3. GC/MS 46

3.1.4. FT-ICR/MS 47

3.1.5. LC/MS/MS 48

3.1.6. NMR 50

3.2. Head Space analyses 50

3.3. Gas phase analyses 51

3.3.1. Sep-Pak Cartridges 51

3.3.2. Tenax cartridges 52

4. Experimental Part 53

4.1. Solvent degradation experiments 53

4.1.1. Pilot plant 53

4.1.2. Laboratory equipment 55

4.2. Experiments for mechanisms validation 60

4.2.1. Experiments in oven 60

4.2.2. Syntheses in stirred reactors 61

5. Identification of degradation products and mechanisms proposal 63

5.1. Products already observed in literature 63

5.2. Novel degradation products 75

5.3. Conclusion 100
6. Recurrent reactions 102
6.1. Introduction 102
6.2. Alkylation/Dealkylation 105
6.3. Aldehydes/ ketones and corresponding acids formation 106
6.4. Aldolisation 108
6.5. Amidification 109
6.6. Glycols formation 112
6.7. Eschweiler-Clarke 114
6.8. Amino acids formation 115
6.9. Ring closure of carbamates 118
6.10. Oxazolidines and tetrahydrooxazines formation 120
6.11. Piperazinones formation 122
6.12. Oxazolines and homologues formation 124
6.13. Imidazoles and homologues formation 126
6.14. Succinimides formation 127
6.15. Pyrroles formation 129
6.16. Pyridines formation 130
6.17. Conclusion 132
7. Conclusion and Perspectives 133
References 135
A. Appendix A – Supplementary information for analytical methods and experiments 145
Appendix – GC parameters 146
Appendix – LC/MS/MS parameters 147
Appendix – List of chemicals 150
Appendix – Experiments protocol 154
B. Appendix B – Chromatograms, NMR spectra and mass spectra of products 156
Appendix – Chromatograms 157
Appendix – HHEA identification 161
Appendix – HEOX identification 163
Appendix – HEHEAA identification 164
Appendix – BHEPDO2,5 identification 165

Appendix – 2-methyloxazolidine identification 166
Appendix – N-nitroso-2-methyloxazolidine identification 167
Appendix – GC/MS-TOF mass spectra of unidentified products 168
Appendix – Pyrazines identification 172
Appendix –Mass spectra of compounds observed in chapter 6 175
C. Appendix C – Publications 190
Figures Captions 240
Tables Captions 244
Schemes Captions 246

Abbreviations

%w pourcentage of weight

Ald Aldehydes

Amu Atomic Mass Unit

ANR Agence Nationale pour la Recherche (National Agency for Research)

APCI Atmospheric-Pressure Chemical Ionization

B molality

Cα Carbon on α position

Cβ Carbon on β position

CCS Carbon Capture and Storage

CI Chemical Impact

CIS Cooled Injection System

CO_2 Carbon dioxide

d days

EI Electron Ionisation

Eq Equivalent

ESI ElectroSpray Ionization

FID Flame Ionization Detector

FT-ICR/MS Fourier Transform Ion Cyclotron Resonance Mass

FTIR Fourier Transform Infrared Spectrocopy

GC Gas Chromatography

GHG Greenhouse Gas

Gt Gigatons

HPLC/DAD High Performance Liquid Chromatography/ Diode Array Detector

HSQC Heteronuclear Single Quantum Coherence

HSS Heat Stable Salt

HS-SPME Head Space Solid Phase Micro-Extraction

IC Ionic Chromatography

ICP-MS Inductively Coupled Plasma - Mass Spectroscopy

IEA International Energy Agency

Ket Ketones

LC Liquid Chromatography

mol moles

MRM Multiple Reaction Monitoring

MS Mass Spectrometry

Mw or M Molecular weight

m/z mass to charge ratio

NCI Negative Chemical Impact

NIST National Institute of Standard Library (for GC-MS)

NL Normal liters

NMR Nuclear Magnetic Resonance

PCC Post Combustion Capture

PCI Positive Chemical Impact

P_{CO2} Partial pressure of CO_2

P_{O2} Partial pressure of O_2

ppm parties per millions

rpm revolution per minutes

rt retention time

SIM selected-ion monitoring

TDU ThermoDesorption unit

TOF Time of Flight

V volts

1. Introduction

1.1.General context

The global temperature increase (~ 0.8 °C) over the last three decades (Seinfeld, 2011) as well as the climate change have become an alarming environmental problem. These phenomena are attributed to the increase of greenhouse gases concentrations (GHG) in the atmosphere and more particularly of carbon dioxide (CO_2), which accounts for about 60% of the heat trapped in the atmosphere. Nowadays, GHG emissions reduction is one of the biggest challenges of our societies.

CO_2 concentration is about 40% higher than before the industrial revolution (International Energy Agency, IEA, 2013) and it tends to increase dramatically. 31.3 Gt of CO_2 ($GtCO_2$) were emitted in 2011. 60% of these emissions were due to fossil fuel combustion (i.e. oil, coal and natural gas): more precisely, coal combustion accounted for 44 % of the global CO_2 emissions (13.7 $GtCO_2$). With the growing demand of energy, without restrictions, CO_2 emissions from coal combustion would go up to 15.7 Gt in 2035. Therefore, different scenarios to reduce emissions were taken into account by IEA (Figure 1.1).

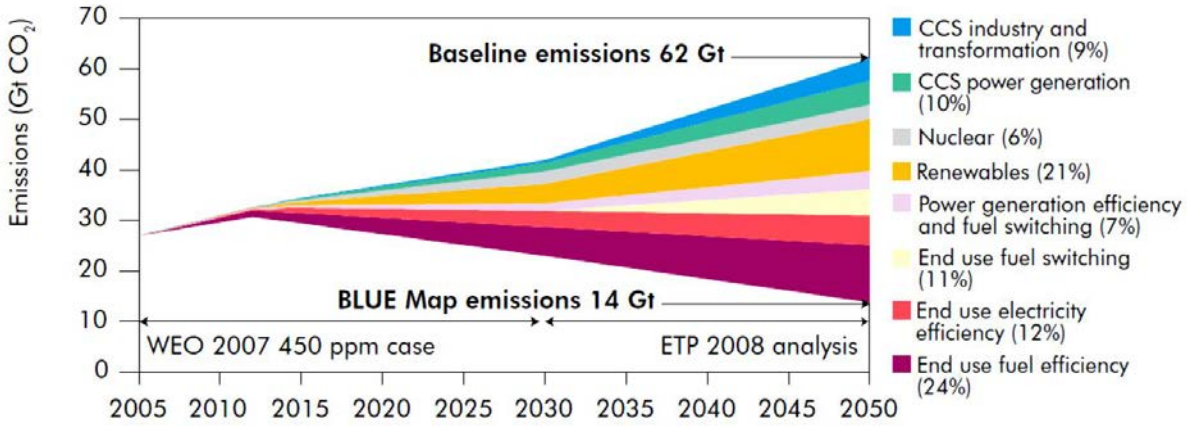


Figure 1.1. Scenarios to reduce CO_2 emissions to the atmosphere (IEA, 2008).

Among them, carbon capture and storage (CCS) may enable about 20% of CO_2 emissions reduction. CCS is a mature technology that could be used rapidly as a mid-term solution to mitigate CO_2 environmental impact. CCS could be involved in different cases : coal or natural gas power plants, refineries, cement plants or steel furnaces.

1.2. Carbon capture and storage

Three main technologies exist to capture CO_2: pre-combustion, oxy-combustion and post-combustion capture (PCC) (Kenarsari et al., 2013; Lepaumier et al., 2010).

Among them, PCC is the most mature technology. It can be implemented on existing plants to treat their emissions, especially coal fired power plants. The main challenge of this technology is to treat high gas flowrates with low CO_2 partial pressure.

Four types of PCC systems are under development: adsorption, membrane separation, cryogenic separation and absorption.

Solvents absorption is the most mature technology, and especially, absorption by an aqueous amine solution, thus taking advantage of the strong experience of industrials in natural gas deacidification (Islam et al., 2011).

Amine scrubbing process, described in Figure 1.2, is a cyclic process where aqueous solutions of amines -usually called solvents - are used to absorb CO_2 from flue gas. In the case of coal-fired power plants, this gas contains typically around 70% of N_2, 15% of CO_2, 10% of H_2O and 5% of O_2. Moreover, some traces of SO_x and NO_x are present (about 20 ppm of SO_x and 100 ppm of NO_x) despite adapted pre-treatments (Bhown and Freeman, 2011).

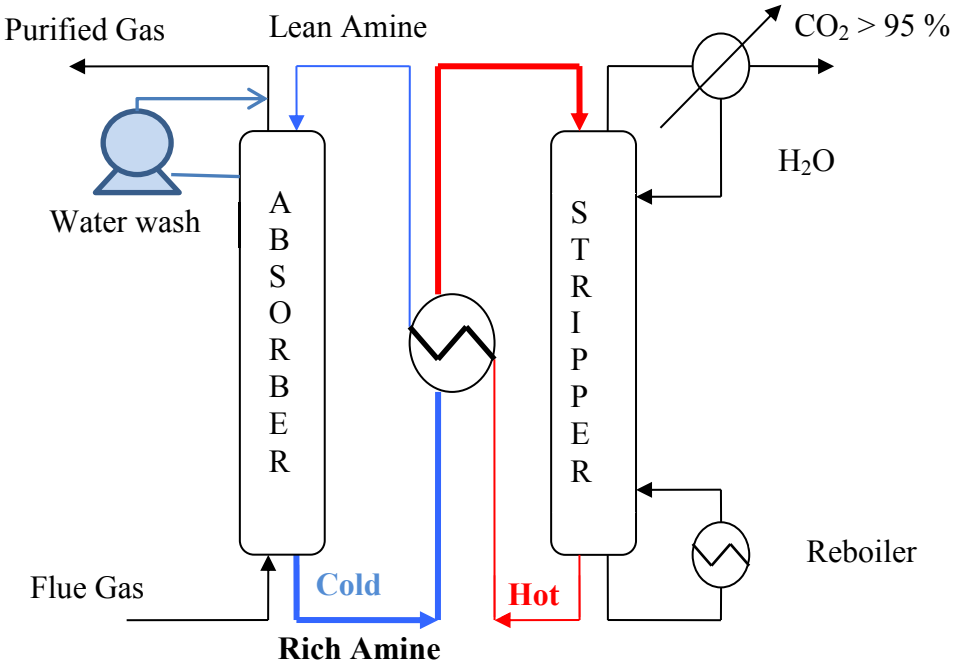


Figure 1.2. Simplified CO_2 capture flow sheet

Solvent goes through two steps, absorption and regeneration:

- In the absorber, CO_2 is absorbed in the solvent, which circulates counter-currently. A reversible exothermic chemical reaction takes place between CO_2 and amine, which leads to carbamate and/or carbonate formation. The temperature ranges usually from 40 to 70°C (depending on the solvent), due to the exothermic reaction. The pressure is close to atmosphere pressure and partial pressure of CO_2 is between roughly 150 mbar (inlet gas) and 15 mbar (outlet gas) whereas partial pressure of O_2 is around 50 mbar.
- In the stripper, the CO_2-rich solvent is heated to regenerate the amine and to produce free CO_2. Pressure is between 1.8 (classical case) and 6 bar. Maximum temperature (in the reboiler) is bounded between 120 and 160°C depending mainly on the boiling point of involved amines: 120°C in the case of the benchmark molecule, i.e. monoethanolamine (MEA). CO_2 partial pressure is close to 1 bar and O_2 partial pressure is unknown but considered much lower than in the absorber due to O_2 stripping at high temperature.

The desorbed CO_2 is compressed (110 bar) for transport and storage.

However before being implemented, this technology needs economic (high energy consumption) but also environmental acceptance.

Indeed, the deployment of this technology is supposed to reduce the thermal efficiency of a modern power plant from a yield of 45 % to 35 %, in the case of MEA. Such efficiency penalties are mainly related to the cost of solvent regeneration and to the CO_2 compression (Bouillon et al., 2009; Rao and Rubin, 2002). Therefore most of the studies are on these aspects.

However, degradation of the solvent due to amines reaction with flue gas components (O_2, CO_2, NO_x, SO_x...) (Gouedard et al., 2012) should be taken in account too. It generates additional costs (solvent loss, foaming, fouling and corrosion) and can have an impact on environment through the contamination of treated flue gas by organic compounds (Islam et al., 2011; Moser et al., 2011). These compounds could be potentially dangerous for humans or environment according to their concentration and their toxicity like nitrosamines (IARC, 1978; NTP, 2012; Thitakamol et al., 2007). This toxicity is a potential showstopper for this technology.

The degradation of different amines has been studied in the case of CO_2 capture and also natural gas treatment applications (Gouedard et al., 2012; Lee et al., 2013); main works

concern monoethanolamine (MEA) (da Silva et al., 2012; Vevelstad, 2013; Voice, 2013; Voice and Rochelle, 2013), diethanolamine (DEA), methyldiethanolamine (MDEA), piperazine (PZ) (Freeman, 2011; Freeman and Rochelle, 2012a; 2012b; Lensen, 2004) and 2-amino-2-methylpropan-1-ol (AMP) (Wang, 2012; Wang and Jens, 2011).

MEA is the benchmark molecule due to its high loading at low CO_2 partial pressure and high CO_2 absorption kinetic. Moreover MEA is highly soluble in water, provides aqueous solutions with a low viscosity and has a low price.

This is the most studied amine with the description of about fifty degradation products. However, Vevelstad, 2013 showed with laboratory experiments that some degradation products were not observed due to unclosed nitrogen mass balances. Moreover, even if many studies were done, few of them were focused on pilot plant degradation and the chemistry involved in degradation was unclear and needed more research. Thus, our work focused on MEA degradation.

1.3.Objectives

Main objectives of this work were to identify as many degradation products as possible, and to propose for most of them a realistic formation pathway that could be transposed to other amines for a prediction of their behaviour.

Firstly, a critical literature review is proposed, which is focused on MEA degradation with a list of degradation products observed and proposed mechanisms. This review is reported in chapter 2.

Secondly, analytical methods are developed to identify novel degradation products. All these methods are reported in chapter 3.

Then, the IFPEN pilot plant, the representative test as well as experiments made to validate our mechanisms proposals or to synthesise standards are described in chapter 4.

Degradation products identified in this work are presented in chapter 5. In the first part, already observed degradation products are reported with some proposals of new mechanisms pathways and in the second part, novel degradation products observed are detailed with their suggested mechanism of formation.

In the chapter 6, some chemical reactions previously observed are generalized. They are applied to three other amines to predict their degradation products and to confirm that some reactions are transposable to other amines.

2. Literature review

Numerous authors described degradation of MEA in laboratory but few papers were about pilot plant degradation (Cotugno et al., 2014; da Silva et al., 2012; Lepaumier et al., 2011a; Reynolds et al., 2013; Strazisar et al., 2003). Moreover, many papers reported degradation products but few mechanisms of formation were proposed.

This chapter is a critical literature analysis*. **Degradation products observed in pilot plants are written in bold in this chapter.**

In the post-combustion capture process, two kinds of degradation occur: thermal degradation and oxidative degradation. Most of the lab studies focused on one of these degradations. Thermal degradation occurs at high temperature and high CO_2 partial pressure in the stripper (Davis, 2009; Holub et al., 1998; Lepaumier, 2008). Oxidative degradation is supposed to occur in the absorber and is mainly due to the presence of a large amount of O_2 in flue gases (Lepaumier et al., 2009b; Rooney et al., 1998a; Sexton, 2008).

In the present chapter, thermal degradation is reported first, then oxidative degradation and finally effect of SO_x and NO_x on degradation is described.

2.1. Thermal degradation

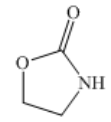
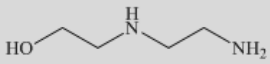
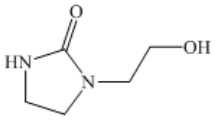
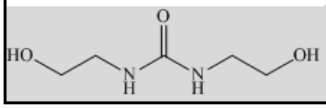
Thermal degradation takes place mainly in the stripper (Davis and Rochelle, 2009; Lepaumier et al., 2011a). Most of the studies postulated that such degradation is due to the combination of high temperature and CO_2.

A fundamental study on degradation due to high temperature without CO_2 was performed to emphasize the role of heat (Lepaumier, 2008). This type of degradation caused dealkylation, dimerization and cyclisation but no mechanism had been proposed, even if a radical pathway was highly likely to occur as for oxidative degradation (Lepaumier, 2008). In this case, most important degradation products were ammonia and N-(2-hydroxyethyl)ethylenediamine (HEEDA).

Because of high partial pressure of CO_2 and high temperature, thermal degradation of MEA could lead to successive degradation compounds. The main ones were given in Table 2.1.

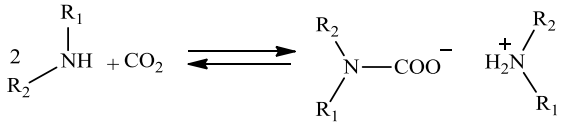
* Update of of a review focused on MEA degradation published by Gouedard et al., 2012 (see Annexe C)

Table 2.1 MEA main thermal degradation products

Chemical structure	Name (Abbreviation)	Mw (g/mol)	References
	**Oxazolidin-2-one (OZD)**	87	Lepaumier et al., 2009a Lepaumier et al., 2011a Strazisar et al., 2001 Strazisar et al., 2003
	**N-(2-hydroxyethyl)ethylenediamine (HEEDA)**	104	Davis and Rochelle, 2009 Lepaumier et al., 2009a Lepaumier et al., 2011 Reynolds et al., 2013 Supap et al., 2006
	**N-(2-hydroxyethyl)imidazolidin-2-one (HEIA)**	130	Davis and Rochelle, 2009 Lepaumier et al., 2009a Lepaumier et al., 2011a Sexton and Rochelle, 2011 Strazisar et al., 2001 Supap et al., 2006
	N,N'-bis(2-hydroxyethyl)urea (BHEU)	148	Davis and Rochelle, 2009 Lepaumier, 2008

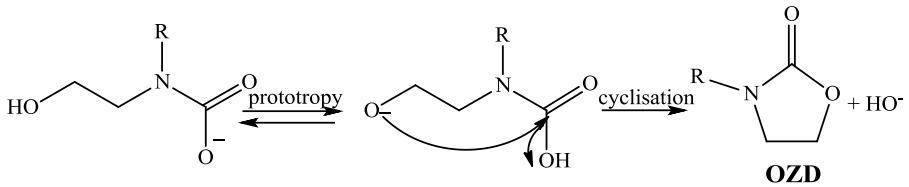
Formation of these compounds had been well established. Proposed mechanisms were listed below (for MEA, R_1 = H in all figures).

Firstly, MEA reacts with CO_2 to form a carbamate (Scheme 2.1), this reaction takes place in the absorber.



Scheme 2.1. Carbamate formation (R^1 = H, R^2 = CH_2CH_2OH)

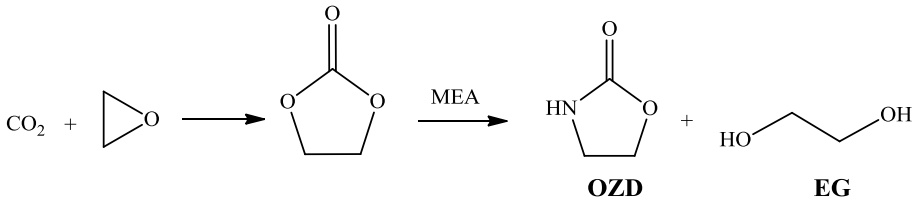
Then the corresponding carbamate can be transformed into oxazolidin-2-one (Scheme 2.2) (Holub et al., 1998; Lepaumier et al., 2009a; Polderman et al., 1955).



Scheme 2.2. Oxazolidin-2-one formation (R^1 = H)

Vevelstad et al., 2013b observed that OZD is strongly affected by oxygen concentration. They proposed another mechanism (Scheme 2.3) based on literature (Patil et al., 2008). CO_2

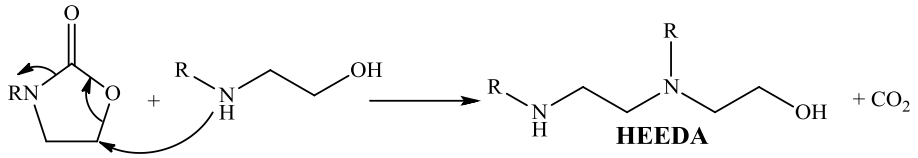
can react with ethylene oxide (formation explained below) to form 1,3-dioxolan-2-one. This intermediate can react with MEA to form OZD.



Scheme 2.3. Oxazolidin-2-one formation adapted from Patil et al., 2008

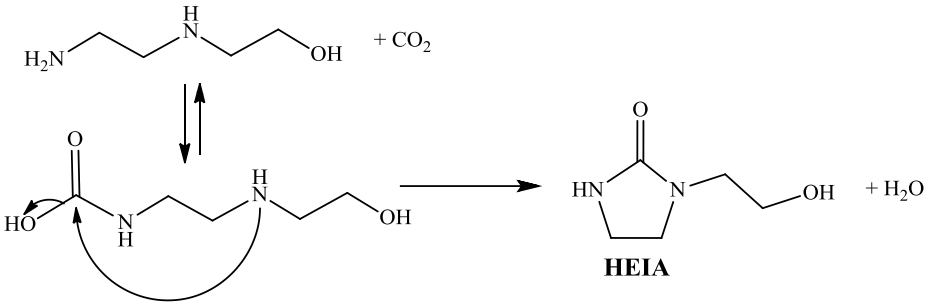
Both mechanisms might occur in pilot plant, even if the first one should be the major mechanism.

Oxazolidin-2-one can react with another molecule of MEA to form HEEDA (Scheme 2.4) (Davis and Rochelle, 2009; Holub et al., 1998; Lepaumier et al., 2009a).



Scheme 2.4. Diamine formation (R^1 = H)

HEEDA can then react with CO_2 to form another carbamate, followed by intramolecular cyclisation giving HEIA (Scheme 2.5), which is not very reactive and can accumulate in the solution (Davis and Rochelle, 2009; Lepaumier et al., 2009a; Sexton and Rochelle, 2011).

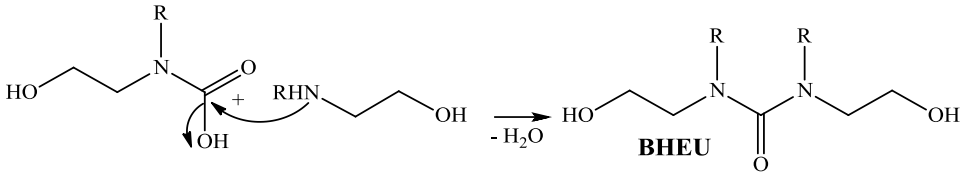


Scheme 2.5. Imidazolidin-2-one formation

The two last schemes can be discussed. Polderman et al., 1955 described HEIA as the precursor of HEEDA but thanks to HPLC analyses, Davis and Rochelle, 2009 and Lepaumier et al., 2011a have shown that it was the opposite. Moreover Lepaumier et al., 2009a showed that HEIA was the major degradation product in thermal conditions and was very stable. These results were in accordance with Fazio, 1984 who described diamines syntheses with oxazolidin-2-ones as starting materials.

Similarly to imidazolidin-2-ones formation, ureas can be obtained by reaction between carbamates and amines (Scheme 2.6) (Davis and Rochelle, 2009; Lepaumier, 2008). This

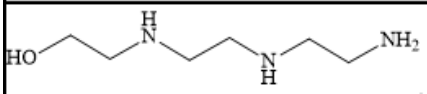
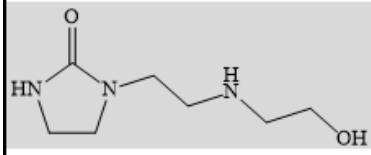
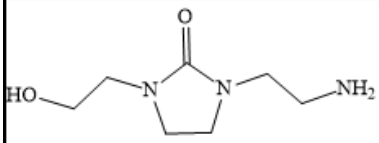
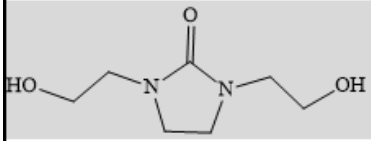
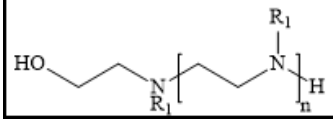
reaction is less favourable than that described in Scheme 2.2 (intermolecular vs intramolecular reaction).



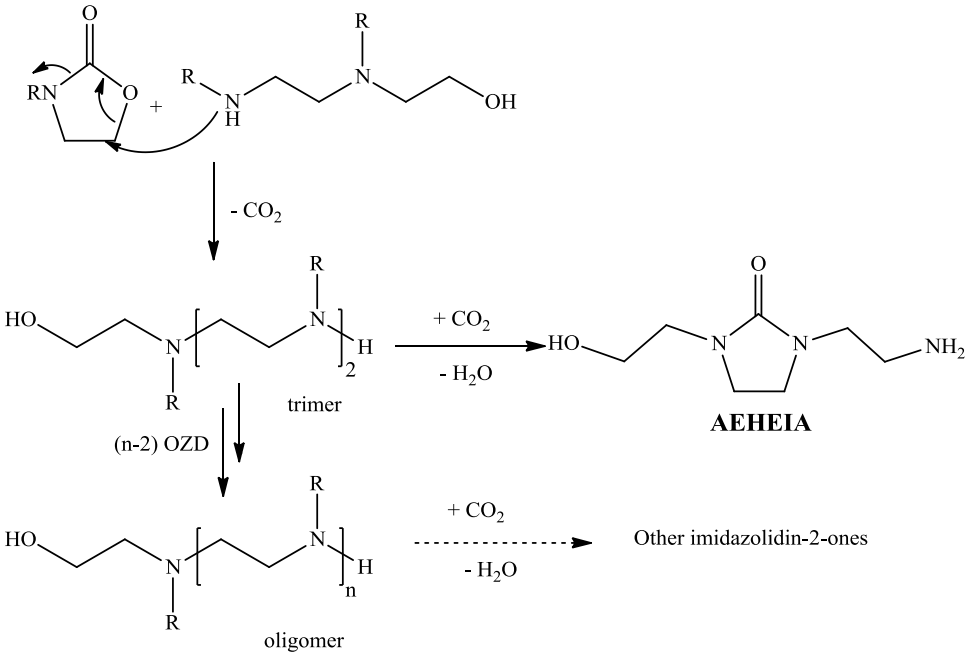
Scheme 2.6. Ureas formation (R^1 = H) according to Davis and Rochelle 2009

Other degradation products are formed starting from HEEDA (Table 2.2).

Table 2.2. MEA thermal degradation products formed from HEEDA.

Chemical structure	Name (Abbreviation)	Mw (g/mol)	References
	N-(2-hydroxyethyl)diethylenetriamine	147	Davis, 2009 Huang et al., 2014
	N-[2-[(2-hydroxyethyl)amino]ethyl]imidazolidin-2-one	173	Davis, 2009 Huang et al., 2014
	N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidin-2-one (AEHEIA)	173	Da silva et al., 2012 Huang et al., 2014 Lepaumier et al., 2011a
	N,N'-bis(hydroxyethyl)imidazolidin-2-one (BHEI)	174	Huang et al., 2014 Lepaumier et al., 2009a
	/	/	Davis, 2009

Davis, 2009; Lepaumier, 2008 showed that successive addition products (Scheme 2.7) can be formed according to the mechanism described in Scheme 2.4 (ring opening of oxazolidin-2-one). Each addition product can form imidazolidin-2-one derivatives as described in Scheme 2.5.



Scheme 2.7. Degradation products formed from HEEDA (R^1 = H)

To the best of our knowledge, no other specific thermal degradation products of MEA have been described in literature.

2.2.Oxidative degradation

Oxidative degradation is mainly described in absorber conditions (O_2, CO_2). Solutions were loaded with CO_2, therefore some similar products as for thermal degradation were observed. Fewer papers studied oxidative degradation in the absence of CO_2 (Lepaumier et al., 2009b; 2011a).

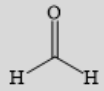
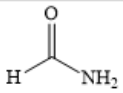
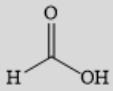
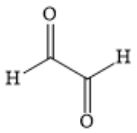
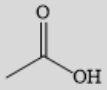
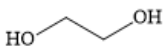
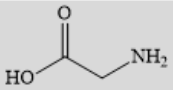
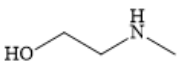
Some authors worked on the catalytic effect of dissolved metallic ions (Fe^{2+}/Fe^{3+}, Cu^{2+}, V^{3+}) on oxidative degradation of MEA (Bello and Idem, 2006; Goff and Rochelle, 2004; 2006; Sexton and Rochelle, 2011). Metallic ions in solution could be generated by corrosion or added through anticorrosion metallic salts ($CuCO_3$, $NaVO_3$).

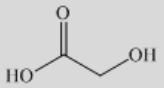
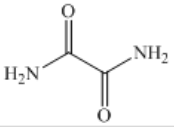
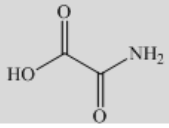
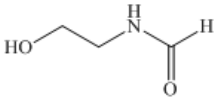
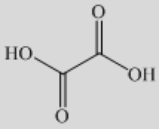
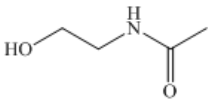
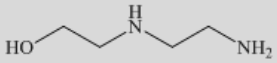
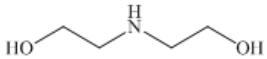
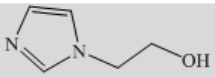
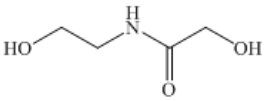
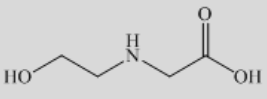
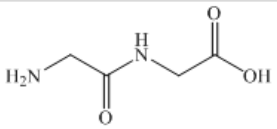
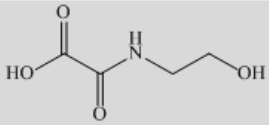
Firstly, the more likely oxidative degradation products were listed. They were cited by two or more teams or their formation was explained by realistic mechanisms. They were listed by increasing molecular weights in Table 2.3. Even if it was not always explained in publications, Confirmation by standards of these products was supposed. Main oxidative degradation reactions are dealkylation, addition and piperazinones formation.

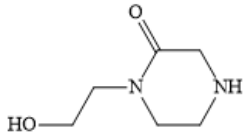
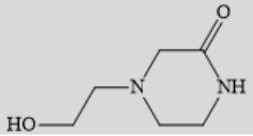
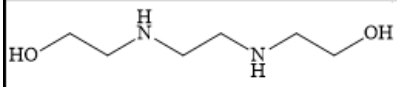
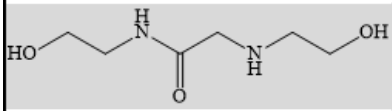
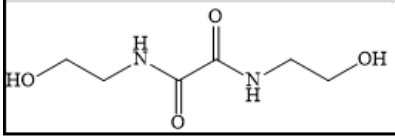
Secondly, degradation products without explained mechanisms were given in Table 2.4 but their formation was proved or very likely.

Finally, some unexpected degradation products were listed.

Table 2.3. Well-described MEA oxidative degradation products (schemes 2.9-2.23).

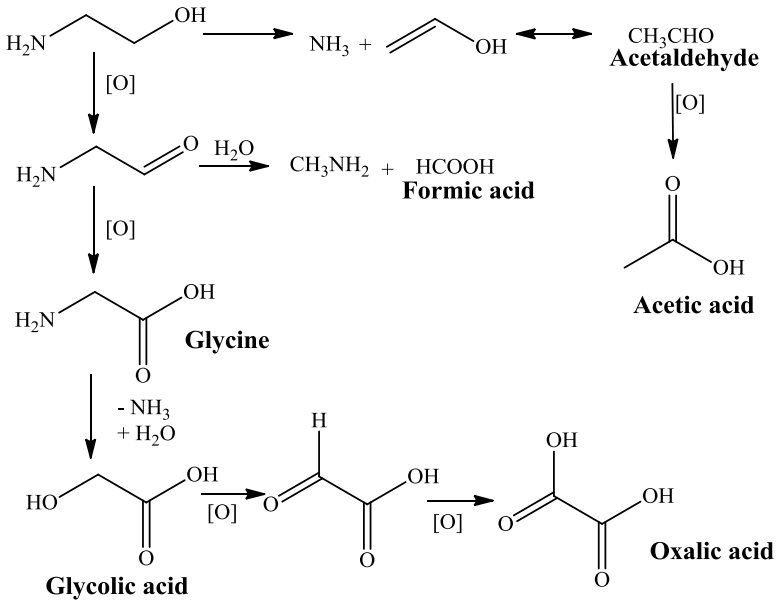
Chemical structure	Name (Abbreviation)	Mw (g/mol)	References
NH_3	**Ammonia**	17	Goff, 2005 Lepaumier et al., 2009b Sexton and Rochelle, 2011 Strazisar et al., 2003 Supap et al., 2006 Vevelstad, 2013
	**Formaldehyde**	30	Goff, 2005 Lepaumier, 2008 Sexton and Rochelle, 2011 Supap et al., 2001 Vevelstad, 2013
$H_3C—NH_2$	Methylamine	31	Lepaumier et al., 2009 Rooney et al., 1998b Sexton and Rochelle, 2011 Strazisar et al., 2003
	**Acetaldehyde**	44	Lepaumier et al., 2011a Rooney et al., 1998b Sexton and Rochelle, 2011 Strazisar et al., 2003 Supap et al., 2006 Vevelstad, 2013
	Formamide	45	Lepaumier et al., 2011a Sexton and Rochelle, 2011
	**Formic acid**	46	Lepaumier, 2008 Lepaumier et al., 2011a Rooney et al., 1998b Sexton and Rochelle, 2011 Strazisar et al., 2003 Supap et al., 2001
	Glyoxal	58	Lepaumier, 2008 Sexton and Rochelle, 2011
	**Acetic acid**	60	Lepaumier, 2008 Lepaumier et al., 2011a Rooney et al., 1998b Sexton and Rochelle, 2011 Strazisar et al., 2003
	Ethylene glycol	62	Lepaumier, 2008 Voice, 2013
	Glycine	75	Bedell, 2011 Lepaumier, 2008 Rooney et al., 1998b
	2-(methylamino)ethanol (MAE)	75	Davis and Rochelle, 2009 Goff, 2005 Lepaumier, 2008 Rooney et al., 1998b

Chemical structure	Name (Abbreviation)	Mw (g/mol)	References
	Glycolic Acid	76	Lepaumier et al., 2009b Rooney et al., 1998b Sexton and Rochelle, 2011 Supap et al., 2011
	Oxalamide, Oxamide	88	Supap et al., 2011
	Oxamic acid	89	Lepaumier, 2008
	**N-(2-hydroxyethyl)formamide (HEF)**	89	Lepaumier et al., 2009b Lepaumier et al., 2011a Strazisar et al., 2003 Supap et al., 2011
	**Oxalic acid**	90	Davis, 2009 Rooney et al., 1998b Sexton and Rochelle, 2011 Supap et al., 2011
	**N-(2-hydroxyethyl)acetamide (HEA) (or N-acetylethanolamine)**	103	Lepaumier et al., 2009b Lepaumier et al., 2011a Strazisar et al., 2003 Supap et al., 2006 Supap et al., 2011
	**N-(2-hydroxyethyl)ethylenediamine (HEEDA)**	104	Davis and Rochelle, 2009 Lepaumier et al., 2009b Lepaumier et al., 2011a Supap et al., 2006
	**Diethanolamine (DEA)**	107	Da silva et al., 2012 Huang et al., 2013 Vevelstad et al., 2013
	**N-(2-hydroxethyl)imidazole (HEI)**	112	Cotugno et al., 2014 Lepaumier et al., 2011a Sexton and Rochelle, 2011
	**2-Hydroxy-N-(2-hydroxyethyl)acetamide (HHEA)**	119	Lepaumier et al., 2011a Supap et al., 2011 Vevelstad, 2013
	**N-(2-hydroxyethyl)glycine (HEGly)**	119	Da silva et al., 2012 Vevelstad et al., 2013 Vevelstad, 2013 Voice, 2013
	N-glycylglycine (Glygly)	132	Strazisar et al., 2001 Supap et al., 2006
	**N-(2-hydroxyethyl)oxamic acid (HEOX)**	133	Lepaumier et al., 2009b Supap et al., 2011 Voice, 2013

Chemical structure	Name (Abbreviation)	Mw (g/mol)	References
	**N-(2-hydroxyethyl)piperazin-2-one ou 1-(2-Hydroxyethyl)piperazin-2-one (1HEPO)**	144	Lepaumier et al., 2009b Lepaumier et al., 2011a Strazisar et al., 2003
	**N-(2-hydroxyethyl)piperazin-3-one (4HEPO)**	144	Cotungo et al., 2014 Lepaumier et al., 2009b Lepaumier et al., 2011a Strazisar et al., 2003
	N,N'-bis(2-hydroxyethyl)ethylenediamine (BHEEDA)	148	Lepaumier, 2008
	**N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA)**	162	Da silva et al., 2012 Lepaumier et al., 2011a Strazisar et al., 2003
	**N,N'-bis(2-hydroxyethyl)oxalamide (BHEOX)**	176	Da silva et al., 2012 Lepaumier et al., 2011a Supap et al., 2011 Vevelstad, 2013

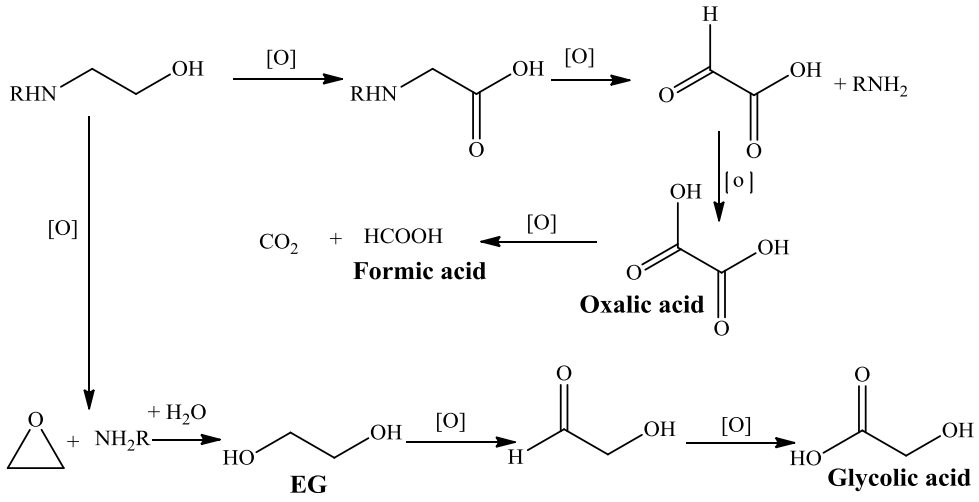
Aldehydes, carboxylic acids, ammonia and methylamine are called first generation degradation products because they are formed by degradation first. Therefore, their formation then their reactions with other compounds are firstly described.

Two general mechanisms were proposed for the generation of carboxylic acids by. Rooney et al., 1998b (Scheme 2.8) and by Lepaumier et al., 2009b (Scheme 2.9). In both of them, volatile amines like ammonia or methylamine are formed as well as aldehydes which are acids precursors. It is noteworthy that the mechanism of methylamine formation described by Rooney et al., 1998b (Scheme 2.8) remains unclear.



Scheme 2.8. Carboxylic acids formation according to. Rooney et al., 1998b

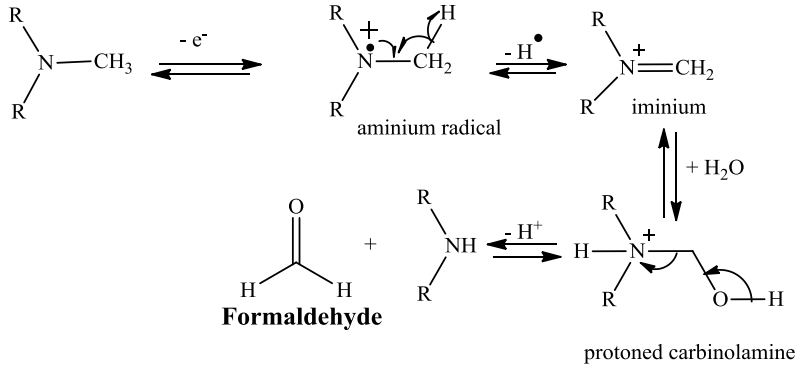
Lepaumier et al., 2009b described the formation of ammonia and ethylene oxide which, according to Ye and Zhang, 2001, can be hydrolysed into ethyleneglycol leading to carboxylic acids (Scheme 2.9). It is well known that aldehydes are rapidly oxidised into acids.



Scheme 2.9. Oxidations and ethyleneglycol formation (R = H) according to Lepaumier, 2008

Some authors described in more detail oxidative fragmentation of amines with radical chemistry. This step can occur for example in the above-mentioned transformation of glycine to ammonia and glyoxilic acid. Two types of radical pathways can lead to the same compound. The first one (Scheme 2.10) is based on electron abstraction (Chi and Rochelle, 2002; Goff, 2005; Goff and Rochelle, 2004; Lindsay Smith and Mead, 1973; Lindsay Smith and Masheder, 1977) and the second one (Scheme 2.11 and Scheme 2.12) is based on hydrogen abstraction (Lepaumier et al., 2009b; Petryaev et al., 1984).

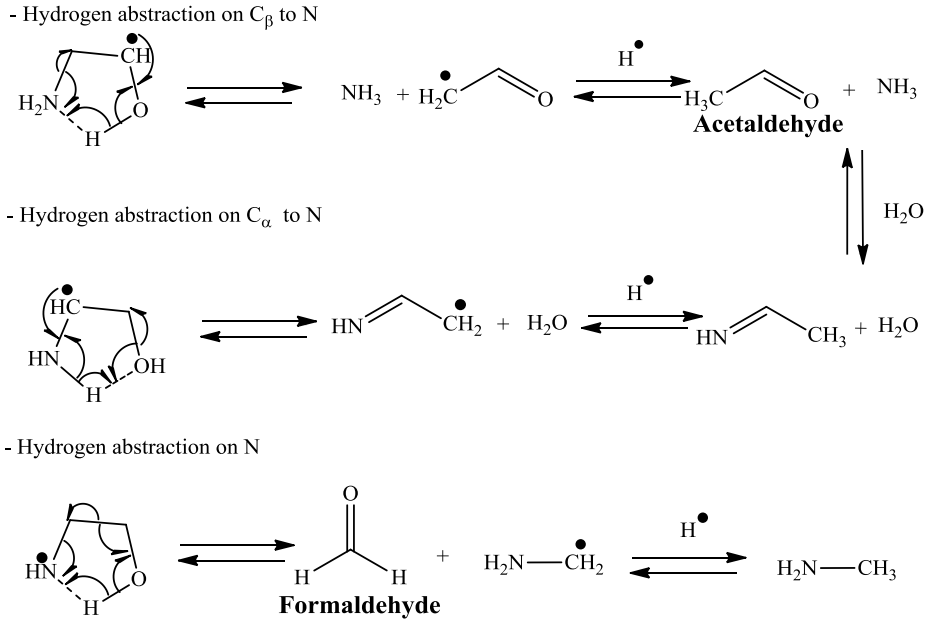
- Electron abstraction has been proved but only for tertiary amines (Dennis et al., 1967; Hull et al., 1967a; 1967b; 1969).



Scheme 2.10. Electron abstraction (R = H or alkyl) according to Lindsay Smith and Masheder, 1977

Scheme 2.10 could be extrapolated for MEA: electron abstraction could take place on the CH_2 on α of nitrogen atom (R = H and CH_3 replaced by CH_2CH_2OH), giving ammonia and glycine.

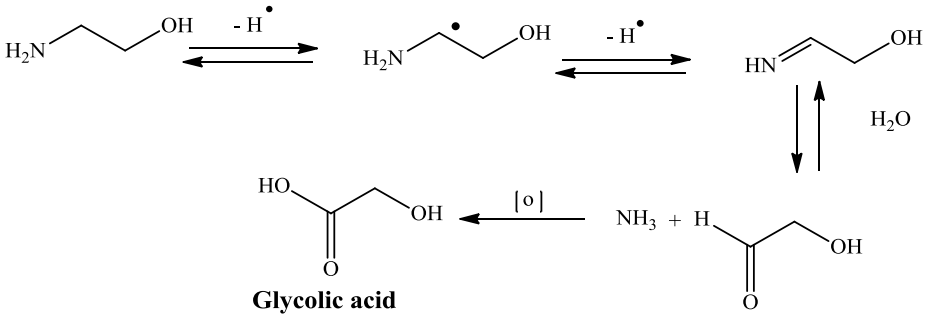
- Hydrogen abstraction in MEA can occur on three sides: C_β to N, C_α to N or N as shown in Scheme 2.11.



Scheme 2.11. Hydrogen abstraction according to Petryaev et al., 1984

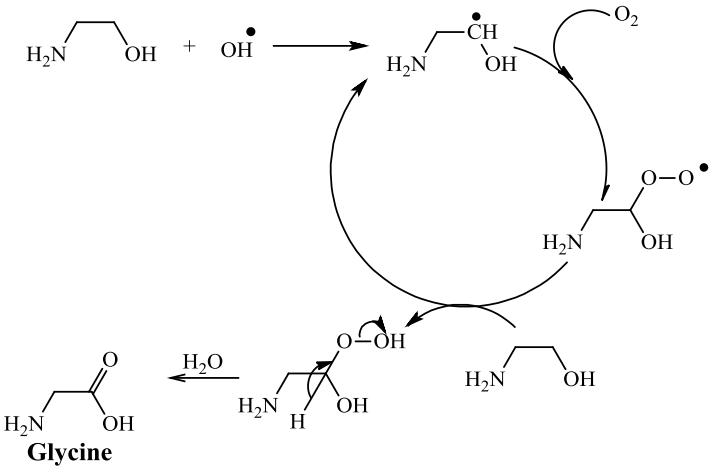
H abstraction could occur thanks to free radicals as $HO^\bullet$ or others oxygenated species. However this intermolecular rearrangement don't take account to presence of O_2, which normally react quickly with free radicals. Petryaev et al., 1984 mechanism would lead to ammonia, acetaldehyde, formaldehyde and methylamine formation.

Lepaumier et al., 2009b proposed another pathway for hydrogen abstraction on C_α to N, which leads after deamination to glycolic acid formation (Scheme 2.12).



Scheme 2.12. Hydrogen abstraction according to Lepaumier et al., 2009b

Scheme 2.13 explains the formation of glycine thanks to hydrogen abstraction by hydroxyl radicals on C_β to N then peroxide formation (Bedell, 2009; 2011). A catalytic cycle was proposed to form glycine.



Scheme 2.13. Radical mechanism proposed for glycine formation according to Bedell, 2009

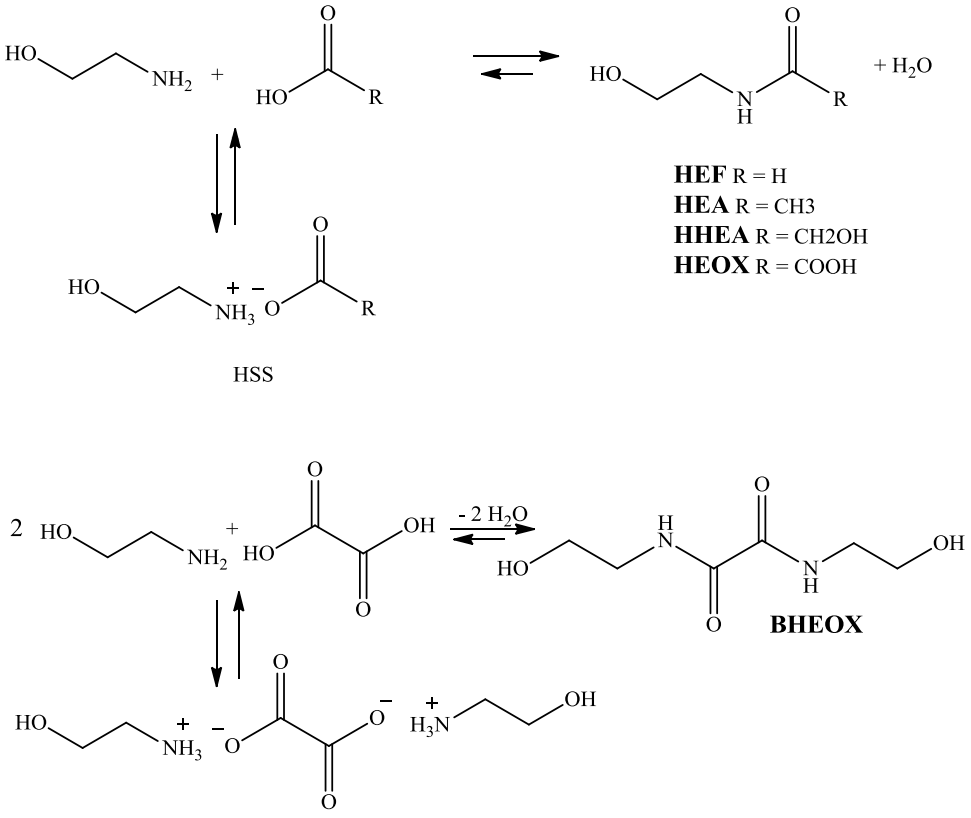
Among all radical mechanisms described in the literature, it remains difficult to favour one rather another (Bedell, 2011; Chi and Rochelle, 2002; Lepaumier et al., 2009b; Lindsay Smith and Masheder, 1977; Petryaev et al., 1984).

However, Karl et al., 2012 and Nielsen et al., 2011 showed using theoretical calculations that hydrogen abstraction would be more favourable on C_α to N (about 80%). Then hydrogen abstraction would be more favourable on N than on C_β to N.

All these mechanisms explained formation of aldehydes and acids, but their formation still remains unclear. It seems important to understand their formation because they are involved in other reactions or they can have an impact on the pilot plant (fouling, corrosion).

They can react first with amines affording salts commonly called HSSs “Heat Stable Salts” (Supap et al., 2011) or HSASs, “Heat Stable Amine Salts”. It is important to point out that all

acids are in HSSs form due to this reaction. These salts and also amides (listed in Table 2.3) are obtained by classical reaction (Scheme 2.14) between carboxylic acids and amines (Lepaumier et al., 2011a). HSSs are not regenerated in stripper conditions because carboxylic acids are more acidic than carbonic acid (Tanthapanichakoon et al., 2006; Veldman, 2000).

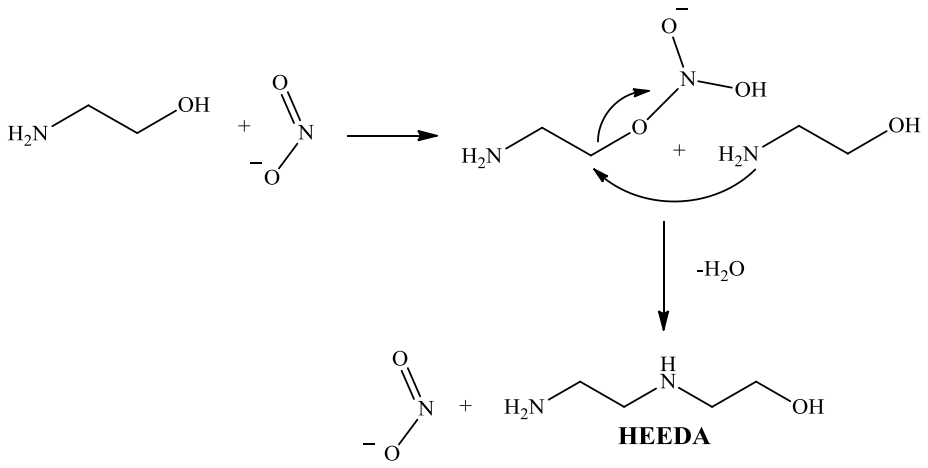


Scheme 2.14. Amides and HSSs formation (R = H, CH_3, CH_2OH or C(O)OH)

Following this mechanism, two molecules of glycine can react together to form N-glycylglycine (Glygly) (Strazisar et al., 2001; Supap et al., 2006).

HEEDA can be obtained by oxidative or thermal degradation (Huang et al., 2014; Lepaumier et al., 2009b).

Huang et al., 2014 observed that HEEDA formation is enhanced by the presence of nitrites. They proposed a mechanism (Scheme 2.15) where nitrites react with hydroxyl group of MEA to form a better leaving group. Then MEA can react with this intermediate by intermolecular substitution to form HEEDA.

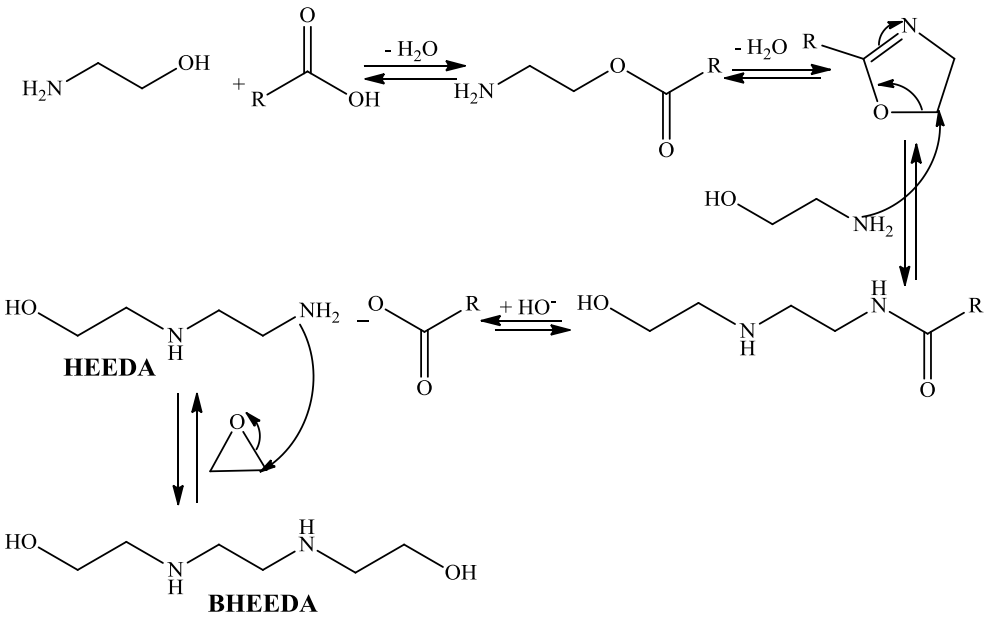


Scheme 2.15. HEEDA formation adapted from Huang et al., 2014

On pilot plant, oxidative and thermal degradation are both involved, therefore activation of alcohol function nitrite (Scheme 2.15) can occur to lead to other amines formation (Huang et al., 2014).

In the case of oxidative degradation, Lepaumier et al., 2009b explained HEEDA formation through the activation of the hydroxyl substituent of MEA due to its esterification in the presence of carboxylic acids (Scheme 2.16). The amino function would then react intra-molecularly with the ester function allowing cyclisation (via oxazolines). Then another molecule of MEA could be involved in a S_N2 reaction on the cyclic intermediate to form an amide, which was hydrolysed thanks to basic conditions leading to HEEDA (Scheme 2.16).. However, esterification seems not to be favourable in solution as explained in chapter 5 of this work. Moreover, many amides are formed in the process and they are relatively stable towards hydrolysis. Therefore, this mechanism appears unlikely.

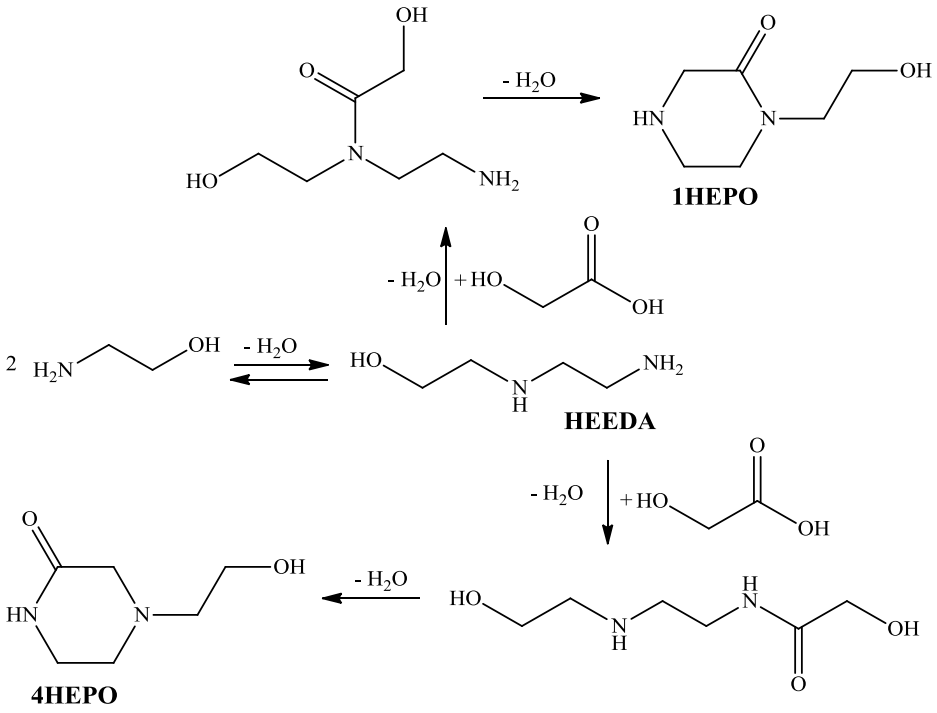
Lepaumier et al., 2009b explained simultaneouosly BHEEDA formation by reaction of HEEDA with ethylene oxide.



Scheme 2.16. HEEDA and BHEEDA formation according to Lepaumier et al., 2009b (R = H, CH_3 or CH_2OH)

In pilot plant, HEEDA formation could be formed following Scheme 2.4 and Scheme 2.15 but mechanism based on CO_2 should be predominant due to carbamate concentration, which is about 2 M.

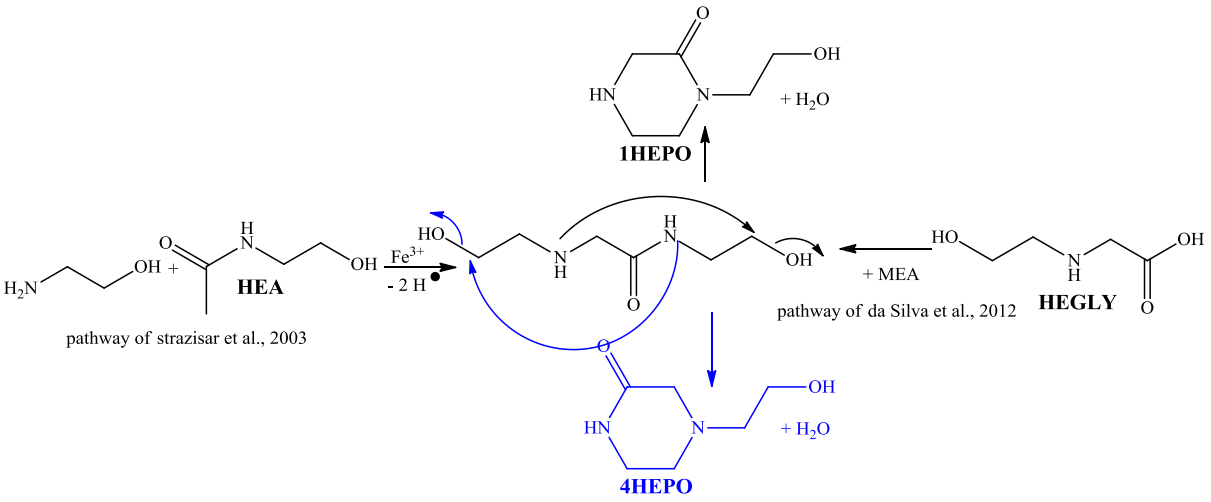
During oxidative degradation, MEA gives piperazinones observed in lab experiments (Lepaumier et al., 2009b) and in pilot plants (da Silva et al., 2012; Lepaumier et al., 2011a; Strazisar et al., 2003). Three mechanistic pathways have been proposed: Lepaumier et al., 2009b explained their formation by a reaction between glycolic acid and HEEDA followed by intramolecular dehydration (Scheme 2.17).



Scheme 2.17. Piperazinones formation according to Lepaumier et al., 2009b

Strazisar et al., 2003 and da Silva et al., 2012 (Scheme 2.18) both proposed a pathway with HEHEAA as intermediate. Difference between these mechanisms is HEHEAA formation. On one hand, Strazisar et al. envisaged a radical pathway, on the other hand, da Silva et al., 2012 explained HEHEAA formation by the reaction between HEGly (a major degradation product) and MEA, which is in accordance with high concentration of 4HEPO.

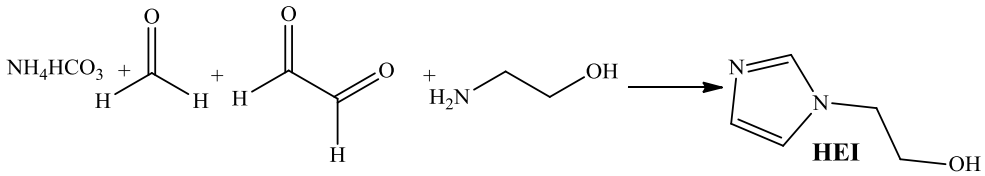
The final step for these two pathways is an intramolecular dehydration of HEHEAA, which can lead to the formation of two isomers.



Scheme 2.18. Piperazinones formation according to Strazisar et al., 2003 and da Silva et al., 2012

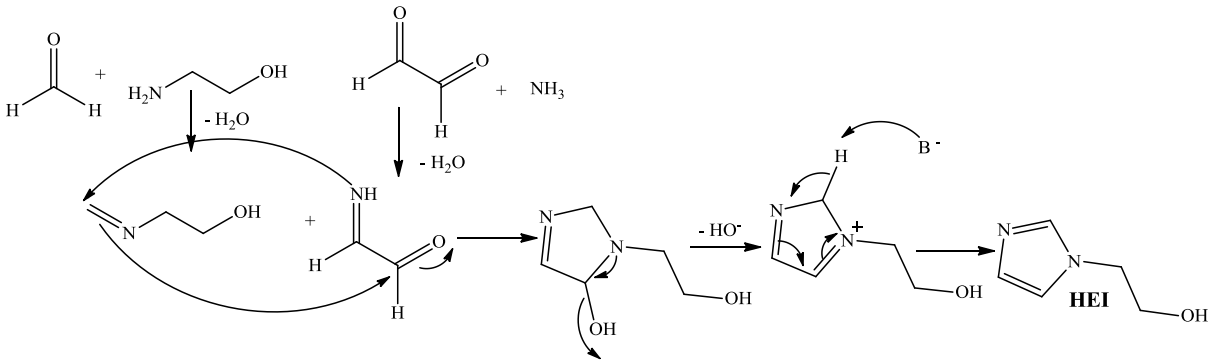
These mechanisms will be discussed in the chapter 5 because intramolecular dehydration seems unlikely to form a major compound as 4HEPO in CO_2 capture conditions.

HEI is a major degradation product. Arduengo et al., 2001 patented HEI and derivate syntheses (no mechanism is given); HEI would be obtained by a reaction between ammonium bicarbonate, formaldehyde, glyoxal and MEA (Scheme 2.19). Since all these compounds are present in degraded solution of MEA, HEI can be formed by this way.



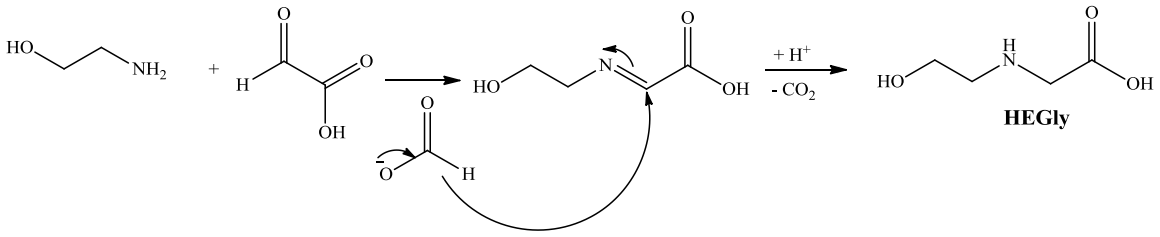
Scheme 2.19. HEI formation according to Arduengo et al., 2001

Vevelstad, 2013 proposed a mechanism based on the patent of Katsuura and Washio, 2005. On one hand, formaldehyde can react with MEA to form an imine, on the other hand, ammonia and glyoxal can react together to form another imine. The two imines react together to form intermediate leading to HEI after dehydration.



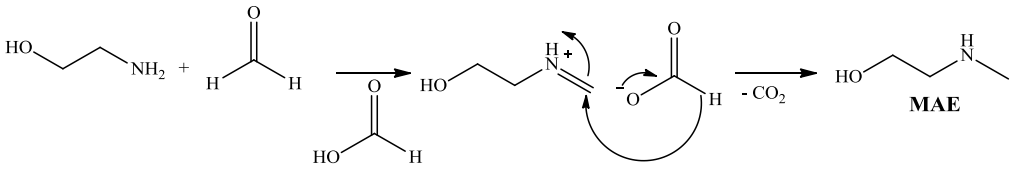
Scheme 2.20. HEI formation according to Katsuura and Washio, 2005 and Vevelstad, 2013

HEGly was discovered recently by da Silva et al., 2012 as one of the major product in pilot plant. Vevelstad, 2013 proposed a mechanism: MEA can react with the aldehyde function of glyoxylic acid to form an imine. This imine can be reduced by formic acid to give HEGly according to a Leuckart-Wallach reaction.



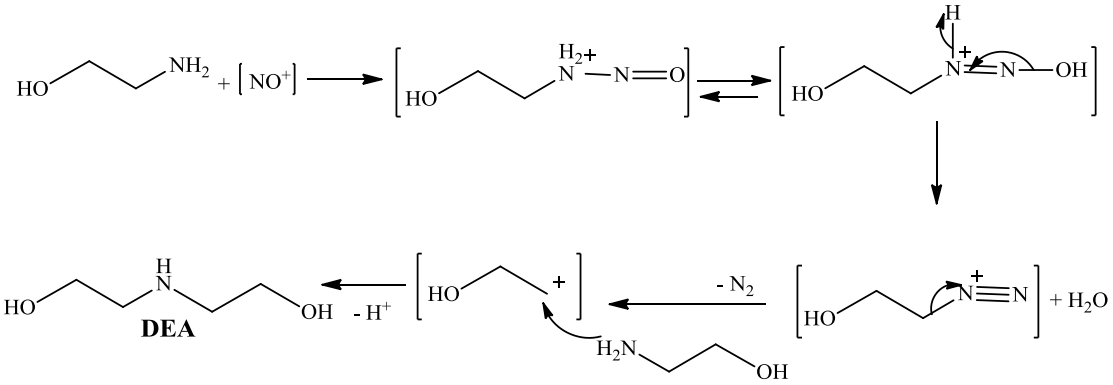
Scheme 2.21. HEGly formation by Leuckart-Wallach reaction according to Vevelstad, 2013.

Leuckart-Wallach reaction is a variant of the Eschweiler-Clarke reaction, which could explain MAE formation (Scheme 2.22) (Lepaumier, 2008).



Scheme 2.22. Methylation of amine by Eschweiler-Clarke reaction (Lepaumier, 2008)

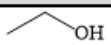
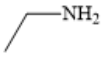
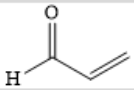
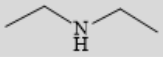
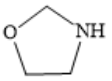
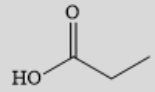
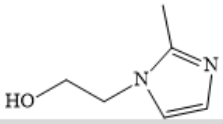
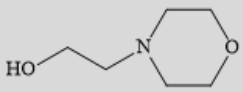
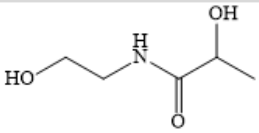
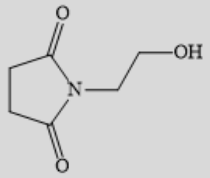
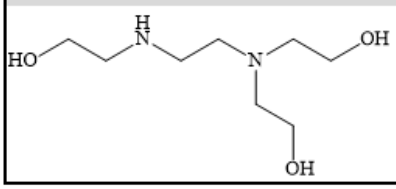
DEA is often observed in very small amount in fresh MEA. This might be due to the contamination of commercial MEA (reaction between MEA and ethylene oxide during MEA synthesis). However, Huang et al., 2014 clearly observed DEA formation during degradation experiments of MEA in the presence of nitrites. Thanks to this result, they proposed a mechanism involving the formation of diazonium salt from the reaction of MEA with nitrosonium cation (NO^+) according to Fostås et al. 2011 and Ridd, 1961. Nitrosonium cations are potential reactants due to the presence of nitrites but their formation was not explained.



Scheme 2.23. DEA formation according to Fostås et al., 2011 and Ridd, 1961

Other degradation products (Table 2.4) are very likely or confirmed by standards but without described mechanisms. Therefore further investigations are needed.

Table 2.4. Degradation products of MEA without any described mechanisms

Chemical structure	Name (Abbreviation)	Mw (g/mol)	References
	Ethanol	46	Supap et al., 2006
	Dimethylamine	45	Lepaumier et al., 2009 Love, 2013 Vevelstad et al., 2013
	Ethylamine	45	Lawal et al., 2005 Love, 2013 Vevelstad et al., 2013
	**Nitrous Acid**	47	Davis, 2009 Strazisar et al., 2001 Vevelstad, 2013
	**Acrolein**	56	Love et al., 2012
	**Nitric Acid**	63	Davis and Rochelle, 2009 Davis, 2009 Strazisar et al., 2001 Vevelstad, 2013
	Oxazoline	71	Voice, 2013*
	Diethylamine	73	Vevelstadt et al., 2013
	Oxazolidine	73	Reynolds et al., 2013* Voice, 2013*
	Propionic acid	74	Love et al., 2012 Strazisar et al., 2003
	N-(2-hydroxyethyl)-2-methylimidazole	126	Velvelstad et al., 2013*
	**N-(2-hydroxyethyl)morpholine**	131	Cotungo et al., 2014
	**N-(2-hydroxyethyl)lactamide**	133	Reynolds et al., 2013 Strazisar et al., 2003
	**N-(2-hydroxyethyl)succinimide**	143	Lepaumier et al., 2011 Reynolds et al., 2013 Strazisar et al., 2003 Supap et al., 2011
	N,N,N'-tris(2-hydroxyethyl)ethylenediamine (THEED)	192	Lepaumier et al., 2009b

* Without standard confirmation

- It is well known that nitrates and nitrites were present in solution but, to the best of our knowledge, no mechanism was proposed.
- Ethanol, dimethylamine, ethylamine and THEED were observed as degradation products but no mechanism was proposed.
- N-(2-hydroxyethyl)succinimide and N-(2-hydroxyethyl)lactamide are reported by two or more authors but Voice, 2013 thought that their formation seemed difficult to explain.
- Acrolein and propionic acid are observed in water wash section (Love, 2012). N-(2-hydroxyethyl)morpholine was observed and confirmed recently (Cotugno et al., 2014) in pilot plants.

Three interesting products were proposed as degradation products but without any confirmation.

- N-(2-hydroxyethyl)-2-methylimidazole (HEMI) was proposed by Vevelstad et al., 2013b. In HEI mechanism (Scheme 2.20), if formaldehyde was replaced by acetaldehyde (proved degradation product), this would obviously lead to MeHEI.
- Oxazoline and oxazolidine were proposed as degradation products too. Voice, 2013 predicted oxazoline formation by reaction between N-hydroxyethanolamine and formic acid and oxazolidine formation by reaction between MEA and formic acid. These two molecules could probably be present in pilot plant because their formation needs only first generation products.

Moreover, about 60 other degradation products are mentioned in five papers without explanation (Bello and Idem, 2005 (45 products); Lawal et al., 2005a (25 products); 2005b (11 products); Strazisar et al., 2003 (6 products); Supap et al., 2006 (20 products)). Some of them are cited several times by the same group, but their formations appear very hard to explain: for example, 1-methylazetidine, pyrimidine, 1,3-dioxane, uracil, 2,6-dimethyl-4-aminopyridine and 18-crown-6. For more details readers should refer to the five cited papers.

Under pilot plant conditions, oxidative and thermal degradation might take place. Lepaumier et al., 2011a showed that MEA degradation is mainly due to oxidation. da Silva et al., 2012, Lepaumier et al., 2011a and Strazisar et al., 2003 obtained as major degradation products 4HEPO, HEHEAA, HEI and HEGly and a compound with a molecular weight of 176 g/mol. Only Strazisar et al., 2003 identified this molecule as N-3- bis(2-hydroxyethyl)-propanamide, it needs further investigation.

2.3. Effect of SO_x and NO_x

SO_x and NO_x present in flue gases can be partially remove before CO_2 capture. Nevertheless it is important to understand their impact on the solvent because "deSOx" or "deNOx" could perhaps not be necessary. Only a few studies are present in the literature. Bonenfant et al., 2007 showed that ammonium sulphate salt formation with SO_2 decreases CO_2 absorption capacity of HEEDA. Supap et al., 2009 and Uyanga and Idem, 2007 showed that SO_2 increases amine loss. However recent publications (Sun et al., 2014 and Zhou et al., 2013) explained that SO_2 effect (inhibition or activation) depends on its concentration. In experiment with 60 ppm of SO_2, they observed a decrease of degradation rate compared with no SO_2, whereas with 150 ppm, this decrease was attenuated. This phenomenon was explained by the scavenging of active oxygen species by SO_2. However, with high concentration of SO_2 corrosion was increased and the presence of metal salts enhanced the degradation of amine.

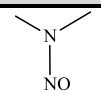
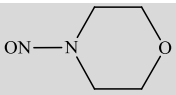
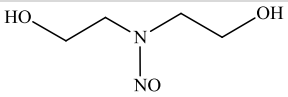
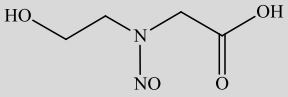
Wen and Narula, 2009 proposed the formation of thioglycolic acid, when MEA reacts with SO_2. These authors did not give more details concerning degradation products or mechanisms.

Gao et al., 2011 had published a pilot-scale study confirming that SO_2 (214 ppm and 317 ppm) increased degradation rate and decreased CO_2 absorption rate due to HSSs formation They observed more sulphate than sulphite and pointed out that concentration of acetate dramatically decreased while concentration of glycolate strongly increased. A paper of the same team (Zhou et al., 2012) related thermal degradation of MEA in the presence of SO_x (Na_2SO_3, SO_2, H_2SO_4) and NO_x (HNO_3). In the presence of SO_2, authors identified sulphite, sulphate and thiosulphate ions in solution and they proposed also structures for three unidentified products based on their molecular weight.

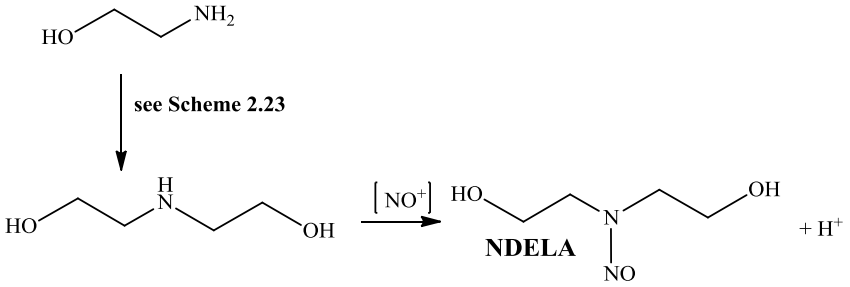
NO_x are known to react with secondary amines to form nitrosamines and nitramines (Challis and Challis, 1982; Loeppky C.J, 1994; Williams, 1988). This reaction can also occur with primary amines (Ridd, 1961), tertiary amines (Mirvish, 1975; Smith and Loeppky, 1967) and quaternary ammoniums (Fiddler et al., 1972; Kemper et al., 2010). Therefore all the amines are able to give nitrosamines.

Nitrosamines observed in the case of MEA were reported in the next table.

Table 2.5. Nitrosamines observed in MEA degradation

Chemical structure	Name (abbreviation)	Mw (g/mol)	References
	N-nitrosodimethylamine (NDMA)	75	Einbu et al., 2013 Fostås et al., 2011
	N-nitrosomorpholine (NMor)	116	Fostås et al., 2011
	N-nitrosodiethanolamine (NDELA)	134	Einbu et al., 2013 Fostås et al., 2011
	N-nitroso-N-(2-hydroxyethylglycine) (NHEGly)	148	Einbu et al., 2013

Strazisar et al., 2003 suggested presence of nitrosamines in pilot plant thanks to the total nitrosamine analysis but they were not identified. Pedersen et al., 2010 observed N-nitrosodiethanolamine (NDELA) and Fostås et al., 2011 proposed a mechanism of formation for this nitrosamine: NO_x could react with MEA to form DEA (Scheme 2.2.24), which could react another time with NO_x to form NDELA. In autoclave, N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMor) were observed too. N-nitrosopiperazine (NPZ) was expected to be formed but was not observed. Recently, in addition to NDELA and NDMA, a novel nitrosamine issued from HEGly, the N-nitroso-N-(2-hydroxyethylglycine) (NHEGly), was observed by Einbu et al., 2013.



Scheme 2.2.24. Nitrosamines formation according to Ridd (1961) and Fostas et al. (2011)

Saavedra, 1981 studied the action of HNO_2 on MEA and AMP (2-amino-2-methyl-1-propanol) and observed the formation of N-nitroso-2-methyl-1,3-oxazolidine from MEA while AMP gave N-nitroso-2-isopropyl-4,4-dimethyl-1,3-oxazolidine. Even if HNO_2 cannot be present in CO_2 capture conditions, NO_x might give the same results. This nitrosamine should be formed in pilot plant.

This is extremely important to list nitrosamines formed during the process because they are well known as carcinogenic agents since many years (IARC, 1978; NTP, 2012) and all must be done to avoid their formation or to quickly destroy them before atmosphere emissions.

2.4.Conclusion

Amine degradation in post-combustion CO_2 capture is a main problem due to its consequences on process units and the potential impact of degradation products on environment. Therefore, knowledge about amine degradation is a key point for CO2 capture acceptance. Degradation products from literature were listed and their proposed mechanisms were discussed. Influence of heat, CO_2, O_2, NO_x and SO_x was described. Ammonia, N-(2-hydroxyethyl)-piperazin- 3-one (4HEPO), N-(2-Hydroxyethyl)glycine (HEGly) and N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA) are the main identified degradation products in pilot plants. Among lab studies, the most cited degradation products are ammonia, carboxylic acids, N-(2-hydroxyethyl)formamide (HEF), N-(2-hydroxyethyl)acetamide (HEA) and N-(2-hydroxyethyl)imidazole (HEI) for oxidative degradation, and oxazolidin-2-one (OZD), N-(2-hydroxyethyl)ethylenediamine (HEEDA) and N-(2-hydroxyethyl)imidazolidin-2-one (HEIA) for thermal degradation. Numerous degradation products have been identified but many are still unknown. Some degradation mechanisms have been proposed but some of them are unclear or need proofs. SOx and NOx effects are still few examined and much work remains to be done concerning volatile degradation products potentially emitted to atmosphere: their identification and their formation mechanisms need further investigations. To conclude, a lot of studies have been already done but understanding of amine degradation is not completely achieved and much work remains to be done.

3. Analytical methods

This chapter details the different analytical methods used during this work to cover the whole type of the MEA degradation products. High concentration of MEA compared with its degradation products, presence of volatile compounds implied combination of different analyses (GC/FID or MS, LC/MS, IC, NMR) and sampling methods (HS-SPME, Sep-Pack and TENAX cartridges). Information on the chemicals used including abbreviation, purity and suppliers can be found in Appendix A – list of chemicals.

Gas chromatography (GC) coupled with flame ionisation detector (FID) or mass spectrometry (MS) were routinely used.

GC/MS was the preferred method for the identification of products due to the availability of data. However, GC/MS was sometimes not sensitive enough or unsuitable for some compounds (carboxylic acids, heavy molecules) because GC is limited to volatile compounds, therefore, LC/MS has been used too, but no database is available, due to the intrinsic variability of ionization and fragmentation inherent to the design of sources. The only way to confirm identification was to use standards. Ion chromatography was chosen to detect and quantify some anionic compounds. ^{1}H, ^{13}C and ^{1}H-^{13}C HSQC NMR was used to confirm the structure of some major syntheses products.

New sampling methods were developed to observe novel compounds:

1) Head space solid phase micro-extraction (HS-SPME) enabled the analysis of volatile products even at trace level present in liquid phase. Amount of MEA adsorbed on the fibre was quite low thus lowering its matrix effect compared to conventional analyses and enabling an increase of GC/MS sensitivity towards other products.

2) Adsorption on solid phase of gaseous sample was also used to trap and thus pre-concentrate products of the gas phase. Sep-Pak and TENAX cartridges have been used. The main differences between these cartridges were the selectivity for products (TENAX cartridges are not selective whereas Sep-Pak cartridges are specific for aldehydes and ketones) and the desorption (thermic for TENAX and by liquid extraction for Sep-Pak).

LC/MS/MS, some GC/MS with direct injection or coupled with HS-SPME or TENAX cartridges analyses were made by ESPCI, IFPEN's partner in an ANR project (DALMATIEN)†. Analyses of Sep-Pack cartridges were done by INERIS.

Figure 3.1 is a sum-up of the analytical strategy used to improve the identification of degradation products.

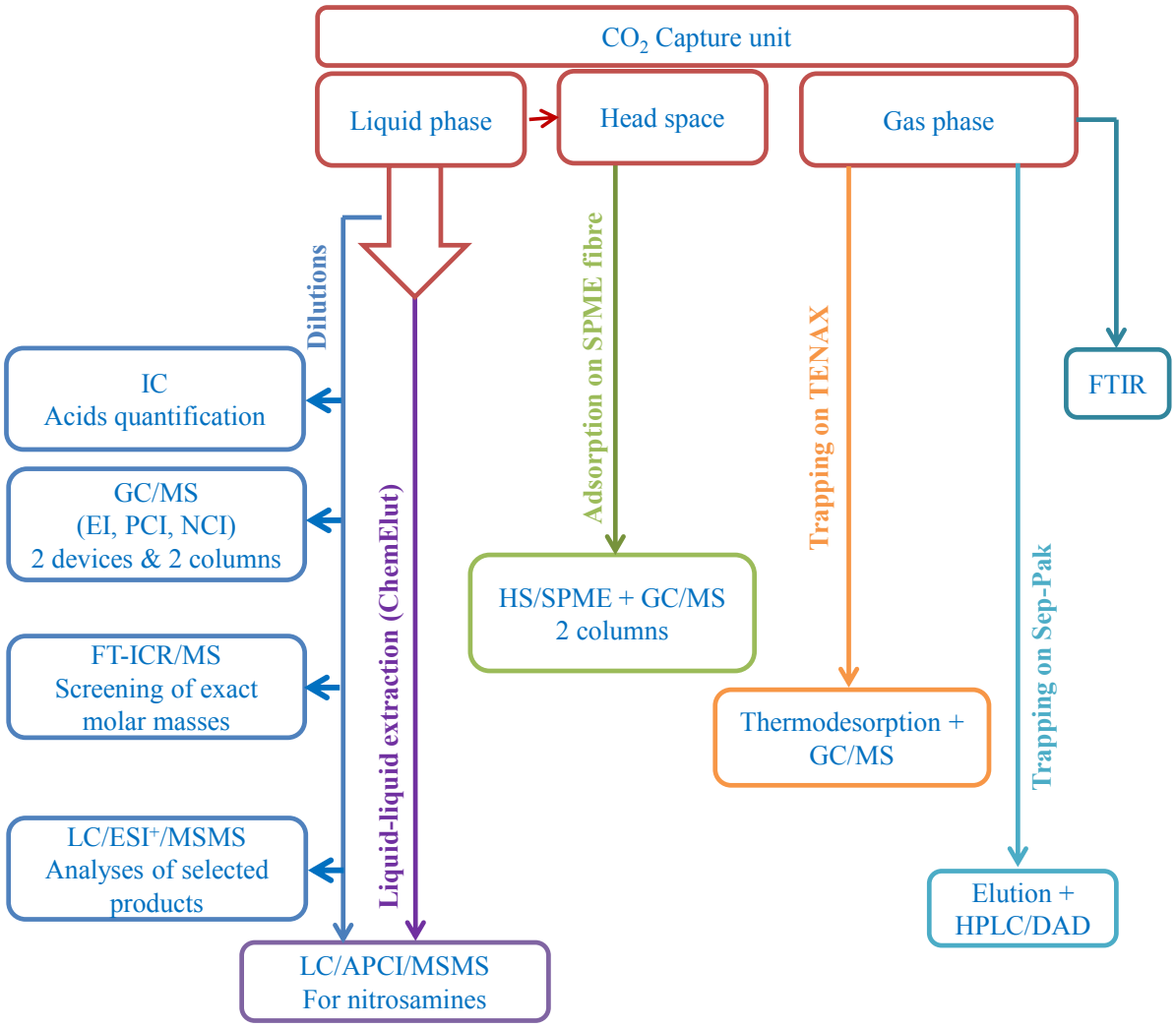


Figure 3.1. Analytical strategy
HPLC/DAD: High performance liquid chromatography with diode array detection

Firstly, analytical methods of the liquid phase will be described, then these for volatile products either dissolved (HS-SPME) or present in the gas phase.

† ANR programme : Systèmes Energétiques Efficaces et Décarbonés (SEED) 2011 Reference : ANR-11-SEED-0006

3.1.Liquid phase analyses

3.1.1. Ion chromatography

Ion chromatography was commonly used to quantify acids in their anionic forms: glycolate, formate, acetate, oxalate, sulphate, nitrite, and nitrate ions. Samples were diluted in ultrapure water depending on acids concentration. 25 µL of the solution was injected twice on a Dionex ICS-3000 ion chromatograph. The column was AS-15 (4 × 250 mm) from Dionex. Eluent was aqueous KOH solution with a concentration gradient (from 8 to 60 mM) at a flow rate of 1 $mL.min^{-1}$. A 60 minutes run time enabled an optimal separation. Quantification was obtained with an uncertainty of ± 10%. Some samples were pre-treated with HNO_3 69 % to reach a pH below 4 and to eliminate MEA carbamate peak which could overlap acetate and glycolate peaks.

3.1.2. GC/FID

GC/FID was used for routine analytical technique to monitor the degradation experiments and to compare the proportions of different well-known products (chapter 4).

Two methods with different columns were implemented because it was impossible to separate all compounds on the same column: one column was with a highly polar column (CARBOWAX-Amines, Agilent) and one with a non-polar column (CPSIL8-CB-Amines, Agilent), respectively on Agilent HP6890 and Agilent 6890N chromatographs. For example, MDEA and DEA were not separated with CPSIL8 but with CARBOWAX. On the other hand, CPSIL8 was more suitable than CARBOWAX for heavy compounds.

For each column, an internal standard (triethyleneglycol, TEG) could be added to facilitate the comparison of chromatograms. Samples should be diluted 15-folds in water.

Details of programs and columns used were summarised in appendix Table A.A.1.

3.1.3. GC/MS

Two kinds of devices, a GC/MS (Agilent) and a GC/MS-TOF (Thermo Finnigan Tempus), were used for the identification of degradation products. GC/MS (Agilent) was used with two columns a polar and a non-polar. In each case, the analytic program was optimised (appendix Table A.A.1).

First device was an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer. It was equipped with a MPS autosampler from Gerstel. The mass spectrometer was used with the electron ionization (EI) source (70 eV) heated at 250°C. Samples were diluted 10-folds. The acquisition was made in scan and SIM (selected-ion monitoring) mode simultaneously. Characteristic ions for SIM mode were selected for each targeted compounds. The scan range was 25-250 amu (atomic mass unit).

Two columns, both purchased from Agilent, were used: CPSIL8-CB-MS and DB-WAX, which is equivalent to CARBOWAX.

On EI mass spectrum, the peak corresponding to the molecular weight [M] could be missing. For this reason, PCI and NCI were both used. PCI allowed to access to [M+1] and NCI to [M-1]. By comparison of these two results, the molecular weight of well-separated compounds could be obtained with high confidence. With CPSIL8 column, the chemical ionization (CI) source (CH_4 as reactant gas) was used either in positive, PCI, (300°C) or negative, NCI, mode (150°C). In the case of the NCI mode, scan range was restricted to 50-250 amu to avoid noise.

Further identification of unknown compounds was brought by GC/MS-TOF. Due to mass calibration, GC/MS-TOF allowed to obtain the exact molecular weight and to predict the possible molecular formula.

This second device was an Agilent 7890A gas chromatograph coupled with an AccuTOFGCV – JMS – T100GCM mass spectrometer. It was equipped with 7693 autosampler from Agilent. GC/MS-TOF was used with the CPSIL8 CB-MS. Mass spectrometer was used with the EI source (70 eV) heated at 200°C. Depending on their concentration, samples were diluted 10-folds or not. The scan range was 10-350 amu. Program was reported in appendix (Table A.A.1). GC/MS-TOF was used to analyse all syntheses mixtures and liquid sample of pilot plant.

3.1.4. FT-ICR/MS

Ultra-high resolution mass spectra were acquired using a LTQ-FT Ultra Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR/MS) (Thermo Fisher Scientific) equipped with a 7 T superconducting magnet and an electrospray (ESI) ion source (IonMax Thermo Fisher Scientific). Sample solutions (100-folds dilution with 0.1 % of acetic acid) were injected by a syringe infusion pump at a flow rate of 5 µL/min in positive ESI mode ([M+1]). All parameters were adjusted to obtain optimal high mass accuracy and mass resolution. The

key measurement parameters for positive ESI ionization were as follows: capillary temperature, 275 °C; capillary voltage, 60 V; tube lens voltage, 80 V; and source voltage, 4.20 kV. The mass range was set to 50−500 amu. The mass spectral resolution was 100 000 with 32 μscans accumulated and coadded prior to the fourier transform to reduce electronic noise and to improve the signal-to-noise ratio of the resulting spectra.

Elemental composition was assigned using CalMix software with the generic molecular formula $C_cH_hN_nO_o$ ($0 \leq c \leq 20$, $0 \leq h \leq 100$, $0 \leq n \leq 10$, $0 \leq o \leq 10$). Mass tolerance should be ≤ 2 ppm.

Intensity of each molecular weight was correlated with capacity of the molecule to be ionized and its concentration in the sample. This analyse was used to confirm or to infirm proposition of molecular formula done by GC/TOF.

3.1.5. LC/MS/MS

Analyses were performed on a LC Thermo Scientific Dionex Ultimate 3000 (Analytical Autosampler WPS-3000SL, Quaternary Analytical Pump LPG-3400SD) coupled with a MS Thermo Scientific TSQ Quantum Access MAX with HESI-II probe (electrospray ionisation). The MS device was used in positive mode with the probe in position C (depth markers on the probe: A, B, C and D), electrospray voltage of 2500V and capillary temperature of 200°C. The sheath gas was at a flow rate of 40mL/min and the auxiliary gas at 8mL/min (nitrogen gases).

Chromatographic separations were conducted on a Thermo HyperCarb column (PGC). The use of a porous graphitic carbon column was found to be relevant according to the matrix complexity and the high polarity range of the degradation compounds.

Samples had to be at least 1000-fold diluted before injection to prevent pollution of the mass spectrometer by MEA. The retention time of MEA was 1.8 min but it could be detected during the whole analysis, impacting on the MS ionization recovery. Moreover, if its concentration was too high, adducts could also be formed and pollute the device.

First, data were acquired in scan mode (from 40 to 300 amu) to screen samples with Xcalibur (Thermo software). This approach enabled to observe major compounds in sample giving a molecular weight. For complete identification, standards were needed to compare retention time and fragmentation with MRM (multiple reaction monitoring) mode. Transitions and collision energy were optimized by infusion of each standard. LC-MS/MS can only identify targeted compounds (appendix A - Table A.2).

LC/MS/MS was also used to look for nitrosamines. Nevertheless, their very low concentrations combined with the dilution needed to avoid pollution of the ESI-MS by MEA made their detection quite impossible.

A specific method using an APCI probe (Atmospheric Pressure Chemical Ionization) and an original sample handling approach based on diatomaceous earth (ChemElut, Agilent Technologies) were developed.

ChemElut was used for a liquid-liquid extraction. Aqueous phase was immobilised by diatomaceous earth and an immiscible solvent (ethyl acetate) was used to perform the extraction (protocol in appendix A – LC/MS/MS parameters). Figure 3.2 described this extraction. Triangles represented annoying molecules (MEA) which were not soluble in the organic solvent (ethyl acetate) and circles represented molecules of interest (nitrosamines) soluble in the organic solvent.

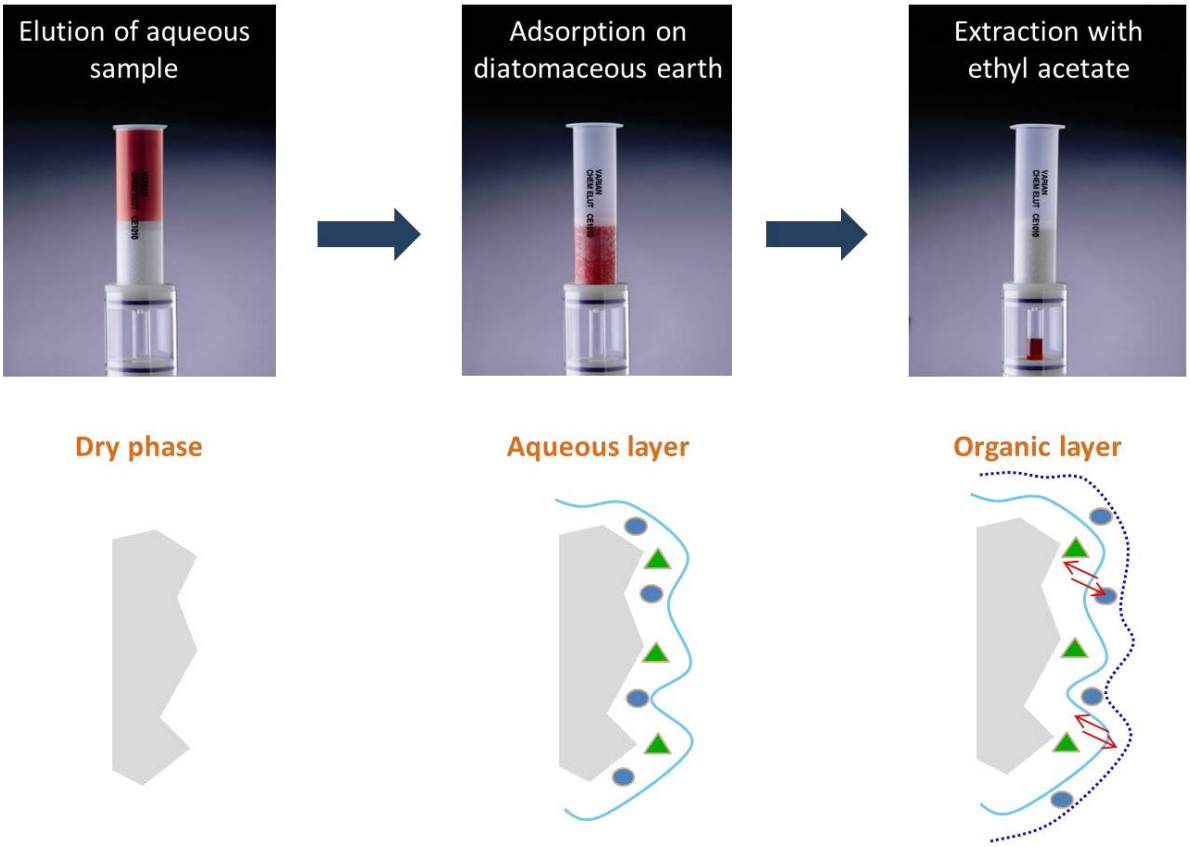


Figure 3.2. ChemElut protocol

This method enabled to selectively extract nitrosamines from samples. At the same time, MEA concentration was decreased from 300 g/L to less than 10 mg/L.

Recovered solutions were analysed with LC-APCI/MS/MS method in MRM mode described above. APCI source was used in positive mode, probe in position C, with a

capillary temperature of 300°C and a corona discharge current of 4 µA. The sheath gas was set at a flow rate of 30 mL/min and the auxiliary gas at 5 mL/min. Same mobile phase gradient as for HESI-II probe was used. MRM transitions were reported in appendix (Table A.3).

3.1.6. NMR

^{1}H, ^{13}C and ^{1}H-^{13}C HSQC NMR spectra were recorded in D_2O using a Bruker AMX 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) at room temperature. This method was mainly used to determine structure of synthesised standards. The HOD signal (δ = 4.79 ppm) was used as internal reference for ^{1}H NMR analysis. HSQC NMR (heteronuclear single quantum coherence) provided correlation between the carbon and its attached protons

3.2. Head Space analyses

The SPME fibre used was a 75 µm Carboxen-PolyDiMethylSiloxane (CAR-PDMS) from Supelco. Standards solutions for HS-SPME procedures were prepared in water/ethanolamine (70/30 v/v) mixtures to mimic real solutions. The volume of solution introduced in the 20 mL HS vial was 5 mL.

The fully automated HS-SPME procedure was as follows (Figure 3.3): First, the vial was equilibrated at 70°C during 5 min, then the CAR-PDMS fibre was placed 30 min at 70°C into the head-space of the sample for the extraction. At the end, the fibre was desorbed directly in a special GC injector for 10 min at 250°C in split mode (1:5). The GC/MS method was the same as for liquid injection with CPSIL8 and DBWAX column. MPS autosampler enabled desorption of the fibre.

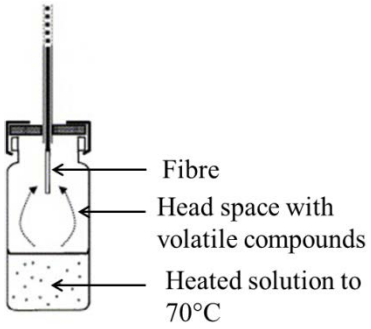


Figure 3.3. HS-SPME procedure

This method enabled to trap the more volatile compounds (see Table 6.1 and 5.2) present in liquid phase. Volatilisation was done at 70°C (like the temperature in absorber). This method gave information about compounds which could be emitted to atmosphere.

3.3. Gas phase analyses

3.3.1. Sep-Pak Cartridges

Sep-Pak DNPH-Silica Plus Short Cartridge (Waters) hold 350 mg of sorbent per cartridge with particle size between 55 and 105 µm. Due to their reaction with acidified 2,4-dinitrophenylhydrazine (DNPH) during sample collection (Figure 3.4), such cartridges trap aldehydes and ketones in air through the formation of stable hydrazone derivatives.

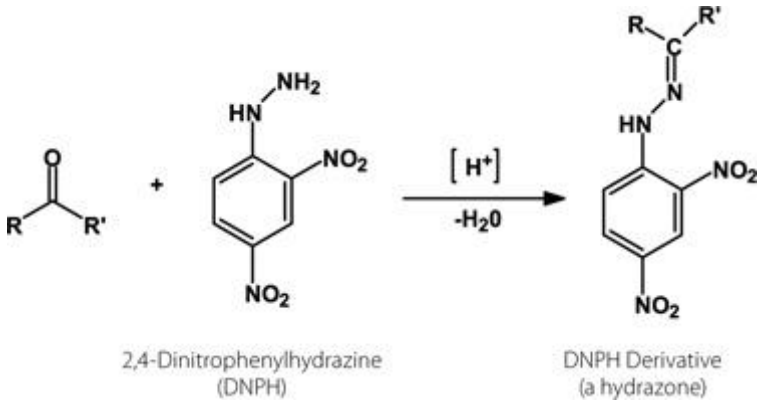


Figure 3.4. DNPH derivation on Sep-Pak cartridge

On pilot plant, the cartridges were connected to the absorber outlet gas line (position V10 in Figure 4.1). On lab experiment, they were connected after the condensers. Adsorption was done during 1 hour with flue gas of 6 NL/h. The derivatives were later desorbed with acetonitrile (about 2 mL) and the collected solution analysed by INERIS using HPLC/DAD. They are quantified thanks to INRS Metropol 001 method.

3.3.2. Tenax cartridges

TENAX TA (Gerstel) is a porous polymer resin based on 2,6-diphenylene oxide. Such trap has been specifically designed for volatiles and semi-volatiles from air or which have been purged from liquid or solid sample matrix (Dettmer and Engewald, 2002). Firstly, all the cartridges have to be conditioned (i.e., heated at 280°C under a flow of inert gas (Helium) at 30 mL/min during 1 hour).

These cartridges were connected to the absorber outlet gas line on pilot plant (position V10 in Figure 4.1) and they were connected after the condensers on lab experiment. Two cartridges were connected in series to check if some compounds could be saturated on the first cartridges and adsorbed on the second one. Sampling was done at 6 NL/h during 1 hour at room temperature. Cartridges were then desorbed with the thermodesorption unit (TDU) coupled with cooled injection system (CIS) (Figure 3.5). Gas flow rate of helium for desorption was 40 mL/min in splitless mode. Initial temperature of desorption was 35°C held for 2 min then raised to 300°C at 120°C/min and held for 6 min. Desorbed molecules were stopped by freezing in CIS injector, which was in "solvent vent" mode (split during desorption and splitless during injection). Then temperature increased from - 40°C to 300°C at 12°C/s and the molecules were injected in the column. Then, the same GC/MS device (Agilent 7890A with CPSIL8 column) as for liquid sample was applied.

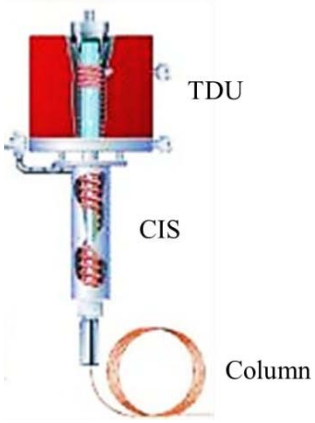


Figure 3.5. TENAX cartridge desorption and injection system

4. Experimental Part

In this chapter, experiments performed during this thesis are described.

- Solvent degradation experiments in pilot plant
- Laboratory solvent degradation experiments
- Syntheses performed to form standards and/or to validate degradation mechanisms.

Information about chemicals (abbreviation, purity and suppliers) is given in appendix (Table A.4).

4.1. Solvent degradation experiments

4.1.1. Pilot plant

A first campaign was done before this work and the degraded solution have been used as a reference sample to establish a laboratory protocol able to reproduce degradation in pilot plant. A second campaign was operated to improve degradation products identification thanks to new analytical methods development.

The pilot plant of IFPEN consists in two columns of around 1 meter each (see Figure 4.1). The first one is the absorber where CO_2 is absorbed in the solvent (MEA). The second column is the stripper where the solvent is regenerated and CO_2 is released. Each column is equipped with high performance packings for ensuring good gas/liquid mass transfer. The absorber outlet gas is directed to a heat exchanger (E10) to condense water. This condensate is separated in separator V10 and is mixed with the CO_2 lean amine in the tank T-01. The released CO_2 is directed to a heat exchanger (E20) to condense water. The condensate is separated in separator V20 and reintroduced on the top of the desorber with the rich amine. At the bottom of the desorber, the lean amine is sent to the tank T-01.

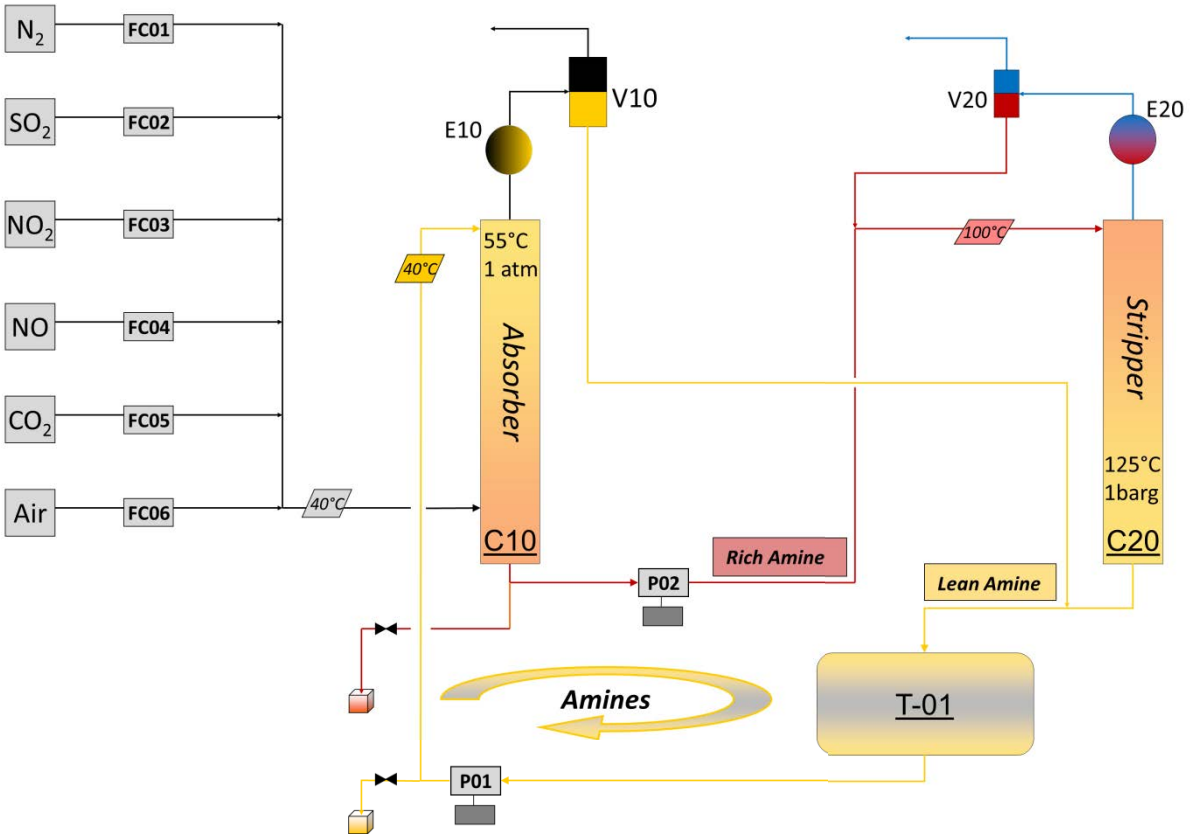


Figure 4.1. IFPEN pilot plant flowsheet

First campaign conditions – C1

The liquid sample from IFPEN CO_2 capture pilot plant was obtained after 1000 hours of operation. The synthetic flue gas composition used was CO_2 14.9% N_2 68.1% and O_2 17%. Gas flow rate was 750 NL/h and liquid flow rate was 2.5 L/h. Absorber temperature profile was 36-58°C and bottom stripper temperature was 108°C at atmospheric pressure. 40% weight MEA solution used for the pilot plant campaign was provided by Carlo Erba (purity of 98%).

Second campaign conditions – C2

The IFPEN CO_2 capture pilot plant was operated during 1652 hours. The synthetic flue gas composition was CO_2 14.12%, N_2 80.74%, O_2 5.13%, 8.9 ppm of SO_2, 4.9 ppm of NO_2 and 97.1 ppm of NO. Gas flow rate was 1000 NL/h and liquid flow rate was 2.5 L/h. Absorber temperature profile was 36-58°C and bottom stripper temperature was 125°C at atmospheric pressure. 30% weight MEA solution used for the pilot plant campaign was provided by Carlo Erba. All analyses described earlier were done on this second campaign especially gas phase analyses.

4.1.2. Laboratory equipment

To the best of our knowledge, there is no laboratory protocol described in literature, which could obtain same degradation products as in pilot plant in short time. The representativeness of this new protocol was validated through comparison of the resulting degradation sample to a previous campaign performed on IFPEN pilot plant.

- Methodology

Purpose of this test was to obtain in shorter time (one week), a noticeable amount of the pilot plant degradation products and if possible in the same proportions. Therefore conditions were close to those of the pilot plant case but more drastic to speed up degradation.

To develop this test, a laboratory unit composed by 6 semi-open batch reactors in hastelloy was used (Figure 4.2).

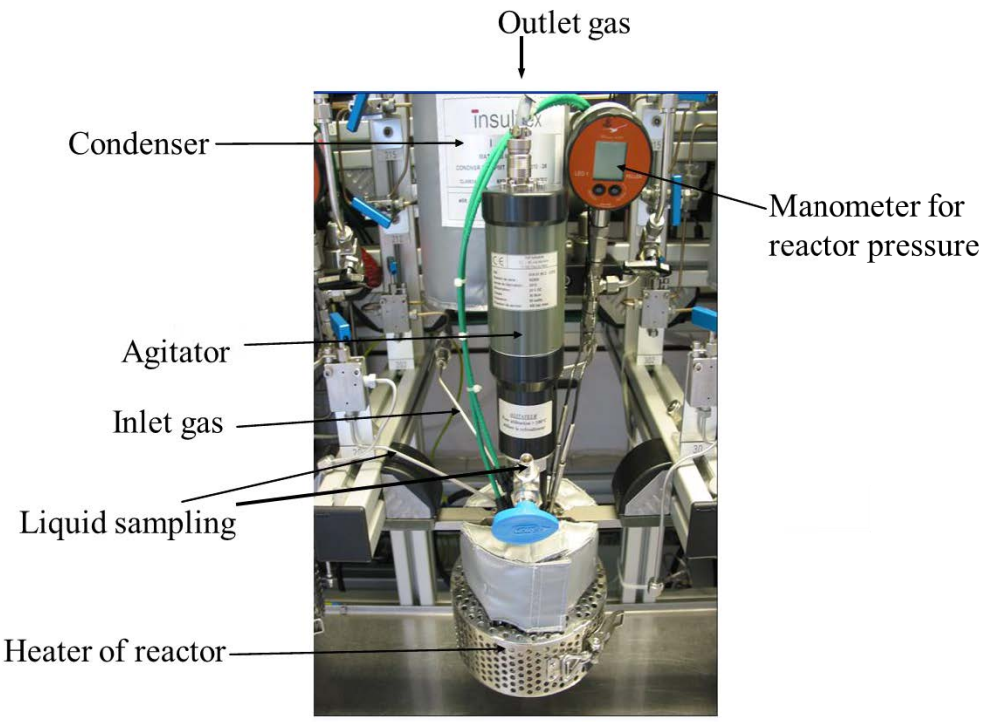


Figure 4.2. Semi-open batch reactor for representative test

This equipment enabled to cycle conditions like in a pilot plant with an absorption step and a regeneration step. Gas flow rates of N_2, CO_2 and air were independent. Condensers were placed after each reactor to limit water losses. Unit programming was online. Outlet gases were analysed online by FTIR detector (Gasmet, FTIR DX4000), which was calibrated for 29 compounds including NH_3, MEA, H_2O and CO_2.

- Representative test

100 g of a 30% wt. aqueous solution of MEA were placed in the reactor with 1000 ppm of Na_2SO_4. This salt was introduced as an internal standard to estimate water loss thanks to quantifications of sodium by ICP and sulphate ions by ionic chromatography. Cycles constituted by an absorption (1), a regeneration (2) and a cooling (3) steps were programmed as shown in Table 4.1.

Table 4.1. Representative test conditions.

Step	Time (min)	Air flow (NL/h)	N_2 flow (NL/h)	CO_2 flow (NL/h)	Temperature (°C)	Pressure (bars)	Stirring (rpm)
1	60	19	14	2.5	60	2	1000
2	60	1	31	0	120	4	1000
3	60	1	31	0	60	4	1000

Partial pressures of oxygen and CO_2 resulting from these choices were reported in Table 4.2

Table 4.2. O_2 and CO_2 partial gas pressures.

Steps	Total flow (NL/h)	P_{CO2} (mbar)	P_{O2} (mbar)
1	35.5	129	206
2	32	/	15
3	32	/	25

Absorber pressure was 2 bars which is the minimum value for a good pressure regulation. Stripper pressure was set to 4 bars to reduce water loss.

Partial pressure of CO_2 was roughly the same as in a pilot plant (100-150 mbar). Nevertheless partial pressure of O_2 was about 4 times higher in absorber to speed up degradation at the lab scale. Oxygen was introduced during regeneration (and cooling) step to simulate the consequence of flue gas entrainment from absorber to stripper in pilot plant. Indeed, thanks to lab experiments, it was anticipated that oxidation processes could occur during the regeneration step but no proof was available before. This protocol gave degradation results in good agreement with those obtained with pilot plants: major products were produced in similar amounts as shown by GC/FID and IC.

As observed in the Table 4.3, fomate was the major acid in both cases, even if lab test was more favourable to formates formation. Others acids were present with almost same amount.

Table 4.3. Comparison of IC results for lab test and pilot plant campaign C1.

	Glycolate ppm	Acetate ppm	Formate ppm	Nitrite ppm	Oxalate ppm	Nitrate ppm
Pilot plant	415	406	2820	/	621	241
Lab test	NQ	100	4142	95	481	83

NQ: no quantification

To know if the degradation was really close to that occurring in pilot plants, samples were collected and analysed at the end of the tests by GC/FID with Carbowax and CPSIL8 columns. Comparison with C1 was done (Figure 4.3 and Figure 4.4).

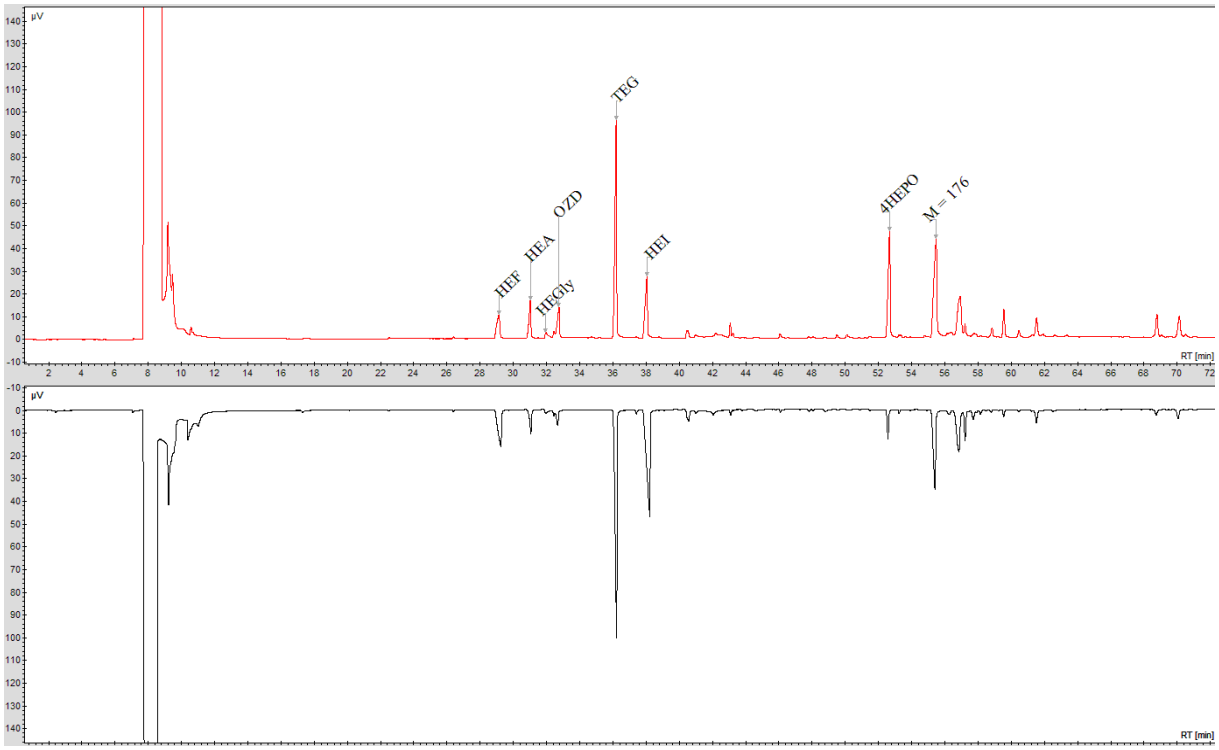


Figure 4.3. Chromatograms comparison of pilot plant (red/up) and representative lab test samples (black/ down) by GC/FID – CPSIL8 column (TEG = internal standard).

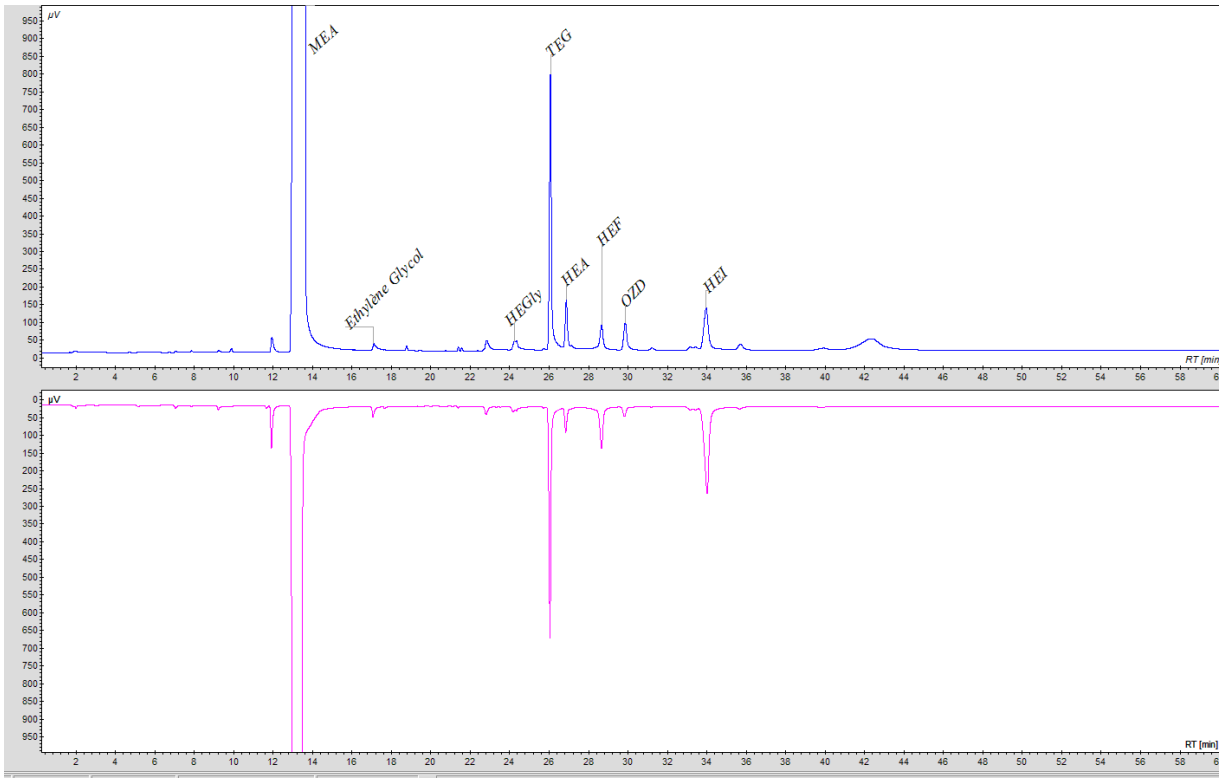


Figure 4.4. Chromatograms comparison of pilot plant (blue/up) and representative lab test samples (pink/ down) by GC/FID- Carbowax (TEG = internal standard).

Same degradation products were observed in these two chromatograms, thus confirming the right choice for lab-test conditions. However, 4HEPO was less concentrated in the laboratory test than in industrial pilot plant, whereas HEI was more concentrated in the laboratory unit. Proportion of other degradation products was comparable but not rigorously the same. These differences did not represent a major drawback because, from one pilot plant to another, degradation products were not formed exactly in same proportion. Hence, the most important thing was to obtain the same degradation products (no more) and same major products as in pilot plant, which was the case here.

FTIR analysis enabled to follow ammonia and CO_2 concentration in outlet gas during the test. The Figure 4.5 focused on analyses realised between 18 and 21 h of test.

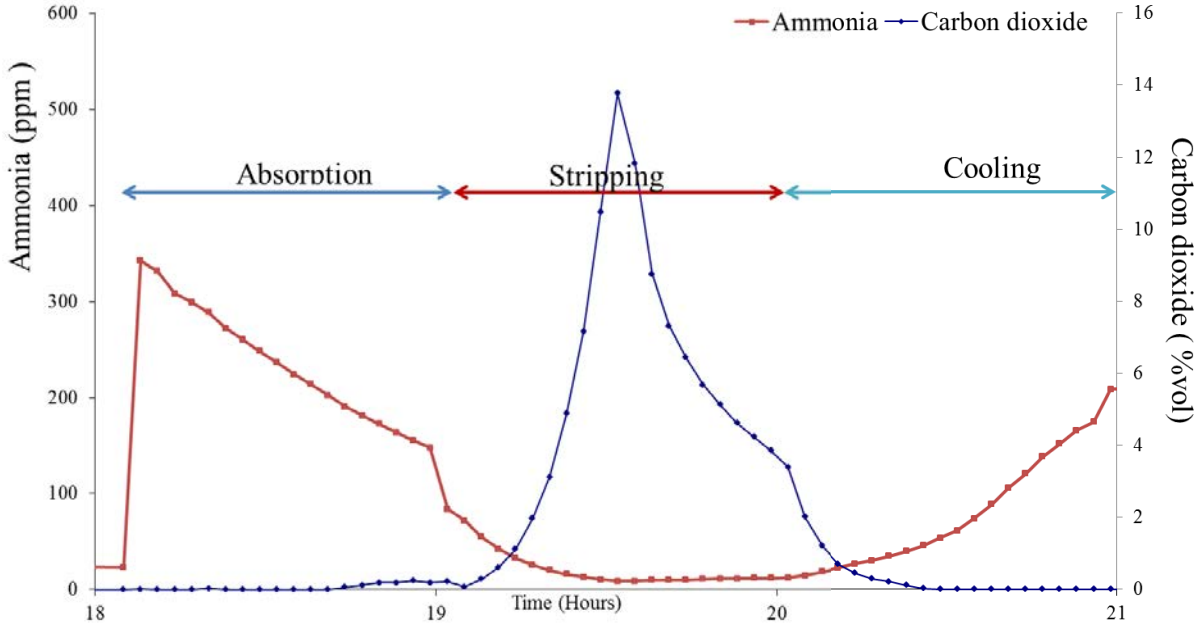


Figure 4.5. Ammonia and CO_2 FTIR profiles

Like in pilot plants, ammonia was detected in the outlet gas during the absorption step, on the other hand, CO_2 was predominant during the regeneration step (desorption) as the result of the increasing of the temperature. Globally, the amount of ammonia was more important at the end of the experiment. It was correlated with degradation: amount of ammonia increased with degradation.

This test was also carried out to degrade other selected molecules (N-methyl-2-aminoethanol (MAE), 3-aminopropan-1-ol (3AP1) and 1-aminopropan-2-ol (1AP2)) to highlight recurrent reactions. Results of these experiments are reported in Part 6.

Molality (b) was used for the sake of comparison: the same number of moles for the same water quantity.

$b = \frac{n\ reactant}{m\ water}$ in mol/kg (m)

7 m was used for all amines. Following formula was considered to determine the weight of the other amines to be used at the same molality.

$$m_{reactant} = \frac{m_{tot}}{1+\frac{1000}{M_{reactant}*b}}$$ (all the masses were in kg).

4.2. Experiments for mechanisms validation

For each newly identified molecule, a mechanism is proposed in the part 5. To do that, some experiments were performed to validate mechanism hypotheses or to get proofs of structure. Generally, these experiments were carried out in flask in oven but when better control of the conditions and/or presence of CO_2 or O_2 were needed, another equipment was used, stirred reactors. Reported experiments were numbered S1 to S28 to simplify the reading of the Part 5.

Reactants were mainly first generation degradation products of MEA (aldehydes, carboxylic acids), other major degradation compounds and/or MEA. All reactants were listed in Table 4.4 and 4.5.

All these experiments were routinely followed by GC/FID and further analyses were performed using GC/MS. When it was required, NMR analyses were done too.

4.2.1. Experiments in oven

Reactants of experiments carried out in oven were summarized in Table 4.4. These solutions were a mixture of reactants in water. More details about these experiments were reported in appendix (Table A.5).

Table 4.4. Sum-up of the experiments carried out in oven.

Names	Reagents
S1	MEA + Glycolic acid
S2	MEA + Oxalic acid
S3	MEA + HEGly
S4	MEA + Glyoxal
S5	MEA + Glyoxylic acid
S6	MEA + Glyoxal bisulphite
S7	MEA + Formaldehyde
S8	HEGly
S10	MEA + Glyoxal + Ammonium formate
S11	MEA + Ethyleneglycol
S12	HEEDA + Ethyleneglycol
S13	HEEDA + Glyoxal
S14	HEGly + OZD
S17	MEA + Glyoxal
S18	MEA + Pyruvic acid + Ammonium formate
S21	MEA + Formic acid
S22	MEA + Acetic acid
S23	HEF
S24	HEA
S25	MEA + Acetaldehyde
S27	MEA + Acetaldehyde + Formaldehyde
S28	OZD + Glycine

4.2.2. Syntheses in stirred reactors

Some experiments needed either a deeper control of the conditions (case of exothermic reactions), to be monitored more carefully, a decrease of the chemical risk (synthesis of nitrosamines) or an addition of gases as O_2 or CO_2. For these reasons, the corresponding tests were carried out in stirred reactor (Table 4.5).

Table 4.5. Sum-up of experiments carried out in stirred reactor

Names	Reagents
S9	MEA + Glyoxal + $NH_4^+HCO3^-$ + Formaldehyde
S15*	MEA + Glyoxal + Acetaldehyde + O_2
S16	MEA + Glyoxal + $NH_4^+HCO3^-$ + Acetaldehyde
S19	MEA + Acrylic acid
S20*	HEEDA + Glyoxal + CO_2
S26	MEA + Acetic acid + Acetaldehyde + $NaNO_3$

*special equipment used: composed by semi-batch glass reactors with inlet gas and condensers to limit water loss. The inlet gas (air or nitrogen) could be mixed with CO_2.

5. Identification of degradation products and mechanisms proposal

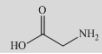
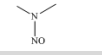
MEA degradation was studied for two campaigns (C1 and C2) in IFPEN pilot plant and for laboratory representative tests. Analyses were done by IFPEN and ESPCI. The liquid phase was analysed and also liquid phase head space and absorber outlet gas. About seventy degradation products were identified. Most of them were present in pilot plant campaigns. Products observed only in laboratory test were clearly emphasized. Firstly, compounds already mentioned in literature were reported with, for some of them, additional mechanisms were proposed. Secondly, products identified for the first time were described with proposed mechanism of formation.

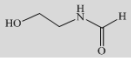
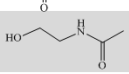
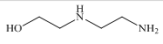
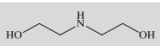
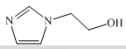
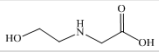
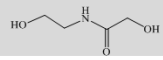
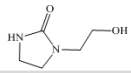
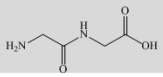
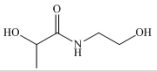
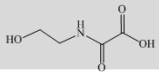
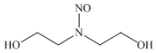
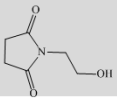
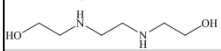
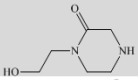
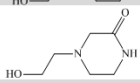
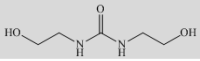
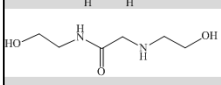
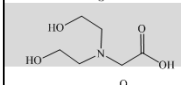
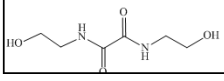
5.1. Products already observed in literature

Products already reported in literature (Cf. chapter 2) were reported in Table 5.1. Associated analytical methods used to identify them in this work were also specified. All the analytical methods are described in chapter 3.

Chromatograms were given in Appendix (Figures B.1 to B.7) with their identification.

Table 5.1. Products observed in this work

			Liquid phase analyses						Head Space analyses		Gas phase analyses	
				GC/MS					SPME		TENAX	
			IC	CPSIL8		DBWAX	LC/MS/MS		DBWAX	CPSIL8	CPSIL8	Sep Pak
Chemical structure	Identification	M g/mol		EI	PCI NCI	EI		PGC	EI	EI	EI	HPLC/DAD
	Formaldehyde	30										X
	Acetaldehyde	44									X	X
	Formic acid	46	X			X						
	Nitrous acid	47	X									
	Acetic acid	60	X			X					X	
	Ethyleneglycol (EG)	62		X	X X	X			X	X	X	
	Nitric acid	63	X									
	Propionic acid	74	X								X	
	(2-Methylamino)ethanol (MAE)	75		X	?							
	Glycine	75						X				
	N-nitrosodimethylamine (NDMA)	75									X	
	Glycolic acid	76	X									

Chemical structure	Identification	M g/mol	Liquid phase analyses						Head Space analyses		Gas phase analyses	
			IC	GC/MS CPSIL8			GC/MS DBWAX	LC/MS/MS PGC	SPME DBWAX	SPME CPSIL8	TENAX CPSIL8	Sep Pak HPLC/DAD
				EI	PCI	NCI	EI		EI	EI	EI	
	Oxazolidin-2-one (OZD)	87		X	X	X	X			X	X	
	N-(2-hydroxyethyl)formamide (HEF)	89		X	X	X	X				X	
	Oxalic acid	90	X									
	N-(2-hydroxyethyl)acetamide (HEA)	103		X	X	X	X					
	N-(2-hydroxyethyl)ethylenediamine (HEEDA)	104						X				
	Diethanolamine (DEA)	105						X				
	N-(2-hydroxyethyl)imidazole (HEI)	112		X	X	X	X				X	
	N-nitrosomorpholine (NMOR)	116						X				
	N-(2-hydroxyethyl)glycine (HEGly)	119		X	X	X	X	X				
	*2-Hydroxy-N-(2-hydroxyethyl)acetamide* (HHEA)	119		X	?	?						
	N-(2-hydroxyethyl)imidazolidin-2-one (HEIA)	130		X	X	X		X				
	N-Glycylglycine (Glygly)	132						X				
	N-(2-hydroxyethyl)lactamide (HEL)	133		X			X					
	*N-(2-hydroxyethyl)oxamic acid* (HEOX)	133	X	?	?	?						
	N-nitrosodiethanolamine (NDELA)							X				
	N-(2-hydroxyethyl)succinimide (HESucc)	143		X	X	X	X					
	N,N'-bis(2-hydroxyethyl)ethylenediamine (BHEEDA)	148						X				
	1-(2-hydroxyethyl)piperazin-2-one (1HEPO)	144		X	X	X						
	4-(2-hydroxyethyl)piperazin-2-one (4HEPO)	144		X	X	X						
	N,N'-bis(2-hydroxyethyl)urea (BHEU)	148						X				
	*N-(2-hydroxyethyl)-2-((2-hydroxyethyl)amino)acetamide* (HEHEAA)	162		X	?	?						
	N,N-bis(2-hydroxyethyl)glycine (Bicine)	163		X	X	X	X	X				
	N,N'-bis(2-hydroxyethyl)oxalamide (BHEOX)	176		X	X	X						

In italic: Standard synthesised

? : Suspected to be observed with the corresponding method

It is important to point out products which could be emitted to atmosphere. Da Silva et al., 2012 observed HEI, HEGly, HEF, BHEOX and OZD in water wash section from Esbjerg pilot plant. These products could come from gas phase, liquid entrainment or they could be formed in the water wash section. Therefore, these results should have been completed by a gas phase analysis.

It is reasonable to think that products observed in head space or gas phase (formaldehyde, acetaldehyde, acetic acid, ethylene glycol, NDMA, HEF, OZD and propionic acid) could be emitted to atmosphere.

Most of products observed in Table 5.1 were confirmed by commercially available standards. Standards were synthesised for HHEA, HEOX and HEHEAA. These products are amides and their formation is well known (Scheme 2.14). They are formed by reaction between an amine and a carboxylic acid:

- **HHEA**

MEA was stirred with glycolic acid (S1) and the mixture was analysed by NMR and GC/MS. Formation of HHEA was confirmed by NMR. Then its mass spectrum was compared with the one obtained at same retention time in the GC/MS analysis of liquid pilot plant sample (Spectra in appendix – Figure B.8 to B.11). That confirmed the presence of HHEA in pilot plant.

- **HEOX**

HEOX is an amide with a carboxylic function. However, due to the basic pH of the solvent used for CO_2 capture, it is in ionic form leading to low intensity and to spread out GC signal. Therefore, IC analysis was preferred. HEOX should be obviously formed by the reaction between MEA and oxalic acid (Scheme 2.14). The reaction mixture obtained from MEA and oxalic acid (S2) was analysed with IC (Figure 5.1) and compared to the pilot plant sample. Formic acid, oxalic acid and an unknown compound were detected. Oxalic acid was the reactant and formic acid came from decarboxylation of oxalic acid. In this synthesis, BHEOX was observed as the major product in GC/MS, leading from the reaction of oxalic acid with two MEA molecules. The first step leading to BHEOX should be the formation of HEOX; therefore it is highly likely that the unknown peak in IC analysis is the monoamide HEOX. Nevertheless, because of the presence of BHEOX, structure of HEOX could not be proved by NMR (see appendix – Figures B.12 and B.13). However, it could be noted that HEOX was

previously observed by Vevelstad, 2013 who made a similar hypothesis thanks to same kind of synthesis.

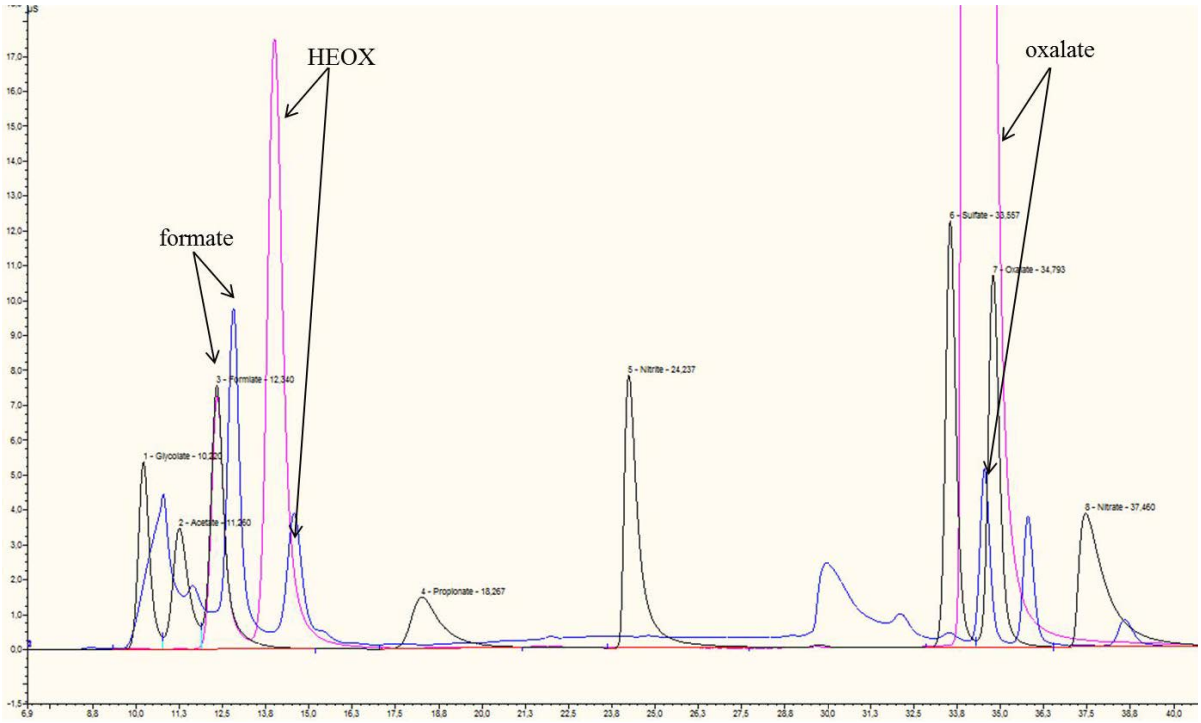


Figure 5.1. Reaction mixture from MEA and oxalic acid (in pink) superposed with standards (20 ppm in black) and pilot plant sample (in blue).

The unidentified peak was observed in pilot plant too (Figure 5.1). Little shift between retention times of pilot plant and synthesis sample was probably due to the column ageing between analyses.

To conclude, presence of HEOX was highly suspected in pilot plant.

- **HEHEAA**

A major compound with a molecular weight of 162 and $C_6H_{14}N_2O_3$ as molecular formula was observed in pilot plant by GC/MS. This product could be HEHEAA. To confirm it, MEA and HEGly were mixed in S3 because HEHEAA formation proposed by da Silva et al., 2012 (Scheme 2.18, way of da silva) was based on an amidification reaction between MEA and HEGly.

By GC/MS comparison, one of the major product observed in S3 corresponded to a major and unknown product observed in pilot plant sample (same mass spectrum and same retention time, see appendix – Figures B.14 and B.15). Regarding to the mechanism proposed by da Silva et al., 2012, this peak could be attributed to HEHEAA. Unfortunately structure

identification by NMR could not be done due to the presence of other important compounds such as MEA, but presence of HEHEAA was highly suspected in pilot plant.

Mechanism comprehension and reaction between MEA and specific reactants (all observed in MEA degradation) had helped us to confirm presence of important degradation products.

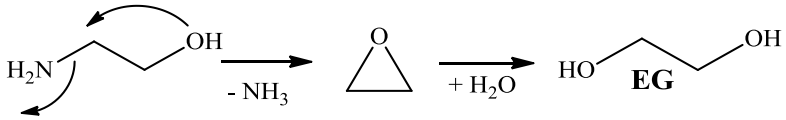
Some teams had proposed mechanism to explain formation of degradation products. Some mechanisms were well described in literature: OZD, HEEDA, HEIA, BHEU (see part 2.1), amides (HEF, HEA, HHEA, HEOX, Glygly, BHEOX), BHEEDA (see part 2.2, Scheme 2.16), DEA.

Some nitrosamines already observed in literature were observed in this work (NDMA, NMOR, NDELA). Mechanism of their formation was previously described by Fostås et al., 2011.

For others, ethylene glycol, aldehydes, carboxylic acids, HEHEAA, HEGly, 1HEPO, 4HEPO, HEI, HESucc, propionic acid and HEL, there was no described mechanism or they were unlikely regarding to organic chemistry, unclear or not proved. Therefore, new mechanisms are proposed in this work.

- **EG**

Ethyleneglycol (EG) was one of the first generation degradation products. A mechanism of deamination has been proposed (Scheme 5.1) for its formation. Unfortunately, ethylene oxide was not observed, probably due to its very high reactivity.

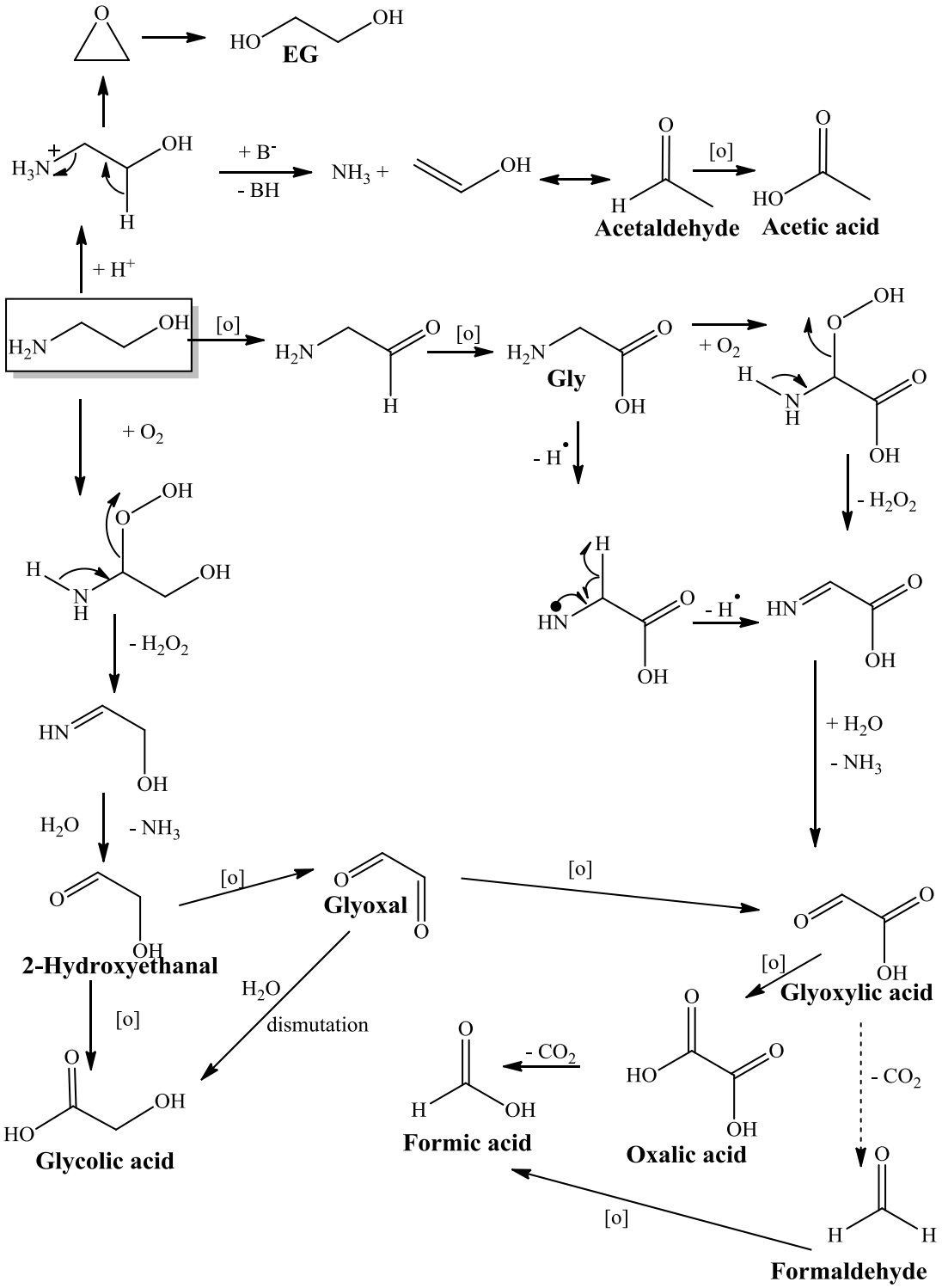


Scheme 5.1. Proposed mechanism for ethyleneglycol formation

- **Aldehydes and carboxylic acids**

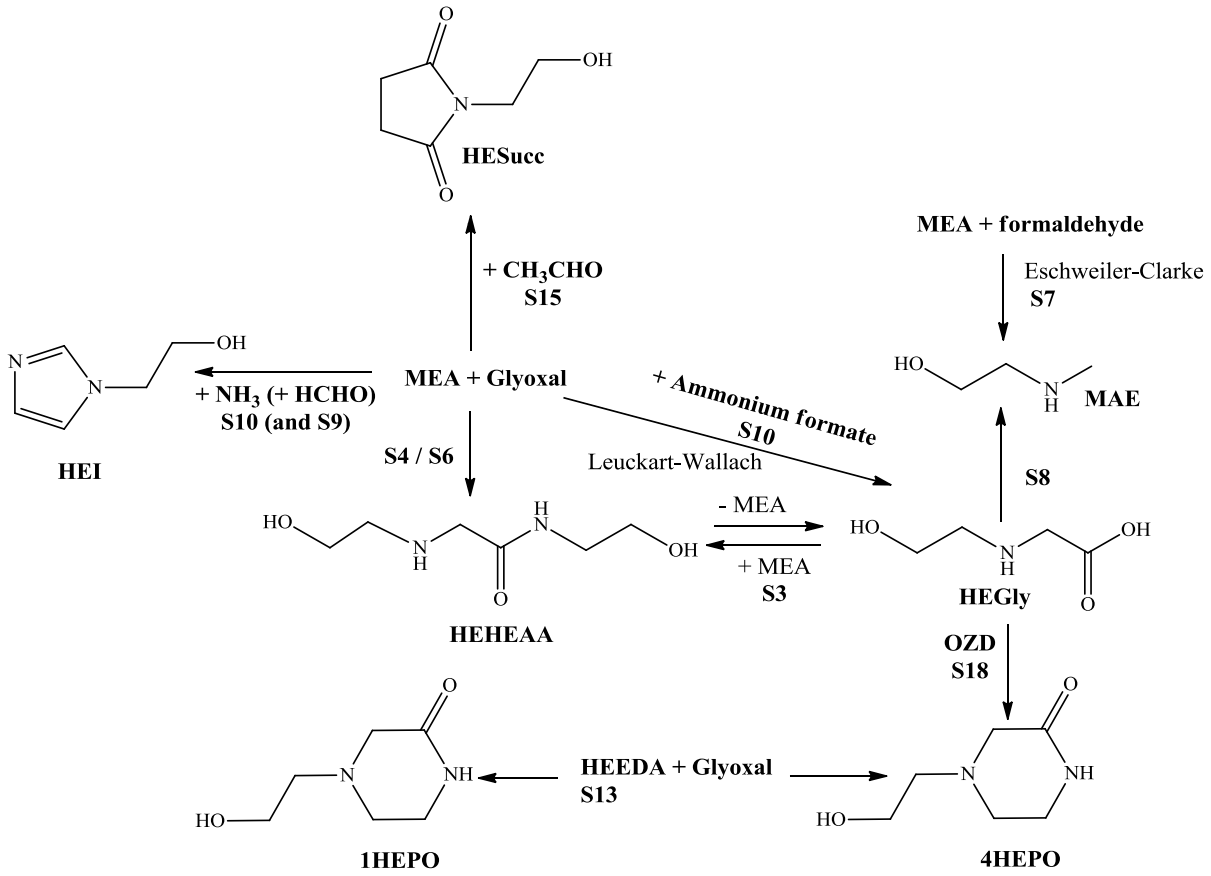
Aldehydes and carboxylic acids are first generation products of MEA degradation. Some mechanisms were already proposed in part 2 (Schemes 2.9; 2.10 and 2.11) but many of them were unclear or incomplete. Therefore, a detailed mechanism is proposed in this work (Scheme 5.2). This mechanism is based on hydrogen abstraction and peroxide formation (Denisov and Afanas'ev, 2005; Nielsen et al., 2011), except for the formation of acetaldehyde (acetic acid after oxidation), which is based on ionic mechanism.

As previously mentioned, formic acid is the main acid. It can be obtained by alpha keto-acid decarboxylation, which is a well-known reaction for oxalic or glyoxylic acid.



Scheme 5.2. Proposed mechanism for carboxylic acids and aldehydes formation

Glyoxal is one of the first degradation products. It is particularly unstable and exists in many species in aqueous solution such as hydrates or glycolic acid. Glyoxal could be involved in numerous reactions as described in Scheme 5.3.

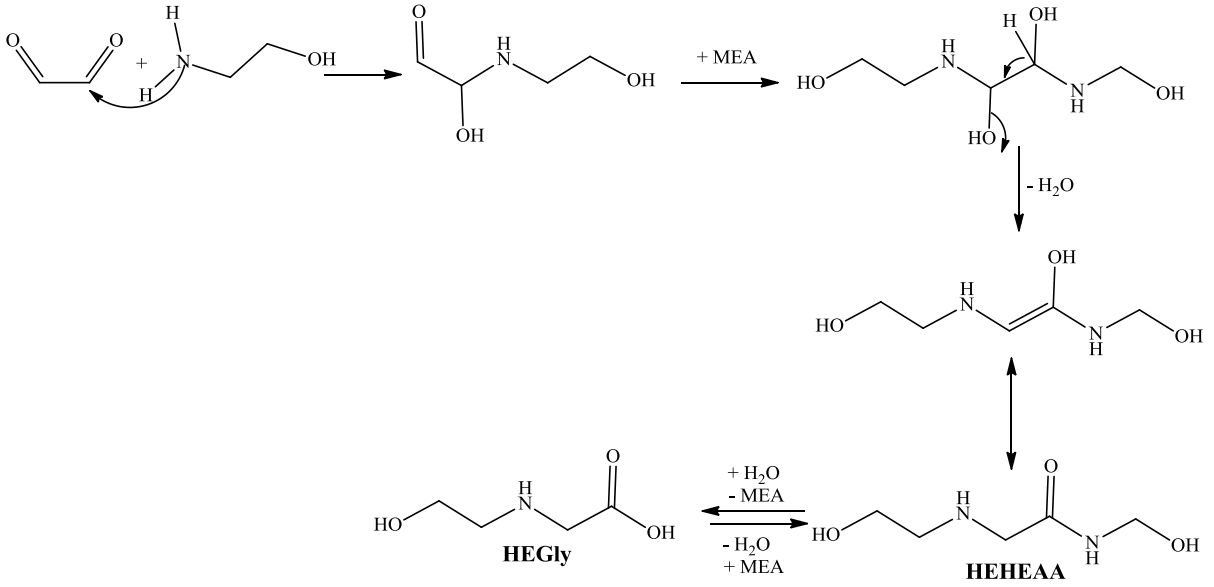


Scheme 5.3. Sum-up of reactions of MEA with glyoxal leading to known degradation products

- **HEGly**

HEGly was observed when MEA was mixed with glyoxal (S4) or with glyoxylic acid (S5). Indeed glyoxal could give glyoxylic acid (Scheme 5.2). This observation is in accordance with Vevelstad mechanism (Scheme 2.21). The proposed reaction pathway involves a reductive amination step thanks to the presence of formate (in this case ammonium formate).

However, another mechanism could be proposed (Scheme 5.4). Reaction of two MEA with glyoxal should lead the diamide HEHEAA. Amides are potentially in equilibrium with the corresponding salts, especially in an aqueous basic solution (Supap et al., 2011). Hence, HEGly should be observed in parallel to HEHEAA.



Scheme 5.4. Proposed mechanism for HEGly formation (based on S6 results)

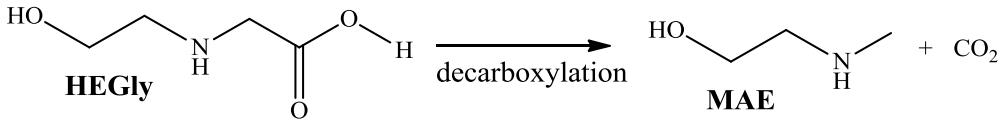
To prove this mechanism, MEA was mixed with glyoxal bisulphite (S6). The later was used in order to work with a stable glyoxal analogue. Major products observed in GC/MS were HEGly and HEHEAA. This result is in perfect accordance with this mechanism.

To conclude, two mechanisms could occur in pilot plant to form HEGly. They only used MEA and first generation products which could explain HEGly abundance.

- **MAE**

MAE was observed in pilot plant sample. Lepaumier, 2008 proposed a mechanism based on Eschweiler-Clarke reaction (Scheme 2.22.). This mechanism was confirmed in the present work with the formation of MAE and N,N-dimethylaminoethanol (DMAE) as major products in S7 synthesis (MEA mixed with formaldehyde).

MAE was also formed in small amount when HEGly was heated (S8). Consequently, another mechanism is proposed: the decarboxylation of HEGly (Snider and Wolfenden, 2000; Steffen et al., 1991) (Scheme 5.5).

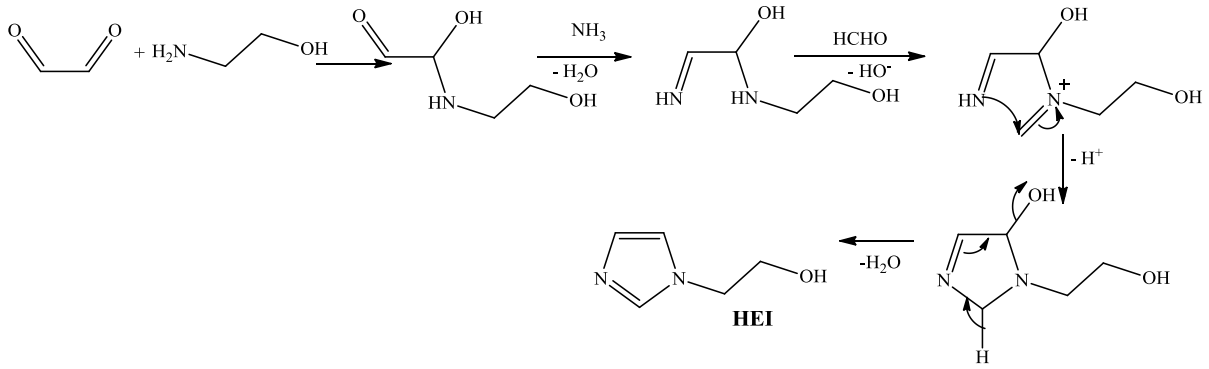


Scheme 5.5. Proposition of mechanism for MAE formation (based on S8 results)

These two mechanisms could occur.

- **HEI**

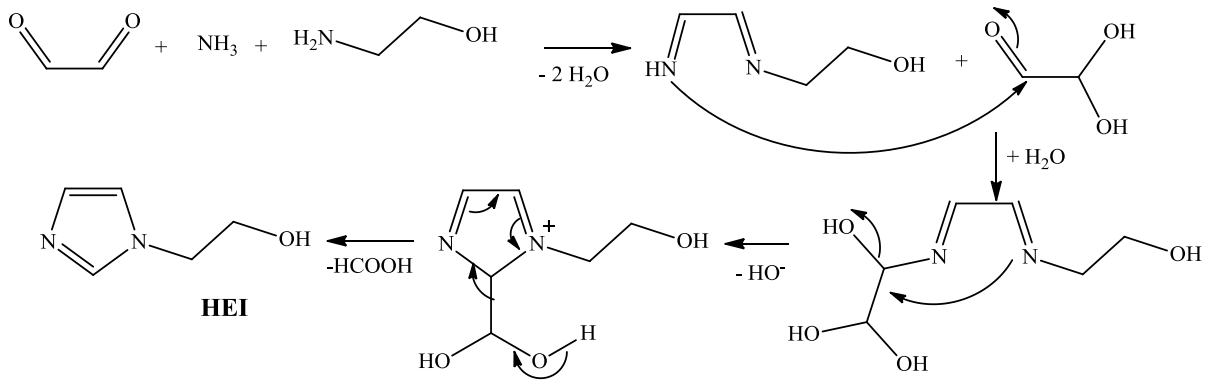
HEI was observed by da Silva et al., 2012; Lepaumier et al., 2011a; Sexton and Rochelle, 2011; Strazisar et al., 2003 as one of the main degradation products. To prove HEI formation, reactants were mixed following Arduengo's patent (Arduengo et al., 2001) (S9). Therefore a likely mechanism could be proposed (Scheme 5.6).



Scheme 5.6. Proposed mechanism for the formation of HEI (Based on S9 results)

Some other patents described the synthesis of HEI by mixing MEA, glyoxal, formaldehyde and ammonia (Ben, 2005; Katsuura and Washio, 2005; Kawasaki et al., 1991). Vevelstad, 2013 proposed a mechanism based on Katsuura and Washio, 2005. This mechanism was verified by synthesis (Scheme 2.20).

When MEA was mixed with glyoxal and ammonium formate in water (S10), HEI was the major product. Another mechanism (Scheme 5.7) without formaldehyde was proposed based on Yu et al., 2011.



Scheme 5.7. Proposed mechanism for the formation of HEI without formaldehyde (based on S10 results)

Moreover in this synthesis HEF was found in high proportion, which is in accordance with the final step and formation of formic acid.

This mechanism seems more probable than the other one because glyoxal should be formed in bigger proportion than formaldehyde.

- **4HEPO and 1HEPO**

4-(2-hydroxyethyl)piperazin-2-one (4HEPO) was described as one of the major degradation product in pilot plants and it seemed the same in our sample. Several authors had proposed mechanisms for its formation as well as for 1HEPO (da Silva et al., 2012; Lepaumier et al., 2009b; Strazisar et al., 2003).

Strazisar et al., 2003 proposed the first mechanism for these compounds (Scheme 2.18). The intermediate, HEHEAA would be formed from reaction between HEA and MEA. Reaction between an amine and a methyl group seemed to be unlikely, even with Fe^{3+} used as a catalyst. da Silva et al., 2012 had proposed an amidification between MEA and HEGly to form HEHEAA (Scheme 2.18). Moreover, HEGly was described by Lepaumier et al., 2011a as a major compound in pilot plant. This could be in accordance with high concentration of 4HEPO but not with the low concentration of 1HEPO, even if steric hindrance would disadvantage 1HEPO formation. As explained before, HEHEAA seems to be formed by reaction between MEA and HEGly (S3). However in this synthesis, 4HEPO was obtained in very small amount and 1HEPO was not observed. Therefore, intramolecular cyclisation of HEHEAA seems unlikely to lead to 4HEPO and 1HEPO (Scheme 2.18).

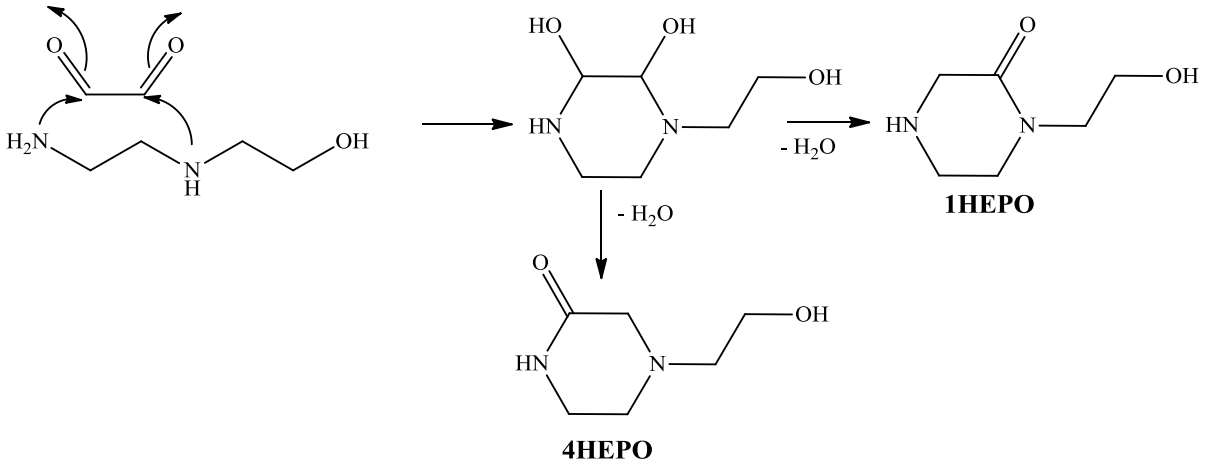
Moreover, intramolecular nucleophilic substitution of alcohol by amine seems generally hard to do in organic chemistry. For example, when MEA was mixed with glycolic acid, HEGly was not observed (S1), even as minor product. To confirm this hypothesis, MEA (or HEEDA) was mixed with ethyleneglycol (S11 and S12); no new compound was observed by NMR or GC/MS. Therefore it could be better to propose ethylene oxide than ethyleneglycol as an electrophile in the mechanisms, although due to its strong reactivity, ethylene oxide was not reported in literature or observed in our syntheses.

Substitution of alcohols with primary or secondary amines in our syntheses conditions didn't occur. However, pilot plant conditions could favour this reaction (presence of nitrite could activate OH as leaving group, Huang et al., 2014, Scheme 2.23).

Lepaumier et al., 2009b described another possible way (Scheme 2.17), but intramolecular nucleophilic substitution of alcohol by amine was involved too.

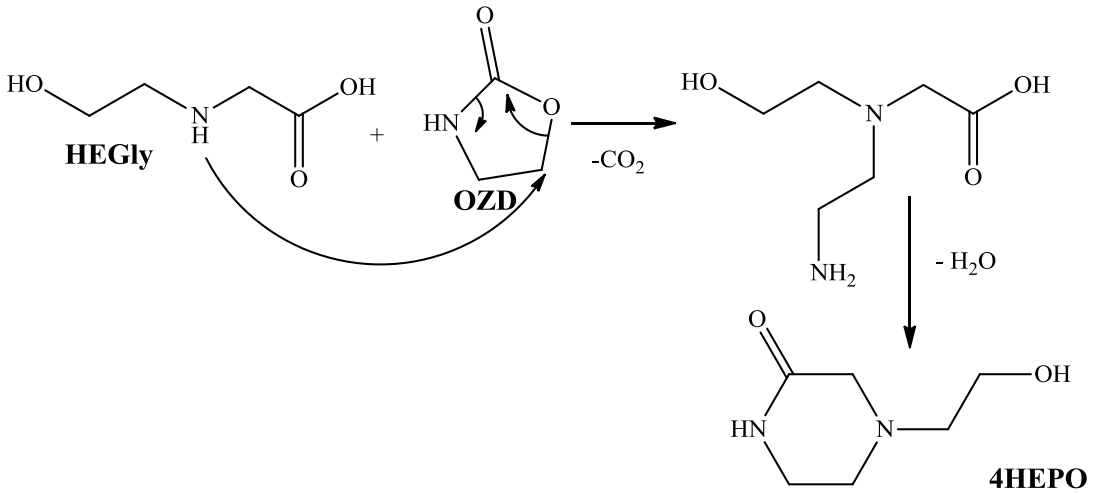
None of these mechanisms was confirmed; therefore we proposed two other ones. The first is for 4HEPO and 1HEPO formation. Major products of the reaction of HEEDA with glyoxal

(S13) were 1HEPO and 4HEPO. Glyoxal could react with the two amino groups of HEEDA to form a vicinal diol, which was converted, after dehydration, either to 1HEPO or 4HEPO (Scheme 5.8).



Scheme 5.8. Proposed mechanism for 1HEPO and 4HEPO formation (based on S13)

Another mechanism was proposed in Scheme 5.9 by the reaction of OZD with amine function of HEGly. Then, amidification, which seemed favourable in pilot plant conditions, occured. 4HEPO was one of the major products of S14 (HEGly + OZD), which was in accordance with this mechanism.



Scheme 5.9. Proposed mechanism for 4HEPO formation (based on S14)

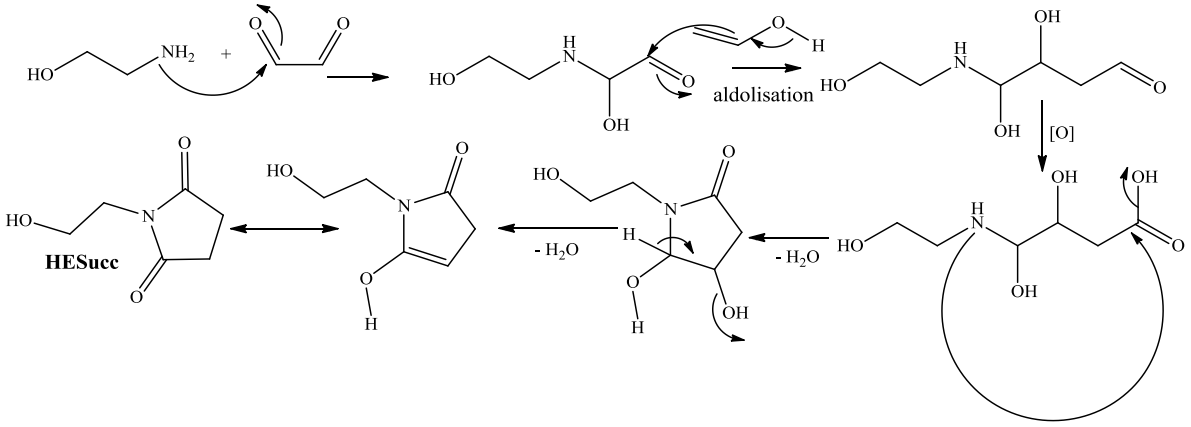
These two mechanisms could both occur in pilot plant. As the second one led to 4HEPO only, it could explain the higher concentration of 4HEPO compared to 1HEPO.

Compared to 4HEPO and its 3 mechanisms proposed, some products observed were not explained with any mechanism: HESucc, propionic acid and HEL. To form these compounds, the carbon chain length was increased compared to MEA, which is rather complex to explain

(Voice, 2013). We propose the involvement of an aldolisation step (reaction between two carbonyl compounds, aldehydes or ketones) in following mechanisms.

- **HESucc (4 carbon atoms chain)**

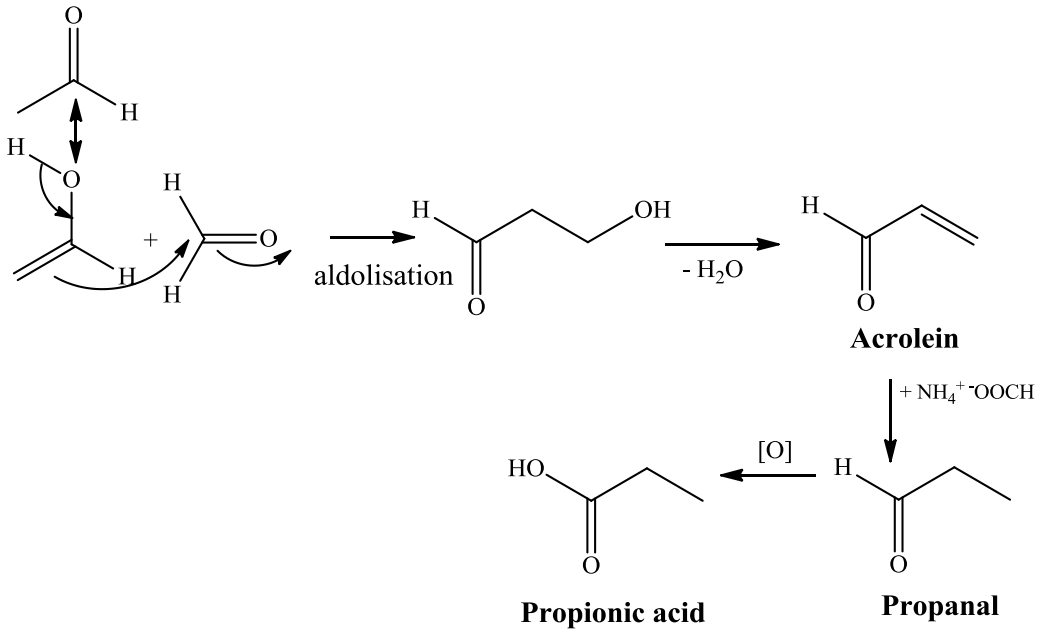
This product has been already reported by Lepaumier et al., 2011a; Reynolds et al., 2013; Strazisar et al., 2003; Supap et al., 2011. To the best of our knowledge, no mechanism was proposed. As shown in Scheme 5.10, this product could be formed by reaction of MEA with glyoxal, then aldolisation could take place with acetaldehyde. Oxidation followed with intramolecular cyclisation (amidification) and dehydration led to HESucc. When MEA was mixed with glyoxal then acetaldehyde and then oxygen was added (S15), HESucc was formed in small amount, which seemed in accordance with the proposed mechanism.



Scheme 5.10. Proposed mechanism HESucc formation (based on S15)

- **Propionic acid**

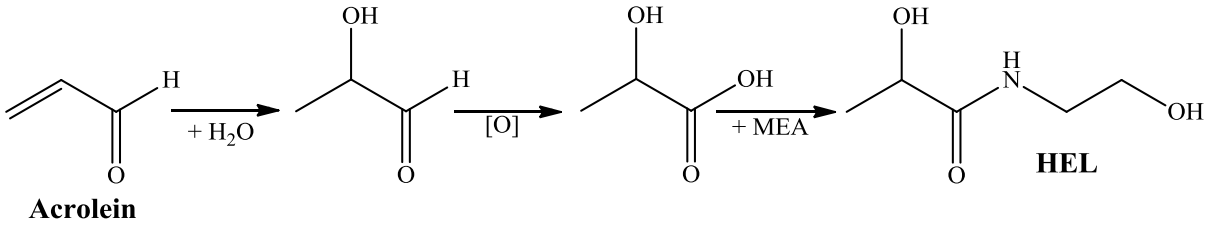
Propionic acid was observed in pilot plant sample. Its formation mechanism was based on aldolisation of acetaldehyde with formaldehyde. This aldolisation led to acrolein, previously observed as volatile compound by Love, 2012. The double bond of acrolein could be reduced and the aldehyde group oxidised giving propionic acid (Scheme 5.11).



Scheme 5.11. Propanal and propionic acid formation via acrolein

- **HEL**

This compounds was reported by Reynolds et al., 2013; Strazisar et al., 2003. However, no mechanism was proposed. A way of formation starting from acrolein was proposed (Scheme 5.12). It was converted into lactaldehyde, then oxidised into lactic acid, which could react with MEA to form HEL.



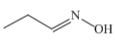
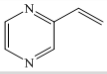
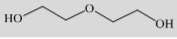
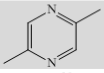
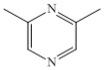
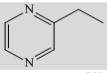
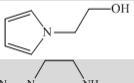
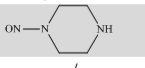
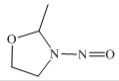
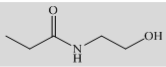
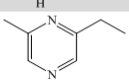
Scheme 5.12. Proposed way of formation for N-(2-hydroxyethyl)lactamide.

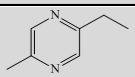
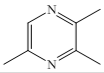
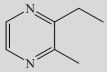
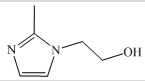
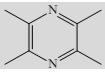
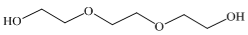
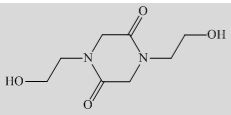
Even if reaction conditions were different to those of pilot plant, syntheses had helped us to propose mechanism. For example we have seen that amino group cannot substitute a hydroxyl group.

5.2.Novel degradation products

Novel products have been identified thanks to new sampling methods. There were listed in Table 5.2.

Table 5.2. Novel products

Chemical structure	Identification	M g/mol	Liquid phase analyses						Head Space analyses		Gas phase analyses	
			GC/MS					LC/MS/MS	SPME		TENAX	HPLC/DAD
			CPSIL8			DBWAX		PGC	DBWAX	CPSIL8	CPSIL8	Sep Pak
			EI	PCI	NCI	EI			EI	EI	EI	
	Propanal	58										X
	Acetaldoxime	59									X	
	Pyrrole	67									X	
	Oxazoline	71	X	X		X			X	X	X	
	**Butan-2-one**	72										X
	**Acetoxime**	73									X	
	**Propanaloxime**	73									X	
	Oxazolidine	73	X	X	X			X			X	
	Pyrazine	80	X	X		X		X	X	X	X	
	2-Methyloxazoline	85	X			X			X	X		
	2-Methyloxazolidine*	87	X								X	
	3-Methylpyridine	93	X								X	
	2-Methylpyrazine	94				X			X	X	X	
	Piperazin-2-one (PO)	100	X	X	X							
	**2-Vinylpyrazine**	106									X	
	Diethyleneglycol (DEG)	106	X			X			X		X	
	2,3-Dimethylpyrazine	108							X	X	X	
	2,5-Dimethylpyrazine	108							X	X		
	2,6-Dimethylpyrazine	108							X	X	X	
	2-Ethylpyrazine	108							X	X	X	
	N-(2-hydroxyethyl)pyrrole (HEPyr)	111	X	X	X	X			X	X	X	
	N-nitrosopiperazine (NPZ)	115						X				
	N-nitroso-2-methyloxazolidine*	116									X	
	N-(2-hydroxyethyl)propanamide (HEPr)	117	X			X						
	2-Ethyl-6-methylpyrazine	122							X	X		

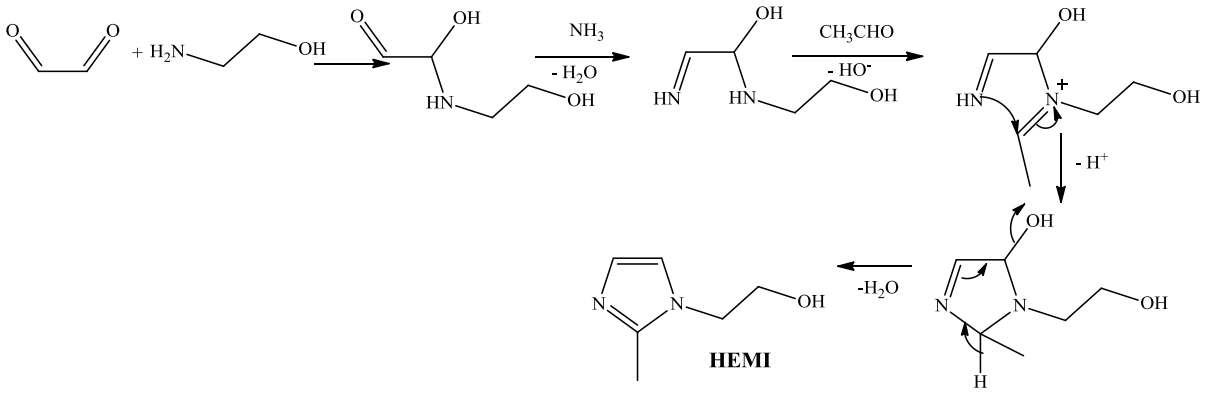
Chemical structure	Identification	M g/mol	Liquid phase analyses GC/MS CPSIL8 EI	CPSIL8 PCI	CPSIL8 NCI	DBWAX EI	LC/MS/MS PGC	Head Space analyses SPME DBWAX EI	SPME CPSIL8 EI	Gas phase analyses TENAX CPSIL8 EI	HPLC/DAD Sep Pak
	2-Ethyl-5-methylpyrazine	122						X	X		
	2,3,5-Trimethylpyrazine	122						X	X	X	
	2-Ethyl-3-methylpyrazine	122						X	X		
	N-(2-hydroxyethyl)-2-methylimidazole (HEMI)	126	X								
	2,3,5,6-Tetramethylpyrazine	136								X	
	Triethyleneglycol (TEG)	150								X	
	*N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione* (BHEPDO2,5)	202	X	X?	X?						

In Italic: Synthetized standards
In bold: Observed in laboratory representative experiment
* No standard confirmation

Firstly, we will describe products, which are supposed to be obtained from MEA and glyoxal as starting material. (Mass spectra of unknown products and synthesised standard are reported in appendix B – Figures B.18 to B.30)

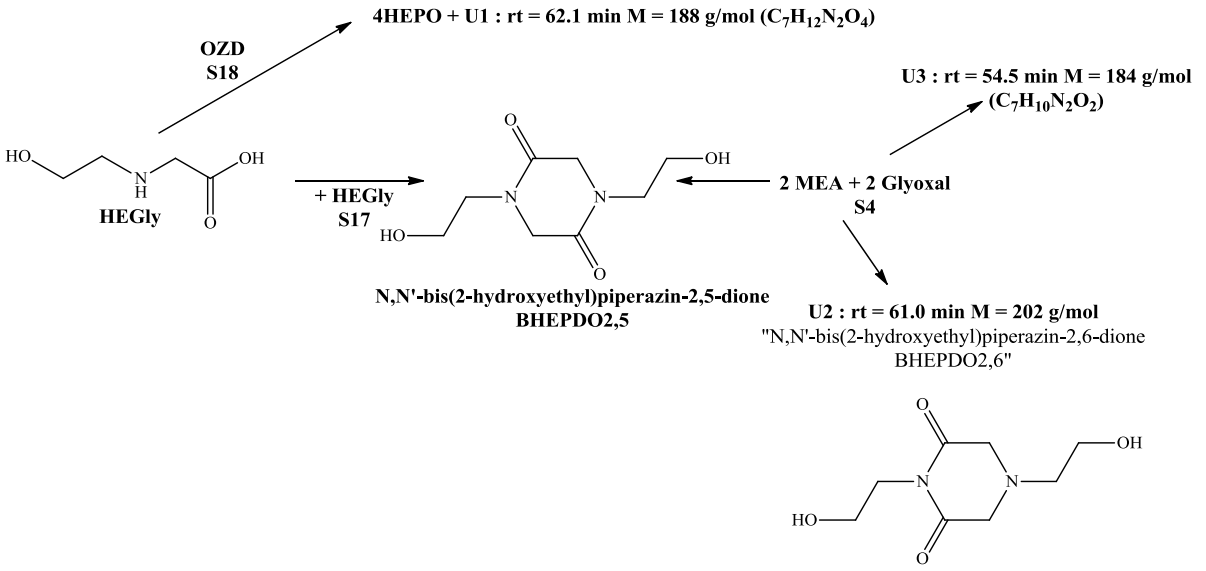
- **1-(2-hydroxyethyl)-2methylimidazole (HEMI)**

Vevelstad et al., 2013b suggested HEMI formation, because a fragment with a molecular weight of 126 was observed in GC/MS. Moreover its fragmentation was similar to that of HEI. For its formation, they proposed same reactants as for HEI (Scheme 2.20) but formaldehyde was replaced by acetaldehyde. Presence of HEMI in the pilot plant sample was confirmed by standard. S16 with MEA, ammonium formate, acetaldehyde and glyoxal led to HEMI formation as major product, therefore mechanism proposed for HEI could be applied with acetaldehyde instead of formaldehyde (Scheme 5.13).



Scheme 5.13. Proposed mechanism for HEMI formation (based on HEI formation and S16)

Scheme 5.14 is a sum-up for the reaction with MEA and glyoxal as starting materials, which lead to new degradation products.



Scheme 5.14. Sum-up of reactions for new degradation products (U1, U2, U3 unknown products see after)

- **BHEPDO2,5**

In the pilot plant sample, a compound with a molecular weight of 202 was observed by GC/MS. This molecular weight was confirmed with positive and negative chemical ionisation: m/z = 203 for PCI, and m/z = 201 for NCI. Moreover, the major product observed in S8 (HEGly in water at 100ºC for 15 days) had the same mass spectrum and same retention time. The structure of this compound was determined by ^{1}H-^{13}C HSQC NMR as BHEPDO2,5 (Figure 5.2). The main differences in ^{1}H NMR (Figure 5.3) between HEGly (precursor), and this product were the shifts of the singlet from 3.65 to 4.20 ppm and of one triplet from 3.20 to 3.56 ppm, which were in accordance with the formation of amido group.

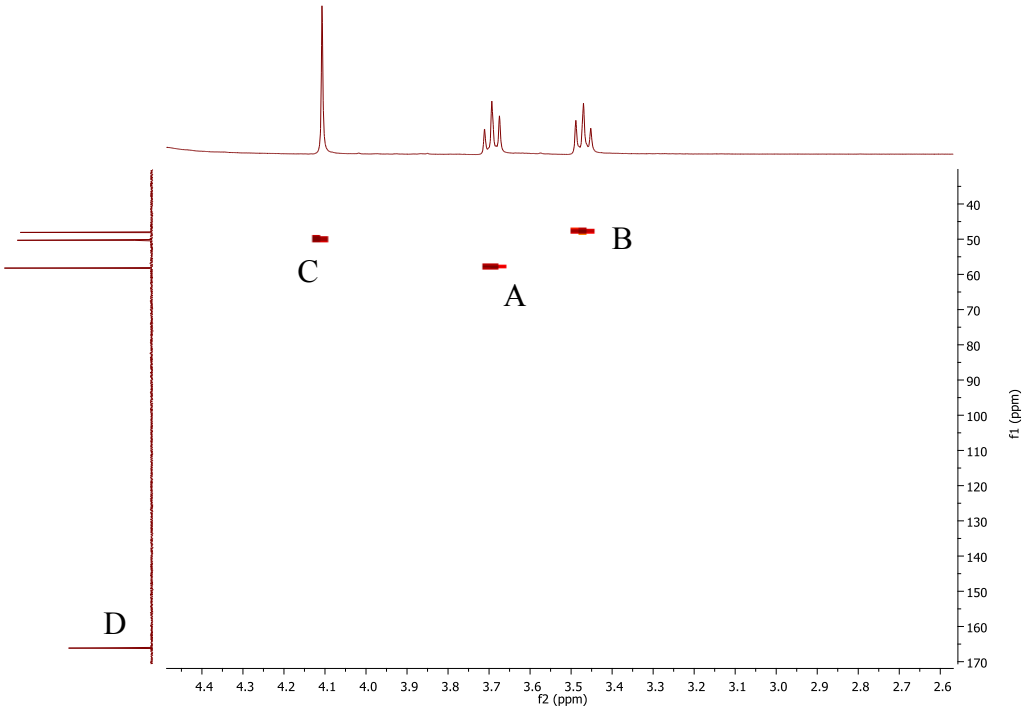


Figure 5.2. ^{1}H-^{13}C HSQC spectrum of S8 in D_2O.

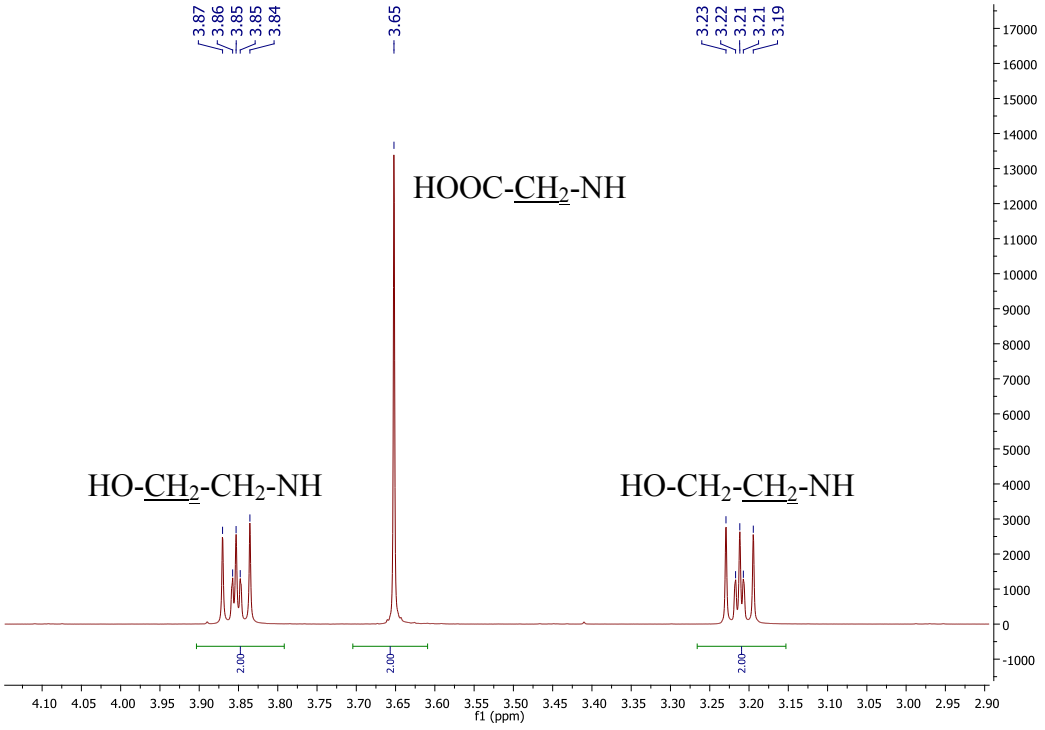
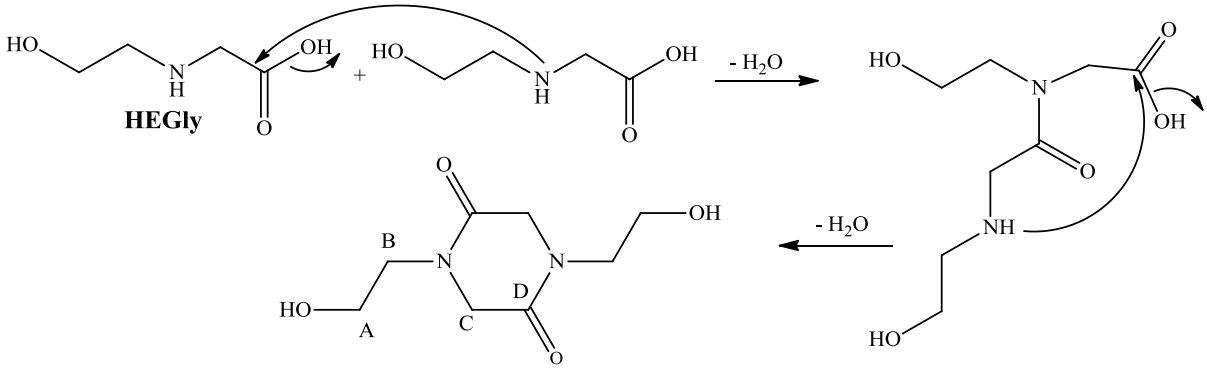


Figure 5.3. ^{1}H NMR spectrum of HEGly in D_2O.

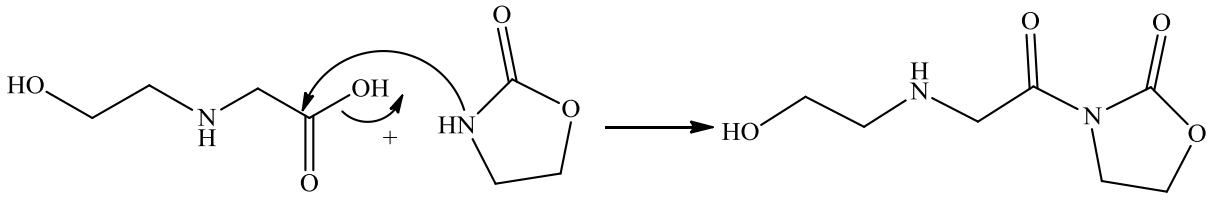
As HEGly is one of the major degradation products (da Silva et al., 2012), 2 molecules of HEGly can react together to form this product. Firstly, amine of HEGly could react with carboxylic acid of the other molecule, then an intramolecular amidification could lead to BHEPDO2,5 (Scheme 5.15).



Scheme 5.15. Proposed mechanism for BHEPDO2,5 formation (based on S8).

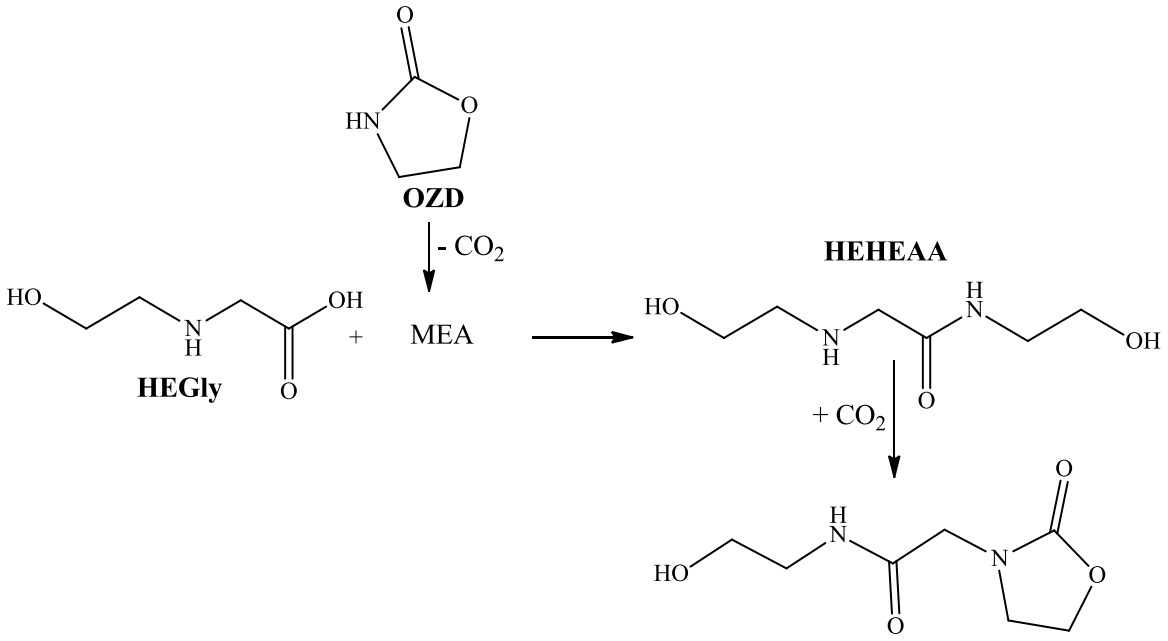
- **Unknown compound with M = 188 g/mol (rt 62.1 min) – U1**

This compound was characterized by a highly intense GC peak. The molecular formula obtained by GC/MS-TOF was $C_7H_{12}N_2O_4$, which was in accordance with FT-ICR/MS results. A fragment at 157 with the molecular formula $C_6H_9N_2O_3$ was also observed, apparently due to the loss of CH_2-OH. Such compound was observed as a major product in S14 synthesis (HEGly and OZD). Some authors described reaction of OZD with carboxylic acids with a high yield thanks to the use of coupling reagents (Andrade et al., 2003; Knol and Feringa, 1996). Therefore, this product could come from amidification between HEGly and OZD (Scheme 5.16).



Scheme 5.16. Proposal for the structure and formation pathway of U1 (based on S14)

Another isomer (Scheme 5.17) could also be proposed for U1; OZD would be opened and to release CO_2. As previously proposed, HEGly could react with MEA to form HEHEAA, then HEHEAA could react with CO_2 to form a new oxazolidinone.



Scheme 5.17. Proposal for the structure and formation pathway of U1 (based on S14)

Unfortunately, these hypotheses could not be yet proved. The second hypothesis seems less favourable because HEHEAA was not observed in S14.

The next table was a sum up of products observed in pilot plant sample without identification. They were indexed with their retention time, on GC/MS-TOF with CPSIL8 column. The corresponding molecular weight obtained thanks PCI and NCI and proposed molecular formula were reported as well as the synthesis number, when they were observed.

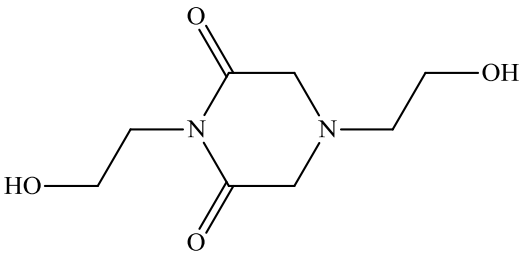
Table 5.3. Products observed without identification in pilot plant sample

				Liquid phase analysis GC/MS				
				CPSIL8			DBWAX	
Name	RT	M	Molecular formula	EI	PCI	NCI	EI	Synthesis
U4	32.8	115	$C_5H_9NO_2$	X	X	X	X	S28
U6	50.6	158	$C_7H_{14}N_2O_2$	X	X	X		S25
U3	54.6	184	$C_8H_{12}N_2O_3$	X	X			S4
U5	56.8	176	$C_7H_{16}N_2O_3$	X	X	X		S26
U8	58.7	188	$C_8H_{16}N_2O_3$	X	X	X		S30
U2	61.0	202	$C_8H_{14}N_2O_4$	X	X	X		S4
U1	62.1	188	$C_7H_{12}N_2O_4$	X	X	X		S14
U7	63.0	216	$C_9H_{16}N_2O_4$	X	X	X		S3

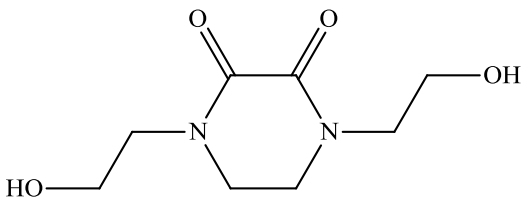
Reasonable molecules could be proposed for some of these unknown compounds by combining synthesis approaches, study of molecules fragmentation in mass spectrometry and reinvestigation of main reaction pathways previously described.

- **Unknown compound with M = 202 g/mol (rt 61.0 min) – U2**

This compound was characterized by a highly intense GC peak. The molecular formula obtained by GC/MS-TOF is $C_8H_{14}N_2O_4$, which was in accordance with FT-ICR/MS results. When MEA was mixed with glyoxal (S4), BHEPDO2,5 and U2 were observed as major products. Therefore, it could be an isomer BHEPDO2,6 or BHEPDO2,3.

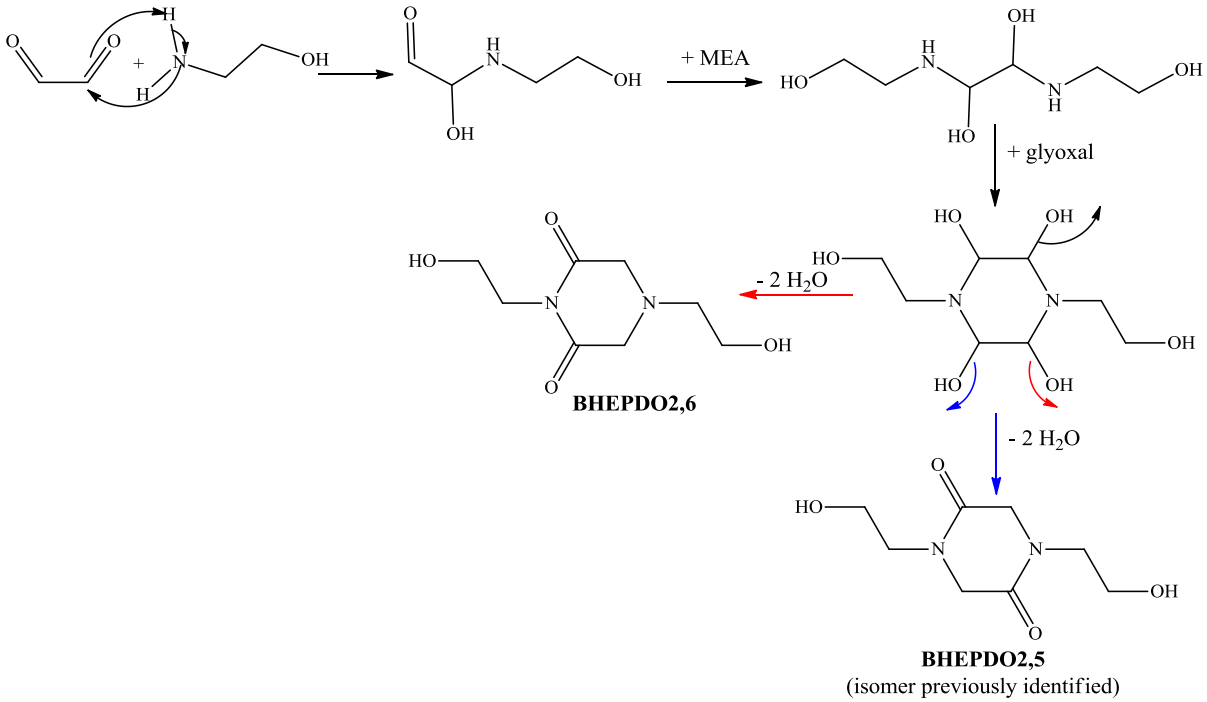


N,N'-bis(2-hydroxyethyl)piperazin-2,6-dione
BHEPDO2,6



N,N'-bis(2-hydroxyethyl)piperazin-2,3-dione
BHEPDO2,3

The tetrol intermediate suggested in the reaction of two MEA with two glyoxal could lead to the formation of two ketones in 2,6 or 2,5, not in 2,3. According to Scheme 5.18, it seemed unlikely to observe the formation of BHEPDO2,3. BHEPDO2,6 was the most favourable isomer and should correspond to this unknown compound.



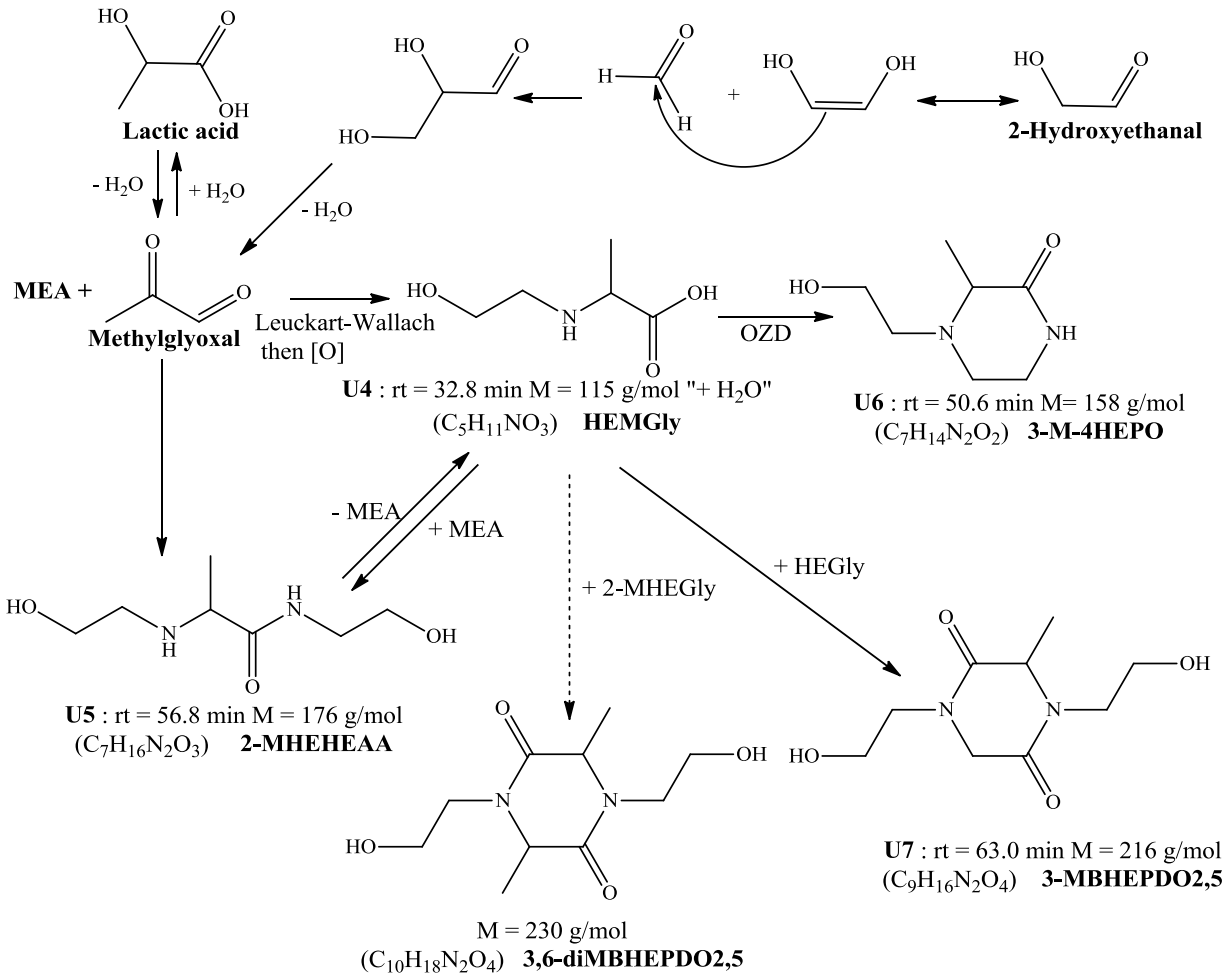
Scheme 5.18. Proposal for the structure and formation pathway of U3 (based on S4)

- **Unknown compound with M = 184 g/mol (rt 54.5 min) – U3**

The GC peak of U3 with $C_8H_{12}N_2O_3$ for molecular formula has a retention time just longer than 4HEPO. Its EI mass spectrum was characterized by two fragments at m/z = 154 and m/z = 111 corresponding to $C_7H_{10}N_2O_2$ and $C_5H_7N_2O$, respectively. This product was also observed when MEA was mixed with glyoxal (S4). In the presence of an excess of MEA, it is the major product (S17). No plausible structure could be proposed.

Regarding the reactions described for the formation of products in the case of MEA with glyoxal, we had transposed these reactions to MEA and methylglyoxal to explain formation of some products. Methylglyoxal is well-known to be in equilibrium with lactic acid (Fedoronko and Koenigstein, 1971; Konigstein et al., 1981) As shown in Scheme 5.12, lactic acid could be obtained through the hydration of acrolein and oxidation of the resulting compound. Another pathway to form this compound was by aldolisation of 2-hydroxyethanal with

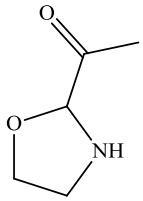
formaldehyde. Even if methylglyoxal was not observed in this work, it could be a reactive intermediate. The sum-up (Scheme 5.19) could help to understand the formation of some products. However, at that time, none of the proposed compounds was confirmed by commercial standards.



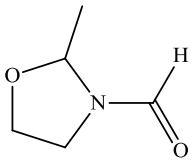
Scheme 5.19. Sum-up of proposed reactions of MEA with methylglyoxal for novel degradation products

- **Unknown compound with M = 115 g/mol (rt 32.8 min) – U4**

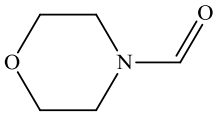
The GC peak of U4 was between those of HEGly and OZD. Its molecular formula obtained with GC/MS-TOF was $C_5H_9NO_2$, which was in accordance with FT-ICR/MS results. Its EI mass spectrum was characterized by a fragment at 86 (C_4H_8NO), loss of 29, which suggest that the molecule could have a formyl group. Three molecules could be envisaged regarding our knowledge on MEA reactions:



2-acetyloxazolidine



N-formyl-2-methyloxazolidine



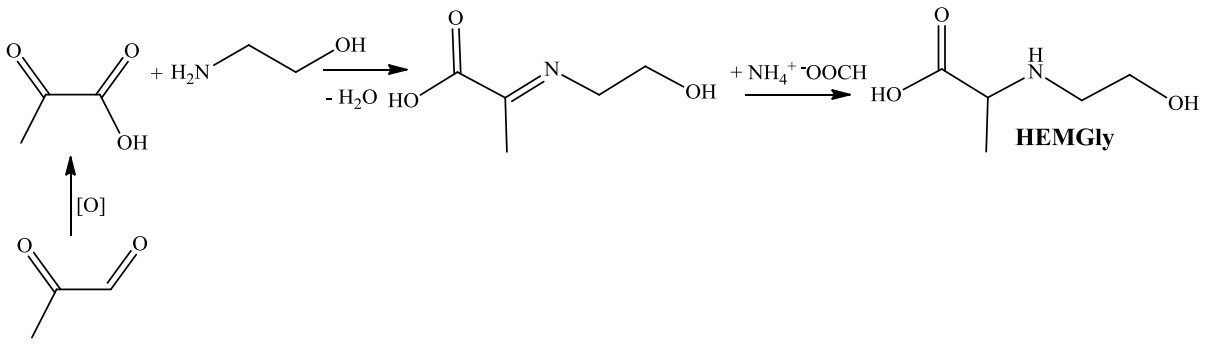
N-formylmorpholine

MEA + methylglyoxal MEA + acetaldehyde + formic acid morpholine + formic acid

N-formylmorpholine is commercially available and was characterized by the same retention time and fragmentation as U4 (M = 115). However, intensity of the fragments was different. Therefore, we cannot prove that it is U4.

N-formyl-2-methyloxazolidine could be formed by amidification of formic acid with 2-methyloxazolidine (already observed and explained in the next part). However, retention time of the GC/MS peak and its relative intensity seemed not in accordance with this proposal. Moreover, if N-formyl-2-methyloxazolidine was formed, it should be in small amount in liquid phase due to intermediate abundance. Same comments could be done for 2-acetyloxazolidine.

A very last hypothesis was that this compound could be an amino acid, more exactly a methyl derivative of HEGly, N-(2-hydroxyethyl)-2-methylglycine (HEMGly). The molecular weight of HEMGly is 133, i.e. 115 + 18 (water), corresponding to $C_5H_{11}NO_3$ ($C_5H_9NO_2$ + H_2O). This loss of water was already observed for HEGly even in PCI and NCI, where the last fragment was observed at 101 instead of 119. Moreover U4 was observed when MEA was mixed with pyruvic acid and ammonium formate (Leuckart Wallach reaction) (S18), which is in accordance with this hypothesis (Scheme 5.20).



Scheme 5.20. Proposal for the structure and formation pathway of U4 (based on S18)

As pyruvic acid was not observed in pilot plant, this compound could be formed *in situ* by reaction of MEA with methylglyoxal. The resulting compound could be oxidised into HEMGly.

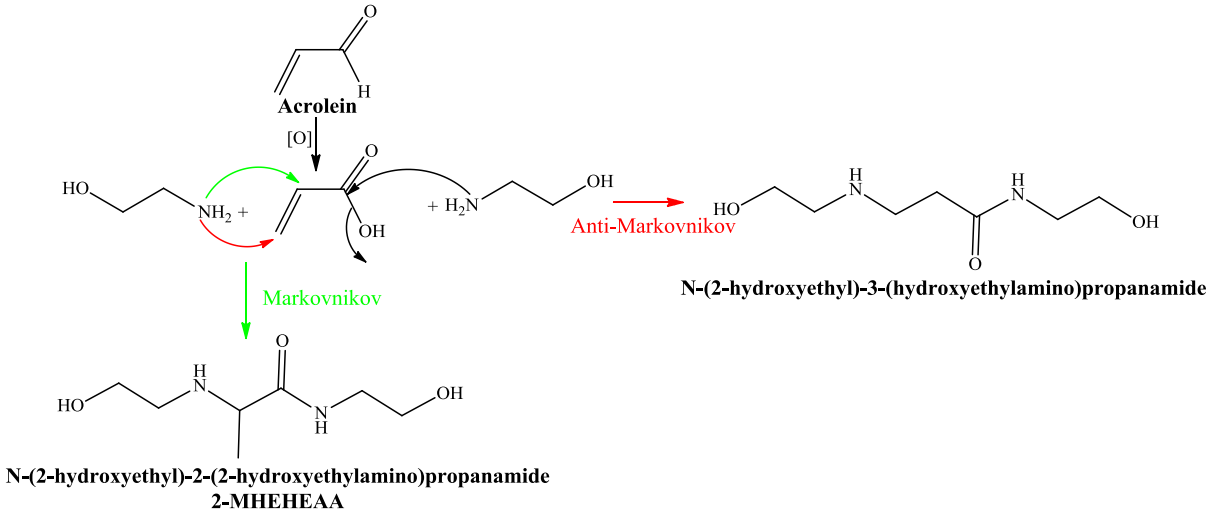
- **Unknown compound with M = 176 g/mol (rt 56.8 min) – U5**

The formula of this compound, which was one of the major products detected by GC/MS, was $C_7H_{16}N_2O_3$ (confirmed by FT-ICR/MS). This molecular weight was also observed by Lepaumier et al., 2011a; Strazisar et al., 2003. More precisely, the mass spectrum was characterized by two fragments, one at 158 corresponding to $C_7H_{14}N_2O_2$ (loss of water) and the other one at 88, which could correspond to HO-CH_2-CH_2-NH-CH_2-CH_2-.

This molecule was already observed by Strazisar et al., 2003 and the assignment proposed was N-(2-hydroxyethyl)-3-(2-hydroxyethylamino)propanamide. They proposed same mechanism as for HEHEAA formation (Scheme 2.18) with propionic acid as reactant instead of acetic acid.

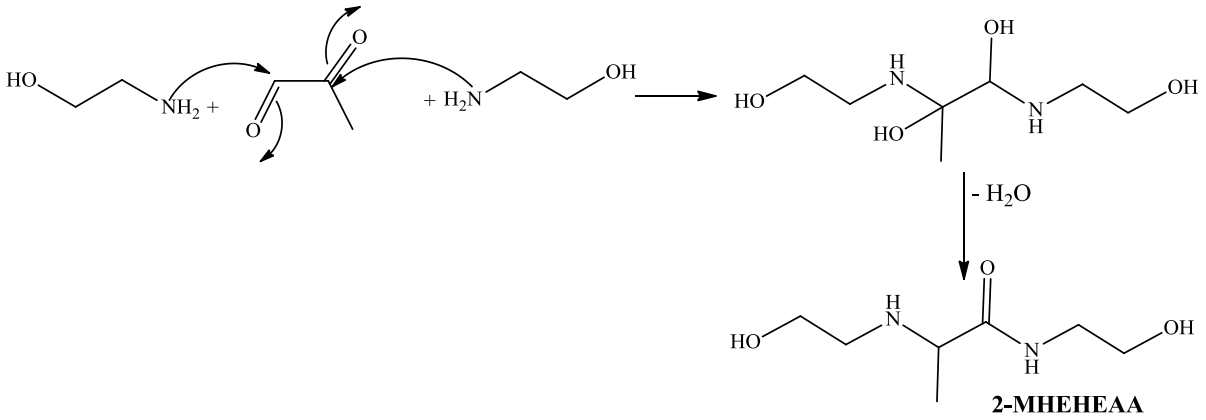
U5 was observed in the sample involving MEA and acrylic acid (S19). In that case, two MEA molecules were expected to react with acrylic acid through amidification and amination pathways. Acrylic acid was not observed in this work but it could be formed by oxidation of acrolein.

Amination following the anti-Markovnikov rule explained the formation N-(2-hydroxyethyl)-3-(2-hydroxyethylamino)propanamide. But this hypothesis was not the best one due to the fact that there was a low probability that radicals were involved in this mixture. Therefore the Markovnikov rule should better apply, thus leading to the formation of N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)propanamide.



Scheme 5.21. Proposal for the structure and formation pathway of U5 (based on S19)

Another mechanism, based on Scheme 5.4, was also proposed. Two MEA could react with methylglyoxal (expected to be formed) to lead to 2-MHEHEAA.



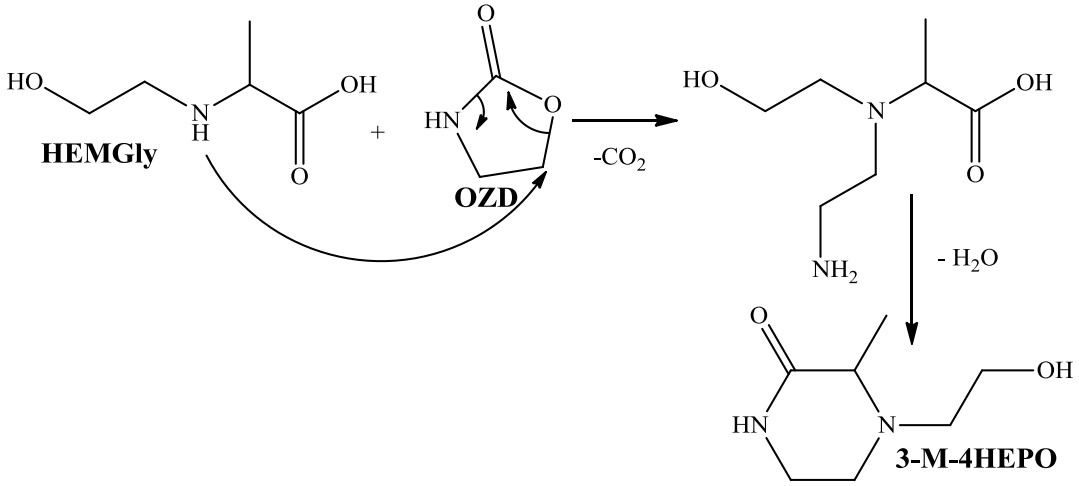
Scheme 5.22. Alternative proposal for the structure and formation pathway of U5

Nowadays, no conclusion could be done between these two propositions.

- **Unknown compound with M = 158 g/mol (rt 50.6 min) – U6**

The GC peak of this compound had a retention time a little bit shorter than 1HEPO's one. The molecular formula proposed by calibration was $C_7H_{14}N_2O_2$, which was confirmed by FT-ICR/MS. The mass spectrum of this compound was characterized by two fragments at 115 and 99 corresponding to $C_5H_{11}N_2O$ (related to the loss of $COCH_3$ or CH_2CHO) and $C_5H_{11}N_2$, respectively.

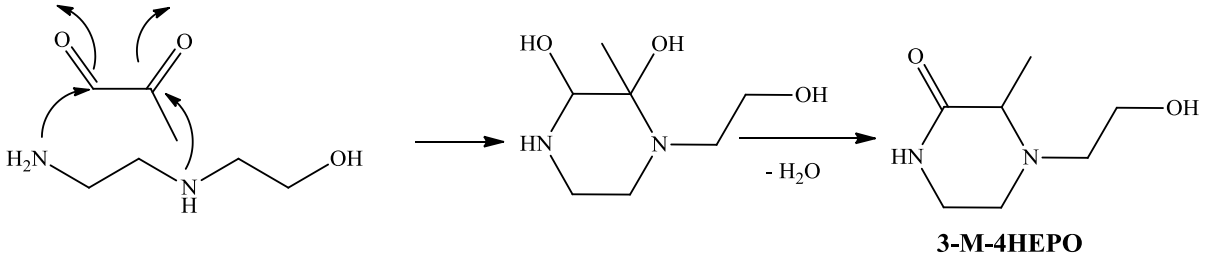
This compound could be 4-(2-hydroxyethyl)-3-methyl-piperazin-2-one obtained by the reaction of N-(2-hydroxyethyl)-2-methylglycine with OZD (Scheme 5.23). This was the same kind of reaction as 4HEPO formation from HEGly with OZD (Scheme 5.9).



Scheme 5.23. Proposal for the structure and formation pathway of U6

Moreover as for 4HEPO (Scheme 5.8), a second mechanism involving HEEDA and methylglyoxal could occur (Scheme 5.24). The GC peak of this compound was observed in small amount in S20, where HEEDA was mixed with glyoxal. In fact, small amount of

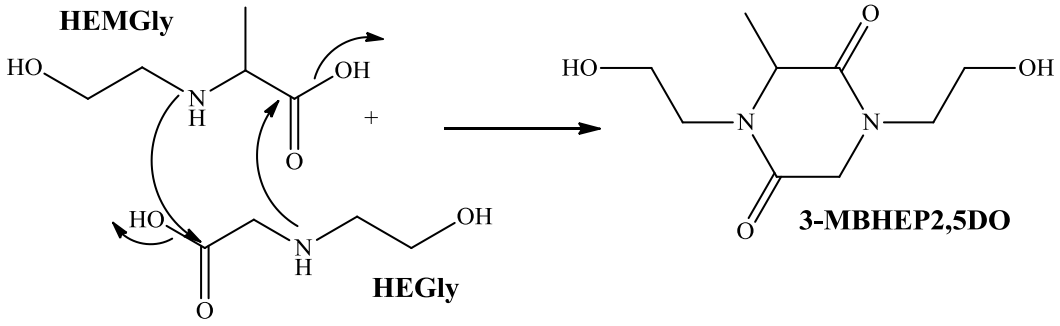
methylglyoxal could be formed in situ and could react with HEEDA. That would explain the low amount of this compound in S20.



Scheme 5.24. Alternative proposal for the structure and formation pathway of U6

- **Unknown compound with M = 216 g/mol (rt 63 min) – U7**

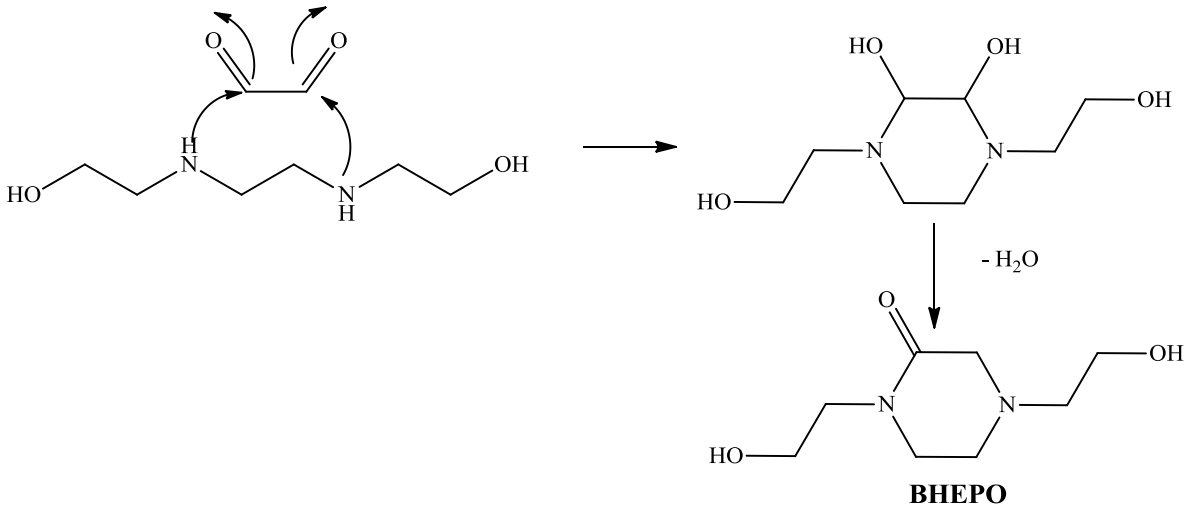
The formula of this compound was $C_9H_{16}N_2O_4$ (confirmed by FT-ICR/MS). Its mass spectrum was characterized by a fragment at 185 ($C_8H_{13}N_2O_3$), which could correspond to loss of CH_2-OH. One hypothesis was the formation of 1,4-bis(2-hydroxyethyl)-3-methylpiperazin-2,5-dione (3-MBHEP2,5DO). It could be obtained by the reaction of HEMGly with HEGly (Scheme 5.25).



Scheme 5.25. Proposal for the structure and formation pathway of U7

- **Unknown compound with M = 188 g/mol (rt 58.7 min) – U8**

The formula of U8 with a retention time shorter than HEHEAA was $C_8H_{16}N_2O_3$ (confirmed by FT-ICR/MS). Our proposal implied the formation of 1,4-bis(2-hydroxyethyl)piperazin-2-one (BHEPO), which was in accordance with a fragment at 157 ($C_7H_{13}N_2O_2$). It could be assigned to a loss of CH_2-OH. BHEPO could be formed by the reaction of BHEEDA (observed in the pilot plant sample) and glyoxal (Scheme 5.26).



Scheme 5.26. Proposal for the structure and formation pathway of U8

More research should be done on all these degradation products (U1 to U8) to confirm their structures or to propose new ones.

Other novel degradation products formed without glyoxal as reactant were classified by chemical family : pyrazines, nitrogen heterocycles, amides, oximes and aldehydes and glycols.

- **Pyrazines**

We have recently published (Rey et al., 2013)[‡] the observation in pilot plant sample of many pyrazines, including pyrazine and nine alkylpyrazines, 2-methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethylpyrazine, 2,3-dimethylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 2,3,5-trimethylpyrazine and 2-ethyl-3-methylpyrazine. They were identified thanks to HS-SPME sampling method used to trap volatile products and to decrease matrix effect. In addition, two others alkylpyrazines, 2,3,5,6-tetramethylpyrazine and 2-vinylpyrazine, were identified through TENAX tubs on the representative experiment .

As observed on MS SIM chromatograms of standards obtained by HS-SPME with non-polar and polar columns (appendix - Figure B.31 and Figure B.32), best separation was obtained with the polar column. This column could separate all the isomers except 2-ethyl-3-methylpyrazine and 2,3,5-trimethylpyrazine but those compounds could be identified by their

[‡] See Annexe C

mass spectra. Nevertheless, m/z 42 used for 2,3,5-trimethylpyrazine was interfered by ethanolamine (appendix - Figure B.32). In consequence, this compound was preferentially analysed with the non-polar column. The 2-ethyl-5-methylpyrazine and 2-ethyl-6-methylpyrazine isomers were well separated and identified by ^{1}H NMR (see appendix - Figure B.33) because the standard was a mixture of both compounds

In addition of identification (Figure 5.4), a semi-quantitative approach was applied to obtain an approximate content of all pyrazines identified in liquid samples of pilot plant. MS SIM chromatogram of pilot plant sample was used to evaluate the amount of the target products as shown in Figure 5.4. An external calibration was made with a mix of the ten pyrazines studied by spiking a solution of water/MEA at three levels of concentration. The results obtained were reported in Table 5.4. The global relative uncertainty on the pyrazines amount determination has been roughly estimated to be around 18% by using two repetitions in intermediate precision conditions, i.e. different columns and days.

To be sure that pyrazines were produced during the degradation process, the water/MEA mixture originally introduced in the pilot plant was analysed before the experience. All pyrazines could be found at traces levels, between 60 times less than in the degraded sample for 2-ethyl-3-methylpyrazine and 300 times less for 2,3-dimethylpyrazine. Pyrazine concentration was compared to some known degradation products to assess its relative abundance: it was very close to acetate and oxalate ions concentrations (55 and 53 ppm respectively). Nevertheless, identified pyrazine derivatives were less concentrated in the liquid phase than carboxylic ions but they were more concentrated in the gas phase because of their much higher volatility. Their presence in the gas phase were proved by HS-SPME method using a temperature (70°C) close to highest temperatures encountered in absorber conditions.

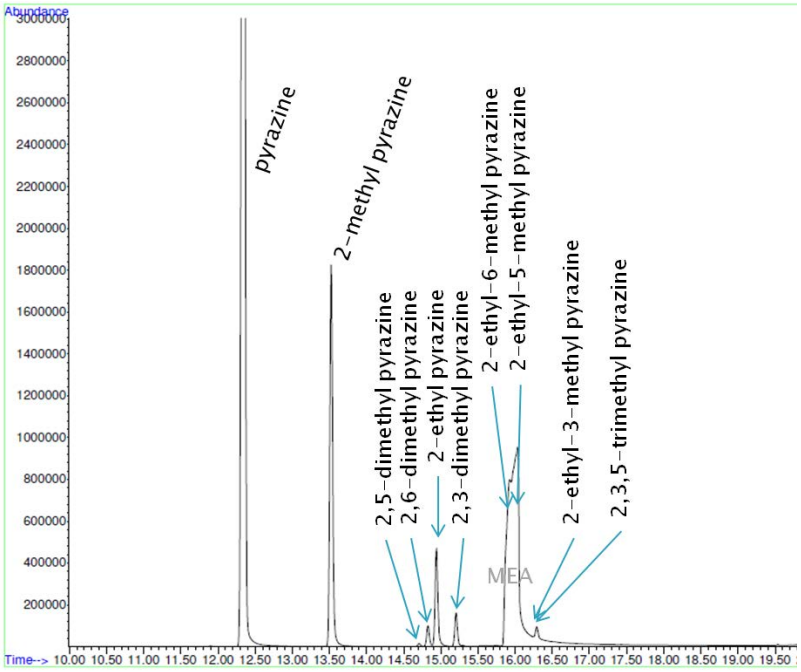


Figure 5.4. SIM (TIC) chromatogram, after HS-SPME, of pilot plant sample using DBWAX

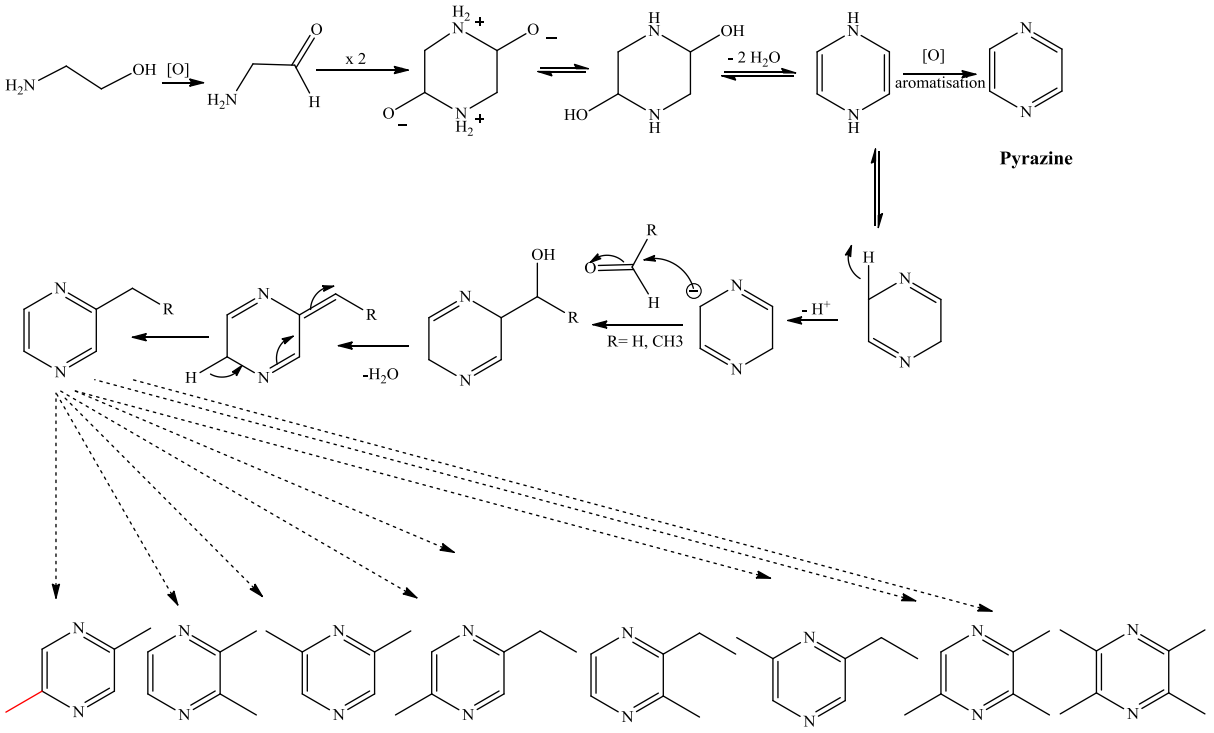
Table 5.4. Average concentrations of ten pyrazines in pilot plant samples

pyrazines	Concentrations in IFPEN pilot sample (mg/L)
pyrazine	50
2-methylpyrazine	3
2,5-dimethylpyrazine	0.02
2,6-dimethylpyrazine	0.13
2-ethylpyrazine	0.28
2,3-dimethylpyrazine	0.20
2-ethyl-6-methylpyrazine	0.04
2-ethyl-5-methylpyrazine	Traces < 0.01
2,3,5-trimethylpyrazine	0.01
2-ethyl-3-methylpyrazine	0.02

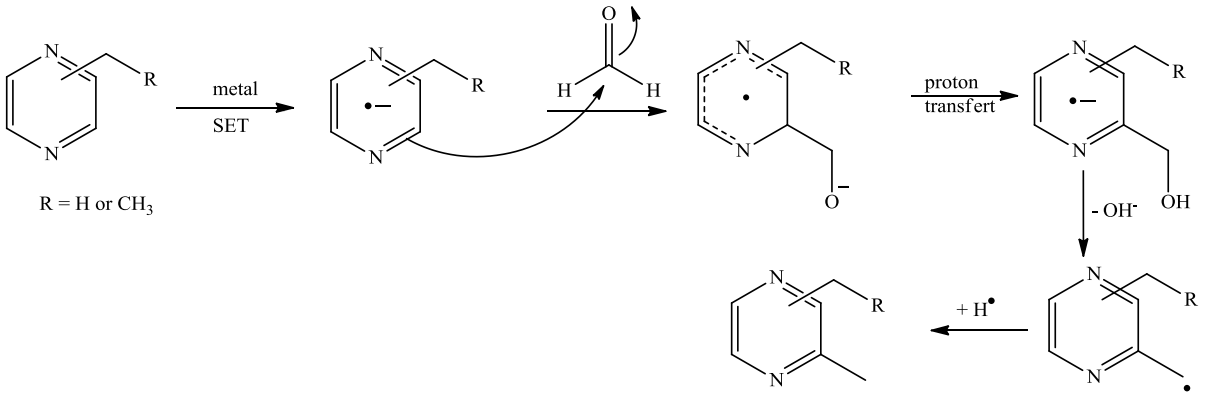
Pyrazine, 2-ethylpyrazine, 2-methylpyrazine, 2,6-dimethyl pyrazine, 2,3-dimethyl pyrazine, 2,3,5-trimethyl pyrazine were identified on TENAX too. Moreover, 2-vinylpyrazine and 2,3,5,6-tetramethylpyrazine could be observed for the first time in small amount on TENAX cartridges from representative test. These compounds were not observed in TENAX cartridges used on pilot plant, maybe due to the low level of these compounds which were

hidden by other observed products. Confirmation with commercial standards was done but with no quantification.

A mechanism for the formation of pyrazine derivatives was proposed in Scheme 5.27 and Scheme 5.28. Their formation was due to the presence of 2-aminoacetaldehyde, formaldehyde and acetaldehyde. Oxidation of MEA to 2-aminoacetaldehyde was very easy in pilot plant conditions (Rooney et al., 1998a) and the presence of formaldehyde and acetaldehyde was previously reported by Rooney et al., 1998a; Sexton and Rochelle, 2011. The first step was a fast condensation of two 2-aminoacetaldehyde molecules followed by a dehydration leading to dihydropyrazine. This molecule was then easily oxidised to pyrazine as explained by Krems and Spoerri, 1947; this oxidation was also observed by Guerra and Yaylayan, 2010 during a pyrolysis at 150°C and by Adams et al., 2008 at 90°C. Conditions used by Adams et al., 2008 could be encountered in the case of CO_2 capture. Moreover, the deprotonated form of dihydropyrazine can react with formaldehyde or acetaldehyde to form 2-methylpyrazine or 2-ethylpyrazine, respectively (Adams et al., 2008; Guerra and Yaylayan, 2010). The formed alkylpyrazines can give di-, tri- or tetraalkylpyrazines by electrophilic addition catalysed by a metal in presence of a base (Bramwell et al., 1971) as shown Scheme 5.28. Thanks to metal, SET (single electron transfer) occured, therefore alkylpyrazines can react with formaldehyde to form dialkylpyrazines, then trialkylpyrazines and finally tetraalkylpyrazines.

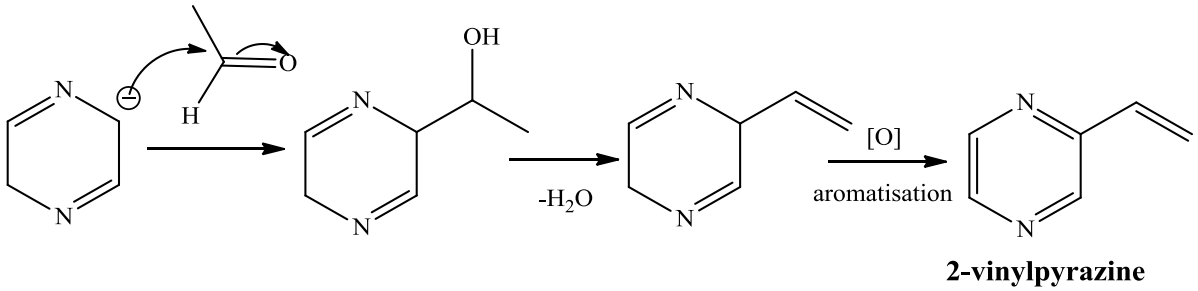


Scheme 5.27. Mechanism of pyrazine and alkyl pyrazines formation (adapted from Adams et al., 2008; Guerra and Yaylayan, 2010; Krems and Spoerri, 1947).



Scheme 5.28. Mechanism of pyrazine alkylation (adapted from Bramwell et al., 1971).

Similarly to 2-ethylpyrazine, the mechanism for vinylpyrazine formation would involve the reaction of the deprotonated form of dihydropyrazine (mentioned in scheme 5.28) with acetaldehyde. Two dehydration pathways of the resulting intermediate were allowed, one led, as previously explained, to 2-ethylpyrazine ; the second led to 2-vinyldihydropyrazine which could be aromatised easily thanks to conjugation with the vinyl function (Scheme 5.29).



Scheme 5.29. Mechanism of vinylpyrazine formation.

These pyrazines are volatile products. They could be released to the atmosphere, so it is important to know their toxicity. In a recent publication (Rey et al., 2013), we have shown that the identified pyrazines (2-vinylpyrazine and 2,3,5,6-tetramethylpyrazine were not studied) are currently not indicating toxicological concern at the level of intake estimated at 0.2–120 µg/day in Europe.

Others new products observed are from nitrogen heterocycle or amides family.

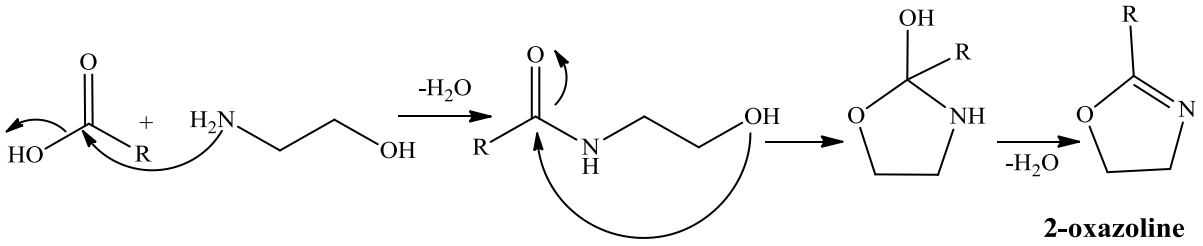
- **Nitrogen heterocycles**

Various nitrogen heterocyclic compounds were observed including oxazoline, oxazolidine, 2-methyloxazoline, 2-methyloxazolidine, N-nitroso-2-methyloxazolidine, HEPyr, pyrrole, 3-methylpyridine and HEMI. Most of these products were described in our last publication (Gouedard et al., 2014).

➢ Oxazoline and 2-methyloxazoline

Oxazoline and 2-methyloxazoline were observed in gas phase (TENAX or HS-SPME), therefore they could be emitted to the atmosphere. They were identified thanks to numerous analyses methods and confirmed by standard for the first time.

Earlier, Voice, 2013 suspected oxazoline formation but no confirmation with standard was done. A mechanism based on literature (Ilkgul et al., 2010; Levine et al., 2008) is proposed to explain oxazoline and 2-alkyloxazolines formation (Scheme 5.30). First step is amidification of MEA by a carboxylic acid (Gouedard et al., 2012), then intramolecular cyclisation leads to an intermediate which dehydrates to form oxazoline or 2-alkyloxazolines. Oxazoline was observed in S21 and S23 and 2-methyloxazoline in S22 and S24, confirming the reaction between MEA and carboxylic acids with amide as intermediate.

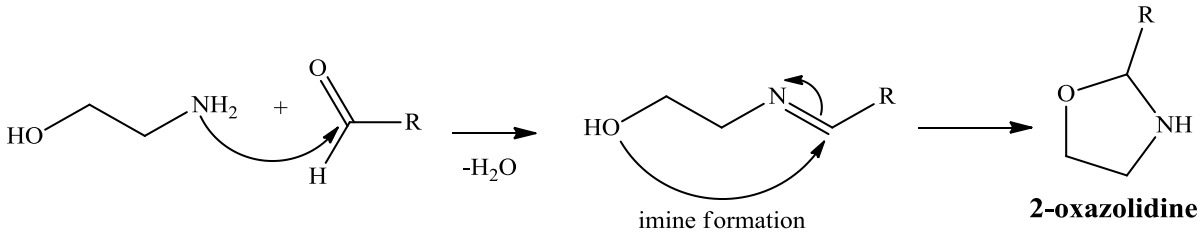


Scheme 5.30. Proposed mechanism for oxazolines (R = H, CH_3).

- Oxazolidine and 2-methyloxazolidine

Oxazolidine and 2-methyloxazolidine are also volatile products observed on gas phase thanks to TENAX cartridges. Oxazolidine was suspected by Reynolds et al., 2013 and Voice, 2013 and was confirmed in this work by standard. Unfortunately, there is no commercial standard for 2-methyloxazolidine. Regarding the proposed reactants for oxazolidine (MEA and formaldehyde, S7), 2-methyloxazolidine was synthesised by mixing MEA with acetaldehyde (S25). However, this synthesis was not enough selective to identify 2-methyloxazolidine by NMR. MEA was the major compound in S25 mixture. Using GC/MS, 2-methyloxazolidine could be identified with high confidence by NIST database (database furnished with the GC/MS).

A mechanism based on literature (Lambert and Wharry, 1982; Saavedra, 1985) is proposed to explain the formation of both oxazolidine and 2-alkyloxazolidines (Scheme 5.31). It is well known that amines and aldehydes react to form imines (first step), then the hydroxyl group of MEA would react on the imine function to form 2-alkyloxazolidine by intramolecular cyclisation. This mechanism was confirmed because oxazolidine and 2-methyloxazolidine were formed in high yield in S7 and S25 respectively.



Scheme 5.31. Proposed mechanism for oxazolidines formation (R = H, CH_3).

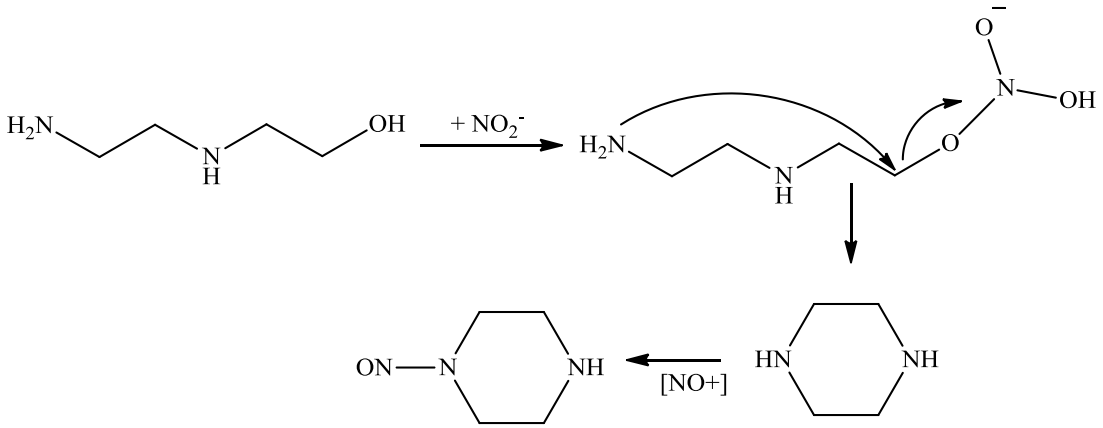
- N-nitroso-2-methyloxazolidine

A compound with a molecular weight of 116, was observed on TENAX cartridges and identified by MS database (NIST) as N-nitroso-2-methyloxazolidine. This identification was confirmed by the synthesis of this nitrosamine following Saavedra, 1981 and Eiter et al., 1972 protocols (S26). GC/MS analysis of S26 gave this compound as the major reaction product (same retention time and mass spectrum, see appendix Figures B.21 to B.22) as observed on TENAX cartridges. Formation of this compound was highly suspected by NMR. Therefore, we conclude that this nitrosamine can be formed in the pilot plant conditions.

The formation of N-nitroso-2-methyloxazolidine was based on the mechanism of nitrosation (Scheme 2.2.24) applied to 2-methyloxazolidine (Scheme 5.31)

- N-Nitrosopiperazine

N-Nitrosopiperazine was observed thanks to ChemElut extraction and LC/MSMS analysis. This molecule could be formed from HEEDA with nitrite activation (adapted from Huang et al., 2014) then by nitrosation of piperazine (Scheme 5.32) (Fostås et al., 2011).



Scheme 5.32. Proposed mechanism for NPZ formation

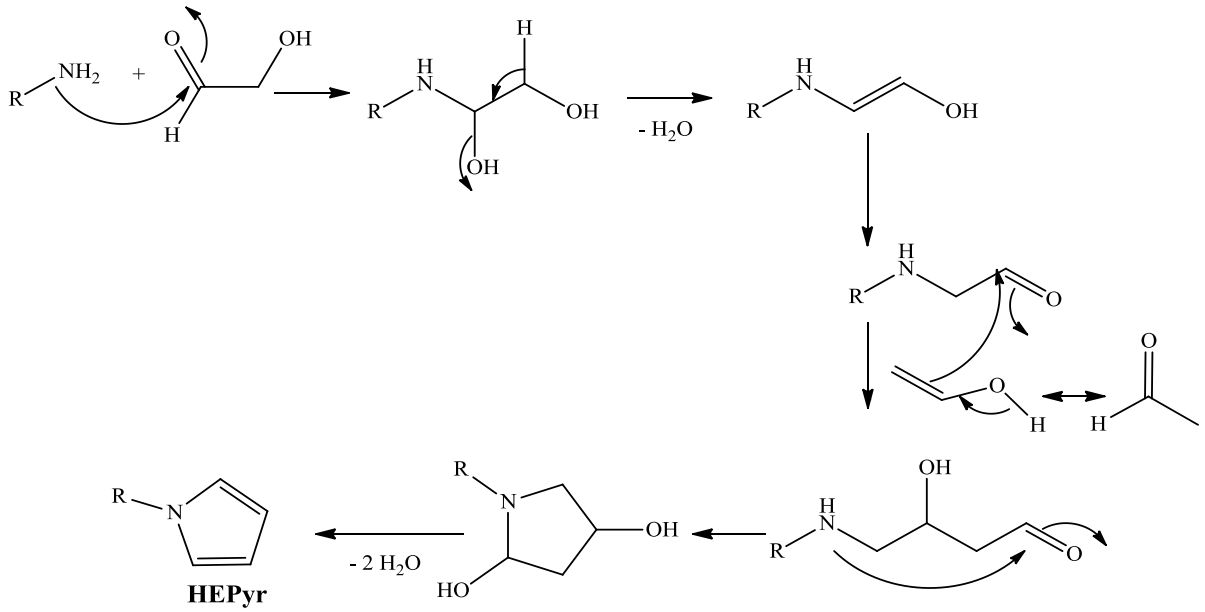
The formation of the following products involves an increase of the carbon chain length explained, as previously mentioned, by an aldolisation step.

- HEPyr and pyrrole

HEPyr was observed in all GC/MS analyses, whereas pyrrole was only observed on TENAX cartridges. Both compounds were confirmed by standards and their formation could be explained with same king of mechanism.

To form N-(2-hydroxyethyl)pyrrole, MEA reacted with glycolaldehyde, a potential intermediate in the glycolic acid synthesis (Goff and Rochelle, 2004). Then, the resulting vicinial diol would be dehydrated leading to an aldehyde which reacted with acetaldehyde via an aldolisation. Finally, the intramolecular cyclisation would lead to a pyrrolidine which could be didehydrated (Scheme 5.33). Result of S15 agreed with this mechanism. When MEA was mixed with glyoxal and acetaldehyde, HEPyr was formed in small amount. Glyoxal is known to be a mix of many chemical species in solution (Lim et al., 2010) including glycolaldehyde.

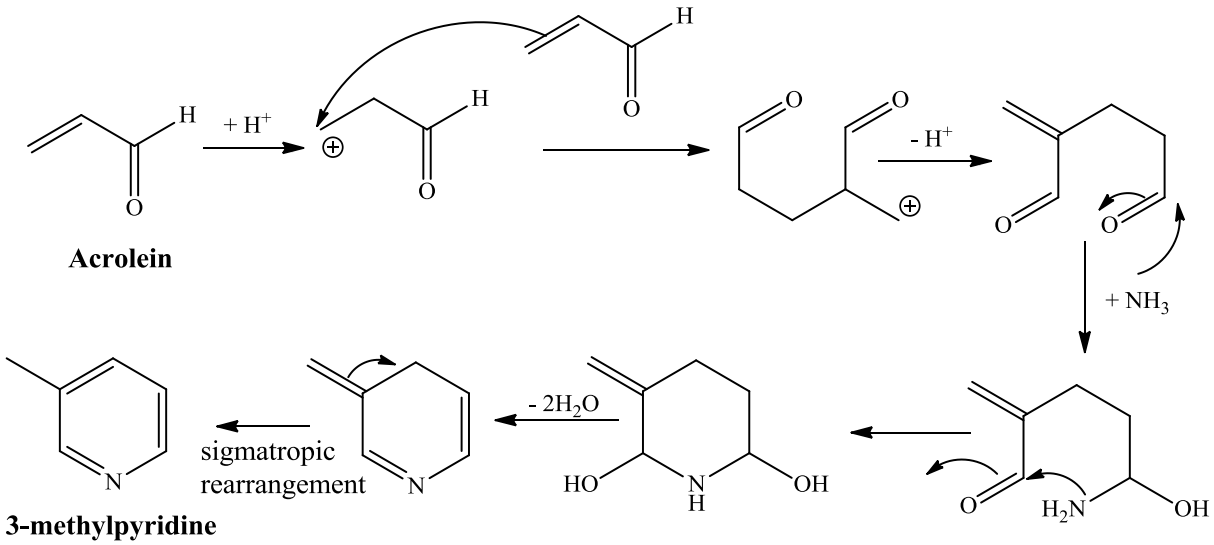
In a similar way, pyrrole could be formed by the reaction of ammonia (instead of MEA) with glycolaldehyde and acetaldehyde.



Scheme 5.33. Proposed way of formation for HEPyr and pyrrole (R = CH_2-CH_2-OH or H)

- 3-methylpyridine

3-methylpyridine (3-picoline) was observed thanks to TENAX cartridges and in direct injection procedures (GC/MS) but it could be hidden by MEA peak. Using literature data (Jin and Li, 2009; Singh et al., 1998), a mechanism was proposed starting from acrolein. This compound could dimerise and the resulting dialdehyde reacted twice with ammonia affording the six-membered ring (Scheme 5.34) leading to 3- methylpyridine after dehydration and aromatisation (sigmatropic rearrangement). When MEA was mixed with acetaldehyde and formaldehyde (reagents for acrolein formation) (S27), 3-methylpyridine was formed in small proportion because ammonia was present in small amount in the fresh MEA, therefore this synthesis seemed to confirm this mechanism.



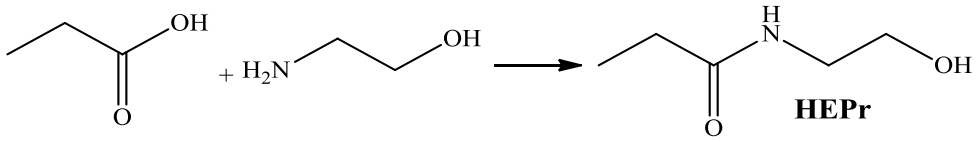
Scheme 5.34. Proposed mechanism for 3- methylpyridine formation (adapted from Jin and Li, 2009; Singh et al., 1998).

- **Amides**

➢ N-(2-hydroxyethyl)propanamide - HEPr

HEPr was observed for the first time using a polar column and confirmed by standard.

Proposed way of formation involved propanoic acid (see Scheme 5.11) and MEA via an amidification (Scheme 5.35).

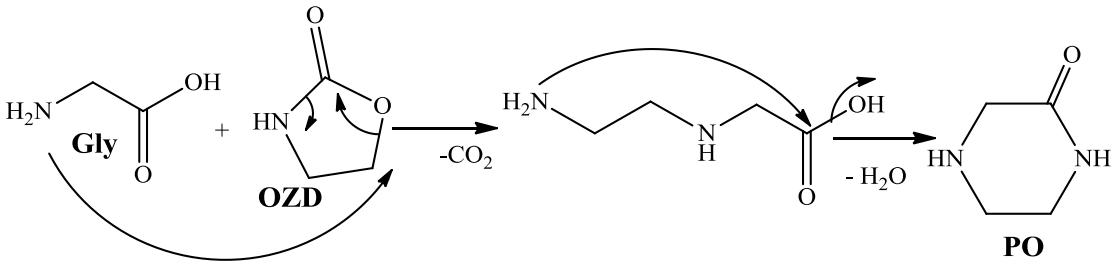


Scheme 5.35. Proposed way of formation for N-(2-hydroxyethyl)propanamide

➢ Piperazin-2-one (PO)

PO was observed by GC/MS and confirmed with a commercially available standard.

The following mechanism explained PO formation (Scheme 5.36) based on its formation in S28. OZD could react with glycine, then PO was formed by intramolecular amidification.



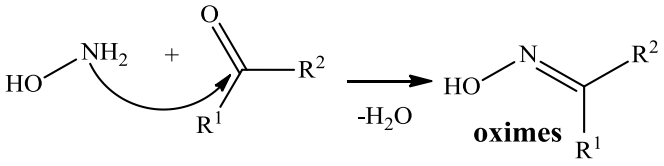
Scheme 5.36. Proposed way of formation for PO

Such a mechanism is similar to that proposed for 4HEPO (Scheme 5.9) with HEGly instead of glycine.

- **Oximes**

Oximes were detected on TENAX cartridges. Acetaldoxime was observed on pilot plant, whereas acetoxime and propanaldoxime were observed on laboratory test. They were confirmed by standards.

Oximes formation was due to the reaction of aldehydes or ketones with hydroxylamine (Wang, 2012), which could come from ammonia oxidation. Carbonyl compounds involved in the formation of acetaldoxime, acetoxime and propanaldoxime were acetaldehyde, acetone and propanal, respectively.



R^1 = H, CH_3 and R^2 = CH_3
or R^1 = H and R^2 = CH_2CH_3

Scheme 5.37. Proposed mechanism for oximes formation

- **Aldehydes/ketones and glycols**

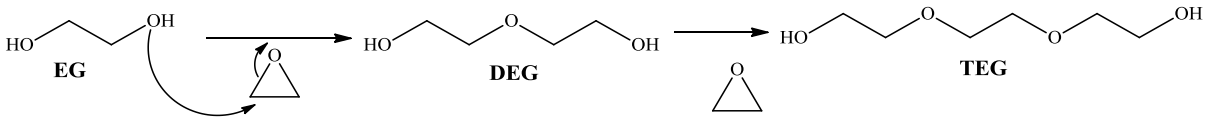
➢ Propanal and butan-2-one

For the first time, propanal was observed thanks to Sep-Pak tubs. Propanal is a precursor of propanoic acid, therefore its formation was already explained in Scheme 5.11.

Butan-2-one was observed on Sep-Pak cartridges. This compound should be formed by aldolisation of two compounds but until present, these reactants were not found. Therefore no mechanism was proposed.

- Di and triethyleneglycol

Diethyleneglycol (DEG) and triethyleneglycol (TEG) were observed in pilot plant. TEG was only seen on TENAX cartridge. A mechanism of deamination was proposed (Scheme 5.1) for the formation of EG. Unfortunately, presence of ethylene oxide is really hard to prove. The oligomerisation of EG in DEG and TEG can be explained by reaction of ethyleneglycol on ethylene oxide (Scheme 5.38).



Scheme 5.38. Proposed mechanism for glycols formation

5.3.Conclusion

More than 60 products were observed during this work. Products already related in literature were reported. New mechanisms were proposed for many of these products as experiments enabling the validation of these mechanisms.

It is noteworthy that 32 new degradation products have been identified thanks a huge analytical development and we proposed for each molecule (except butan-2-one) a mechanism based on well-known reaction in organic chemistry. Even if 8 products (U1 to U8) have not been identified, we proposed a molecular formula with a potential structure if possible.

A pathway (Figure 5.5), which resumes MEA degradation, is proposed. All products firmly observed in this work are reported in this sum-up; sometimes only the name of an entire family is noted for clarity.

Some of these reactions occurring for MEA could be applied to other amines to predict their degradation products.

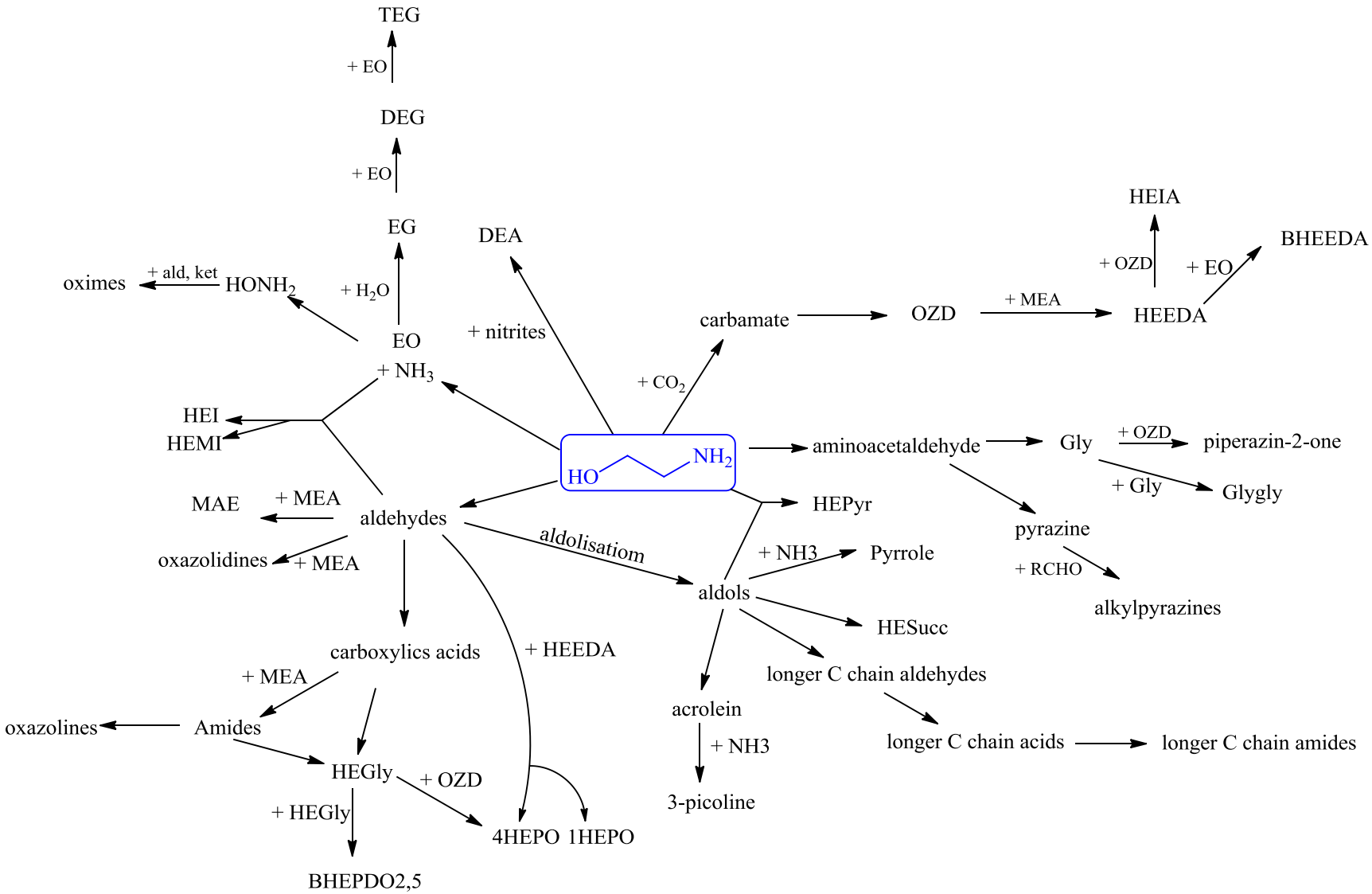


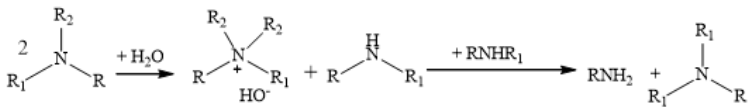
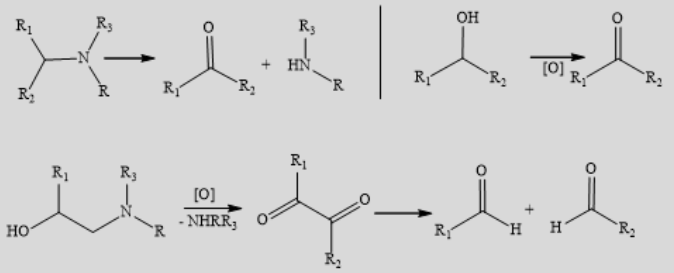
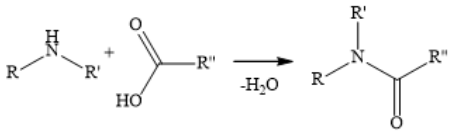
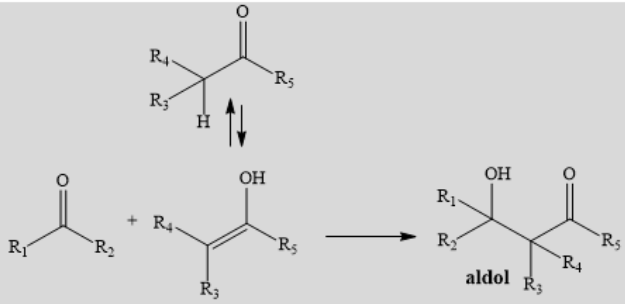
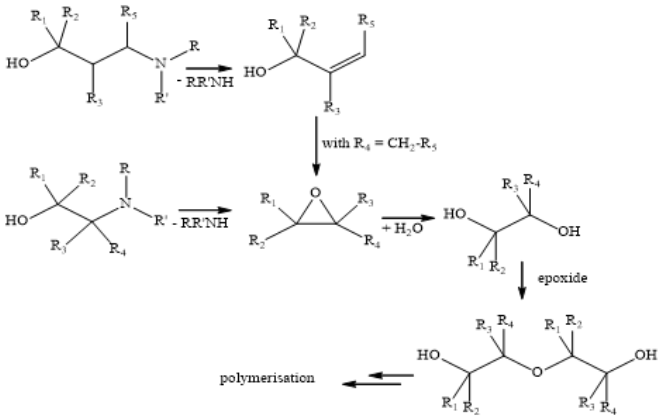
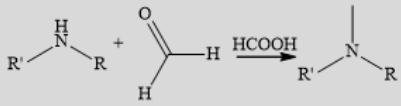
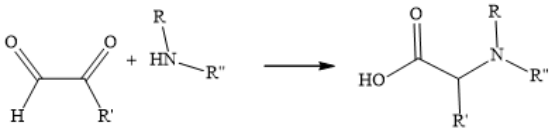
Figure 5.5. Sum up of MEA degradation

6. Recurrent reactions

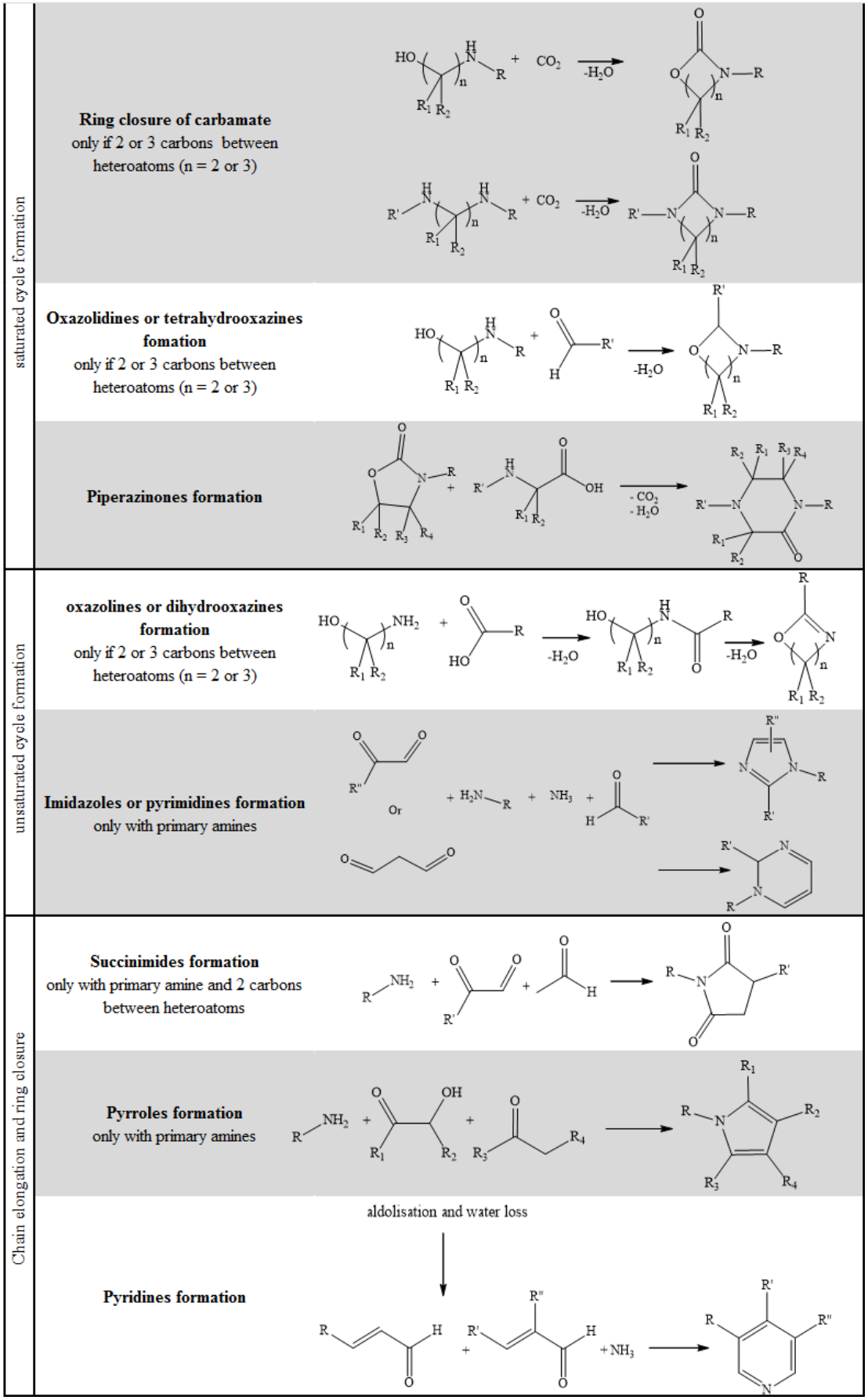
6.1. Introduction

Some reactions proposed in the case of MEA degradation (chapter 5) could also occur with other amines (candidates for CO_2 capture). Table 6.1 lists these reactions and some others already described in literature as dealkylation/alkylation (Lepaumier et al., 2009b). This table specifies type of amine structures which could be involved with these reactions. Classification on the table is based on reaction types and products formed.

Table 6.1. Recurrent reactions for amine degradation

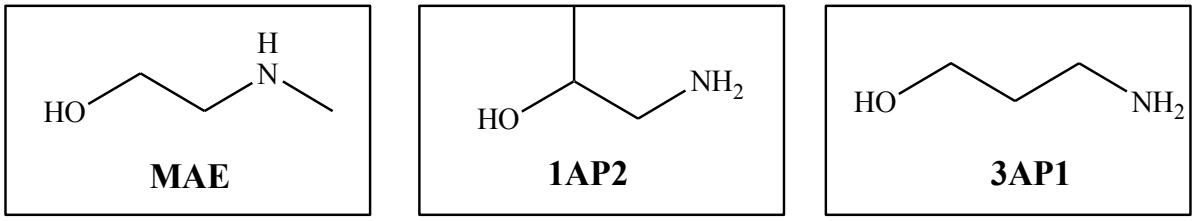
Reaction	Scheme
Dealkylation / Alkylation	
Aldehydes/ Ketones formation (see Scheme 5.2)	
Amidification only for primary or secondary amines	
Aldolisation	
Glycol formation only if 2 or 3 carbons between heteroatoms	
Eschweiler-Clarke only for primary or secondary amines in presence of formaldehyde	
Amino acids formation only for primary or secondary amine (see Scheme 2.21 and Scheme 5.8)	

elementary reaction



R, R', R'', R_1, R_2, R_3, R_4 = H, alkyl or hydroxyalkyl

In this chapter, the idea is to use such database of reactions as a toolbox to identify degradation products of other amines. Demonstration of this concept is proposed with three amines, N-methylaminoethanol (MAE), 1-aminopropan-2-ol (1AP2) and 3-aminopropan-1-ol (3AP1). They were degraded following the representative test established in the case of MEA and described in part 4.



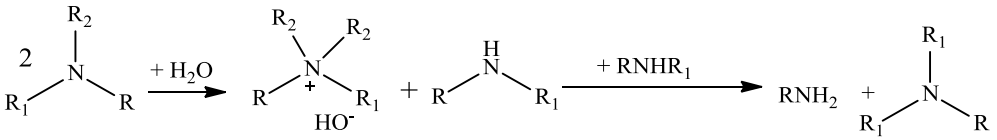
Assumptions were made thanks to the knowledge acquired with the study of MEA and analyses at our disposal but they were not confirmed with standards or syntheses. Written publications on these molecules were used to confirm our results. (Davis, 2009; Eide-Haugmo et al., 2011; Lepaumier, 2008; Lepaumier et al., 2011b; Vevelstad et al., 2013a).

As for MEA, samples were analysed by GC/MS-TOF with CPSIL8 column, IC and FT-ICR/MS.

Products expected to be formed for each types of reactions were reported in tables with their molecular weight and GC/MS retention times (rt). **Products observed in GC/MS or IC were written in bold** and *products only observed in FT-ICR/MS were written in italic*.

6.2.Alkylation/Dealkylation

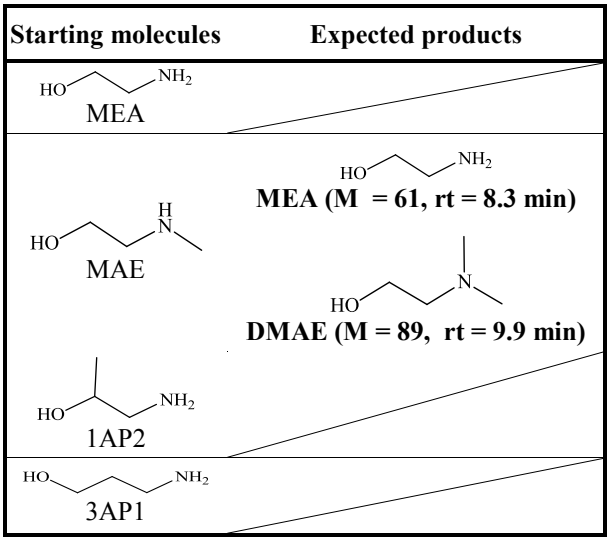
N-alkyl substituted amines could be dealkylated and/or alkylated (Scheme 6.1). This reaction could not be observed in the case of primary amine (MEA, 1AP2 and 3AP1).



Scheme 6.1. Alkylation/dealkylation mechanism

Lepaumier et al., 2009b proposed this reaction to explain formation of DMAE and MEA in the case of MAE degradation, therefore, this reaction was reported in this work. Tertiary amines should be dealkylated first. Secondary amines, like MAE, should lead to the corresponding primary and tertiary amines (as shown in Table 6.2) because alkylation and dealkylation are parallel reactions.

Table 6.2. Expected products from alkylation/dealkylation pathways

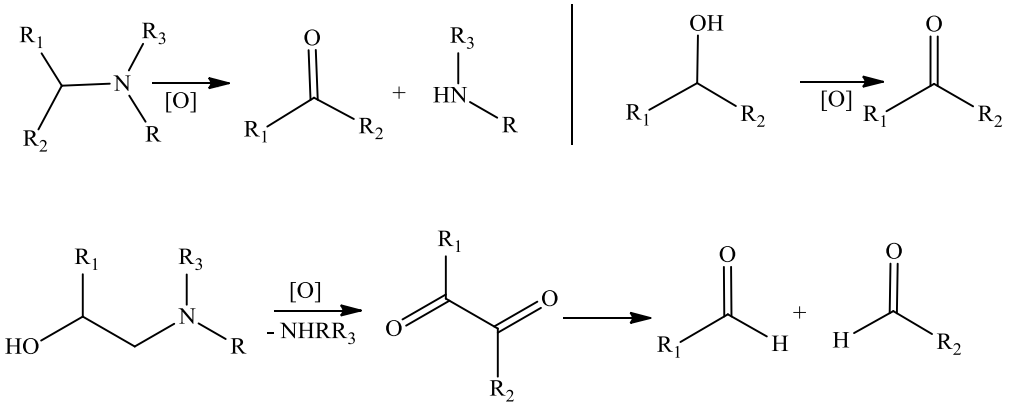


As expected MAE, MEA and DMAE were observed in the case of MAE. This reaction turned out to be the most important reaction occuring in presence of CO_2 (Lepaumier et al., 2009a).

Due to the presence of MEA in MAE degradation test, its major degradation products (see chapter 5) should be observed too but at low concentration.

6.3. Aldehydes/ ketones and corresponding acids formation

Aldehydes / ketones and then carboxylic acids are assumed to be formed in the presence of oxygen. As observed for MEA, these first generation products are later involved in the formation of other degradation products.

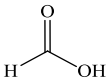
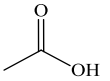
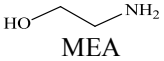
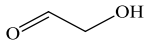
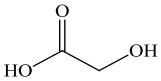
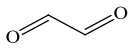
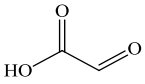
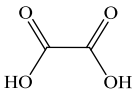
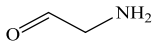
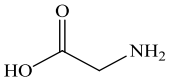
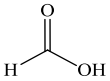
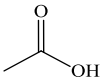
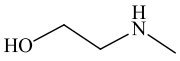
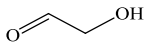
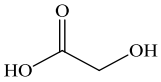
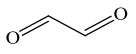
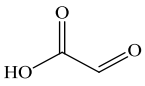
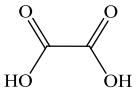
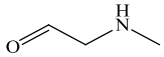
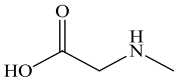
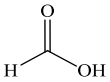
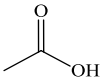
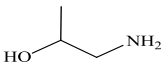
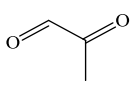
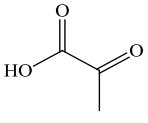
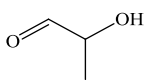
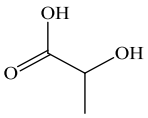
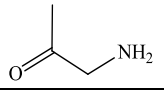


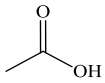
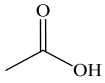
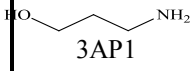
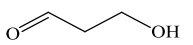
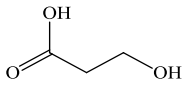
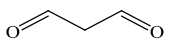
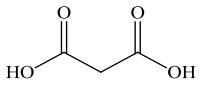
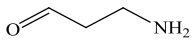
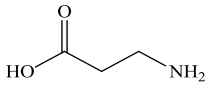
Scheme 6.2. Sum-up of aldehydes and carboxylic acids fornation based on Scheme 5,2

Based on Scheme 6.2, expected aldehydes or ketones, and the corresponding acids (formed by aldehyde oxidation), were listed in the Table 6.3 for MEA and the new tested amines. Even

if aldehydes were not detected in this study, they were considered to be present when the corresponding acid was observed in IC.

Table 6.3. Expected aldehydes/ketones and corresponding acids

Starting molecules	Expected products		Corresponding acids	
		**Formaldehyde**		**Formic acid**
		**Acetaldehyde**		**Acetic acid**
 MEA		2-Hydroxyethanal		**Glycolic acid**
		Glyoxal	 Glyoxylic acid	 **Oxalic acid**
		Aminoacetaldehyde		**Glycine**
		Formaldehyde		**Formic acid**
		Acetaldehyde		**Acetic acid**
 MAE		2-Hydroxyethanal		**Glycolic acid**
		Glyoxal	 Glyoxylic acid	 **Oxalic acid**
		N-methylaminoacetaldehyde		Sarcosine
		Formaldehyde		**Formic acid**
		Acetaldehyde		**Acetic acid**
		Acetone		
 1AP2		Methylglyoxal		**Pyruvic acid**
		Lactaldehylde		**Lactic acid**
		1-Aminopropan-2-one		

Starting molecules	Expected products		Corresponding acids	
		Formaldehyde		**Formic acid**
		Acetaldehyde		**Acetic acid**
 3AP1		3-Hydroxypropanal		3-Hydroxypropanoic acid
		Propandial		Propandioic acid
		3-Aminopropanaldehyde		3-Aminopropanoic acid

Products observed in CI

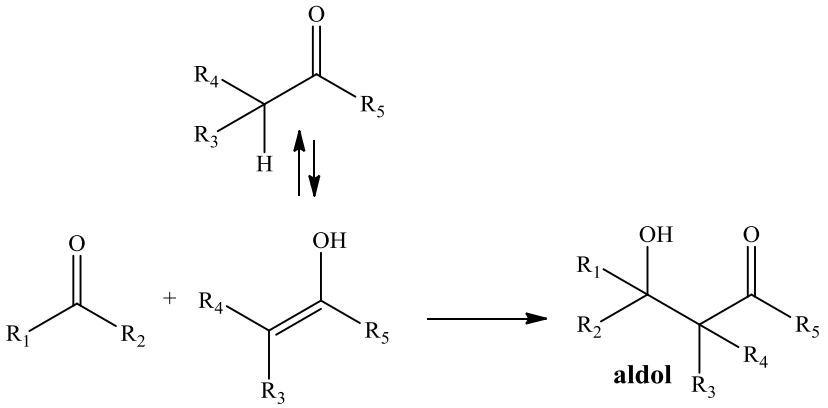
As expected, same acids were observed for MEA and MAE.

In the case of 1AP2, pyruvic and lactic acids were actually supposed to be present with a high probability after standard comparison. Oxalic acid was also detected in small amount. Moreover an unknown acid (UA1) was observed.

In the case of 3AP1, formic and acetic acid was observed as well as UA1 and another unknown acid (UA2).

6.4. Aldolisation

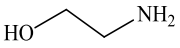
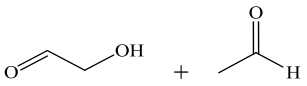
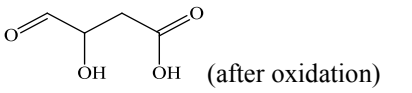
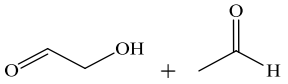
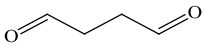
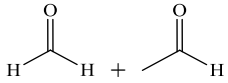
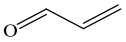
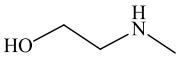
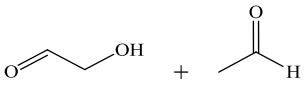
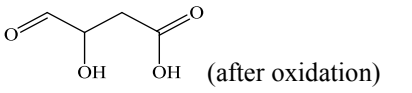
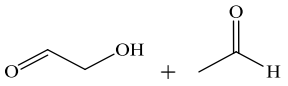
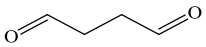
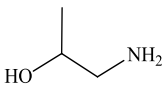
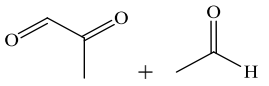
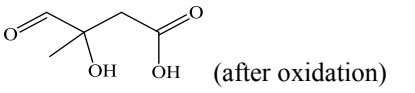
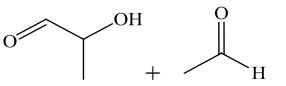
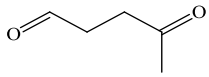
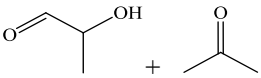
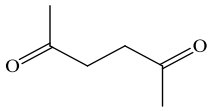
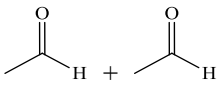
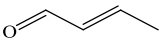
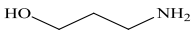
Aldehydes can react together through an aldolisation reaction (Scheme 6.3).



Scheme 6.3. Mechanism of aldolisation

In the case of MEA, this reaction was supposed to explain the elongation of the carbon chain length and formation of compounds like HEL, HEPr or pyrrole (see chapter 5). Dehydration, oxidation or rearrangement of formed aldols could lead to many different products. Only the compounds obtained by the afore-mentioned reactions were reported in Table 6.4.

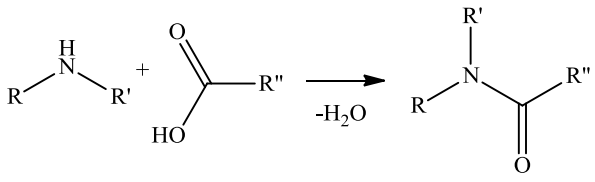
Table 6.4. Expected products issued of aldolisation

Starting molecules	Intermediate (aldolisation)	Expected products
 MEA		 (after oxidation) 3-hydroxy-4-oxo-butanoic acid
		 (after rearrangement) succinaldehyde
		 (after dehydration) acrolein
 MAE		 (after oxidation) 3-hydroxy-4-oxo-butanoic acid
		 (after rearrangement) succinaldehyde
 1AP2		 (after oxidation) 3-hydroxy-3-methyl-4-oxobutanoic acidl
		 (after rearrangement) 4-ketopentanal
		 (after rearrangement) hexane-2,5-dione
		 (after dehydration) 2-butenal
 3AP1		

Products mentioned in Table 6.4 were not detected but were supposed to be intermediates involved in the formation of other compounds proposed later in this chapter.

6.5.Amidification

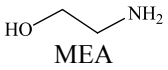
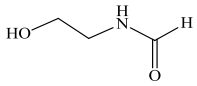
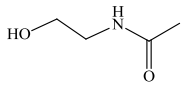
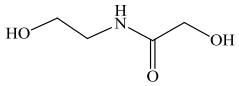
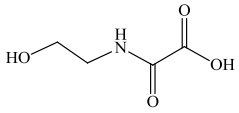
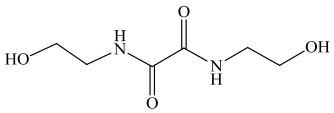
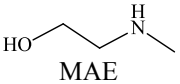
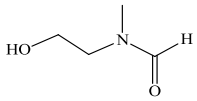
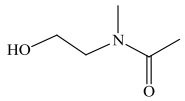
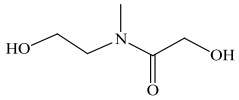
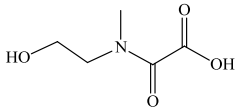
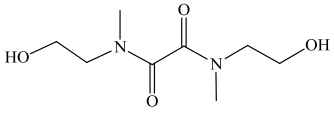
Another elementary reaction is amidification: secondary and primary amines can react with carboxylic acids to form amides (Scheme 6.4).

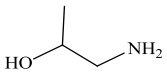
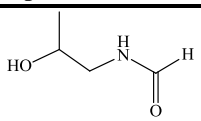
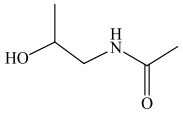
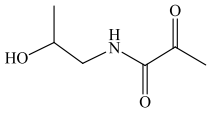
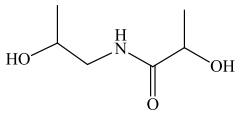
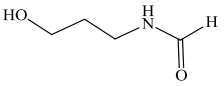
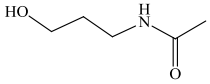
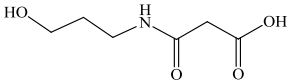
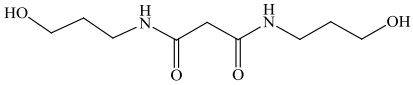
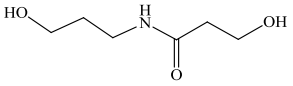


Scheme 6.4. Mechanism of amidification

This reaction has often been observed in MEA degradation (see chapter 5). Table 6.5 lists expected products when starting amines react with carboxylic acids from first generation degradation products (such as formic acid, acetic acid, oxalic acid …). However, this reaction could occur with any other primary and secondary amines and any other carboxylic acids.

Table 6.5. Expected products from amidification reaction

Starting molecules	Expected Products
 MEA	 **HEF (M = 89, rt = 29.8 min)**  **HEA (M = 103, rt = 31.9 min)**  **HHEA (M = 119, rt = 45 min)**  **HEOX (M = 133)**  **BHEOX (M = 176, rt = 59.2 min)**
 MAE	 **N-(2-hydroxyethyl)-N-methylformamide (M = 103, rt 30.3 min)**  **N-(2-hydroxyethyl)-N-methylacetamide (M = 117, rt 33.4 min)**  2-hydroxy-N-(2-hydroxyethyl)-N-methylacetamide (M = 133)  N-(2-hydroxyethylmethyl)oxamic acid (M = 147)  *N,N'-bis(2-hydroxyethyl)-N,N'-dimethyloxalamide (M = 204)*

Starting molecules	Expected Products
 1AP2	 **N-(2-hydroxypropyl)formamide (M = 103, rt = 33.8 min)**  **N-(2-hydroxypropyl)acetamide (M = 117, rt = 32.6 min)**  N-(2-hydroxypropyl)pyruvamide (M = 145)  *N-(2-hydroxypropyl)lactamide (M = 147)*
 3AP1	 N-(3-hydroxypropyl)formamide (M = 103)  N-(3-hydroxypropyl)acetamide (M = 117)  N-(3-hydroxypropyl)malonamide (M = 161)  *N,N'-Bis(2-hydroxypropyl)-propanediamide (M= 218)*  **3-hydroxy-N-(3-hydroxypropyl)propanamide (M = 147, rt = 48 min)**

Products observed in GC/MS

Products observed only in FT-ICR/MS

In the case of MAE, two amides were observed in GC/MS-TOF.

- The major degradation product had molecular weight of 103. As for HEF, the most intense fragment corresponded to a loss of CH_2-OH and a small fragment at m/z = 85 corresponded to a loss of water (Figure B.36, Appendix B). In addition, the retention time (30.3 min) was close to that of HEF (29.8 min), therefore this product could be N-(2-hydroxyethyl)-N-methylformamide (already observed by Lepaumier et al., 2011b; Vevelstad et al., 2013a).
- The formation of N-(2-hydroxyethyl)-N-methylacetamide was suggested from the observation of another peak at 33.4 min characterized by m/z = 117.

Another amide already observed by Vevelstad et al., 2013a was suspected to be N,N'-bis(2-hydroxyethyl)-N,N'-dimethyloxalamide thanks to FT-ICR/MS.

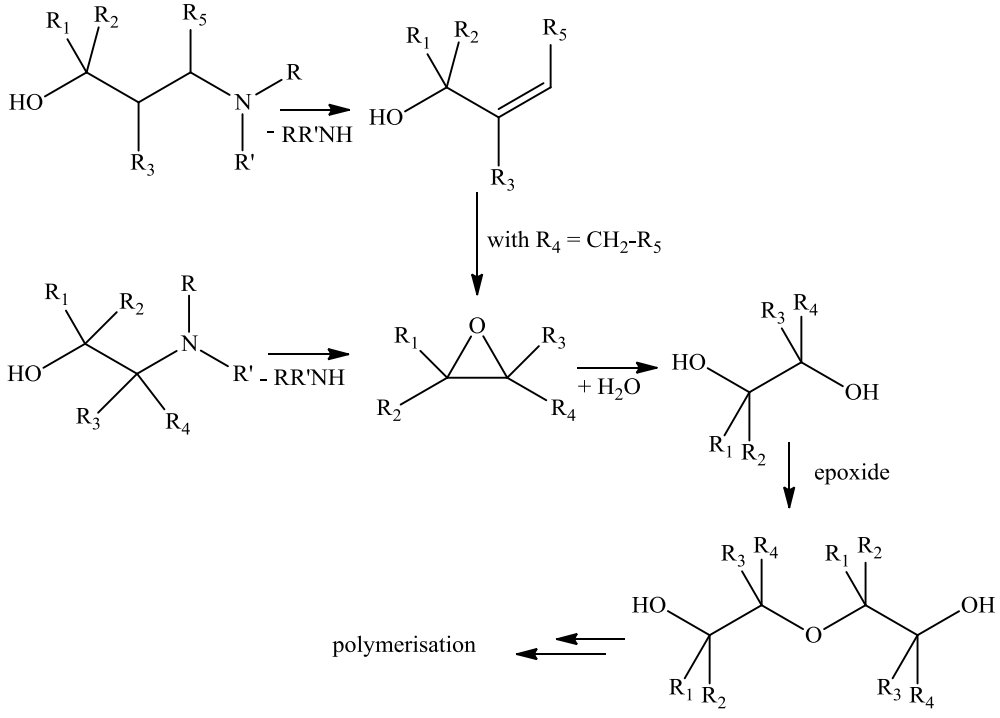
For 1AP2, N-(2-hydroxypropyl)acetamide was proposed by the database for the peak at 32.6 min with m/z = 99 which corresponds to [M-18]. The peak at 33.8 min (m/z = 85) was assigned to N-(2-hydroxypropyl)formamide.

In the case of 3AP1, 3-hydroxy-N-(3-hydroxypropyl)propanamide could correspond to the GC signal with m/z = 147 observed at 48 min.

Some expected products were not observed. Their GC signals could be hidden in GC/MS by those of other products or not detected (too low concentrations for example). Moreover amides derived from formic, acetic, glycolic, 3-hydroxypropanoic and oxalic acids were not observed by FT-ICR/MS with parameters used in our case.

6.6. Glycols formation

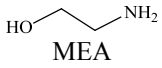
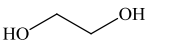
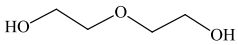
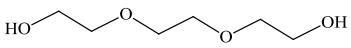
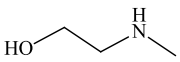
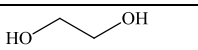
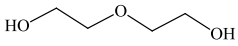
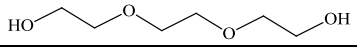
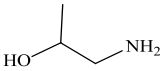
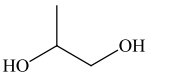
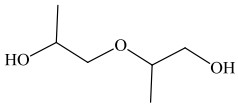
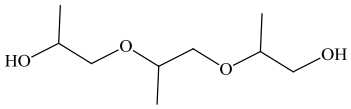
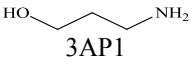
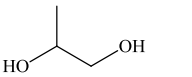
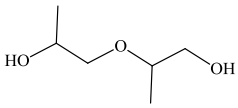
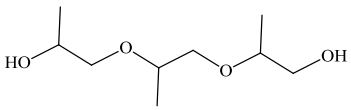
Alkanolamines with two or three carbon atoms between the nitrogen and oxygen atoms could be deaminated leading to the formation of an epoxide and ammonia or the corresponding alkylamine. Epoxide may react with water to form glycols (Scheme 6.5).



Scheme 6.5. Glycols formation

Epoxides could polymerise as previously observed in the case of MEA which formed DEG and TEG.

Table 6.6. Expected glycols

Starting molecules	Expected products	
 MEA		**EG (M = 62, rt = 8,8 min)**
		**DEG (M = 106)**
		**TEG (M = 150)**
 MAE		EG (M = 62, rt = 8,8 min)
		DEG (M = 106)
		TEG (M = 150)
 1AP2		Propane-1,2-diol
		2-methyl-3-oxa-hexane-1,5-diol
		2,5- dimethyl-3,6-dioxanonane-1,8-diol
 3AP1		Propane-1,2-diol
		**2-methyl-3-oxa-hexane-1,5-diol (M = 134, rt = 20.4 min)**
		2,5- dimethyl-3,6-dioxanonane-1,8-diol

Products observed in GC/MS

Glycols are not easily detected with the analytical conditions used for this part and could not be observed in FT-ICR/MS as observed in the case of MEA.

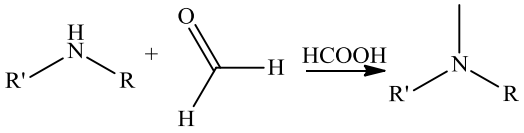
In the case of MAE, none of the expected glycols were observed. As shown before, DBWAX columns and TENAX cartridges were more adapted for the detection of DEG and TEG. It was also highly probable that the GC peak corresponding to EG was hidden by MAE. However, in accordance with our assumption, EG was previously observed by Lepaumier, 2008 in MAE degradation.

In the case of 3AP1, after deamination of alkanolamine, hydroxyl group could attack the resulting double bond to form an epoxide. Therefore, 2-methyl-3-oxa-hexane-1,5-diol was proposed for rt = 20.4 min on the basis of a good match between its mass spectrum and the one proposed by NIST database. This suggested that propane-1,2-diol was formed too following the mechanism proposed in Scheme 6.5.

2-methyl-3-oxa-hexane-1,5-diol should be observed in the case of 1AP2 too, but it was not the case. This could be explained by the presence of other peaks at same retention time.

6.7. Eschweiler-Clarke

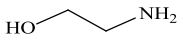
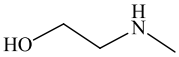
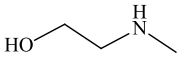
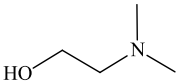
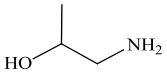
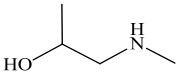
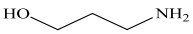
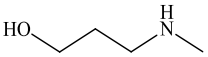
Eschweiler-Clarke reaction leads to the methylation of primary or secondary amines. This reaction requires the presence of formaldehyde (Scheme 6.6).



Scheme 6.6. Eschweiler-Clarke reaction

Expected products were given in the Table 6.7.

Table 6.7. Expected products from Escheweiler-Clarke reaction

Starting molecules	Expected products
 MEA	 **MAE** **(m/z = 75, rt = 10 min)**
 MAE	 **DMAE** **(m/z = 89, rt = 9.9 min)**
 1AP2	 N-methyl-1-aminopropan-2-ol (M = 89)
 3AP1	 **3-Methylaminopropan-1-ol (M = 89, rt = 16.7 min)**

Products observed in GC/MS

This reaction was proved in the case of MEA by the formation of MAE.

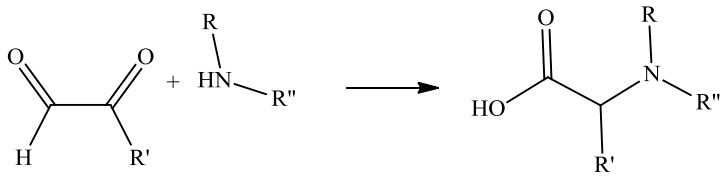
In the case of MAE, DMAE was detected as a major degradation product. It may be formed by this reaction and with the alkylation/dealkylation reaction mentioned previously (part 6.2, alkylation/dealkylation).

In the case of 3AP1, formaldehyde was supposed to be an intermediate involved in the formation of observed formic acid. The GC peak at 16.7 min with m/z = 89 could correspond to the expected N-methylated derivative of 3AP1 (3-methylaminopropan-1-ol). In accordance with our assumption, $C_4H_{11}NO$ was proposed in FT-ICR/MS for m/z = 89.

In the case of 1AP2, the expected product was not observed even in FT-ICR/MS.

6.8. Amino acids formation

Amino acids could be formed by the reaction of dialdehyde or ketoaldehyde with a primary or a secondary amine (Scheme 6.7).

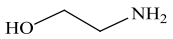
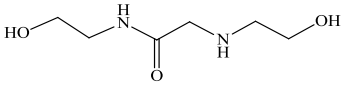
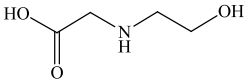
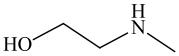
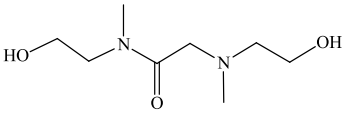
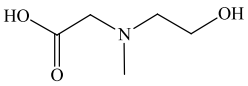
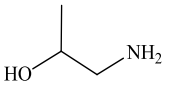
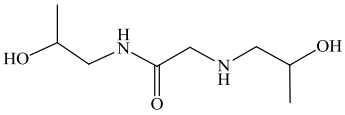
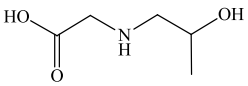
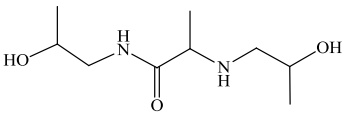
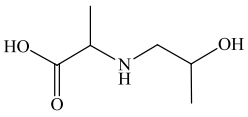
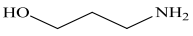
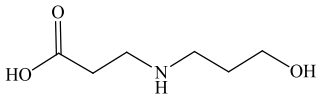


Scheme 6.7. General reaction for amino acids formation

Two mechanisms were proposed previously (chapter 2 and 5):

- The first one, from the literature, was based on the reduction of an imine formed by reaction of an amine with aldehyde or ketone functions, by ammonium formate (Leuckart-Wallach) (Scheme 2.21). Such pathway could be applied with any kind of dialdehyde or ketoaldehyde.
- The other one, proposed in this work, was based on the reaction of two amines with glyoxal or alkylglyoxal and the hydrolysis of the formed amide (Scheme 5.4). This mechanism could occur only if glyoxal or alkylglyoxal were formed. Amine would react twice with glyoxal or alkylglyoxal to form, after rearrangement and oxidation, an amide (intermediate proposed in the Table 6.8), which could be hydrolysed into the corresponding amino acid.

Table 6.8. Expected amino-acids and their intermediates

Starting molecules	Intermediate (2nd mechanism)	Expected products
 MEA	 **HEHEAA (M = 162, rt = 58.2 min)**	 **HEGly (M = 119, rt = 32.3 min)**
 MAE	 **2-[methyl-(2-hydroxyethyl)]amino-N-(2-hydroxyethyl)-N-methylacetamide (MHEAHEMAA) (M = 190, rt = 56.3 min)**	 **N-(2-hydroxyethyl)-N-methylglycine (N-MHEGly) (M = 133, rt = 28.7 min)**
 1AP2	 *N-(2-hydroxypropyl)-2-(2-hydroxypropylamino)acetamide (HPHPAA) (M = 190)*	 N-(2-hydroxypropyl)glycine (HPGly) (M = 133)
	 **N-(2-hydroxypropyl)-2-(2-hydroxypropylamino)propanamide (HPHPPA) (M = 204, rt = 56.9 min)**	 *N-(2-hydroxypropyl)alanine (HPAla) (M = 147)*
 3AP1		 N-(3-hydroxypropyl)-β-alanine (HPβala) (M = 147)

Products observed in GC/MS

Products observed only in FT-ICR/MS

In the case of MEA, HEGly formation could be explained by these two mechanisms. The intermediate of the second mechanism was HEHEAA.

As for HEGly, only [M-18] was expected to be seen on the mass spectrum for all amino acids.

In the case of MAE, a GC peak at 28.7 min with m/z = 115 was observed and its retention time was compatible with the HEGly homologue: N-(2-hydroxyethyl)-N-methylglycine (MHEGly, M = 133 g/mol). Moreover, $C_5H_{12}NO_3$ was proposed with a high intensity in FT-ICR/MS. 2-[methyl-(2-hydroxyethyl)]amino-N-(2-hydroxyethyl)-N-methylacetamide (MHEHEAHEMAA, M= = 190) which is a potential intermediate in the formation of this amino acid was detected by FT-ICR/MS. On GC/MS, a product at 56.3 min with m/z = 88 ($HO\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)\text{-}CH_2$ fragment) as highest peak in mass spectrum could correspond to

MHEHEAHEMAA. This assumption was made because in HEHEAA mass spectrum, highest peak was m/z = 74 which corresponded to the same fragmentation. Therefore, presence of N-MHEGly and MHEHEAHEMAA were highly suspected

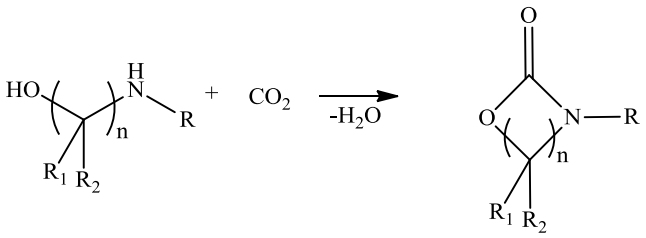
In the case of 1AP2, two amino acids could be formed due to the expected presence of glyoxal (in fact of oxalic acid) and methylglyoxal.

- 1AP2 reaction with glyoxal should lead to N-(2-hydroxypropyl)-2-(2-hydroxylpropylamino)acetamide (HPHPAA) and the corresponding acid N-(2-hydroxypropyl)glycine (HPGly). Using FT-ICR/MS, the molecular formula of HPHPAA was observed but maybe due to a low concentration, HPHPAA was not detected by GC/MS. The corresponding acid was not observed in GC/MS nor in FT-ICR/MS. It was maybe the result of a very low concentration of glyoxal which was corroborated with the low concentration of oxalic acid.
- Methylglyoxal should be present in higher concentration than glyoxal, thus increasing the probability of N-(2-hydroxypropyl)-2-(2-hydroxypropylamino)-propanamide (HPHPPA) and N-(2-hydroxypropyl)alanine (HPAla) formation. A molecular weight corresponding to the formula $C_6H_{13}NO_3$ (HPAla) was seen in FT-ICR/MS, but was not confirmed by GC/MS. It was probably due to the low response of amino acids in GC/MS as already observed with HEGly. On the other hand, its intermediate (HPHPPA) was found in FT-ICR/MS and highly suspected in GC/MS (rt = 56.9 min). On mass spectrum, the peak with the highest intensity was m/z = 102, which should correspond to the fragment HO-CH(CH_3)-CH_2-NH-CH(CH_3). Same kind of fragmentation was previously observed for HEHEAA. It is highly likely that HPHPPA and HPAla were present as degradation products.

In the case of 3AP1, only Leuckart-Wallach mechanism could explain the formation of N-(3-hydroxypropyl)-β-alanine (HPβala) but this product was not observed both in GC/MS and in FT-ICR/MS. Presence of propanedialdehyde or the corresponding acid was not proved, they might be not present in the solution, which could explain the absence of HPβala. Another assumption was on the availability of Leuckart-Wallach mechanism in CO_2 capture conditions. This mechanism was maybe disfavoured.

6.9. Ring closure of carbamates

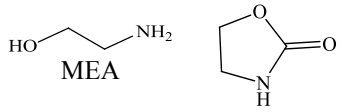
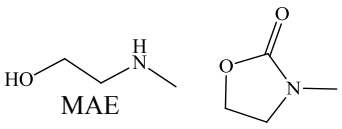
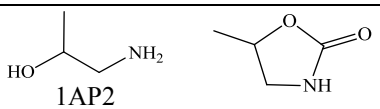
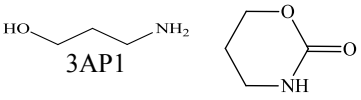
Formation of carbamate with primary or secondary amines is the key reaction in CO_2 capture. In the case of alkanolamines, cyclisation of the carbamate can occur (Scheme 6.8) with starting molecules having two or three carbon atoms between hydroxyl and amino functions.



Scheme 6.8. Ring closure of carbamates

This reaction is disfavoured for more than 3 carbon atoms.

Table 6.9. Expected products from carbamate cyclisation

Starting molecules	Expected products
 MEA	**OZD (M = 87, rt = 33.4 min)**
 MAE	**N-methyloxazolidinone (MOZD) (M = 101, rt = 29.5 min)**
 1AP2	**5-methyloxazolidinone (M = 101, rt = 34.4 min)**
 3AP1	**1,3-oxazin-2-one (M = 101, rt = 40.9 min)**

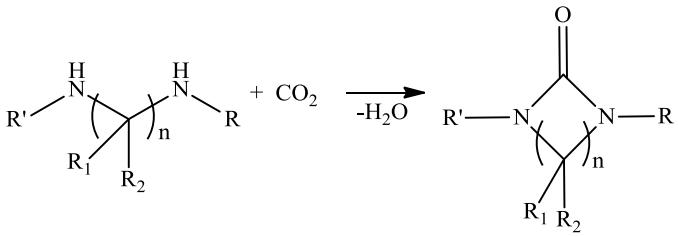
Products observed in GC/MS

Products observed only in FT-ICR/MS

Expected OZD, N-methyloxazolidinone, 5-methyloxazolidinone, 1,3-oxazin-2-one molecules were observed starting from MEA, MAE, 1AP2, 3AP1, respectively. All these products were proposed with high confidence by NIST database and retention times were in accordance with this of OZD. In addition, these products were already reported by Lepaumier, 2008, Lepaumier et al., 2011, Vevelstad et al., 2013; Eide-Haugmo et al., 2011 and Davis, 2009 respectively.

Imidazolidinone or six-membered ring homologues formation:

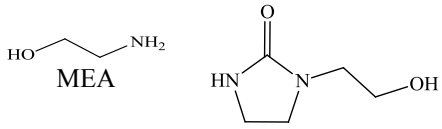
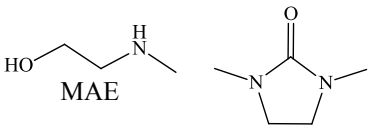
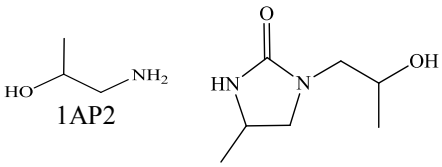
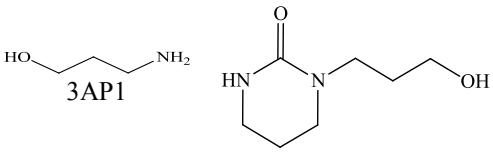
Oxazolidinones or six-membered rings homologues issued from primary alkanolamines (MEA, 1AP2 and 3AP1) can react with the amine in excess to form imidazolidinones or six-membered ring homologues (Scheme 6.9).



Scheme 6.9. Imidazolidinone or six-membered ring homologues formation

The expected products were reported in the next table.

Table 6.10. Expected imidazolidinones or six-membered rings homologues

Starting molecules	Expected products
 MEA	**HEIA (M = 130, rt = 49.4 min)**
 MAE	1,3-dimethylimidazolidin-2-one (M = 114, rt = 37.4 min)*
 1AP2	*1-(2-hydroxypropyl)-4-methylimidazolidin-2-one (M = 158)*
 3AP1	*N-(3-hydroxypropyl)tetrahydropyrimidin-2-one* (M = 158)

* formed by reaction of methylamine instead of MAE

Products observed in GC/MS

Products observed only in FT-ICR/MS

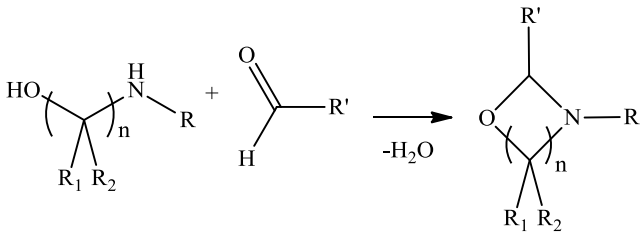
For MEA, this reaction led to HEIA.

For 1AP2 and 3AP1, the expected products, listed in Table 6.10, were not observed by GC/MS but corresponding molecular formulas were proposed in FT-ICR/MS. In addition , Davis, 2009; Eide-Haugmo et al., 2011 already observed these products. Therefore 1-(2-hydroxypropyl)-4-methylimidazolidin-2-one and N-(3-hydroxypropyl)tetrahydropyrimidin-2-one might be present.

MAE is a secondary amine and, regarding to Scheme 2.4 and 2.5, it cannot react with its oxazolidinone to form and imidazolidinone. However, another imidazolidinone, 1,3-dimethylimidazolidin-2-one was proposed with high confidence by NIST database for the GC peak with m/z = 114 at 37.4 min in GC/MS. A formula in accordance with this assignment was found in FT-ICR/MS. Moreover, this compound was already noted by Lepaumier et al., 2011b. It could be formed by the reaction of methylamine with MOZD following the mechanism previously described (see Scheme 2.4 and 2.5). Methylamine (Vevelstad et al., 2013a) is a first generation degradation product of MAE whose formation pathway is aimilar to this one occurred for NH_3 in the case of MEA (Scheme 5.2).

6.10. Oxazolidines and tetrahydrooxazines formation

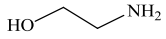
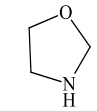
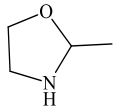
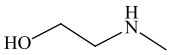
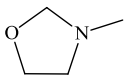
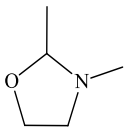
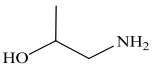
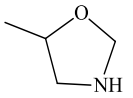
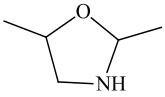
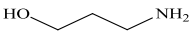
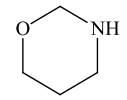
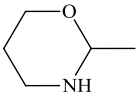
Aldehydes can react with alkanolamines with 2 or 3 carbon atoms between heteroatoms leading to the corresponding oxazolidines or tetrahydrooxazine rings.



Scheme 6.10. Oxazolidines and tetrahydrooxazines formation

The cases with formaldehyde and acetaldehyde as reactants were given in Table 6.11.

Table 6.11. Expected oxazolidines and tetrahydrooxazines

Starting molecules	Expected products
 MEA	 **Oxazolidine (M = 73, rt = 8.3 min)**
	 **2-methyloxazolidine (M = 87, rt = 9.84 min)**
 MAE	 **N-methyloxazolidine (M = 87, rt = 9.7 min)**
	 *2,3-dimethyloxazolidine (M = 101)*
 1AP2	 *5-methyloxazolidine (M = 87)*
	 *2,5-dimethyloxazolidine (M = 101)*
 3AP1	 **tetrahydro-1,3-oxazine (M = 87, rt = 12.45 min)**
	 *2-methyl-tetrahydro-1,3-oxazine (M = 101)*

Products observed in GC/MS
Products observed only in FT-ICR/MS

MEA reacts with aldehydes to form oxazolidine and 2-methyloxazolidine as explained in chapter 5. MAE and 1AP2, with also 2 carbon atoms between heteroatoms can react on the same way giving 1,3-oxazolidine derivatives, whereas 3AP1 should form tetrahydrooxazines.

In the case of MAE, N-methyl-1,3-oxazolidine involving formaldehyde as a reactant was highly suspected to be formed (peak at 9.7 min). The database proposal and retention time in GC/MS as well as the molecular formula in FT-ICR/MS were in accordance with this structure. Molecular weight and corresponding formula of the oxazolidine involving acetaldehyde as reactant was deduced by FT-ICR/MS but the corresponding GC peak could not be observed, maybe due to peaks overlapping.

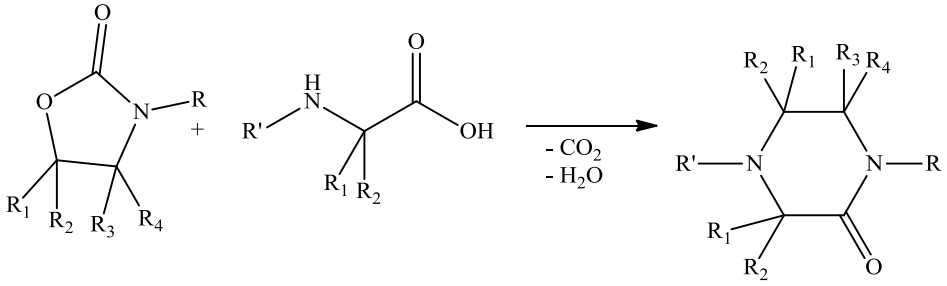
In the case of 1AP2, molecular formulas of expected oxazolidines were observed in FT-ICR/MS but the GC peak were not observed maybe due to peaks overlapping with 1AP2.

In the case of 3AP1, a GC peak at 12.45 min with a molecular weight of 87 was detected in GC/MS. This product was supposed to be the tetrahydro-1,3-oxazine coming from the reaction of 3AP1 with formaldehyde. A highly intense peak with a molecular formula

compatible with tetrahydro-1,3-oxazine was observed in FT-ICR/MS. However, no reference mass spectrum could use for comparison. The other expected product coming from reaction of #AP! With acetaldehyde, 2-methyl-tetrahydro-1,3-oxazine, was not observed by GC/MS but the corresponding molecular formula was found in FT-ICR/MS.

6.11. Piperazinones formation

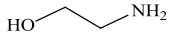
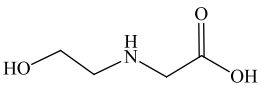
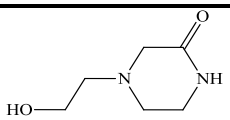
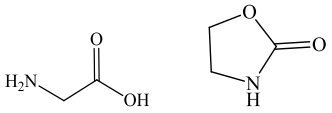
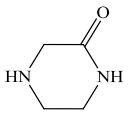
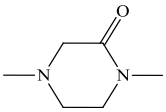
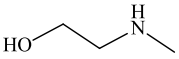
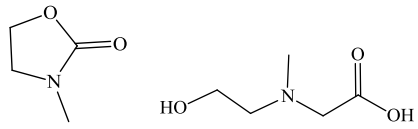
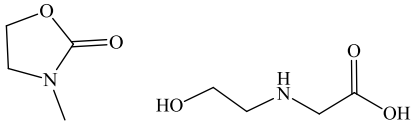
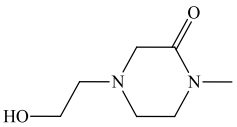
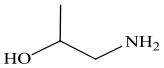
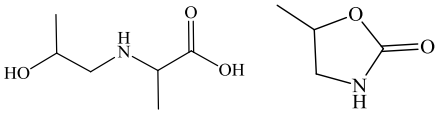
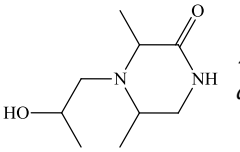
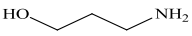
As proposed for MEA in chapter 5 (Scheme 5.9), piperazinones could be formed by the reaction of amino acids with oxazolidinones (Scheme 6.11) obtained from alkanolamines having 2 carbon atoms between hydroxyl and amino functions.



Scheme 6.11. Piperazinones formation

, Expected products were listed in Table 6.12 as well as amino acids and oxazolidinones involved in the reaction.

Table 6.12. Expected piperazinones with their reactants

Starting molecules	Intermediate	Expected products
 MEA	 HEGLY + OZD	 **4HEPO (M = 144, rt = 53.5 min)**
	 Glycine + OZD	 **PO (M = 100, rt = 39.52 min)**
	 Sarcosine + MOZD	 **1,4-dimethylpiperazin-2-one (DMPO) (M = 128, rt = 35.5 min)**
 MAE	 MOZD + N-MHEGly Or  MOZD + HEGly	 **4-(2-hydroxyethyl)-1-methylpiperazin-2-one (M = 158, rt = 51 min)**
 1AP2	 HPala + 5-MOZD	 *4-(2-hydroxypropyl)-3,5-dimethyl-piperazin-2-one (M = 186)*
 3AP1	8 atoms ring ⇒ not favourable	

Products observed in GC/MS
Products observed only in FT-ICR/MS

For MEA, piperazinones formed with this mechanism were 4HEPO and PO.

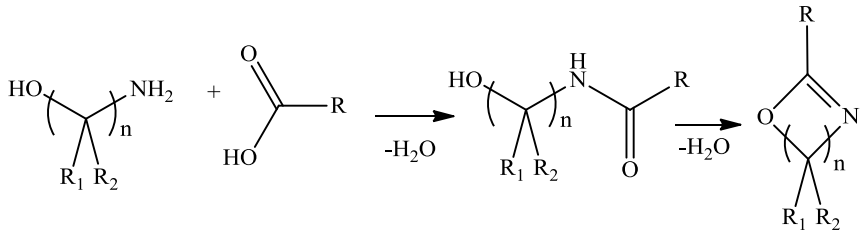
In the case of MAE, a product with M = 128 (rt = 35.5 min) and $C_6H_{13}N_2O$ as molecular formula could correspond to 1,4-dimethylpiperazin-2-one. It could be formed by reaction of sarcosine (from MAE oxidation) with N-methyloxazolidinone. Another product, 4-(2-hydroxyethyl)-1-methylpiperazin-2-one was suggested as a potential product from the observation of M = 158 at rt = 51 min in GC/MS and $C_7H_{15}O_2N_2$ as molecular formula in FT-ICR/MS. Moreover, this unexpected products was characterised by a MS fragmentation similar to that of 4HEPO. This product could be formed by the reaction of MOZD with N-MHEGly followed by demethylation or by reaction of MOZD with HEGly. HEGly was not observed in this work but was previously reported by Vevelstad et al., 2013a. Moreover as

observed in this work, HEGly signal was spread out in GC/MS. High concentration of this compound was needed to observe it. Small amounts of 4HEPO was formed that could be in accordance with the presence of HEGly because HEGly seemed to be a reactant in 4HEPO formation.

For 1AP2, a product with M = 186 was observed at 56.9 min but the highest intensity on mass spectrum was at m/z = 102. It seemed more in accordance with the formation of HPHPPA as suggest in part 6.8. The steric hindrance of 5-MOZD on the target carbon could disfavoured the attack by the amino group of HPala, which made difficult the formation of the expected piperazinone. Therefore, this peak was attributed to HPHPPA rather than the expected piperazinone (Table 6.8). However, a highly intense peak with molecular formula of 4-(2-hydroxypropyl)-3,5-dimethyl-piperazin-2-one was observed in FT-ICR/MS. Therefore, presence of this product was not excluded.

6.12. Oxazolines and homologues formation

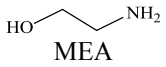
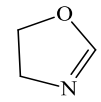
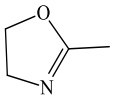
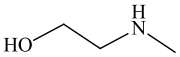
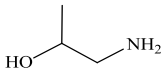
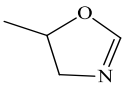
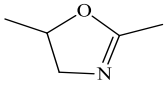
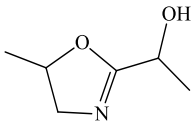
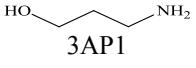
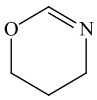
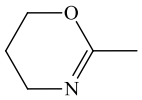
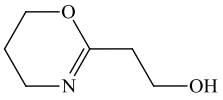
Primary alkanolamines can react with carboxylic acids to form amides as previously shown (see part 6.5, amidification) which can be converted into oxazolines (MEA, 1AP2) or homologues (3AP1) as a result of intramolecular cyclisation and water loss (Scheme 6.12).



Scheme 6.12. Oxazolines and homologues formation

This reaction cannot be considered for alkanolamines with more than three carbon atoms between the hydroxyl and amino groups. Expected oxazolines or homologues were reported in the Table 6.13.

Table 6.13. Expected oxazolines and homologues

Starting molecules	Expected products
 MEA	 **Oxazoline (M = 71, rt = 7.5 min)**
	 **2-methyloxazoline (M = 85, rt= 10.71 min)**
 MAE	
 1AP2	 5-methyloxazoline (M = 85)
	 2,5-dimethyloxazoline (M = 99)
	 *2-(1-hydroxyethyl)-5-methyloxazoline (M = 129)*
 3AP1	 *5,6-dihydro-4H-1,3-oxazine (M = 85)*
	 *5,6-dihydro-4H-2-methyl-1,3-oxazine (M = 99)*
	 *5,6-dihydro-4H-2-(2-hydroxyethyl)-1,3-oxazine (M = 129)*

Products observed in GC/MS
Products observed only in FT-ICR/MS

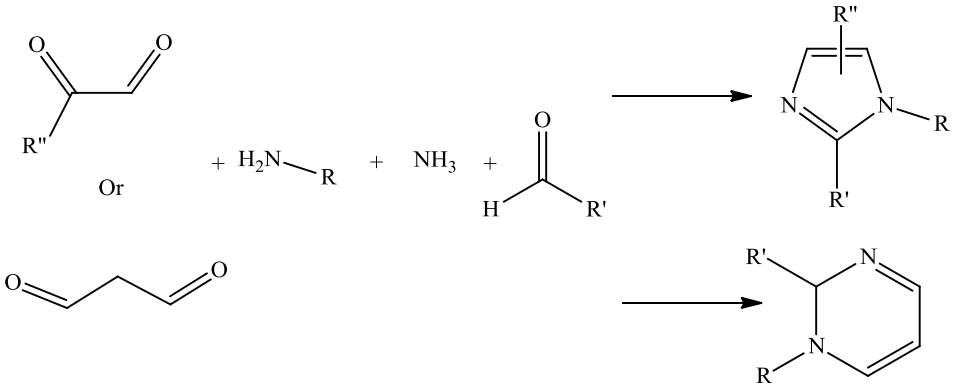
MAE is a secondary amine, therefore dehydration, involved in the mechanism (Scheme 5.30), was impossible due to the presence of the methyl group on amine.

In the case of 1AP2, none of the expected oxazolines (5-methyloxazoline and 2,5-dimethyloxazoline) were observed in GC/MS. Moreover, in FT-ICR/MS, their molecular formulas were not proposed. Therefore, these two products did not seem to be formed maybe because formic and acetic acid should not be present as major acids. Nevertheless, the molecular formula corresponding to 2-(1-hydroxyethyl)-5-methyloxazoline (lactic acid and 1AP2) was found in FT-ICR/MS. Formation of this product was highly probable because lactic acid should be present as one of the major acids (Table 6.3).

In the case of 3AP1, none of the expected dihydro-4H-oxazines were observed in GC/MS, but their corresponding molecular formulas were proposed in FT-ICR/MS. Therefore, these products were suspected to be formed.

6.13. Imidazoles and homologues formation

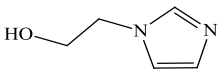
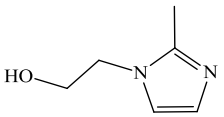
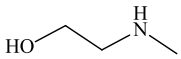
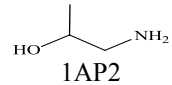
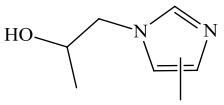
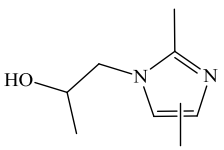
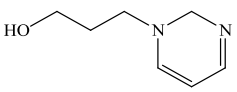
Alkylglyoxal (n=2) or malondialdehydes (n=3) can react with monoaldehydes, primary amines (MEA, 1AP2 and 3AP1) and ammonia to form imidazoles (Scheme 5.6) or pyrimidines (Scheme 6.13).



Scheme 6.13. Imidazoles and homologues formation

Dialdehydes such as succinaldehyde and higher homologues (n ≥ 4) cannot react similarly because seven-membered rings formation is not favourable.

Table 6.14. Expected imidazoles or six-membered ring homologues

Starting molecules	Expected products
 MEA	 **HEI (M = 112, rt = 39 min)**  **HEMI (M = 126, rt= 41.8 min)**
 MAE	
 1AP2	 **1-(2-hydroxypropyl)-4 or 5-methylimidazole (M = 140, rt = 41.3 min and rt = 44.5 min)**  **1-(2-hydroxypropyl)-2,4 or 2,5-dimethylimidazole (M = 154, rt = 46.6 min)**
 3AP1	 *1,2-dihydro-1-(3-hydroxypropyl)pyrimidine (M = 140)*

Products observed in GC/MS
Products observed only in FT-ICR/MS

In the case of MEA, HEI (glyoxal and formaldehyde) and HEMI (glyoxal and acetaldehyde) were observed as degradation products.

MAE is a secondary amine which could not form imidazoles due the absence of ammonia.

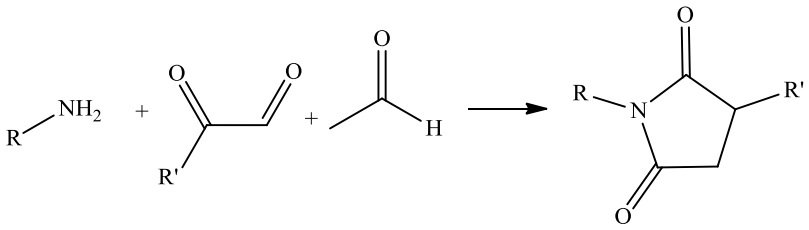
In the case of 1AP2, two molecules with the same molecular weight, i.e. 140, were observed in GC/MS at rt = 41.3 and 44.5 min. An intense peak corresponding to $C_7H_{12}N_2O$ was found by FT-ICR/MS. Therefore, molecules observed in GC/MS were supposed to correspond to the two isomers N-(2-hydroxypropyl)-4-methylimidazole and N-(2-hydroxypropyl)-4-methylimidazole. However, without standard, the peaks could not be attributed more precisely.

Another molecule with a molecular weight of 154 was observed at 46.6 min and an intense peak attributed to $C_8H_{14}N_2O$ was found in FT-ICR/MS. Therefore, N-(2-hydroxypropyl)-2,4 or 2,5-methylimidazole was supposed to be formed.

In the case of 3AP1, 1,2-dihydro-1-(3-hydroxypropyl)pyrimidine should be formed by the reaction of 3AP1, ammonia, formaldehyde and propanedial. However, this product was not observed in GC/MS but the corresponding formula was found in FT-ICR/MS.

6.14. Succinimides formation

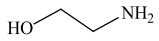
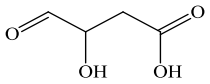
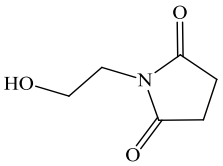
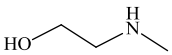
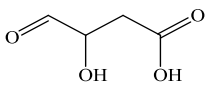
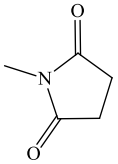
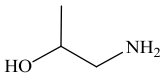
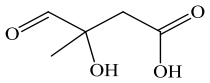
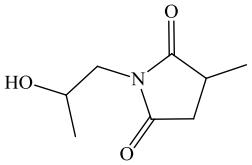
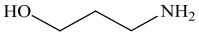
Primary amines (MEA, 1AP2) having 2 carbon atoms between heteroatoms can react with (alkyl)glyoxal and acetaldehyde to form succinimides as proposed in Scheme 6.14.



Scheme 6.14. Succinimidees formation

First step is aldolisation of (alkyl)glyoxal in the presence of acetaldehyde. Resulting aldehyde can be further oxidised to carboxylic acid intermediates (reported in Table 6.15 and Table 6.4). Then reaction with amine leads to different succinimide derivatives.

Table 6.15. Expected succinimides

Starting molecules	Intermediate (aldolisation)	Expected products
 MEA		 **HESucc (M = 143, rt = 43.9 min)**
 MAE		 **N-methylsuccinimide* (M = 113, rt = 45.3 min)**
 1AP2		 *N-(2-hydroxypropyl)-3-methylsuccinimide (M = 171)*
 3AP1		

* formed by reaction of methylamine instead of MAE

Products observed in GC/MS

Products observed only in FT-ICR/MS

In the case of MEA, as shown before (chapter 5.1), HESucc formation was explained from the aldolisation reaction between glyoxal and acetaldehyde, followed by oxidation then reaction of the intermediate (proposed in Table 6.15) with MEA.

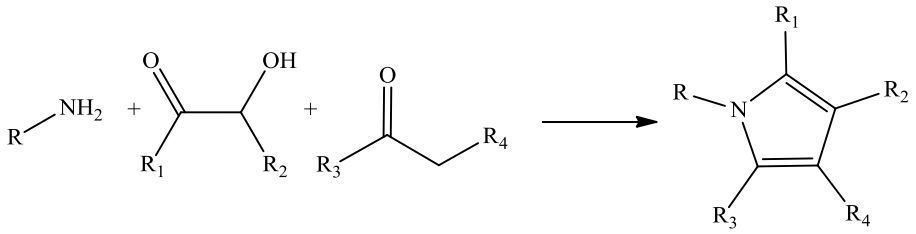
In the case of the secondary amine as MAE, succinimides should not be formed. However methylamine (first generation product of MAE) could react with glyoxal and acetaldehyde to form N-methylsuccimide. This product was proposed with good match by NIST database for a peak at 45.3 min and molecular formula in accordance with this product was observed in FT-ICR/MS too.

In the case of 1AP2, the expected product with 171 as molecular weight was not detected by GC. Studying HESucc fragmentation to predict mass spectrum of N-(2-hydroxypropyl)-3-methylsuccinimide was not helpful. Therefore, it was not possible to find this product by GC/MS without using a standard. On the other hand, $C_8H_{13}NO_3$ was proposed as molecular formula for M = 171 in FT-ICR/MS which could be a proof of the formation of the expected N-(2-hydroxypropyl)-3-methylsuccinimide.

In the case of 3AP1, formaldehyde should be involved to form a linear chain of 4 carbon atoms by aldolisation. However it was supposed to be formed in low amount, therefore, succinimides were not expected.

6.15. Pyrroles formation

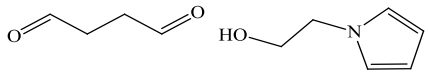
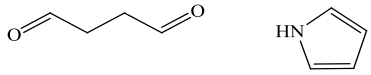
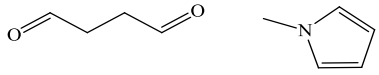
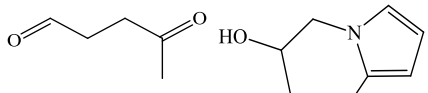
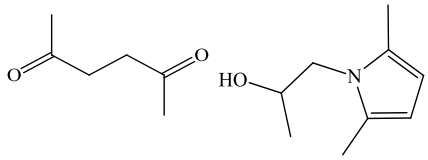
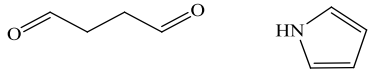
Pyrroles can be formed by reaction of primary amines (MEA and 1AP2) with α-ketols and any aldehyde (Scheme 6.15).



Scheme 6.15. Pyrroles formation

Intermediates issued from aldolisation then rearrangement, as well as expected products were reported in Table 6.16.

Table 6.16. dicarbonyl intermediates and expected pyrroles

Starting molecules	Intermediate (aldolisation)	Expected products
MEA		**HEPyr (M = 111, rt = 27.3 min)**
		**Pyrrole (M = 67)**
MAE		N-methylpyrrole (M = 81)
1AP2		*N-(2-hydroxypropyl)-2-methylpyrrole (M = 139)*
		**N-(2-hydroxypropyl)-2,5-dimethylpyrrole (M = 153, rt = 32.9 min)**
		**Pyrrole (M = 67)**
3AP1		

Products observed in GC/MS
Products observed only in FT-ICR/MS

In the case of MEA, HEPyr was formed from 2-hydroxyethanal and acetaldehyde aldolisation, followed by dehydration and rearrangement, then reaction of the intermediate

(proposed in Table 6.4 and Table 6.16) with MEA. Pyrrole was also observed by reaction of the same intermediate with ammonia.

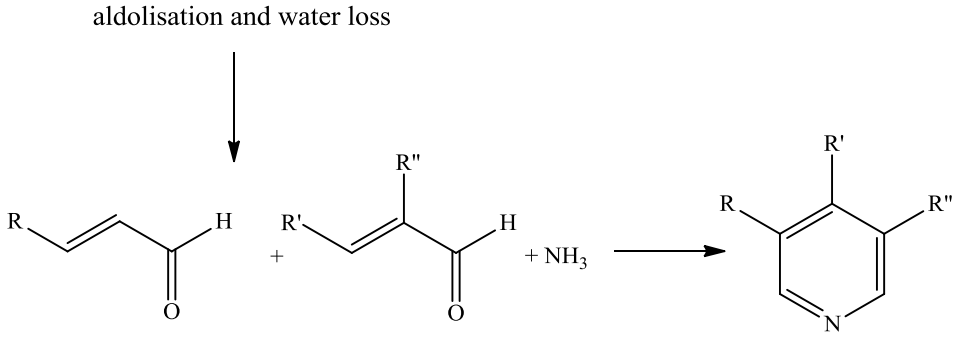
In the case of MAE, pyrroles could not be formed by reaction with MAE. However, as for succinicimide, methylamine could be involved to form N-methylpyrrole but this product was not observed even in FT-ICR/MS.

In the case of 1AP2, N-(2-hydroxypropyl)-2,5-dimethylpyrrole was supposed to be formed (peak at 32.9 min with m/z = 153, $C_9H_{15}NO$ - FT-ICR/MS) by reaction of 1AP2 with 2-hydroxypropanal and acetone, followed by dehydration, rearrangement and then reaction of the intermediate (proposed in Table 6.4 and Table 6.16) with 1AP2. Another product with $C_8H_{13}NO$ as formula was observed in FT-ICR/MS. It could correspond to N-(2-hydroxypropyl)-2-methylpyrrole, which was formed by aldolisation of 2-hydroxypropanol and acetaldehyde, followed by dehydration and rearrangement. Then the intermediate could react with 1AP2.

In the case of 3AP1, as for succinimides, pyrroles were not expected.

6.16. Pyridines formation

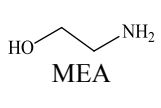
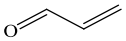
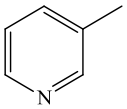
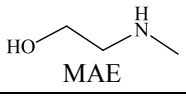
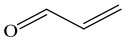
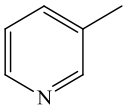
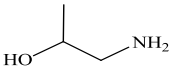
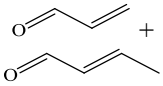
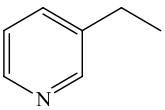
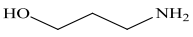
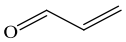
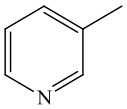
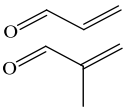
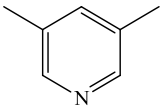
Pyridine derivatives could be obtained by dimerization of conjugated aldehydes in presence of ammonia. These aldehydes were usually formed by aldolisation, followed by dehydration; but in some particular cases, the conjugated aldehydes were formed by dehydration of aldehydes.



Scheme 6.16. Pyridines formation

The expected pyridines were reported in Table 6.16 with their intermediates.

Table 6.17. Alkenal intermediate and expected pyridine

Starting molecules	Intermediate (aldolisation)	Expected products
 MEA		 **3-methylpyridine (M = 111, rt = 17.4 min)**
 MAE		
		 **3-methylpyridine (M = 93, rt = 17.4 min)**
 1AP2		 **3-ethylpyridine (M = 107, rt = 22 min)**
 3AP1		 **3-methylpyridine (M = 93, rt = 17.4 min)**
		 **3,5-dimethylpyridine (M = 107, rt = 23 min)**

Products observed in GC/MS

Products observed only in FT-ICR/MS

As ammonia was not formed in MAE degradation, no pyridines were expected.

In the case of 1AP2, 3-methylpyridine and 3-ethylpyridine were observed in GC/MS and their presence was confirmed by FT-ICR/MS. For 3-methylpyridine, the conjugated aldehyde, acrolein, came from dehydration of 2-hydroxypropanal. The same mechanism as proposed in Scheme 5.34 occurred. 3-ethylpyridine was formed by reaction of acrolein but with 2-butenal and ammonia. 2-butenal was issued from two acetaldehyde aldolisation and dehydration.

3-methylpyridine was also observed in 3AP1 degradation. Acrolein was obtained by dehydration of 3-hydroxypropanal, then same mechanism as proposed in Scheme 5.34 occurred. Formation of 3,5-dimethylpyridine was supported by FT-ICR/MS. This compound could be obtained by reaction of acrolein with 2-methylacrolein and ammonia. 2-methylacrolein could be obtained by the reaction of the double bond of acrolein with formaldehyde (Markovnikov addition) then dehydration.

6.17. Conclusion

To conclude, seventeen generic reactions involved in MEA degradation were reported in this chapter (Table 6.1). When possible, these reactions were transposed to three other alkanolamines (MAE, 1AP2, 3AP1) to predict their degradation products. Expected products of each key reaction were listed in tables and searched in each degraded sample (obtained with the representative test) thanks to analyses by IC, GC/MS and FT-ICR/MS. Many of these expected products were observed. No conclusion could be made for the non-observed products because the study could not be complete as for MEA. Although analyses were not as developed as for MEA, all highlighted reactions seem to occur at least with one of the degraded amine.

We have proved that understanding MEA degradation could help to predict the degradation of other amines thanks to three examples.

7. Conclusion and Perspectives

The aim of this work was to identify novel degradation products of monoethanolamine (MEA) under CO_2 capture conditions, to understand their formation (realistic mechanisms proposal) and then to generalize mechanisms to others amines. A representative laboratory test was established to degrade amines.

First of all, a critical literature review was done for MEA degradation. Degradation products were listed with proposed mechanisms of formation. This chapter showed the important diversity of degradation products and the lack of works concerning oxidative degradation and gas phase analysis.

To improve degradation products identification, several analytical methods and gas sampling technics were developed. Synergy between these methods enabled us to identify sixty products formed during pilot pant campaign carried out at IFPEN.

The first campaign results were used to establish a representative test in lab because no test was representative to pilot plant degradation. This test was established to have the same degradation products as in pilot plant conditions. This test was used to complete gas phase analyses and to study the degradation of others amines.

During this work, more than sixty products issued from MEA degradation were observed in liquid or gas phase. Some of them were previously reported in literature but it is noteworthy that about thirty novel degradation products were identified. These identifications were mainly due to an extensive research on the gas phase.

Generally, products already observed had no described mechanism or some of them were not convincing. To understand MEA degradation, we proposed for each novel molecule (except butan-2-one) and some products already observed, mechanisms based on well-known reactions in organic chemistry. These mechanisms were most of the times validated thanks to experiments. As a result, a key reaction was highlighted in this work: aldolisation. This reaction was a key point for formation of C3 or C4 carbon chains and explained formation of about ten novel compounds observed in this work.

To account for MEA degradation, a general pathway was proposed with all the products observed in this work.

Furthermore, several reactions observed for MEA were generalised. After studying degradation of three other amines (N-methylaminoethanol, 1-aminopropan-2-ol, 3-

aminopropan-1-ol), we have concluded that these reactions could be transposed to other amines. Same families of products could be observed: oxazolines, oxazolidines, amino acids, pyridines, piperazinones. This can help for amine degradation prediction and for the study of their environmental impact.

In future work hypotheses for unknown products would be confirmed thanks to proposed mechanisms of formation, which would help to suggest new syntheses adapted to the proposed formula. Moreover, presence of some compounds as methylglyoxal or acrolein should be confirmed.

Effects of SOx and NOx on degradation were not in the scope of this work. However, it should be useful to study their effects on degradation because some mechanisms suggested formation of products thanks to nitrites and/or NO^+ (HEEDA, DEA). Some laboratory experiments to validate influence of these species on degradation have to be done. For example, activating effect of nitrite in the reaction of amine function on hydroxyl group must be studied.

Even if some works studied metals effects in solutions, it would be interesting to look after degradation due to metallic coupons as stainless steel 316L or hastelloy. It was proved that metallic ions catalyse the degradation but this catalytic mechanism is not well understood as well as reactions which could be involved at the coupon surface.

Thanks to our first proposal of transposable mechanisms, some candidate molecules for CO2 capture could be studied with the same method to confirm these transpositions. This transposition could be used to have a better knowledge of products formed during the degradation.

Volatile products have to be quantified for toxicity assessment to evaluate potential impact of emitted products to the atmosphere. For environmental acceptance, a toxicological study should be done systematically for any novel degradation products, more particularly for products observed in gas phase.

Considering all these ideas, we can conclude that a lot of work remains to be done!

References

Adams, A., Polizzi, V., van Boekel, M., De Kimpe, N., 2008. Formation of pyrazines and a novel pyrrole in Maillard model systems of 1,3-dihydroxyacetone and 2-oxopropanal. J. Agric. Food Chem. 56, 2147–2153.

Andrade, C.K.Z., Rocha, R.O., Vercillo, O.E., Silva, W.A., Matos, R.A.F., 2003. DCC/DMAP-mediated coupling of carboxylic acids with oxazolidinones and thiazolidinethiones. Synlett 2351–2352.

Arduengo, A.J., Gentry, F.P., Taverkere, P.K., Simmons, H., 2001. Process for manufacture of imidazoles. US 6177575 B1, E.I . du pont de Nemours and compagny, Wilmington.

Bedell, S., 2009. Oxidative degradation mechanisms for amines in flue gas capture. Energy Procedia 1, 771–778.

Bedell, S., 2011. Amine autoxidation in flue gas CO_2 capture-Mechanistic lessons learned from other gas treating processes. Int. J. Greenh. Gas Control 5, 1–6.

Bello, A., Idem, R.O., 2005. Pathways for the formation of products of the oxidative degradation of CO_2-loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases. Ind. Eng. Chem. Res. 44, 945–969.

Bello, A., Idem, R.O., 2006. Comprehensive study of the kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during CO_2 absorption from flue gases. Ind. Eng. Chem. Res. 45, 2569–2579.

Ben, D.P., 2005. Process for the preparation of 1-(2-hydroxyethyl)imidazole. IN 195358, India.

Bhown, A.S., Freeman, B.C., 2011. Analysis and Status of Post-Combustion Carbon Dioxide Capture Technologies. Environ. Sci. Technol. 45, 8624–8632.

Bonenfant, D., Minleault, M., Hausler, R., 2007. Estimation of the CO_2 absorption capacities in aqueous 2-(2-aminoethylamino)ethanol and its blends with MDEA and TEA in the presence of SO_2. Ind. Eng. Chem. Res. 46, 8968–8971.

Bouillon, P.-A., Hennes, S., Mahieux, C., 2009. ECO2: Post-combustion or Oxyfuel–A comparison between coal power plants with integrated CO_2 capture. Energy Procedia 1, 4015–4022.

Bramwell, A.F., Payne, L.S., Riezebos, G., Ward, P., Wells, R.D., 1971. The nuclear alkylation of pyrazines by ketones and aldehydes. J. Chem. Soc. C Org. 1627–1632.

Challis, B.C., Challis, J.C., 1982. 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, pp. 1151–1223.

Chi, S., Rochelle, G.T., 2002. Oxidative Degradation of Monoethanolamine. Ind. Eng. Chem. Res. 41, 4178–4186.

Cotugno, P., Monopoli, A., Nacci, A., Zambonin, C.G., Calvano, C.D., Universita, C., Moro, A., Orabona, V., Iccom, C.N.R., Chimica, D., Aldo, B., 2014. MALDI-MS and HILIC ESI-MS / MS as Versatile Tools for Detection of Monoethanolamine Degradation Products in a Real Postcombustion Carbon Dioxide Capture Plant. Energy and Fuels 28, 1295–1303.

Da Silva, E.F., Lepaumier, H., Grimstvedt, A., Vevelstad, S.J., Einbu, A., Vernstad, K., Svendsen, H.F., Zahlsen, K.K., 2012. Understanding 2-Ethanolamine Degradation in Postcombustion CO2 Capture. Ind. Eng. Chem. Res. 51, 13329–13338.

Davis, J., Rochelle, G., 2009. Thermal degradation of monoethanolamine at stripper conditions. Energy Procedia 1, 327–333.

Davis, J.D., 2009. Thermal degradation of aqueous amines used for carbon dioxide capture. Thesis, University of Texas at Austin.

Denisov, E., Afanas'ev, I., 2005. Oxidation and Antioxidants in organic chemistry and biology. Taylor & Francis.

Dennis, W.H., Hull, L.A., Rosenblatt, D.H., 1967. Oxidations of amines. IV. Oxidative fragmentation. J. Org. Chem. 32, 3783–3787.

Dettmer, K., Engewald, W., 2002. Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds. Anal. Bioanal. Chem. 373, 490–500.

Eide-Haugmo, I., Lepaumier, H., Einbu, A., Vernstad, K., da Silva, E.F., Svendsen, H.F., 2011. Chemical stability and biodegradability of new solvents for CO_2 capture. Energy Procedia 4, 1631–1636.

Einbu, A., DaSilva, E., Haugen, G., Grimstvedt, A., Lauritsen, K.G., Zahlsen, K., Vassbotn, T., 2013. 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. Energy Procedia 37, 717–726.

Eiter, K., Hebenbrock, K.-F., Kabbe, H.-J., 1972. Neue offenkettige und cyclische alpha-Nitrosaminoalkyläther. Liebigs Ann. Chem. 765, 55–77.

Fazio, M.J., 1984. Nucleophilic Ring-Opening of 2-Oxazolines with Amines - A Convenient Synthesis for Unsymmetrically Substituted Ethylenediamines. J. Org. Chem. 49, 4889–4893.

Fedoronko, M., Koenigstein, J., 1971. Kinetics and mechanism of the disproportionation of methylglyoxal into latic acid. Collect. Czechoslov. Chem. Commun. 36, 3424–3430.

Fiddler, W., Pensabene, J.W., Doerr, R.C., Wasserman, A.E., 1972. Formation of N-Nitrosodimethylamine from Naturally Occurring Quaternary Ammonium Compounds and Tertiary Amines. Nature 236, 307.

Fostås, B., Gangstad, A., Nenseter, B., Pedersen, S., Sjøvoll, M., Sørensen, A.L., 2011. Effects of NOx in the flue gas degradation of MEA. Energy Procedia 4, 1566–1573.

Freeman, S.A., 2011. Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture. Thesis, Universty of Texas at Austin.

Freeman, S.A., Rochelle, G.T., 2012a. 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.

Freeman, S.A., Rochelle, G.T., 2012b. Thermal Degradation of Aqueous Piperazine for CO_2 Capture: 2. Product Types and Generation Rates. Ind. Eng. Chem. Res. 51, 7726–7735.

Gao, J., Wang, S., Zhao, B., Qi, G., Chen, C., 2011. Pilot-Scale Experimental Study on the CO_2 Capture Process with Existing of SO_2 : Degradation , Reaction Rate , and Mass Transfer. Energy and Fuels 25, 5802–5809.

Goff, G.S., 2005. Oxidative degradation of aqueous monoethanolamine in CO_2 capture processes: Iron and copper catalysis, inhibition, and O_2 mass transfer. Thesis, University of Texas at Austin.

Goff, G.S., Rochelle, G.T., 2004. Monoethanolamine degradation: O2 mass transfer effects under CO2 capture conditions. Ind. Eng. Chem. Res. 43, 6400–6408.

Goff, G.S., Rochelle, G.T., 2006. Oxidation inhibitors for copper and iron catalyzed degradation of monoethanolamine in CO_2 capture processes. Ind. Eng. Chem. Res. 45, 2513–2521.

Gouedard, C., Picq, D., Launay, F., Carrette, P.-L., 2012. Amine degradation in CO2 capture. I. A review. Int. J. Greenh. Gas Control 10, 244–270.

Gouedard, C., Rey, A., Cuzuel, V., Brunet, J., Delfort, B., Picq, D., Dugay, J., Vial, J., Pichon, V., Launay, F., Assam, L., Ponthus, J., Carrette, P.-L., 2014. Amine degradation in CO2 capture. 3. New degradation products of MEA in liquid phase: amides and nitrogenous heterocycles. Int. J. Greenh. Gas Control (submitted).

Guerra, P. V, Yaylayan, V.A., 2010. Dimerization of Azomethine Ylides: An Alternate Route to Pyrazine Formation in the Maillard Reaction. J. Agric. Food Chem. 58, 12523–12529.

Holub, P.E., Critchfield, J.E., Su, W.Y., 1998. Amine degradation chemistry in CO_2 service. 48th Laurance Reid Gas Cond.Conf., 146–160.

Huang, Q., Thompson, J., Bhatnagar, S., Chandan, P., Remias, J.E., Selegue, J.P., Liu, K., 2014. Impact of Flue Gas Contaminants on Monoethanolamine Thermal Degradation. Ind. Eng. Chem. Res. 53, 553–563.

Hull, L.A., Davis, G.T., Rosenblatt, D.H., Mann, C.K., 1969. Oxidations of amines. VII. Chemical and electrochemical correlations. J. Phys. Chem. 73, 2142–2146.

Hull, L.A., Rosenblatt, D.H., Davis, G.T., Williams, H.K.R., Weglein, R.C., 1967a. Oxidations of Amines. III. Duality of Mechanism in the Reaction of Amines with Chlorine Dioxide. J. Am. Chem. Soc. 89, 1163–1170.

Hull, L.A., Rosenblatt, D.H., Davis, G.T., Williams, H.K.R., Weglein, R.C., De Luca, D.C., 1967b. Oxidations of Amines. II. Substituent Effects in Chlorine Dioxide Oxidations. J. Am. Chem. Soc. 89, 1158–1163.

IARC, 1978. Monographs on the Evaluation of Carcinogenic Risks to Humans. Some N-Nitroso Compounds. http://monographs.iarc.fr/ENG/Monographs/vol17/volume17.pdf

IEA, 2008. Energy technology perspectives. OECD, Paris.

IEA, 2013. CO_2 emissions from fuel combustion highlights 2013.

Ilkgul, B., Gunes, D., Sirkecioglu, O., Bicak, N., 2010. Synthesis of 2-oxazolines via boron esters of N-(2-hydroxyethyl)amides. Tetrahedron Lett. 51, 5313–5315.

Islam, M.N.S., Yusoff, R., ALi, B.S., Chakrabarti, M.H., 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. Int. J. Phys. Sci. 6, 5883–5895.

Jin, F., Li, Y., 2009. The Effect of H_2 on Chichibabin Condensation Catalyzed by Pure ZSM-5 and Pt/ZSM-5 for Pyridine and 3-Picoline Synthesis. Catal. Letters 131, 545–551.

Karl, M., Dye, C., Schmidbauer, N., Wisthaler, A., Mikoviny, T., D'Anna, B., Müller, M., Borrás, E., Clemente, E., Muñoz, A., Porras, R., Ródenas, M., Vázquez, M., Brauers, T., 2012. Study of OH-initiated degradation of 2-aminoethanol. Atmos. Chem. Phys. 12, 1881–1901.

Katsuura, A., Washio, N., 2005. Preparation of imidazoles from imines and iminoacetaldehydes. JP2005200305A, Japan.

Kawasaki, N., Noguchi, Y., Aoki, H., Fujii, K., 1991. Preparation of 1-substituted imidazoles. JP 03169865, Japan.

Kemper, J.M., Walse, S.S., Mitch, W.A., 2010. Quaternary Amines as Nitrosamine Precursors: a Role for Consumer Products? Environ. Sci. Technol. 44, 1224–1231.

Kenarsari, S.D., Yang, D., Jiang, G., Zhang, S., Wang, J., Russell, A.G., Wei, Q., Fan, M., 2013. Review of recent advances in carbon dioxide separation and capture. RSC Adv. 3, 22739–22773.

Knol, J., Feringa, B.L., 1996. Direct coupling procedure for the synthesis of N-acyl-2-oxazolidinones derived from α,β-unsaturated carboxylic acids. Synth. Commun. 26, 261–268.

Konigstein, J., Anderle, D., Fedoronko, M., 1981. Determination of kinetic data for the transformation of methylglyoxal. Chem. Zvesti 35, 471–479.

Krems, I.J., Spoerri, P.E., 1947. The Pyrazines. Chem. Rev. 40, 279–358.

Lambert, J.B., Wharry, S.M., 1982. Heterocyclic deformations from molecular enlargement. J. Org. Chem. 47, 3890–3893.

Lawal, O., Bello, A., Idem, R., 2005a. 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.

Lawal, O., Bello, A., Idem, R., Systems, P., 2005b. Pathways and reaction products for the oxidative degradation of CO_2 loaded and concentrated aqueous MEA and MEA/MDEA mixtures during CO_2 absorption from flue gases. Greenh. Gas Control Technol. 7, 1159–1164.

Lee, A.S., Eslick, J.C., Miller, D.C., Kitchin, J.R., 2013. Comparisons of amine solvents for post-combustion CO_2 capture: A multi-objective analysis approach. Int. J. Greenh. Gas Control 18, 68–74.

Lensen, R., 2004. The promoter effect of piperazine on the removal of carbon dioxide. http://www.bsdfreaks.nl/files/hoofd6.pdf

Lepaumier, H., 2008. Etude des mécanismes de dégradation des amines utilisées pour le captage du CO_2 dans les fumées. Thesis, Laboratoire des matériaux organiques à propriétés spécifiques (Université de Savoie).

Lepaumier, H., da Silva, E.F., Einbu, A., Grimstvedt, A., Knudsen, J.N., Zahlsen, K.K., Svendsen, H.F., 2011a. Comparison of MEA degradation in pilot-scale with lab-scale experiments. Energy Procedia 4, 1652–1659.

Lepaumier, H., Grimstvedt, A., Vernstad, K., Zahlsen, K., Svendsen, H.F., 2011b. Degradation of MMEA at absorber and stripper conditions. Chem. Eng. Sci. 66, 3491–3498.

Lepaumier, H., Picq, D., Carrette, P.L., 2009a. New Amines for CO_2 Capture. I. Mechanisms of Amine Degradation in the Presence of CO_2. Ind. Eng. Chem. Res. 48, 9068–9075.

Lepaumier, H., Picq, D., Carrette, P.L., 2010. CO_2 capture: why, how, with what constraints? Actual. Chim. 36–40.

Lepaumier, H., Picq, D., Carrette, P.-L., 2009b. New Amines for CO_2 Capture. II. Oxidative Degradation Mechanisms. Ind. Eng. Chem. Res. 48, 9068–9075.

Levine, M., Kenesky, C.S., Zheng, S., Quinn, J., Breslow, R., 2008. Synthesis and catalytic properties of diverse chiral polyamines. Tetrahedron Lett. 49, 5746–5750.

Lim, Y.B., Tan, Y., Perri, M.J., Seitzinger, S.P., Turpin, B.J., 2010. Aqueous chemistry and its role in secondary organic aerosol (SOA) formation. Atmos. Chem. Phys. 10, 10521–10539.

Lindsay Smith, J.R., Masheder, D., 1977. Amine oxidation. Part 13. Electrochemical oxidation of some substituted tertiary alkylamines. J. Chem. Soc. Perkin Trans. 2, 1732–1736.

Lindsay Smith, J.R., Mead, L.A. V, 1973. 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.

Loeppky C.J, R.N.M., 1994. Nitrosamines and Related N-Nitroso Compounds, in: ACS Symposium Series.

Love, D.H., 2012. Emissions of amines and their degradation products from post-combustion CO_2 capture, in: Atmospheric Chemical Conference.

Mirvish, S., 1975. Formation of N-nitroso compounds: Chemistry, kinetics, and in vivo occurrence. Toxicol. Appl. Pharmacol. 31, 325–351.

Moser, P., Schmidt, S., Stahl, K., 2011. Investigation of trace elements in the inlet and outlet streams of a MEA-based post-combustion capture process results from the test programme at the Niederaussem pilot plant. Energy Procedia 4, 473–479.

Nielsen, C.J., D'Anna, B., Dye, C., Graus, M., Karl, M., King, S., Maguto, M.M., Müller, M., Schmidbauer, N., Stenstrøm, Y., Wisthaler, A., Pedersen, S., 2011. Atmospheric chemistry of 2-aminoethanol (MEA). Energy Procedia 4, 2245–2252.

NTP, 2012. http://ntp.niehs.nih.gov/go/roc.

Patil, Y.P., Tambade, P.J., Jagtap, S.R., Bhanage, B.M., 2008. Synthesis of 2-oxazolidinones/2-imidazolidinones from CO_2, different epoxides and amino alcohols/alkylene diamines using $Br^-Ph_3^-P$-PEG600-$P^-Ph_3Br^-$ as homogenous recyclable catalys. J. Mol. Catal. A Chem. 289, 14–21.

Pedersen, S., Sjøvoll, M., Fostås, B.F., 2010. Flue gas degradation of amines, in: IEAGHG Workshop.

Petryaev, E.P., Pavlov, A. V, Shadyro, O.I., 1984. Homolytic deamination of amino alcohols. J. Org. Chem. USSR 20, 25–29.

Polderman, L.D., Dillon, C.P., Steele, A.B., 1955. Why monoethanolamine solution breaks down in gas-treating service. Oil Gas J. 53, 180–183.

Rao, A.B., Rubin, E.S., 2002. 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.

Rey, A., Gouedard, C., Ledirac, N., Cohen, M., Dugay, J., Vial, J., Pichon, V., Bertomeu, L., Picq, D., Bontemps, D., Chopin, F., Carrette, P.-L., 2013. Amine degradation in CO_2 capture. 2. New degradation products of MEA. Pyrazine and alkylpyrazines: Analysis, mechanism of formation and toxicity. Int. J. Greenh. Gas Control 19, 576–583.

Reynolds, A.J., Verheyen, T.V.V., Adeloju, S.B., Meuleman, E., Chaffee, A., Cottrell, A.J., Feron, P., 2013. Chemical Characterization of MEA Degradation in PCC pilot plants operating in Australia. Energy Procedia 37, 877–882.

Ridd, J.H., 1961. Nitrosation, diazotisation, and deamination. Q. Rev. Chem. Soc. 15, 418–444.

Rooney, P.C., Dupart, M.S., Bacon, T.R., 1998a. Oxygen's role in alkanolamine degradation. Hydrocarb. Process. 77, 109–113.

Rooney, P.C., Dupart, M.S., Bacon, T.R., 1998b. The role of oxygen in the degradation of MEA, DGA, DEA and MDEA. 48th Laurence Reid gas Cond.Conf. 335–347.

Saavedra, J.., 1981. Deamination of primary aminoalkanols. Formation of substituted N-nitroso-1,3-oxazolidines and N-nitroso-1,3-tetrahydrooxazines. J. Org. Chem. 46, 2610–2614.

Saavedra, J.E., 1985. Reductive alkylation of beta-alkanolamines with carbonyl compounds and sodium borohydride. J. Org. Chem. 50, 2271–2273.

Seinfeld, J.H., 2011. Insights on Global Warming 57, 3259–3284.

Sexton, A.J., 2008. Amine oxidation in carbon dioxide capture processes. Thesis, University of Texas at Austin.

Sexton, A.J., Rochelle, G.T., 2011. Reaction Products from the Oxidative Degradation of Monoethanolamine. Ind. Eng. Chem. Res. 50, 667–673.

Singh, B., Roy, S.K., Sharma, K.P., Goswami, T.K., 1998. Role of acidity of pillared inter-layered clay (PILC) for the synthesis of pyridine bases. J. Chem. Technol. Biotechnol. 71, 246–252.

Smith, P.A.S., Loeppky, R.N., 1967. Nitrosative Cleavage of Tertiary Amines. J. Am. Chem. Soc. 89, 1147–1157.

Snider, M.J., Wolfenden, R., 2000. The rate of spontaneous decarboxylation of amino acids. J. Am. Chem. Soc. 122, 11507–11508.

Steffen, L.K., Glass, R.S., Sabahi, M., Wilson, G.S., Schoeneich, C., Mahling, S., Asmus, K.D., 1991. Hydroxyl radical induced decarboxylation of amino acids. Decarboxylation vs bond formation in radical intermediates. J. Am. Chem. Soc. 113, 2141–2145.

Strazisar, B.R., Anderson, R.R., White, C.M., 2001. Degradation of monoethanolamine used in CO_2 capture from flue gas of a coal-fired electric power generating station. J. Energy Environ. Res. 1, 32–39.

Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Degradation pathways for monoethanolamine in a CO_2 capture facility. Energy and Fuels 17, 1034–1039.

Sun, C., Wang, S., Zhou, S., Chen, C., 2014. SO_2 effect on monoethanolamine oxidative degradation in CO_2 capture process. Int. J. Greenh. Gas Control 23, 98–104.

Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C., 2006. 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.

Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C., 2009. 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 Control 3, 133–142.

Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C., 2011. Mechanism of formation of heat stable salts (HSSs) and their roles in further degradation of monoethanolamine during CO_2 capture from flue gas streams. Energy Procedia 4, 591–598.

Tanthapanichakoon, W., Veawab, A., Mcgarvey, B., 2006. Electrochemical investigation on the effect of heat-stable salts on corrosion in CO_2 capture plants using aqueous solution of MEA. Ind. Eng. Chem. Res. 45, 2586–2593.

Thitakamol, B., Veawab, A., Aroonwilas, A., 2007. 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 Control 1, 318–342.

Uyanga, I.J., Idem, R.O., 2007. 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.

Veldman, R.R., 2000. Alkanolamine Solution Corrosion Mechanisms and Inhibition From Heat Stable Salts and CO_2. Corros. 2000.

Vevelstad, S.J., 2013. CO2 absorbent degradation. Thesis, NTNU at Trondheim.

Vevelstad, S.J., Grimstvedt, A., Einbu, A., Knuutila, H., da Silva, E.F., Svendsen, H.F., 2013a. Oxidative degradation of amines using a closed batch system. Int. J. Greenh. Gas Control 18, 1–14.

Vevelstad, S.J., Grimstvedt, A., Elnan, J., da Silva, E.F., Svendsen, H.F., 2013b. Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation. Int. J. Greenh. Gas Control 18, 88–100.

Voice, A.K., 2013. Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing. Thesis, The University of Texas at Austin.

Voice, A.K., Rochelle, G.T., 2013. Products and process variables in oxidation of monoethanolamine for CO_2 capture. Int. J. Greenh. Gas Control 12, 472–477.

Wang, T., Jens, K.-J., 2011. Oxidative degradation of 2-Amino-2-Methyl-1-Propanol, in: Post-combustion capture conference Abu Dhabi, 1st (Ed.), IEAGHG.

Wang, T.L., 2012. Degradation of Aqueous 2-Amino-2-methyl-1-propanol for Carbon Dioxide Capture. Thesis, Telemark University College.

Wen, H., Narula, R., 2009. Impacts of Carbon Capture on Power Plant Emissions, in: 12th International Post-Combustion Capture Network.

Williams, L.H., 1988. N-Nitrosation. Cambridge University Press, Cambridge, pp. 77–112.

Ye, Q.-G., Zhang, S.-S., 2001. The methyldiethanolamine degradation products in desulphurization process for acid waste gas. Gaoxiao huaxue Gongcheng Xuebao 15, 35–39.

Yu, G., Bayer, A.R., Galloway, M.M., Korshavn, K.J., Fry, C.G., Keutsch, F.N., 2011. Glyoxal in Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects. Environ. Sci. Technol. 45, 6336–6342.

Zhou, S., Wang, S., Chen, C., 2012. Thermal Degradation of Monoethanolamine in CO_2 Capture with Acidic Impurities in Flue Gas. Ind. Eng. Chem. Res. 51, 2539–2547.

Zhou, S., Wang, S., Sun, C., Chen, C., 2013. SO_2 effect on degradation of MEA and some other amines. Energy Procedia 37, 896–904.

Appendix A – Supplementary information for analytical methods and experiments

Appendix – GC parameters

Table A.A.1. Specifications of GC/FID and GC/MS programs

	GC/FID		GC/MS-TOF EI	GC/MS (ESPCI) EI		PCI (methane)	NCI (methane)
Column	CARBOWAX	CPSIL8	CPSIL8	CPSIL8	DBWAX	CPSIL8	CPSIL8
Length	15 m	25 m	30	30 m	30 m	30 m	30 m
Internal diameter	530 µm	320 µm	250 µm	250 µm	250 µm	250 µm	250 µm
Thickness	1.0 µm	1.2 µm	1 µm	1 µm	0,5 µm	1 µm	1 µm
Parameters							
Split ratio	4	30	10 ml.min-1	5	5	5	5
Injected volume	0,2 µl	0,2 µl	0,5 µl	1 µl	1 µl	1 µl	1 µl
Initial temp.	60 °C	35 °C	35 °C	40 °C	40 °C	40 °C	40 °C
Initial hold time	5 min	0 min	0 min	2 min	2 min	2 min	2 min
Oven ramp (1)	5 °C.min^{-1}	3 °C.min^{-1}	3 °C.min^{-1}	7 °C.min^{-1}	7 °C.min-1	7 °C.min^{-1}	7 °C.min^{-1}
Intermediate temp.	75 °C	/	/	130 °C	130 °C	130 °C	130 °C
Oven ramp (2)	8 °C.min^{-1}	/	/	13 °C.min^{-1}	10 °C.min-1	13 °C.min^{-1}	13 °C.min^{-1}
Final temp.	200 °C	230 °C	230 °C	280 °C	200 °C	280 °C	280 °C
Final hold time	11,37 min	15 min	50 min	10 min	7 min	10 min	10 min
Flow rate (constant)	3.9 ml.min^{-1}	1,6 ml.min^{-1}	0,9 ml.min^{-1}	1 ml.min^{-1}	1 ml.min-1	1 ml.min^{-1}	1 ml.min^{-1}
Injector temp.	280 °C	280 °C	230 °C	250 °C	250 °C	250 °C	250 °C
Detector temp.	250 °C	250 °C		280°C	280°C	280°C	280°C
Carrier gas	helium	helium	helium	helium	helium	helium	helium

Appendix – LC/MS/MS parameters

LC device was used with a PGC column PGC having these dimensions: 150 mm x 3 mm, 5 µm-particles. 5 µL of samples were injected.

The mobile phase was a mixture of (A) water with 0.1% formic acid and (B) methanol with 0.1% formic acid at a flow rate of 350 µL/min. A pre-run rinse of 100% A was performed systematically during 8 min. After sample injection, eluent A was maintained from 0 to 10 min then it was changed gradually to 80:20 (A:B v:v) in 8 min and held for 12 min. Total duration of the gradient was 30 min.

A list of targeted compounds with their MRM transition is reported in Table A.2

Table A.2**.** MRM transition of target compounds

Compounds	Parent ion (m/z)	Transitions (m/z)	Collision energy (V)
Oxazolidine	74.3	42.6	5
		56.5	10
Glycine	76.2	30.6	10
		31.6	26
Pyrazine	81.2	54.4	19
		52.4	19
HEEDA	105.2	88.3	10
		70.4	15
DEA	106.0	88.2	11
		70.4	13
HEGly	120.2	74.4	12
		56.4	19
HEIA	131.1	113.2	12
		70.4	19
Glygly	133.1	76.4	8
		115.2	5
BHEEDA	149.2	88.3	13
		70.4	21
BHEU	149.2	62.4	11
		44.6	19
Bicine	164,1	118.2	14
		146.2	12

Chromatogram of these target compounds was presented below, following by the chromatogram of transition.

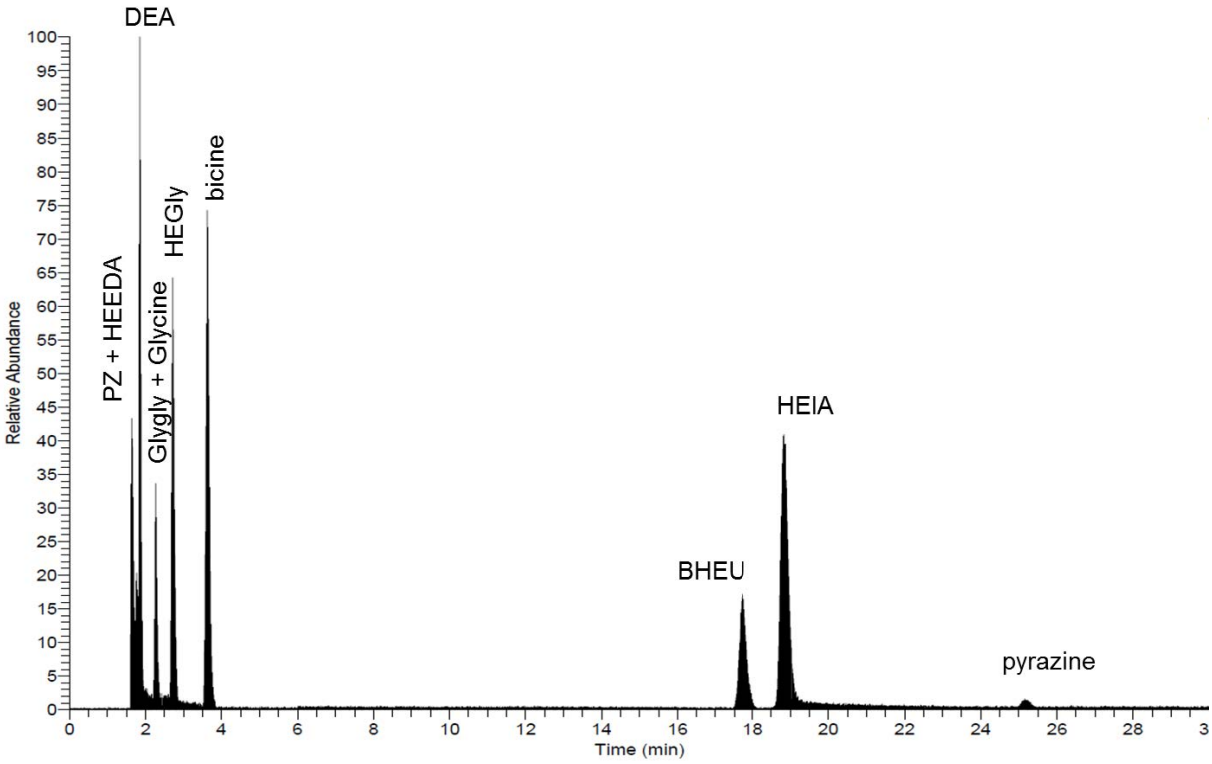


Figure A.1. Chromatogram (LC/MSMS) of a mix of 13 standards (1 mg/L in water) + MEA (100 mg/L)

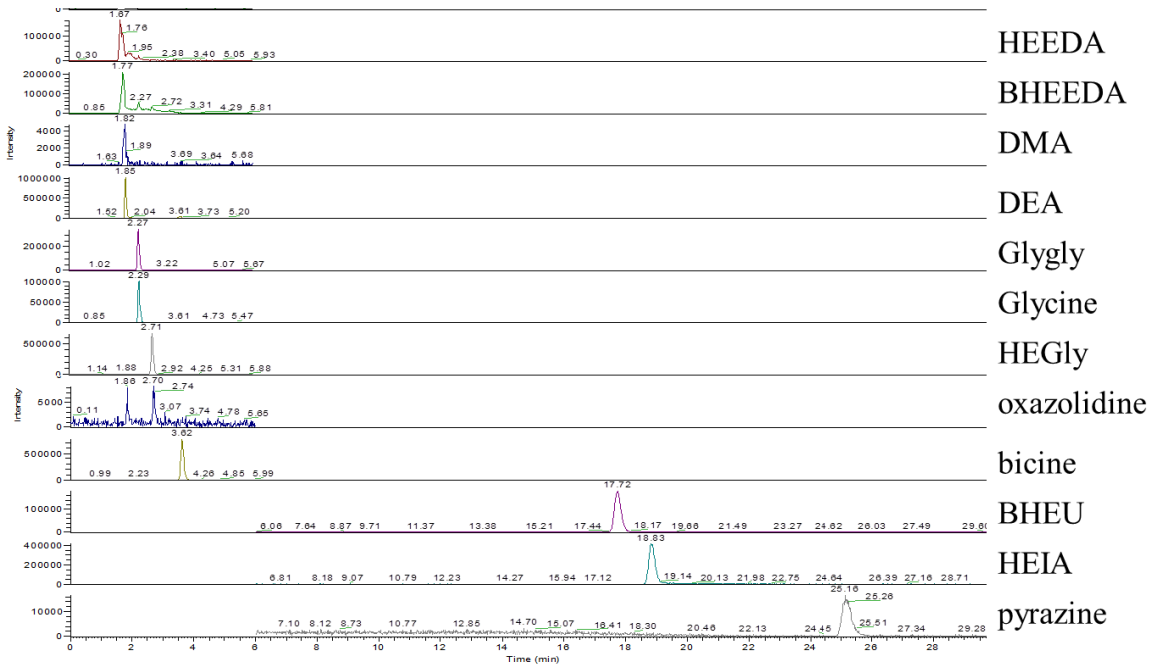


Figure A.2. Chromatograms of transitions (LC-ESI-MSMS) of a mix of 13 standards (1 mg/L in water) + MEA (100 mg/L)

The next table reported MRM transition of a list of targeted nitrosamines. Protocol to use ChemElut cartridges was explained below.

Table A.3. MRM transition of target nitrosamines

Compounds	Parent ion (m/z)	Transitions (m/z)	Collision energy (V)
NPZ	116.3	57.5	15
		86.4	10
NDELA	135.4	74.3	10
		104.4	5
NDMA	75.4	43.7	20
		58.5	20
Nmor	117.3	45.6	22
		86.4	22
NDEA	103.3	29.7	22
		75.5	20
Npip	115.3	41.7	10
		69.5	20

Protocol ChemElut extraction: 3 mL of phosphate buffer (pH = 7.4) were mixed with 250 µL of reaction sample (10-fold dilution). The resulting mixture was adsorbed on ChemElut with 5 min of impregnation, then cartridges were extracted with 8 mL of ethyl acetate (Figure 3.2). After, 100 µL of distilled water were added and the organic solvent evaporated thanks to nitrogen flux gas.

Appendix – List of chemicals

Table A.4. Lists of chemicals

Reagents	Abbreviations	CAS	Mw g/mol	Purity %	suppliers
Acetaldehyde		75-07-0	44	99	Sigma-aldrich
Acetaldoxime		107-29-9	59	98	Sigma-aldrich
Acetic acid		64-19-7	60	99.8	Carlo-Erba
Acetoxime		667463-85-6	73	98	Sigma-aldrich
1-Aminopropan-2-ol	1AP2	78-96-6	75	93	Sigma-aldrich
3-Aminopropan-1-ol	3AP1	156-87-6	75	99	Alfa-aesar
Ammonium formate		540-69-2	63	97	Alfa-aesar
Ammonium hydrogenocarbonate		1066-33-7	79	99	Fluka
Bicine		150-25-4	163	99.5	Fluka
N,N'-bis(2-hydroxyethyl)ethylenediamine	BHEEDA	4439-20-7	148	97	Sigma-aldrich
N,N'-bis(2-hydroxyethyl)oxalamide	BHEOX	1871-89-2	176	99	Alfa-aesar
N,N'-bis(2-hydroxyethyl)urea	BHEU	15438-70-7	148	/	Chemos GMBH
Diethanolamine	DEA	111-42-2	105	99	Sigma-aldrich
Diethyleneglycol	DEG	111-46-6	106	99	Alfa-aesar
2,3-Dimethylpyrazine		5910-89-4	108	99%	Sigma-aldrich
2,5-Dimethylpyrazine		123-32-0	108	99%	Sigma-aldrich
2,6-Dimethylpyrazine		108-50-9	108	99%	Sigma-aldrich

Reagents	Abbreviations	CAS	Mw g/mol	Purity %	suppliers
Ethanolamine	MEA	141-43-5	61	99 et 98 98	Sigma-aldrich Carlo-Erba
Ethyleneglycol	EG	107-21-1	62	99.5	Fluka
2-Ethyl-3-methylpyrazine		15507-23-0	122	99%	Sigma-aldrich
2-Ethyl-5(6)-methylpyrazine		36731-41-6	122	98%	Sigma-aldrich
2-Ethylpyrazine		13925-00-3	108	99%	Sigma-aldrich
Formaldehyde		50-00-0	30	37	Alfa-aesar
Formic acid		64-18-6	46	97	Alfa-aesar
Glycine	Gly	56-40-6	75	99.7	Merck
Glycolic acid		79-14-1	76	99	Sigma-aldrich
Glycylglycine	Glygly	556-50-3	132	99	Alfa-aesar
Glyoxal		107-22-2	58	40	Sigma-Aldrich
Glyoxal bisulfite		517-21-5	266	90	Sigma aldrich
Glyoxylic acid		563-92-2	72	98	Sigma aldrich
N-(2-hydroxyethyl)acetamide	HEA	142-26-7	103	90	Alfa-aesar
N-(2-hydroxyethyl)ethylenediamine	HEEDA	111-41-1	104	99	Sigma-aldrich
N-(2-hydroxyethyl)formamide	HEF	693-06-1	89	97	Alfa-aesar
N-(2-hydroxyethyl)glycine	HEGly	5835-28-9	119	95	Enamine
N-(2-hydroxyethyl)imidazole	HEI	1615-14-1	112	97	Sigma-aldrich
N-(2-hydroxyethyl)imidazolidin-2-one	HEIA	3699-54-5	130	97	Alfa-aesar
N-(2-hydroxyethyl)lactamide	HEL	5422-34-4	133	/	Sigma-aldrich

Reagents	Abbreviations	CAS	Mw g/mol	Purity %	suppliers
N-(2-hydroxyethyl)-2-methylimidazole	HEMI	1615-15-2	126	/	Sigma-aldrich
1-(2-Hydroxyethyl)piperazinone hydrochloride	1HEPO	59702-23-7	180	/	BBV
4-(2-Hydroxyethyl)piperazinone	4HEPO	23936-04-1	144	/	Tyger
N-(2-hydroxyethyl)propanamide	HEPr	18266-55-2	117	/	Sigma-aldrich
N-(2-hydroxyethyl)pyrrole	HEPyr	6719-02-4	111	99	TCI
N-(2-hydroxyethyl)succinimide	HESucc	18190-44-8	143	95	Alfa-aesar
N-methylaminoethanol	MAE	109-83-1	75	98	Sigma-aldrich
2-Methyloxazoline		1120-64-2	85	99%	Alfa-aesar
2-Methylpyrazine		109-08-0	94	99%	Sigma-aldrich
3-Methylpyridine		108-99-6	93	99	Alfa-aesar
N-nitrosodiethanolamine	NDELA	1116-54-7	134	90	Sigma-aldrich
N-nitrosdimethylamine	NDMA	62-75-9	74	5000ug/ml in methanol	Sigma-aldrich
N-nitrosomorpholine	NMOR	59-89-2	116	5000ug/ml in methanol	Sigma-aldrich
N-nitrosopiperazine	NPz	5632-47-3	115	/	Sigma-aldrich
Oxalic acid		144-62-7	90	97	Fluka
Oxazolidine		504-76-7	73	/	Selectlab
Oxazolidin-2-one	OZD	497-25-6	87	99	Alfa-aesar
Oxazoline		504-77-8	71	96	Interchim
Piperazin-2-one	PO	5625-67-2	100	97	Alfa-aesar

Reagents	Abbreviations	CAS	Mw g/mol	Purity %	suppliers
Propanaloxime		627-39-4	73	96	Sigma-aldrich
Propionic acid		79-09-4	74	99	Sigma-aldrich
Pyrazine		290-37-9	80	≥ 99%	Sigma-aldrich
Pyruvic acid		127-17-3	88	97	Sigma-aldrich
Pyrrole		109-97-7	67	98	Sigma-aldrich
Sodium sulphate		7757-82-6	142	99	Sigma-aldrich
2,3,5-Trimethylpyrazine		14667-55-1	122	≥ 99%	Sigma-aldrich
Triethyleneglycol	TEG	112-27-6	150	99	Fluka
2-Vinylpyrazine		4177-16-6	106	≥ 97%	Sigma-aldrich
2,3,5,6-Tetramethylpyrazine		1124-11-4	136	98	alfa

Appendix – Experiments protocol

The following table summarized chemical conditions for experiments made in oven cited in this work. Then detailed protocols for others experiments were reported.

Table A.5. Chemical conditions of oven experiments

Names	Reagent 1	Other reagents	T °C	t
S1	MEA (10 % w) 1 eq	Glycolic acid 1 eq	100	15 d
S2	MEA (10 % w) 1 eq	Oxalic acid 1 eq	100	15 d
S3	MEA (3% w) 2 eq	HEGly 1eq	100	15 d
S4	MEA (30%w) 1 eq	Glyoxal 1 eq	80	15 d
S5	MEA (30%w) 1 eq	Glyoxylic acid 1 eq	70	15 d
S6	MEA (10 % w) 1 eq	Glyoxal bisulfite 1 eq	85	40 min
S7	MEA (30%w) 1 eq	Formaldehyde 1 eq	70	15 d
S8	HEGly (3%w)		100	15 d
S10	MEA (30%w) 1 eq	Glyoxal + Ammonium formate 1 eq 1 eq	85	15 d
S11	MEA (30%w) 1 eq	Ethyleneglycol 1 eq	100	15 d
S12	HEEDA (30%w) 1 eq	Ethyleneglycol 1 eq	100	15 d
S13	HEEDA (30%w) 1 eq	Glyoxal 1 eq	85	15 d
S14	HEGly (3%w) 1 eq	OZD 1 eq	100	15 d
S17	MEA (30%w) 2 eq	Glyoxal 1 eq	RT	15 d
S18	MEA (30%w) 1 eq	Pyruvic acid + Ammonium formate 1 eq 1 eq	85	15 d
S21	MEA (30%w) 1 eq	Formic acid 1 eq	70	15 d
S22	MEA (30%w) 1 eq	Acetic acid 1 eq	70	15 d
S23	HEF (1%w)		85	3 d
S24	HEA (30%w)		100	15 d
S25	MEA (30%w) 1 eq	Acetaldehyde 1 eq	70	15 d
S27	MEA (30%w) 1 eq	Acetaldehyde + formaldehyde 1 eq 2.5 eq	RT	15 d
S28	OZD (30%w) 1 eq	Glycine 1 eq	100	15 d

S9 and S16: Protocol issued of Arduengo et al., 2001.

Formaldehyde or acetaldehyde (1.5 mL or 0.75 g (17 mmol)) were diluted in 4 mL of methanol. A solution of 4.86 mol/L of MEA in methanol (4 mL) was added at 0°C. Then, 1.58 g of ammonium hydrogen carbonate (20 mol) was added with 10 mL of methanol. Finally, glyoxal (40 % in water, 1.92 g, 13.2 mmol) was introduced. The resulting mixture was stirred one night at room temperature.

S19: Pure MEA (30 mL, 501 mmol) was introduced in a three necks round-bottom flask. Then acrylic acid (1.38 mL, 20 mmol) was added slowly to avoid quick increase of temperature. The resulting reaction mixture was followed by ^{1}H and ^{13}C NMR. To accelerate the reaction after 1 hour, the mixture was heated up to 70°C during 2 days, then to 120°C during one day.

S26: Protocol adapted to Eiter et al., 1972 and Saavedra, 1981

First MEA (0.530 g, 8.7 mmol) was diluted in 32 mL of acidified water (16 mL of water with 16 mL of glacial acetic acid, pH < 5) in a three necks round-bottom flask. Then, acetaldehyde (450 µL, 8.2 mmol) was added to this solution at 0°C. Finally, a solution of 3.33 mol/L $NaNO_2$ (1.15 g in 5 mL of water) was introduced. The resulting reaction mixture was stirred at room temperature during 2 hours.

S15: In glass reactor, MEA (15.07 g, 247 mmol) was mixed with glyoxal (40% in water, 37.29 g, and 257 mmol) in water (81.3 g, i.e. MEA at 13 wt. % in water). This mixture was stirred during 3 hours at room temperature then acetaldehyde (13.5 mL, 245 mmol) was added. Flow gas of air was adjusted to 7NL/h after 1 hour. Solution was stirred during 21h then heated up to 80°C during 3 days.

S20: In glass reactor, HEEDA (31.29 g, 300 mmol) was mixed with glyoxal (40 % in water, 43.51 g, 300 mmol) in water (104 g, i.e. HEEDA at 23 wt. %). Solution was stirred with a flow gas of 7 NL/h of N_2 and 0.033 NL/h of CO_2 at 80°C during 7 days.

Appendix B – Chromatograms, NMR spectra and mass spectra of products

Appendix – Chromatograms

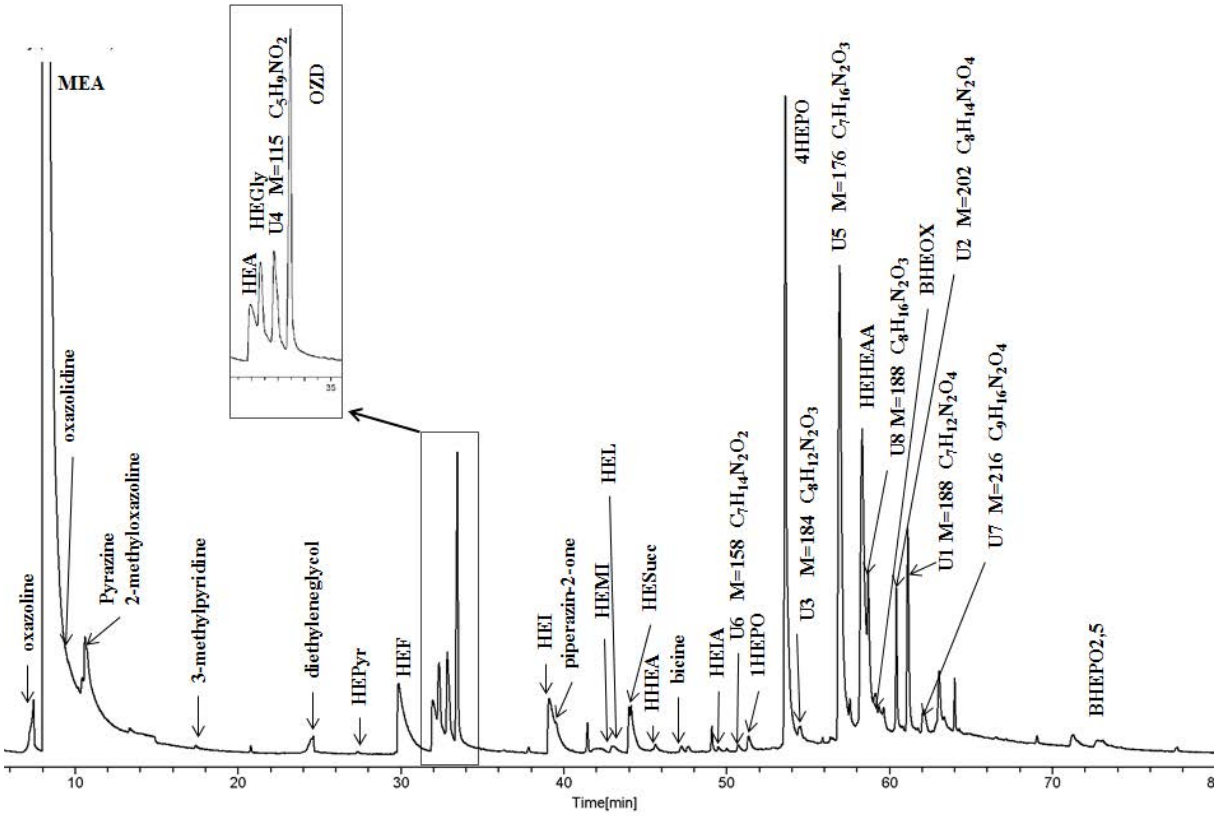


Figure B.1. Chromatogram Scan (GC/MS/TOF) of a liquid sample from pilot plant with CPSIL8

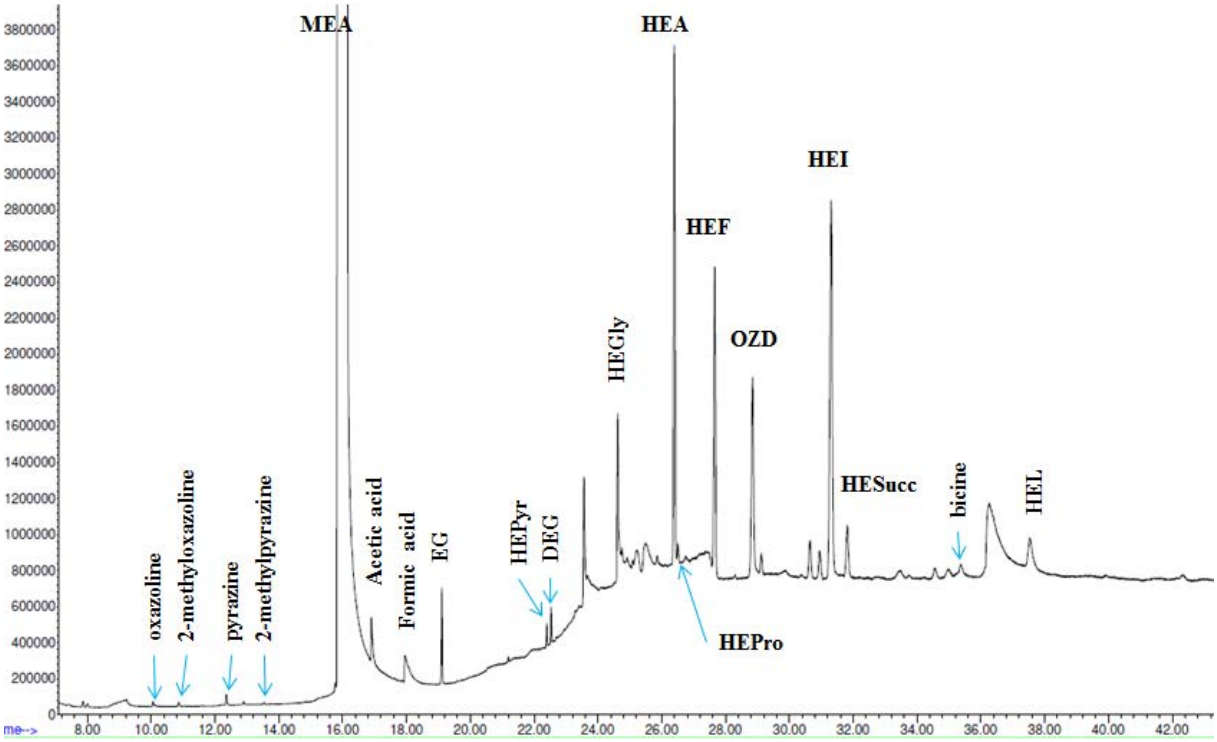


Figure B.2. Chromatogram Scan (GC-EI-MS) of a liquid sample from pilot plant with DBWAX.

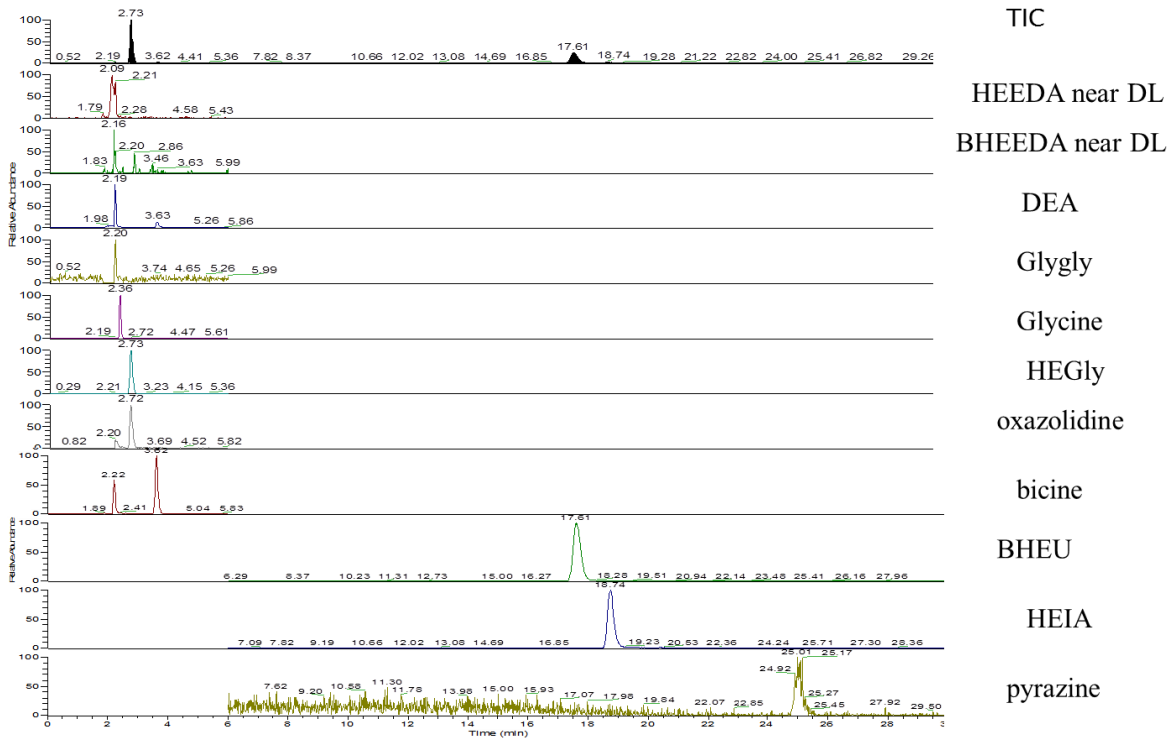


Figure B.3. Chromatogram (LC/MSMS) of liquid sample from pilot plant (100-folds diluted)

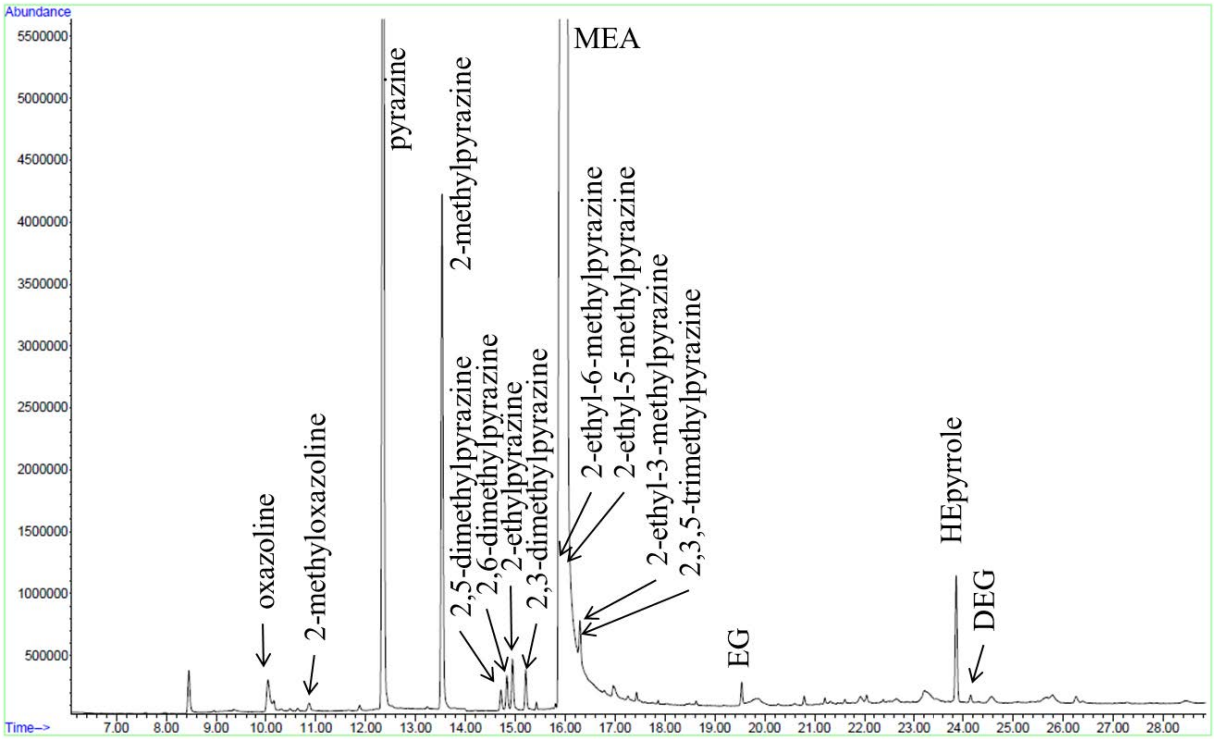


Figure B.4. Chromatogram (HS-SPME-GC-EI-MS) of pilot plant sample with DBWAX

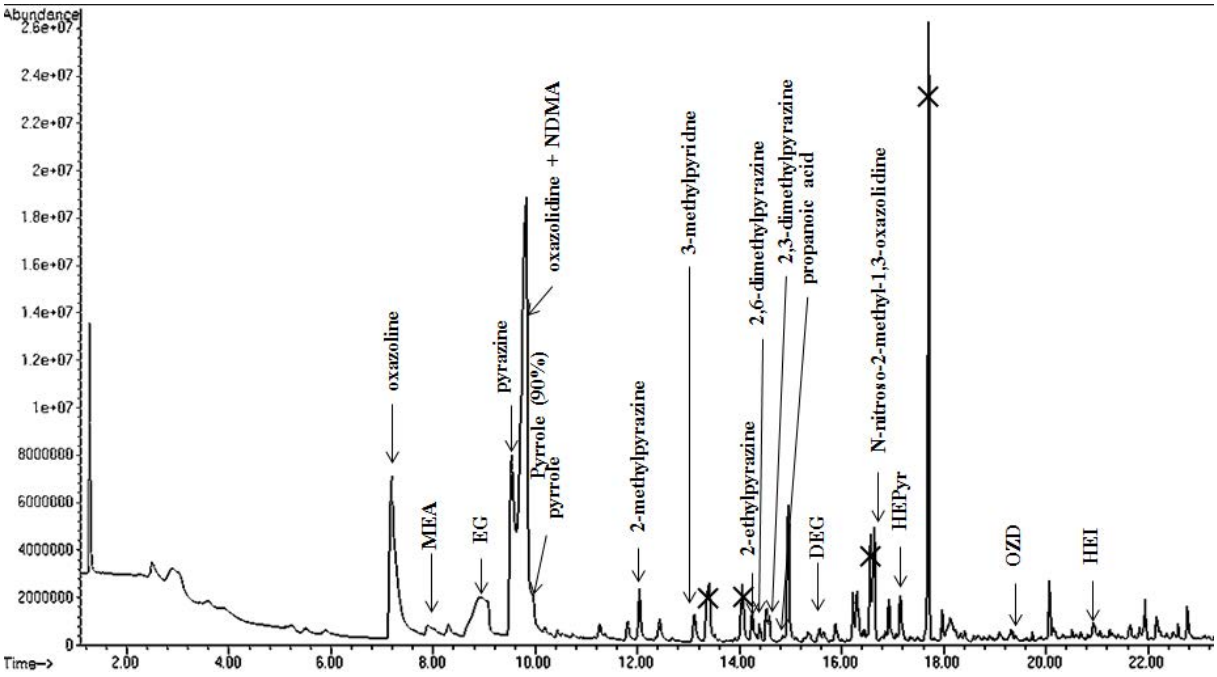


Figure B.5. TENAX Chromatogram with CPSIL8 from pilot plant (C2) after 1600 hours

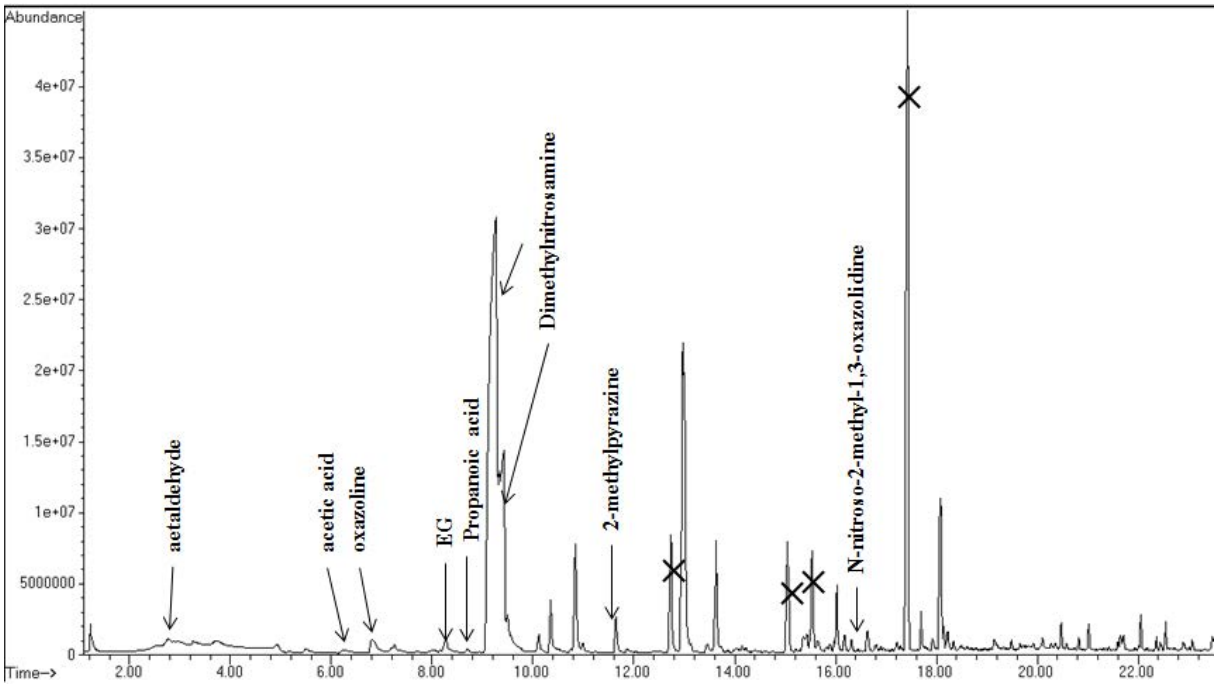


Figure B.6. TENAX Chromatogram with CPSIL8 from pilot plant (C2) after 1000 hours

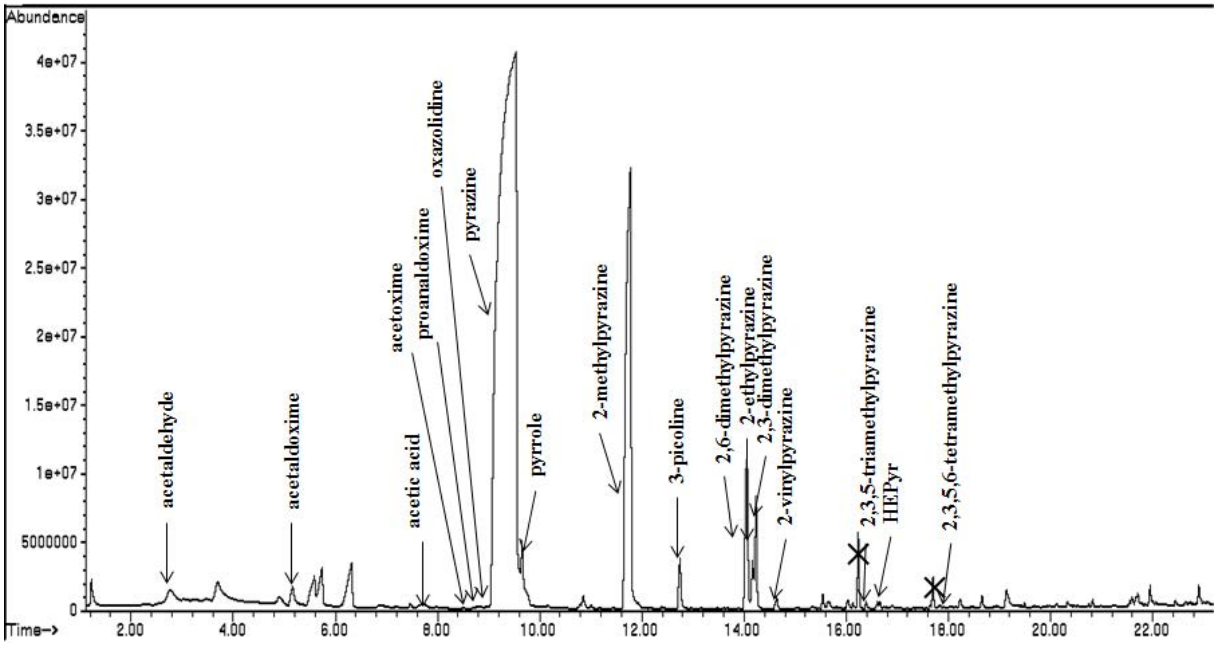


Figure B.7. TENAX Chromatogram with CPSIL8 from lab test

Adsorption on TENAX is a very sensitive method to catch compounds. However, on each chromatogram, pollutions were observed. They came from atmosphere (others plants near to IFPEN one) or from TENAX phase. Indeed, some authors observed phase degradation of TENAX with oxidant gases (presence of O_2, NO_x …) (Dettmer and Engewald, 2002), which was our case. Therefore, analyses of these cartridges should be made with precaution. In our case, only products with a realistic mechanism were reported.

Appendix – HHEA identification

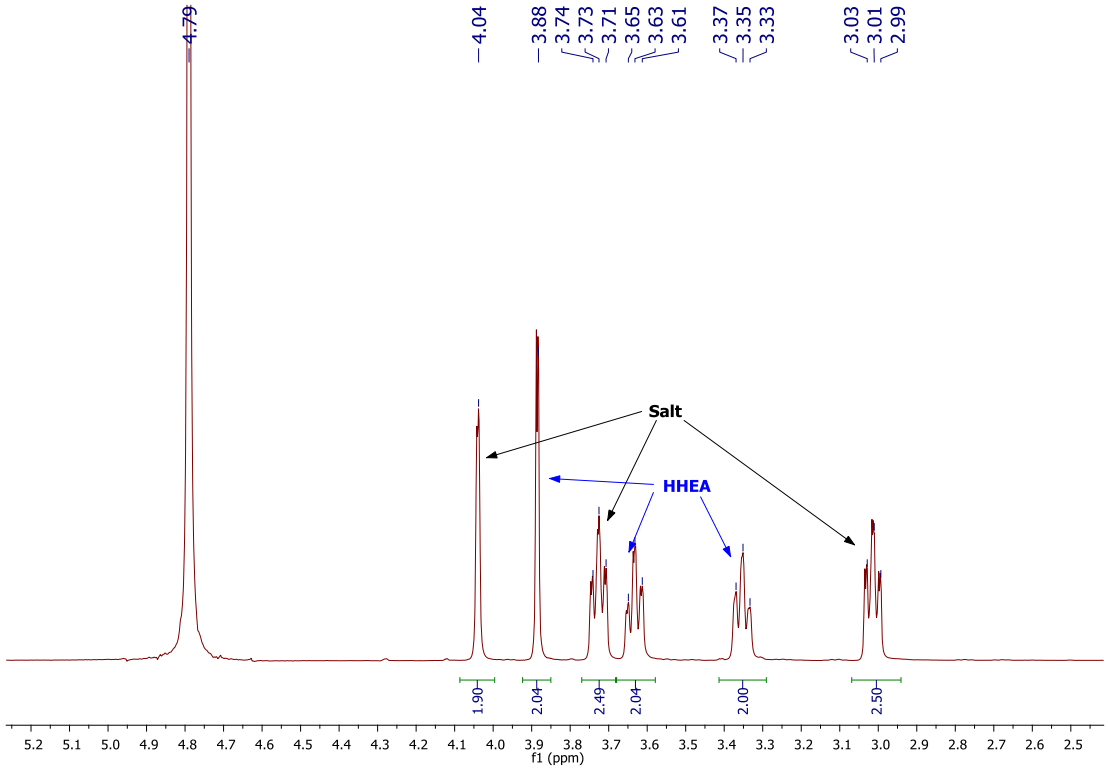


Figure B.8. NMR ^{1}H of S1 in D_2O

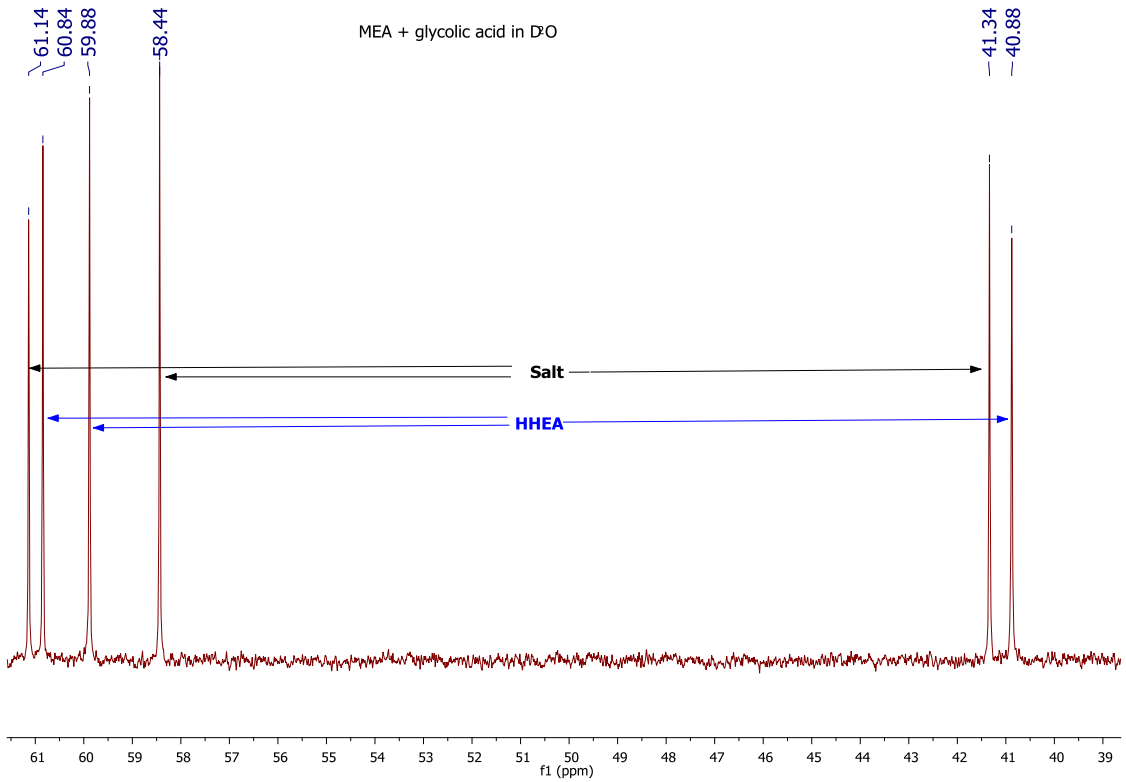


Figure B.9. NMR ^{13}C of S1 in D_2O

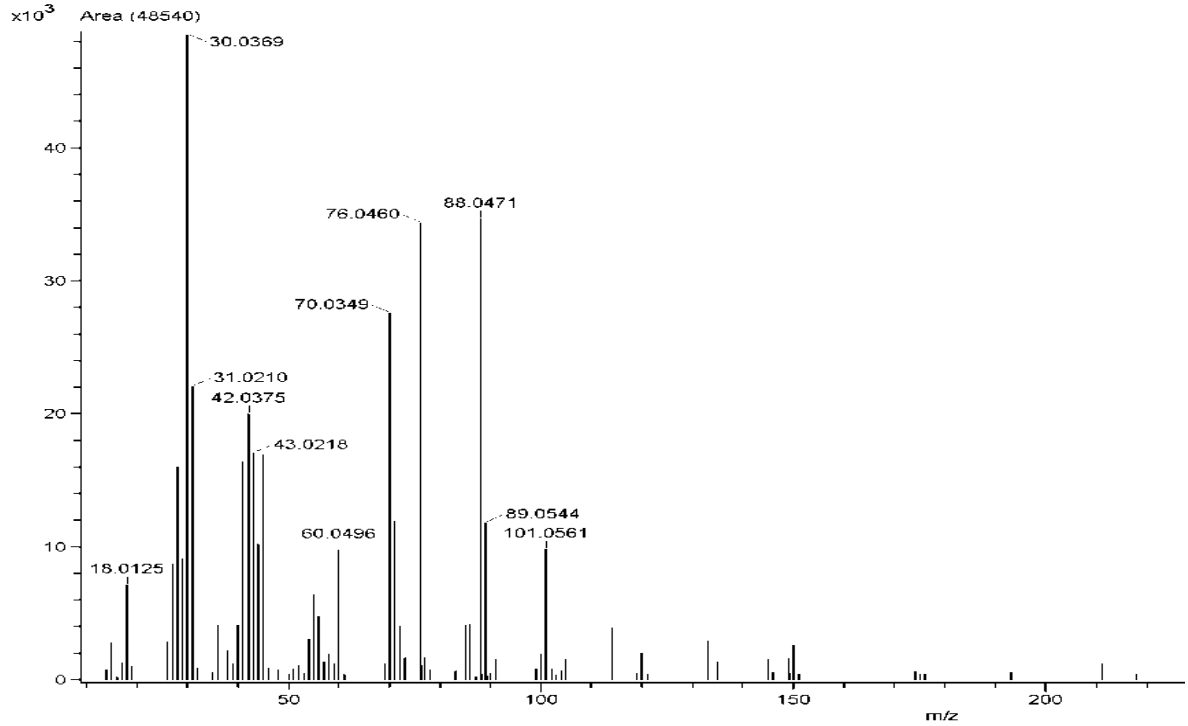


Figure B.10. Mass spectrum of HHEA in S1 (M = 119 g.mol^{-1}, rt = 45.5 min, GC/MS TOF)

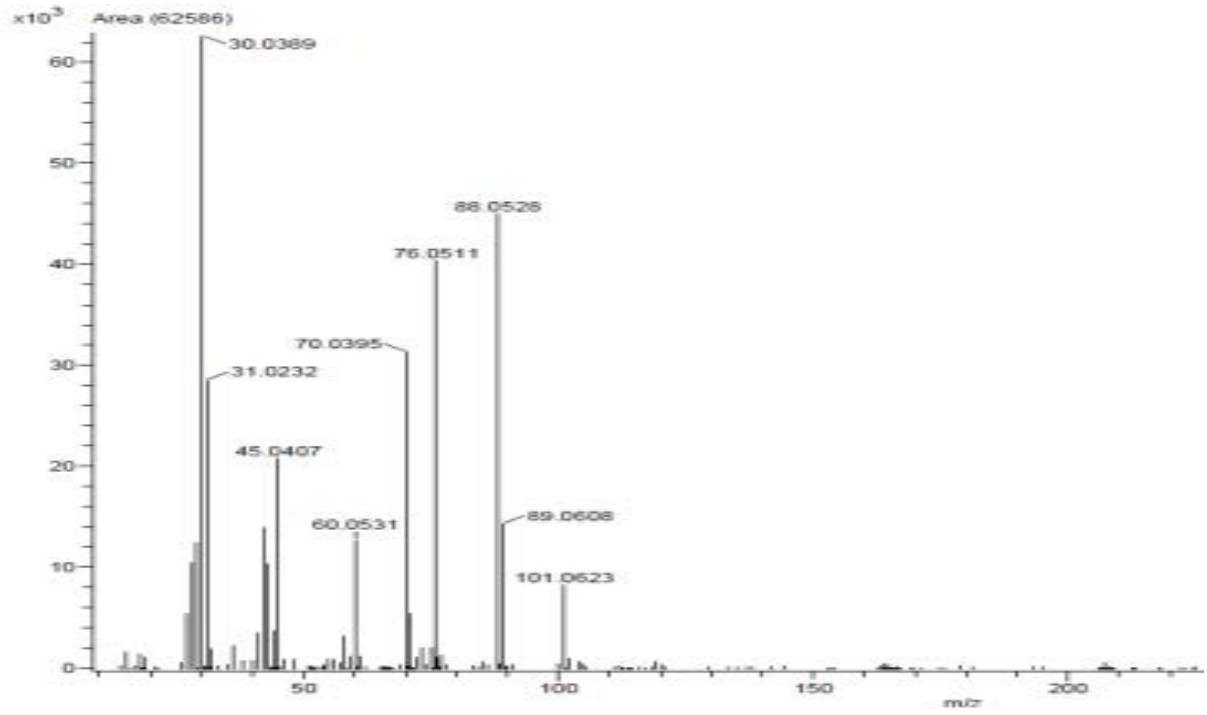


Figure B.11. Mass spectrum of HHEA in pilot plant (M = 119 g.mol^{-1}, rt = 45.1 min GC/MS-TOF

Appendix – HEOX identification

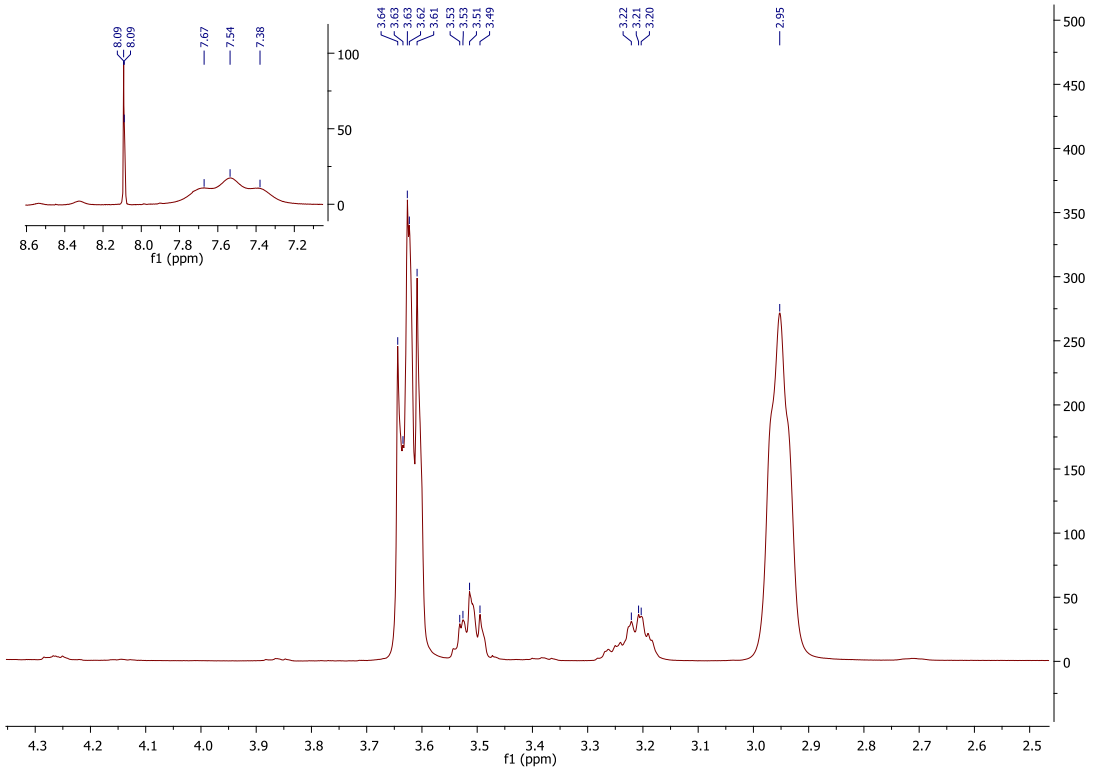


Figure B.12. NMR ^{1}H of S2 in D_2O

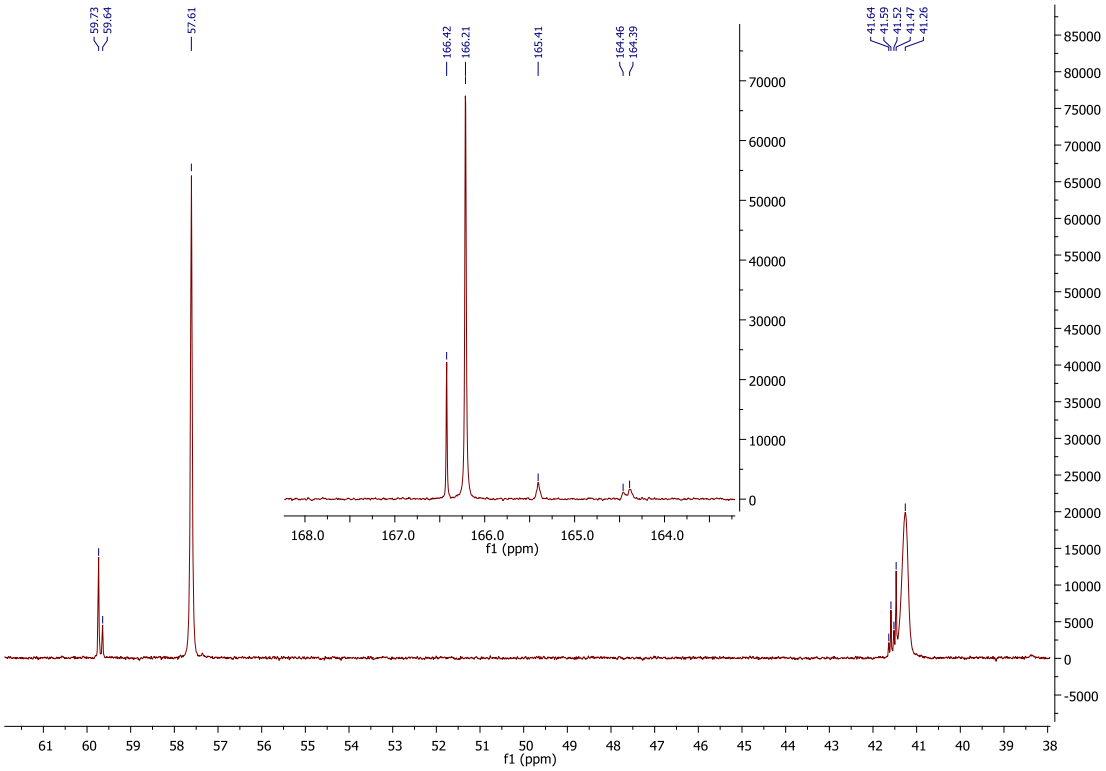


Figure B.13. NMR ^{13}C of S2 in D_2O

Appendix – HEHEAA identification

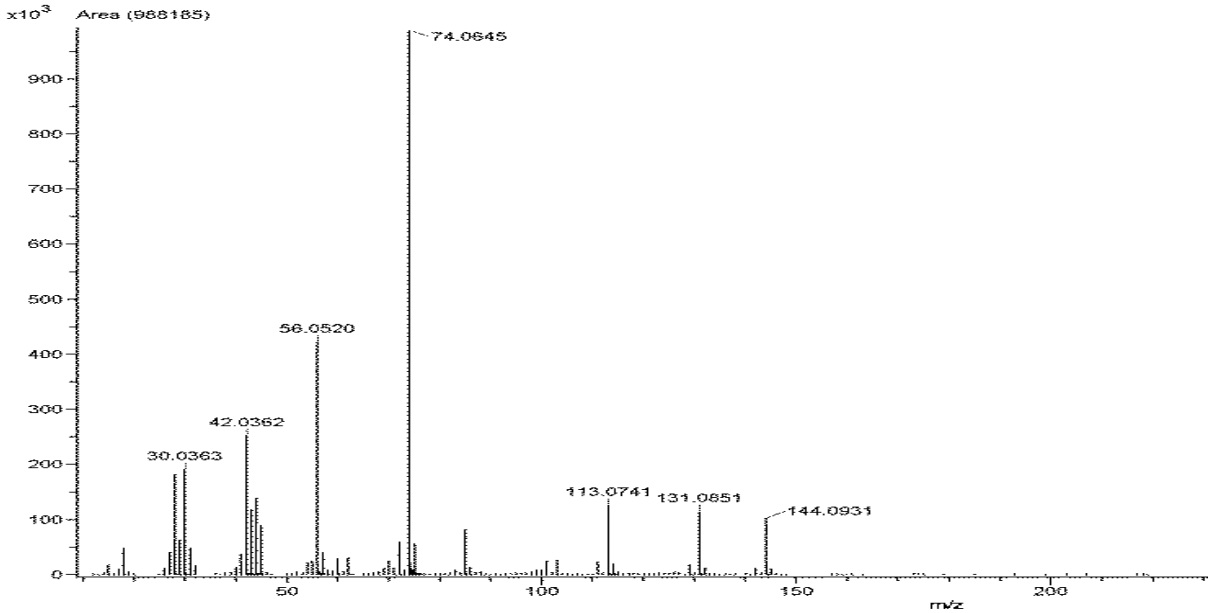


Figure B.14. Mass spectrum of S3 at 58.06 min

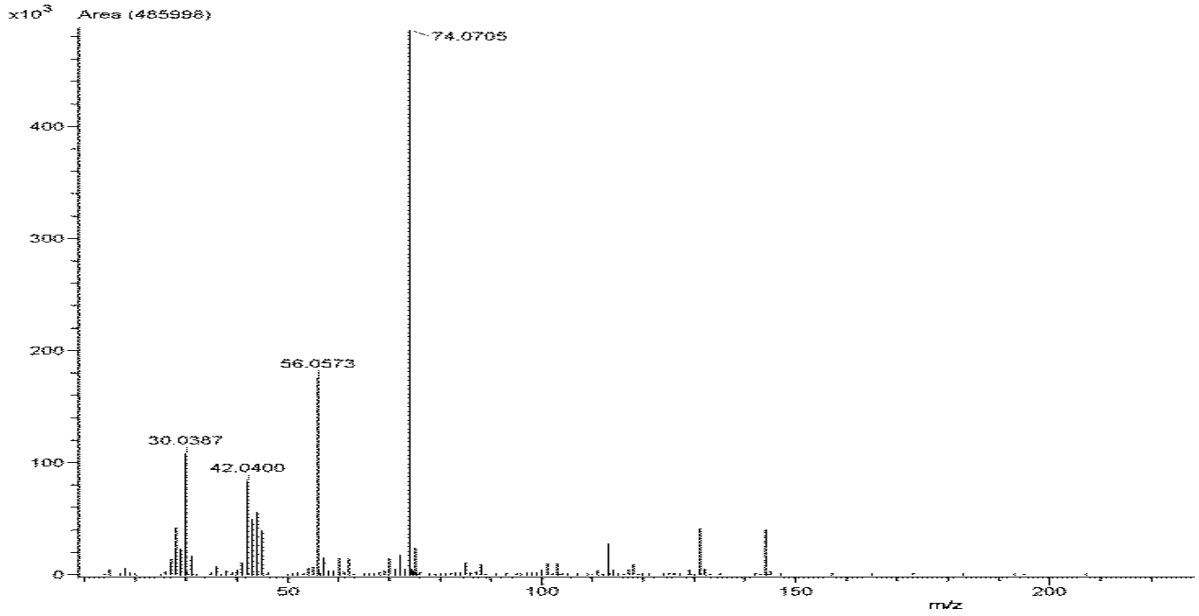


Figure B.15. Mass spectrum of pilot plant at 58.22 min

Appendix – BHEPDO2,5 identification

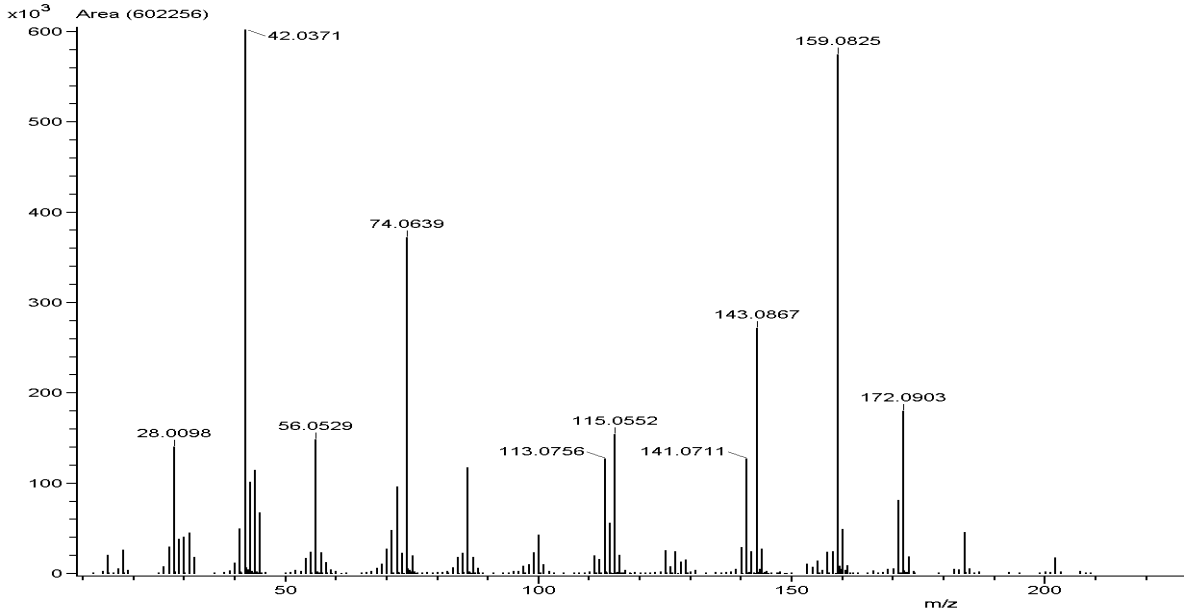


Figure B.16. Mass spectrum of major peak for S8 at 71.6 min (BHEPDO2,5)

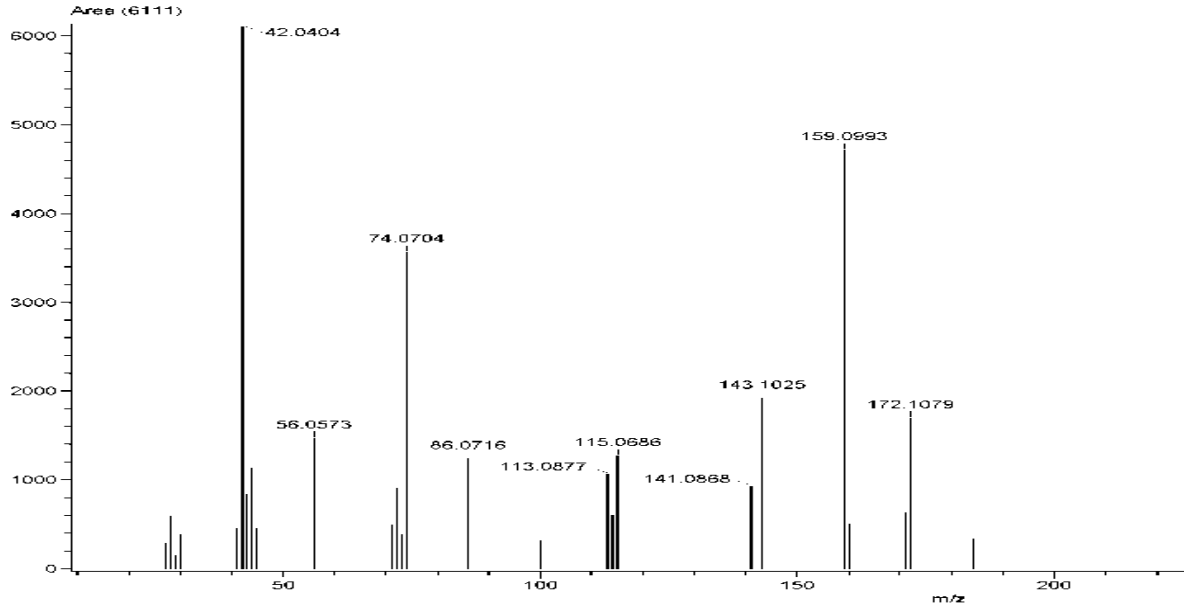


Figure B.17. Mass spectrum of pilot plant at 72.6 min

Appendix – 2-methyloxazolidine identification

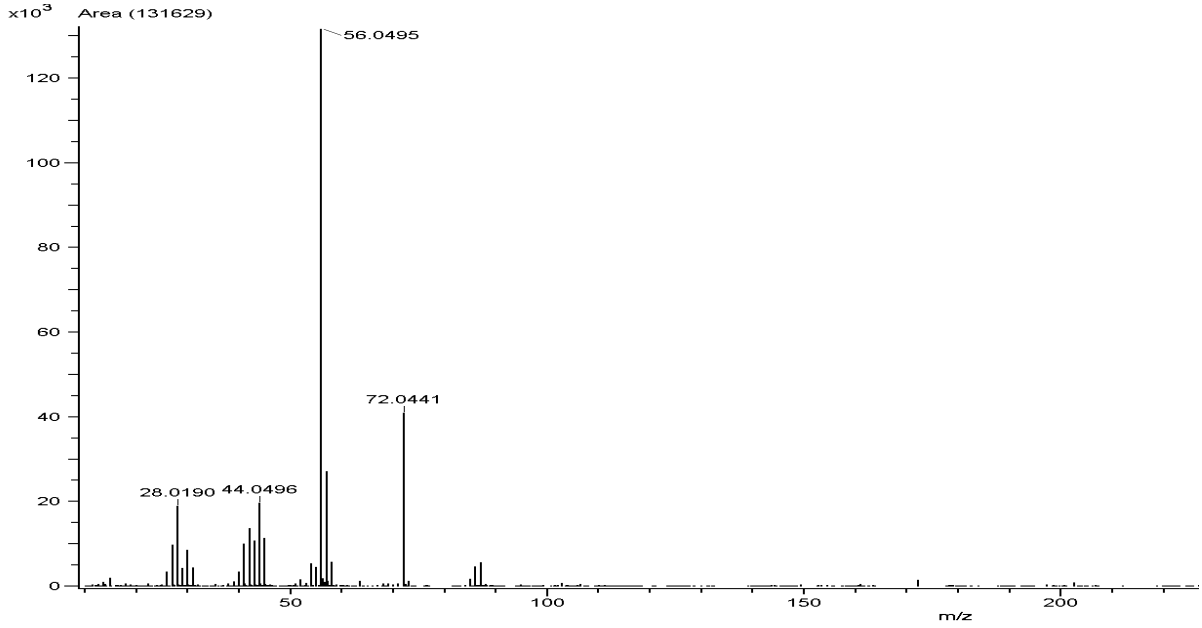


Figure B.18. Mass spectrum of S25 at 9.61 min

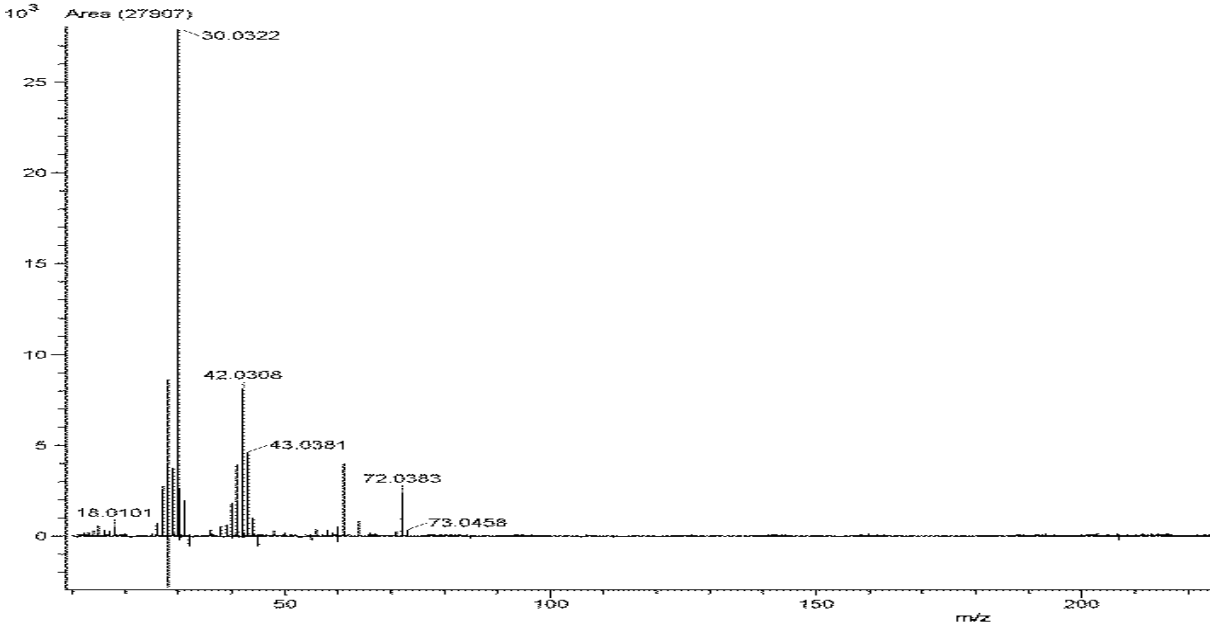


Figure B.19. Mass spectrum of pilot plant at 9.58 min

Appendix – N-nitroso-2-methyloxazolidine identification

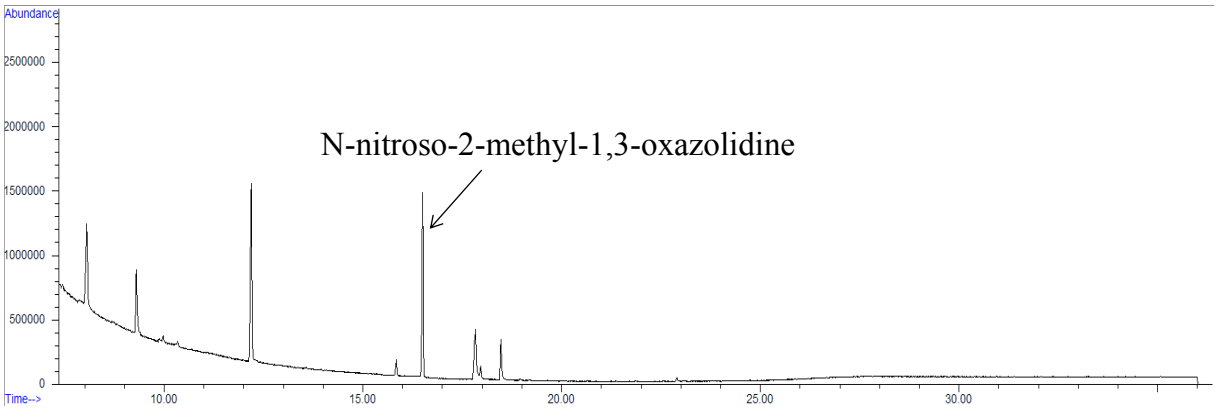


Figure B.20. chromatogram of S28

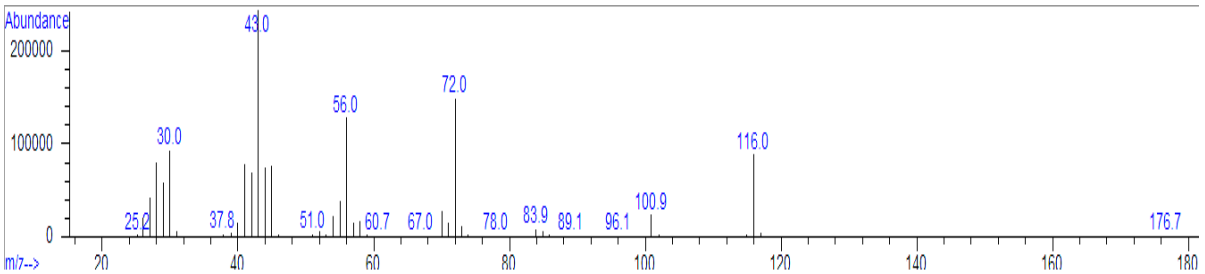


Figure B.21. Mass spectrum of major peak for S28 at 16.8 min

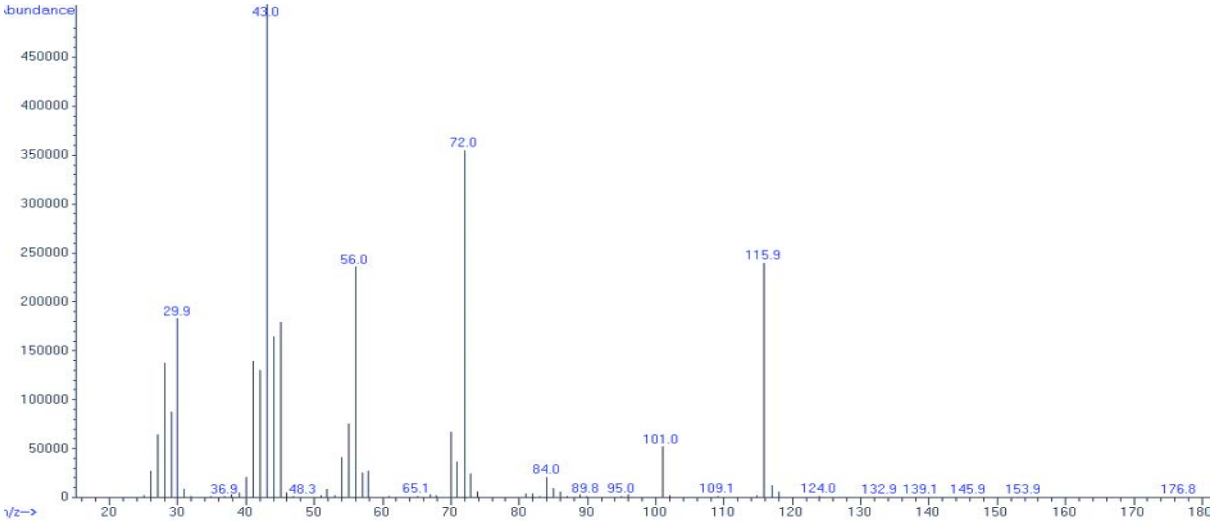


Figure B.22. Mass spectrum on TENAX cartridges at 16.9 min

Appendix – GC/MS-TOF mass spectra of unidentified products

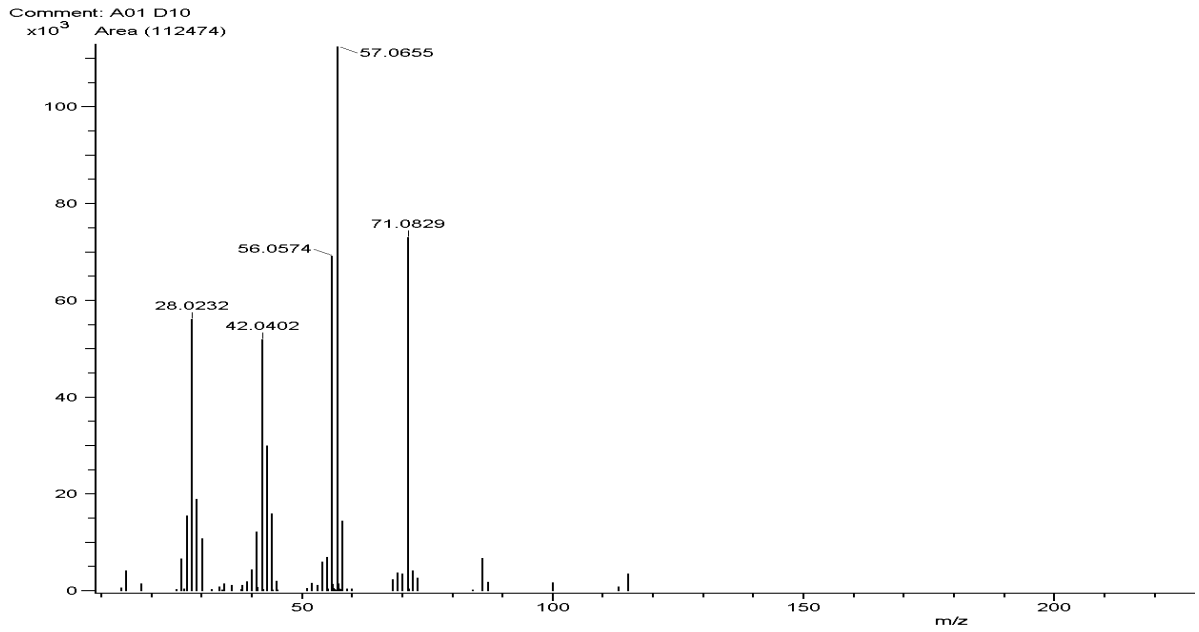


Figure B.23. Mass spectrum of U4 at 32.8 min (M = 115 g/mol)

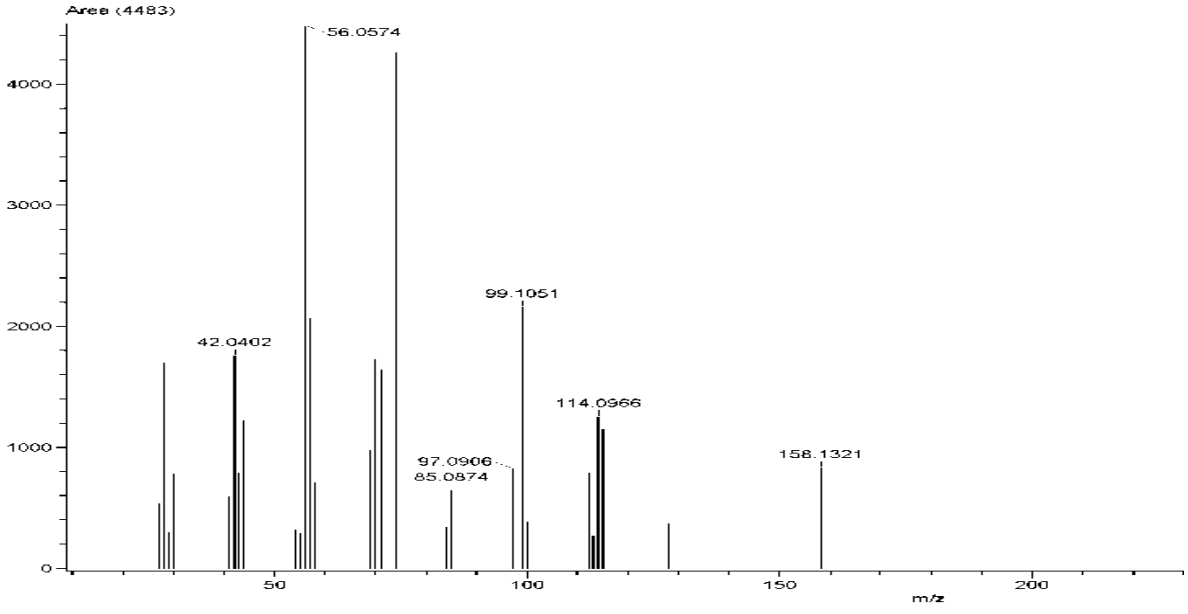


Figure B.24. Mass spectrum of U6 at 50.6 min (M = 158 g/mol)

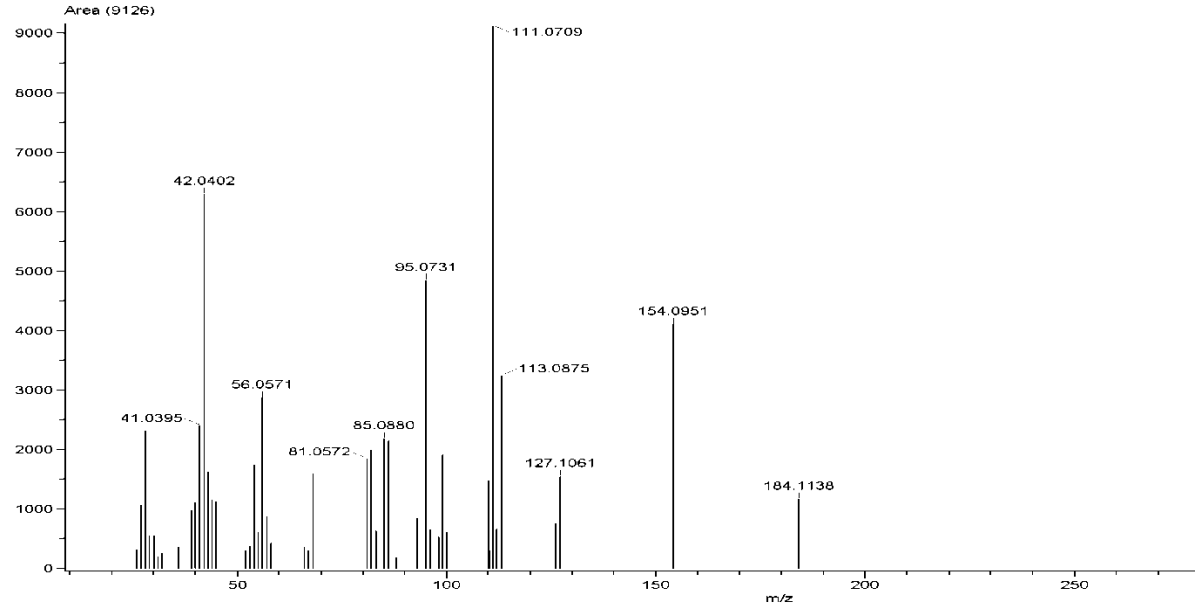


Figure B.25. Mass spectrum of U3 at 53.6 min (M = 184 g/mol)

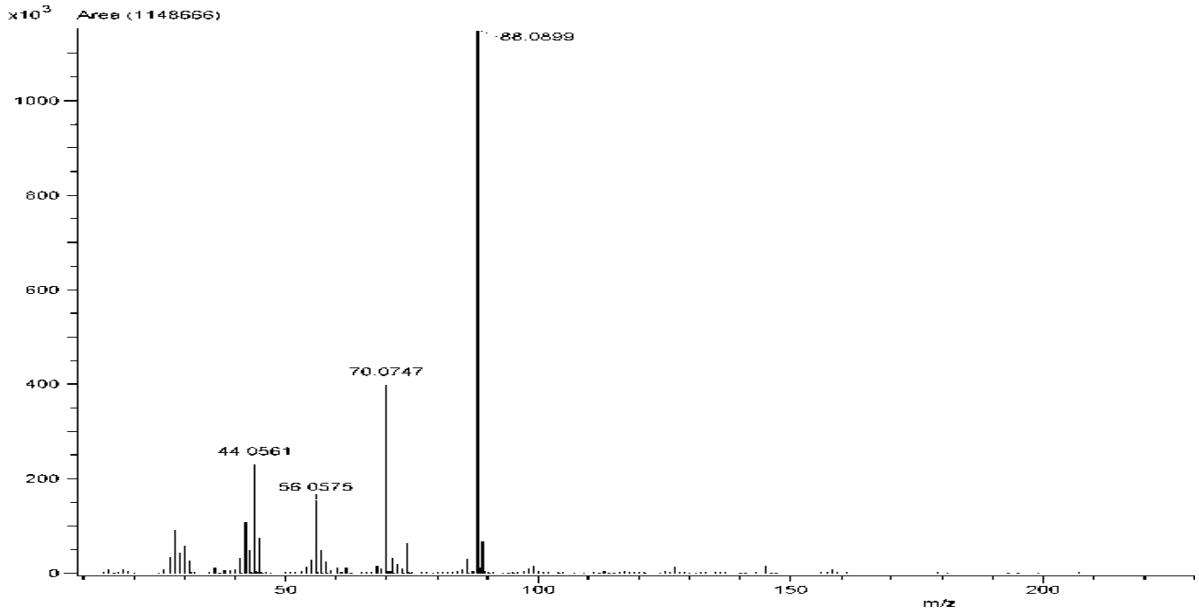


Figure B.26. Mass spectrum of U5 at 56.8 min (M = 176 g/mol)

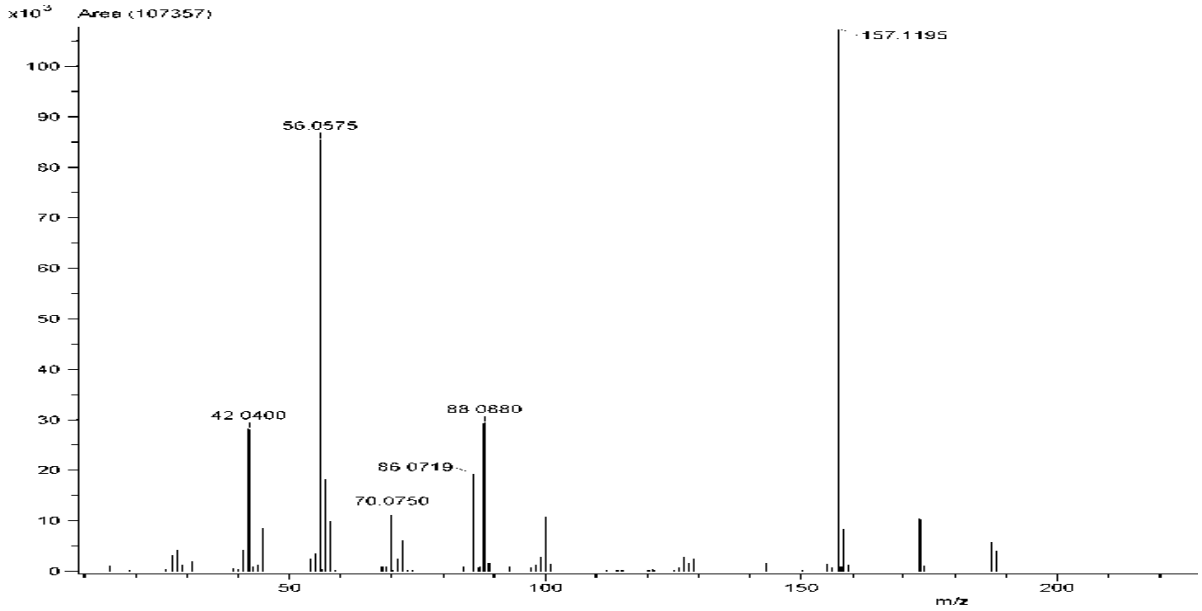


Figure B.27. Mass spectrum of U8 at 58.7 min (M = 188 g/mol)

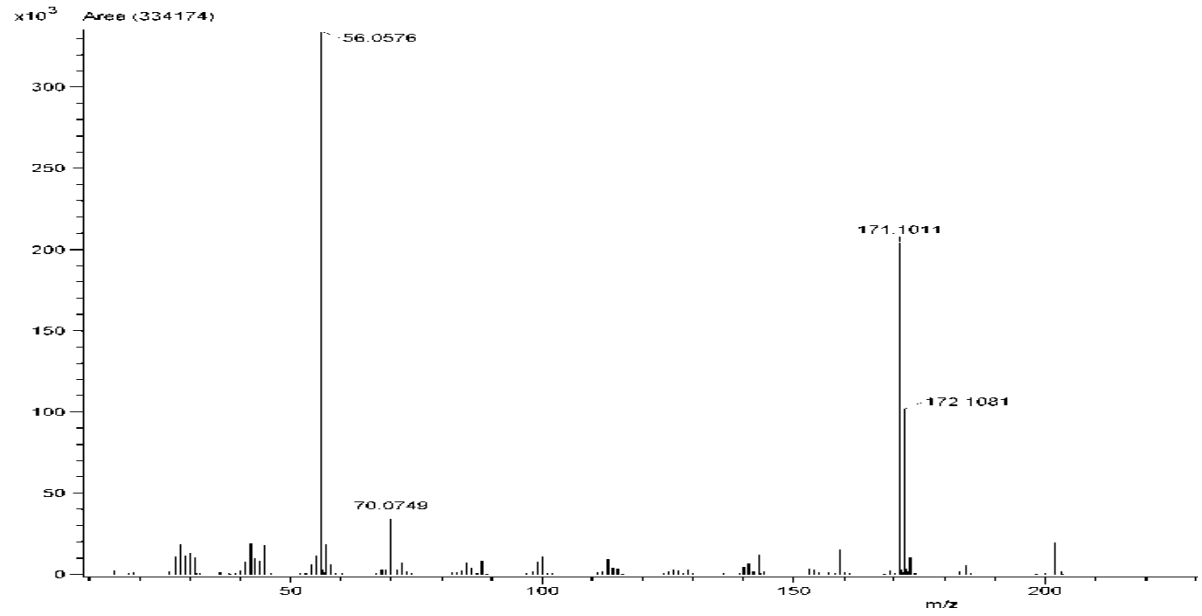


Figure B.28. Mass spectrum of U2 at 61.0 min (M = 202 g/mol)

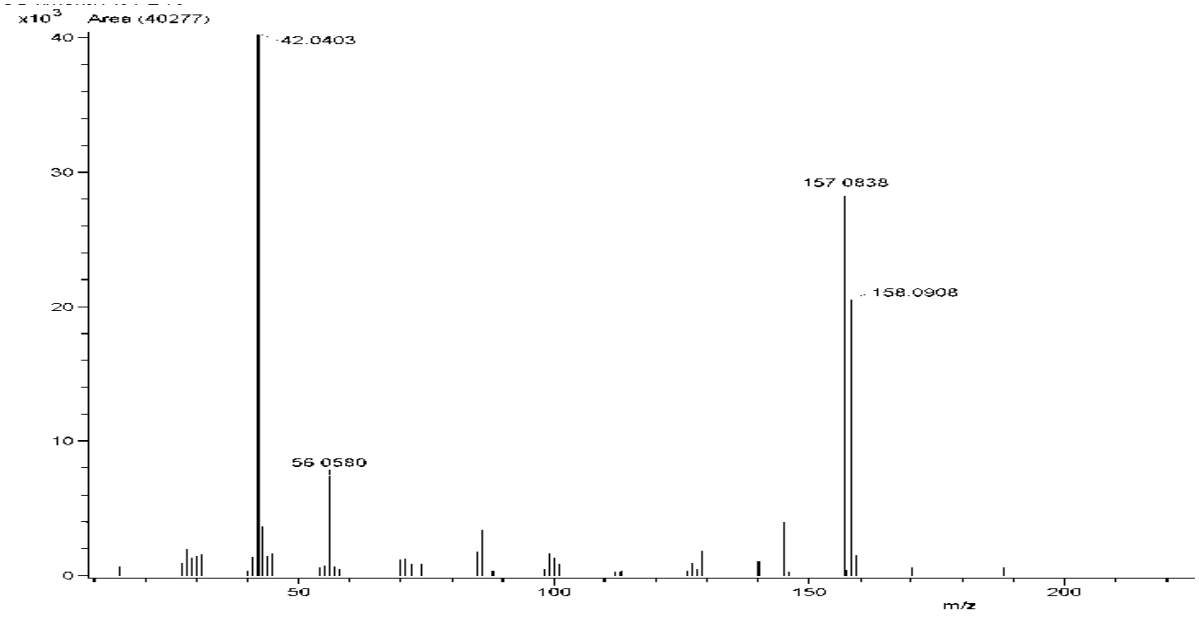


Figure B.29. Mass spectrum of U1 at 62.1 min (M = 188 g/mol)

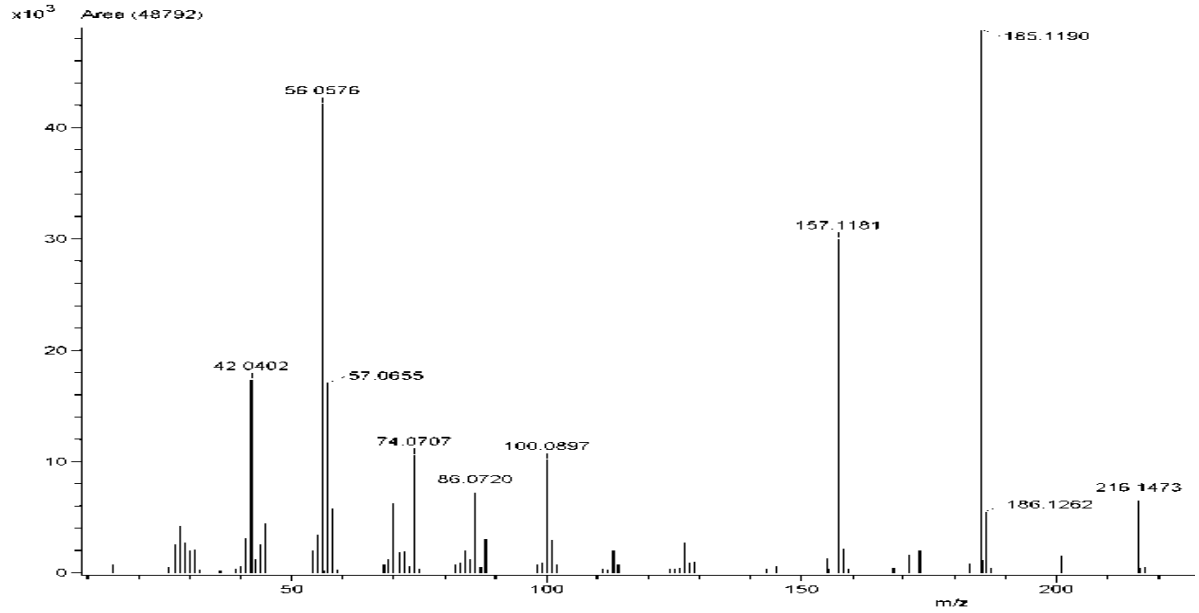


Figure B.30. Mass spectrum of U1 at 63.0 min (M = 216 g/mol)

Appendix – Pyrazines identification

Table B.1. Pyrazine and alkyl pyrazines studied standards, with the selected ion for detection in MS SIM mode and their retention times on both columns.

pyrazines	MW (g/mol)	m/z	RT (min)	
			CPSIL8	DBWAX
pyrazine	80	80	9.3	12.4
2-methylpyrazine	94	94	11.9	13.6
2,5-dimethylpyrazine	108	108	14.3	14.7
2,6-dimethylpyrazine	108	108	14.3	14.8
2-ethylpyrazine	108	107	14.4	14.9
2,3-dimethylpyrazine	108	67	14.5	15.2
2-ethyl-6-methylpyrazine	122	121	16.4	15.9
2-ethyl-5-methylpyrazine	122	121	16.5	16.1
2,3,5-trimethylpyrazine	122	42	16.5	16.3
2-ethyl-3-methylpyrazine	122	121	16.5	16.3

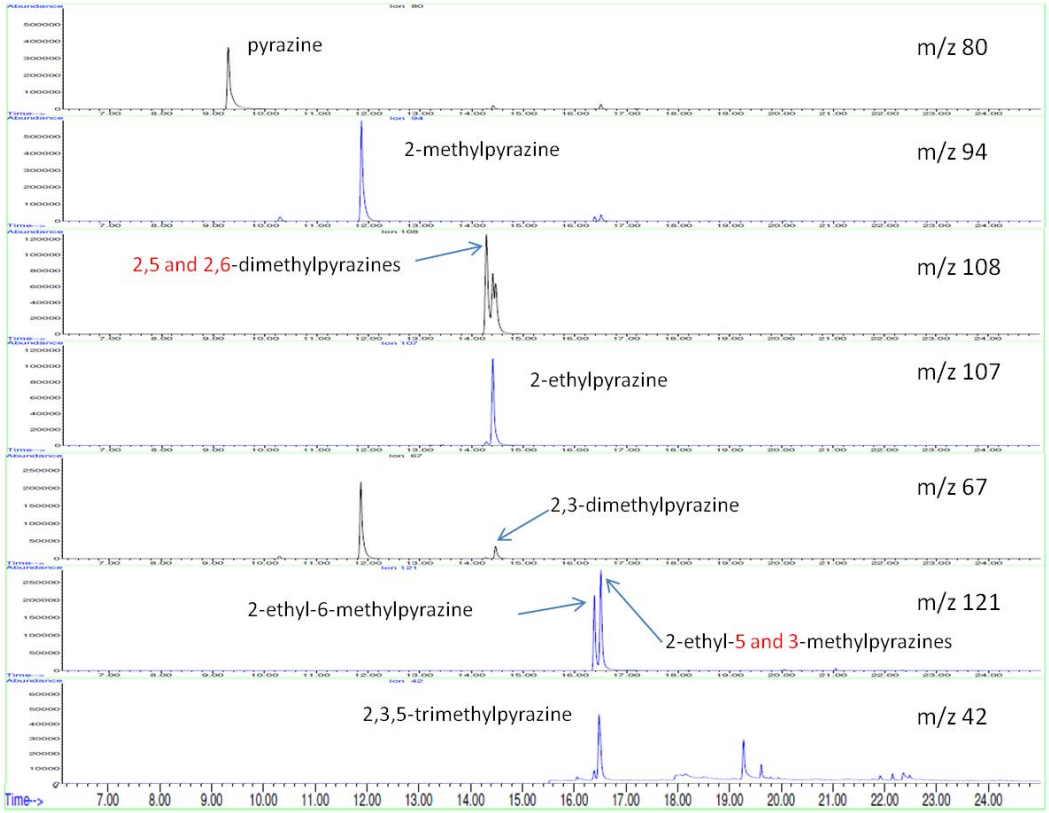


Figure B.31. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 10 mg/L, other alkyl pyrazines were at 0.1 mg/L) in a water/MEA solution with CPSIL8.

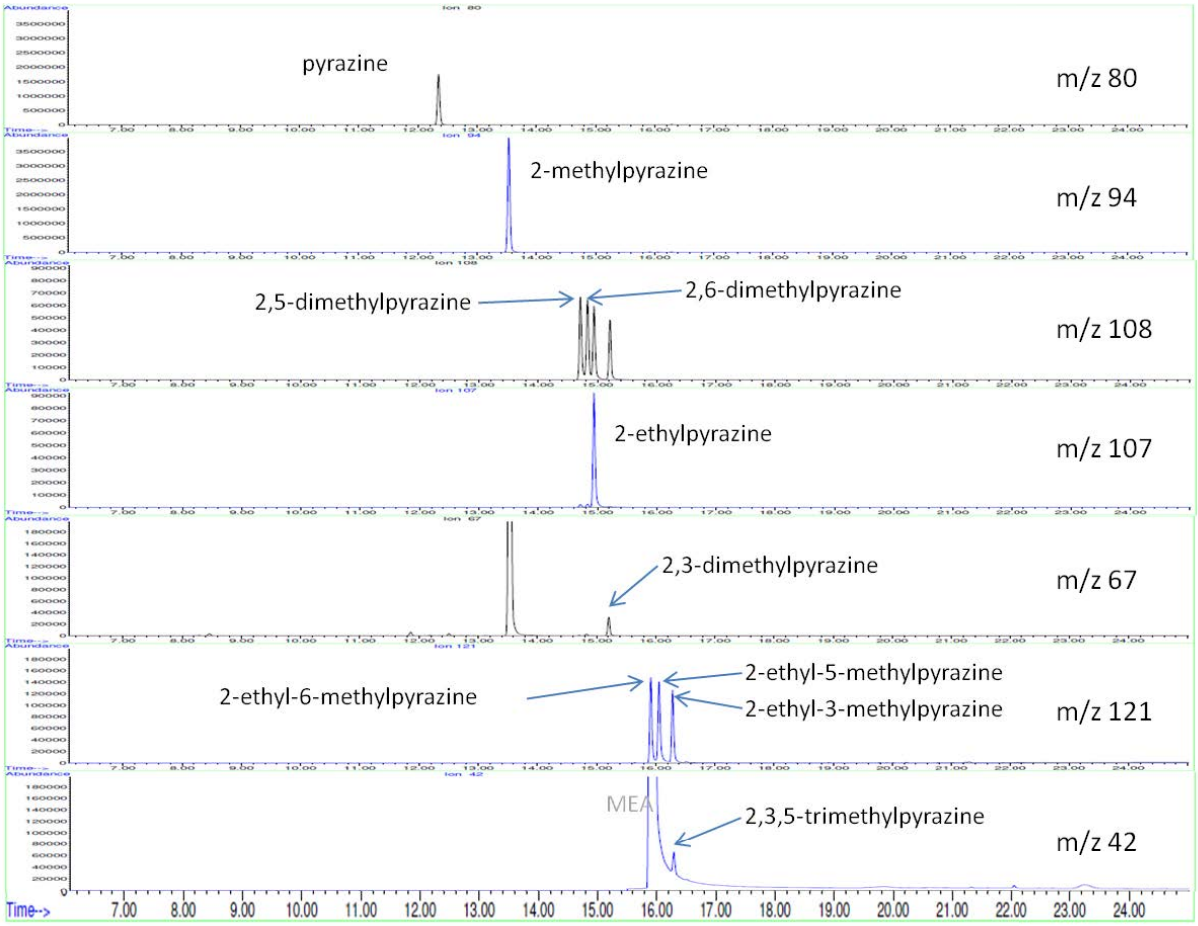


Figure B.32. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 10 mg/L, other alkyl pyrazines were at 0.1 mg/L) in a water/MEA solution with the DBWAX.

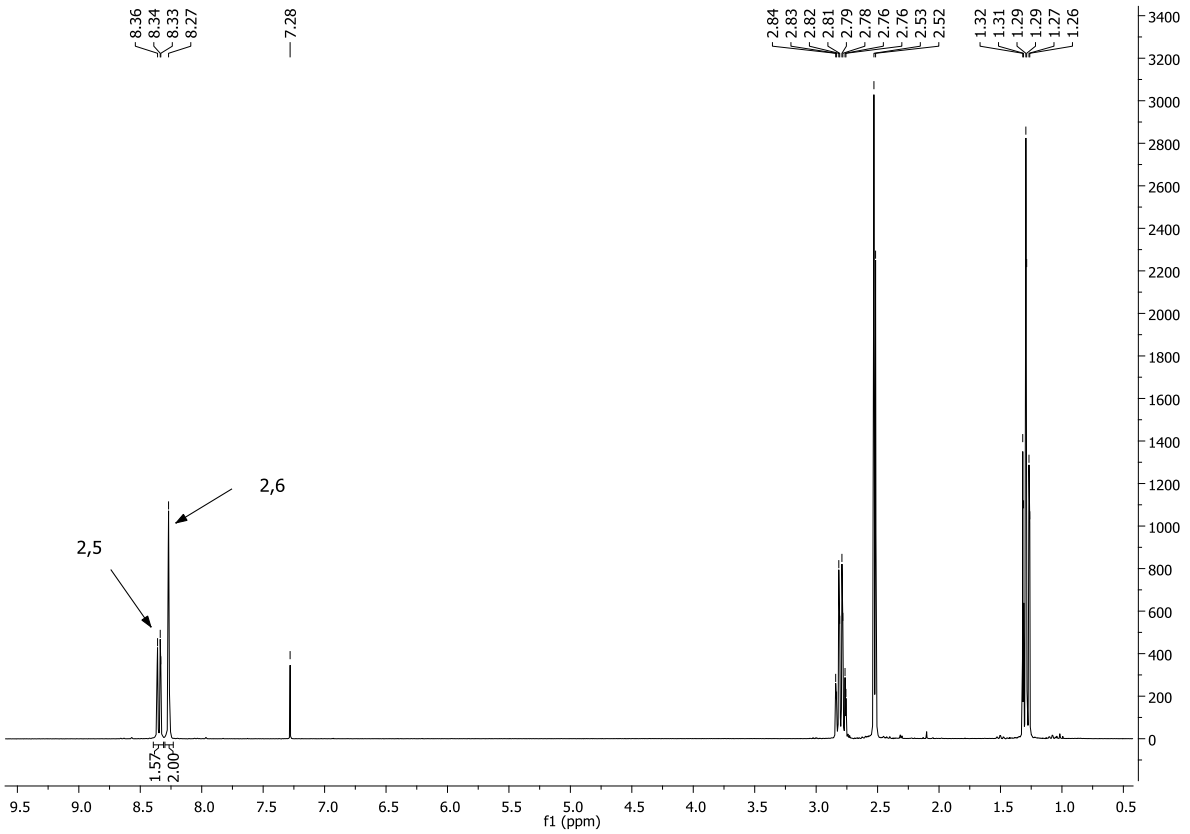


Figure B.33. ^{1}H NMR spectrum of standard mixture of 2,5 and 2.6-dimethylpyrazine

Indeed, aromatic protons of the 2,6 isomer are less shifted compared to those of the 2,5 one (NMR prediction), so the peak at 8.27 ppm correspond to the 2 protons of 2,6 whereas protons of 2,5 are at 8.34 and 8.36. Integration of peak at 8,27 give 2 and integration of the two peaks at 8.34 and 8.36 give 1,57. So there is in the mixture 55% of 2,6 and 45% of 2,5.

Appendix –Mass spectra of compounds observed in chapter 6

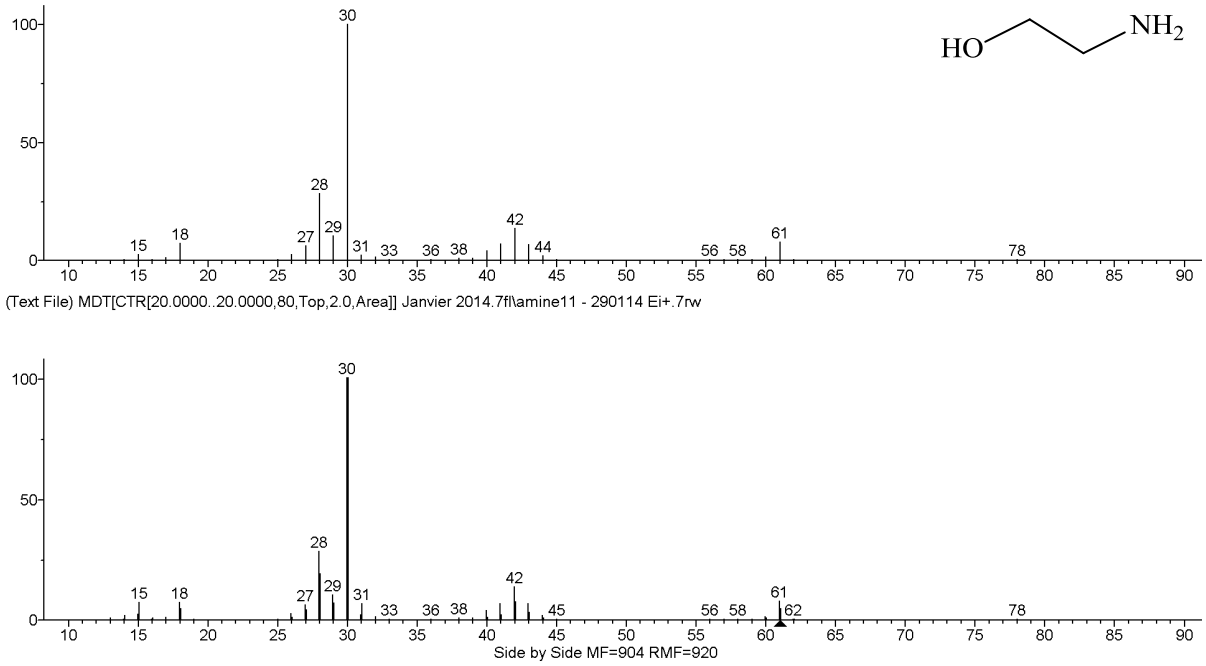


Figure B.34. Comparison mass spectra of the GC peak (MAE, m/z = 61 at rt = 8,3) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition).

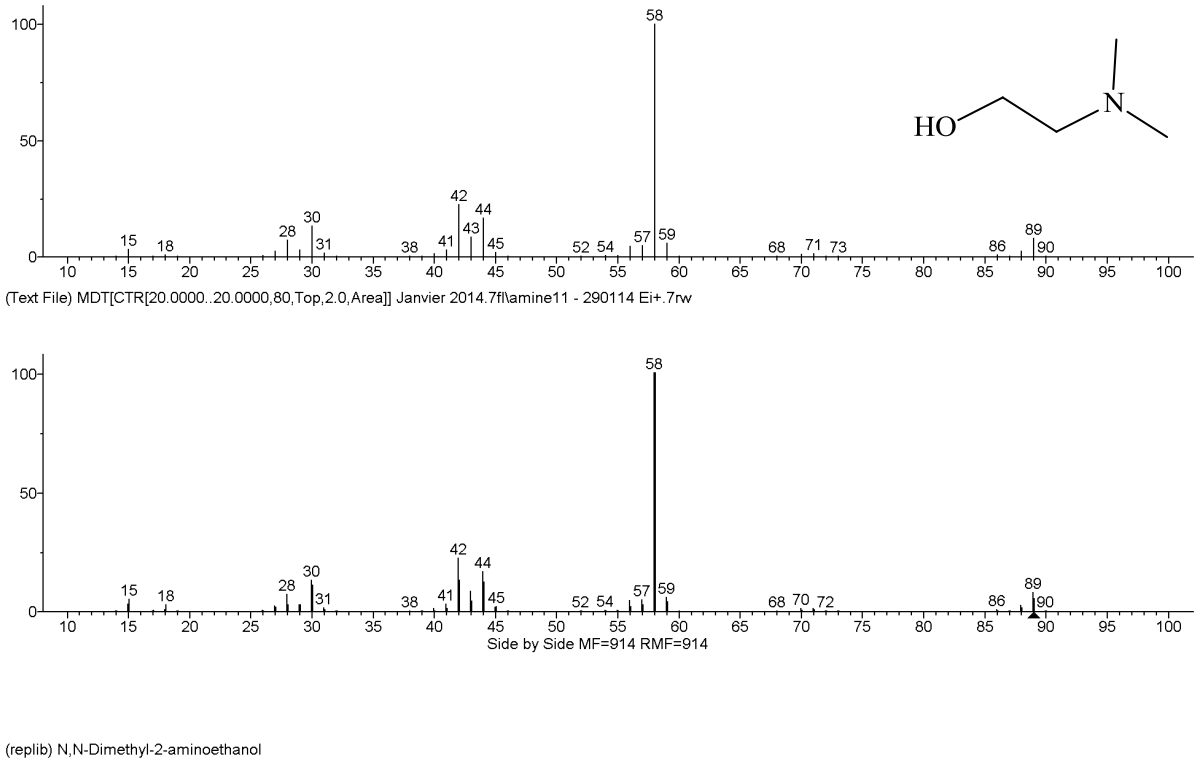


Figure B.35. Comparison mass spectra of the GC peak (MAE, m/z = 89 at rt = 9.9) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition).

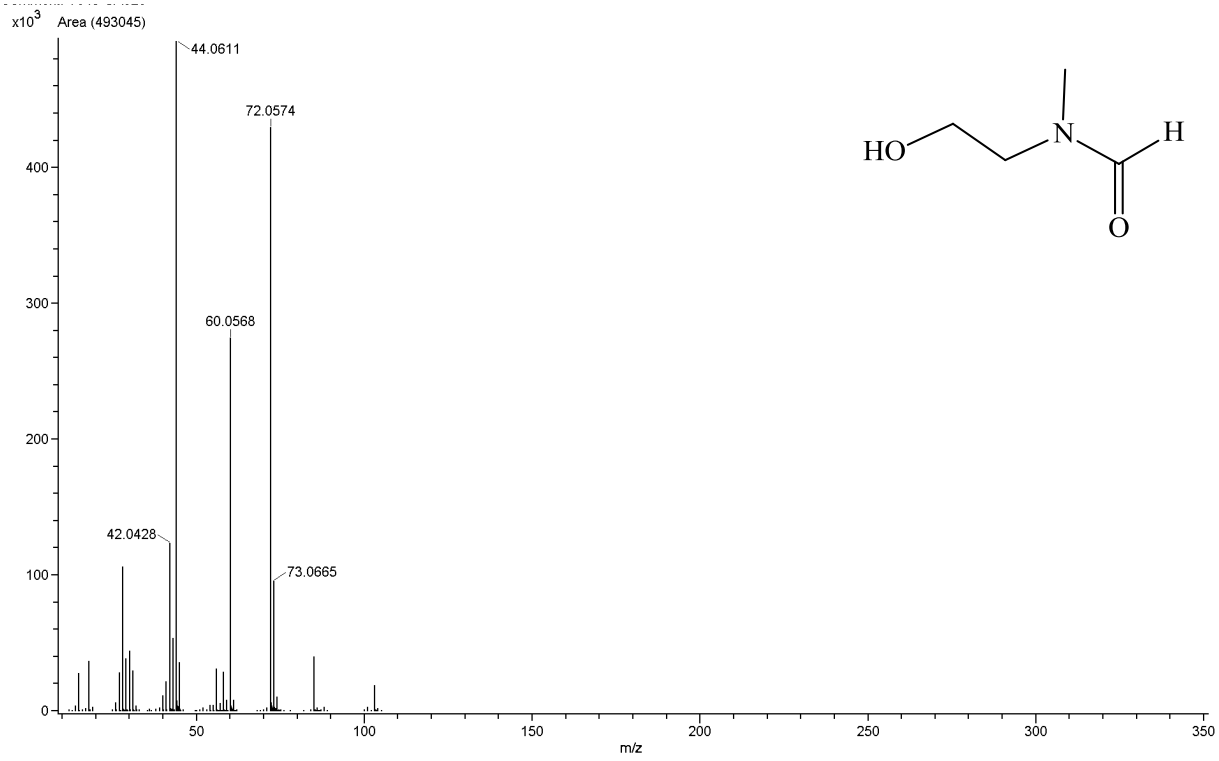


Figure B.36. MAE, m/z = 103 at rt 30.3 min

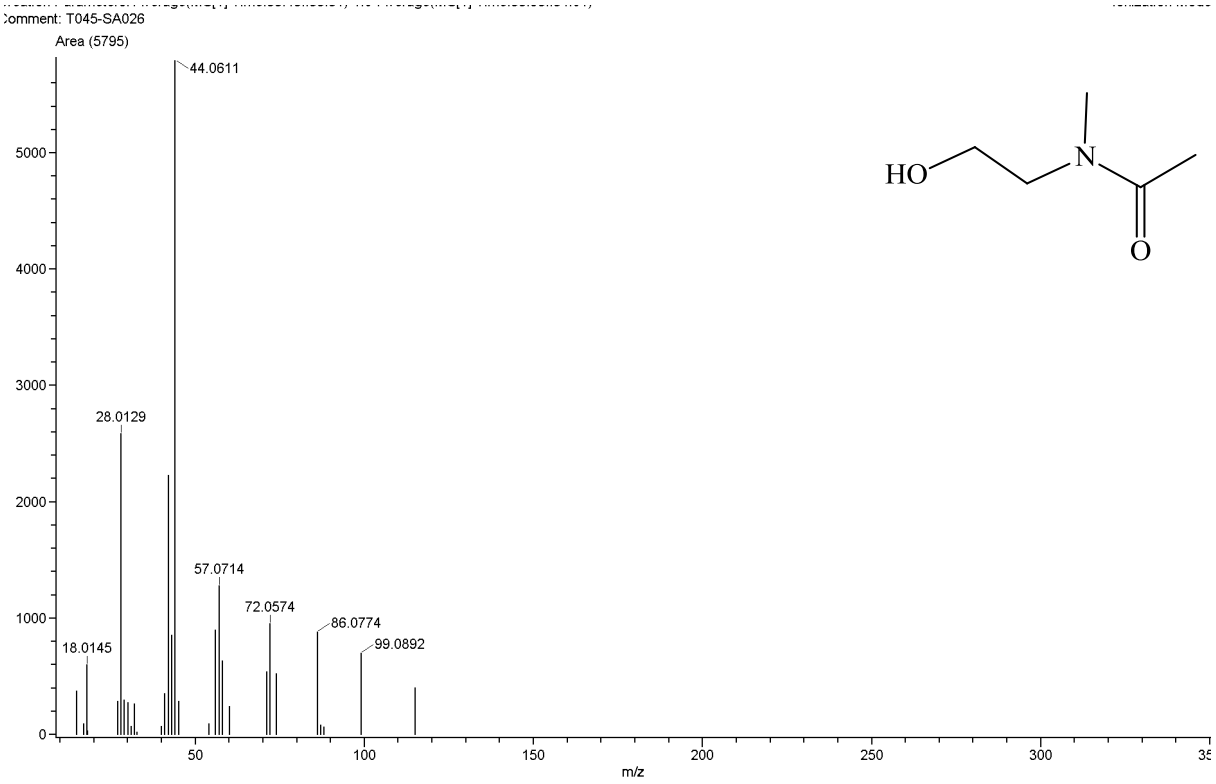


Figure B.37. MAE, m/z = 117 at rt 33.4 min

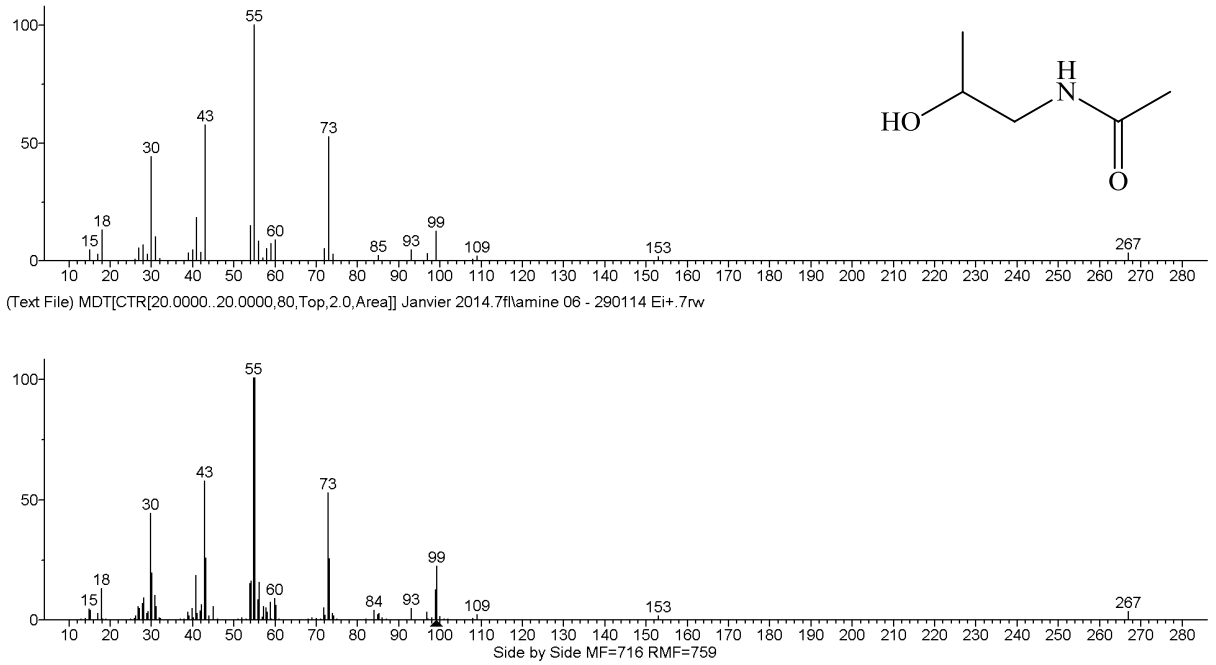


Figure B.38. Comparison mass spectra of the GC peak (1AP2, m/z = 99 at rt = 32.6) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

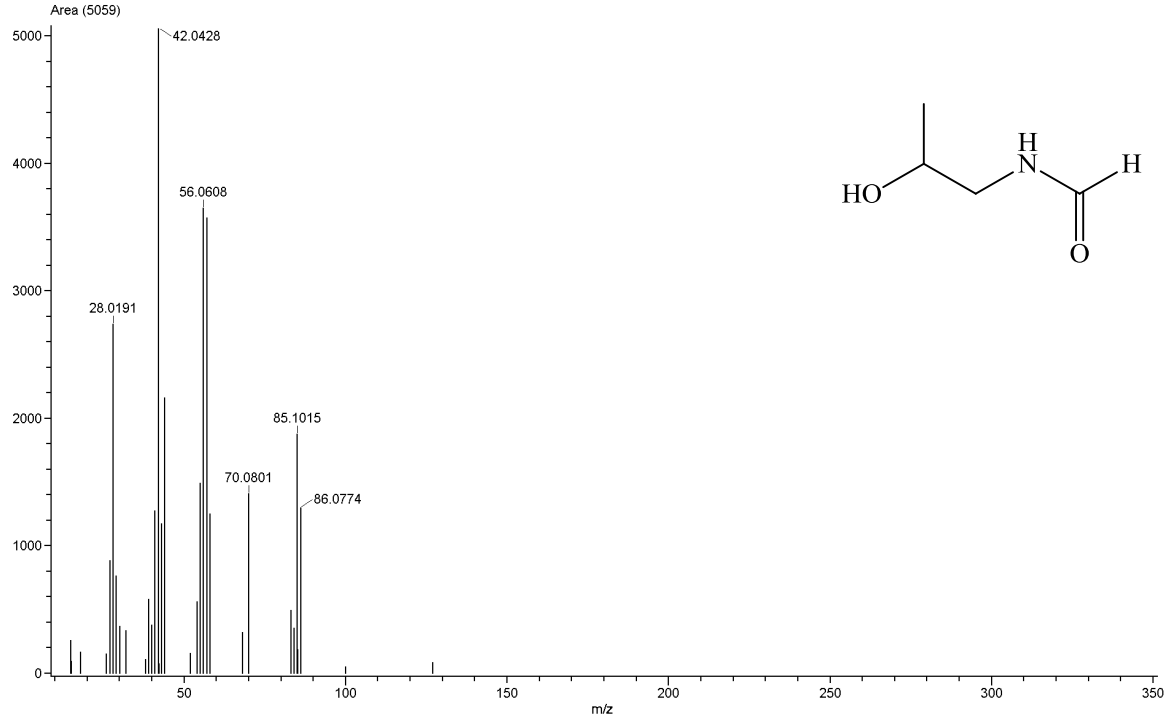


Figure B.39. 1AP2, m/z = 85 at rt = 33.8 min

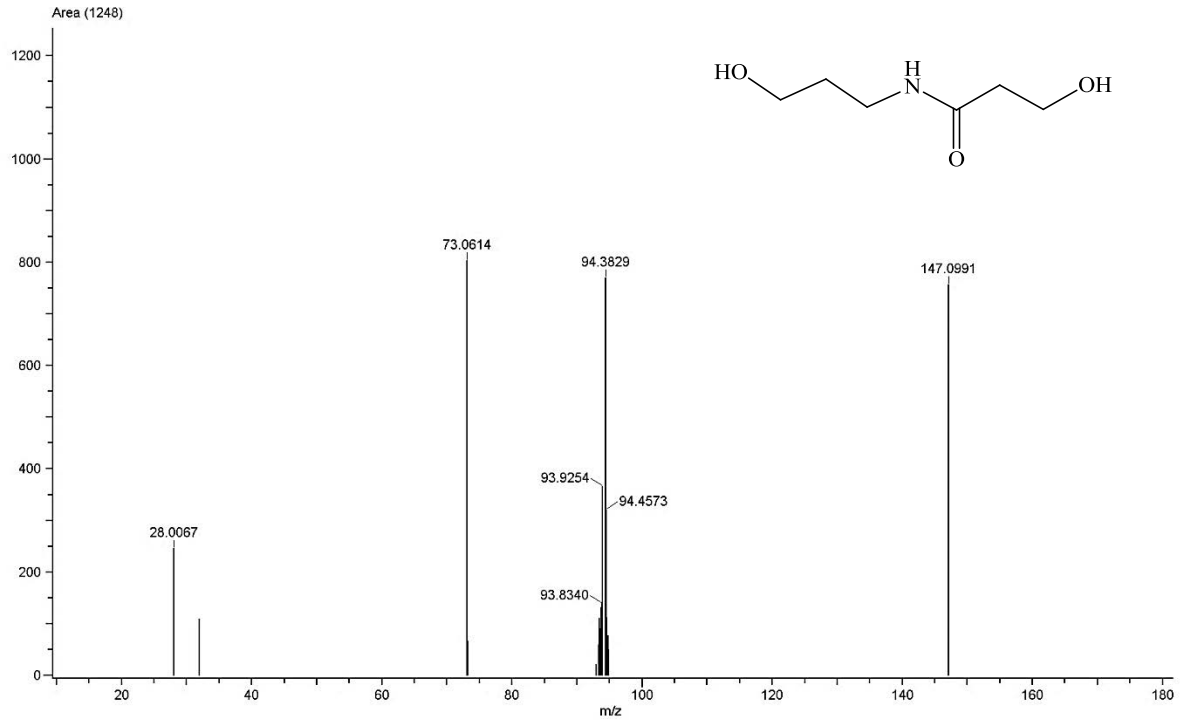


Figure B.40. 3AP1, m/z = 147 at rt = 48 min

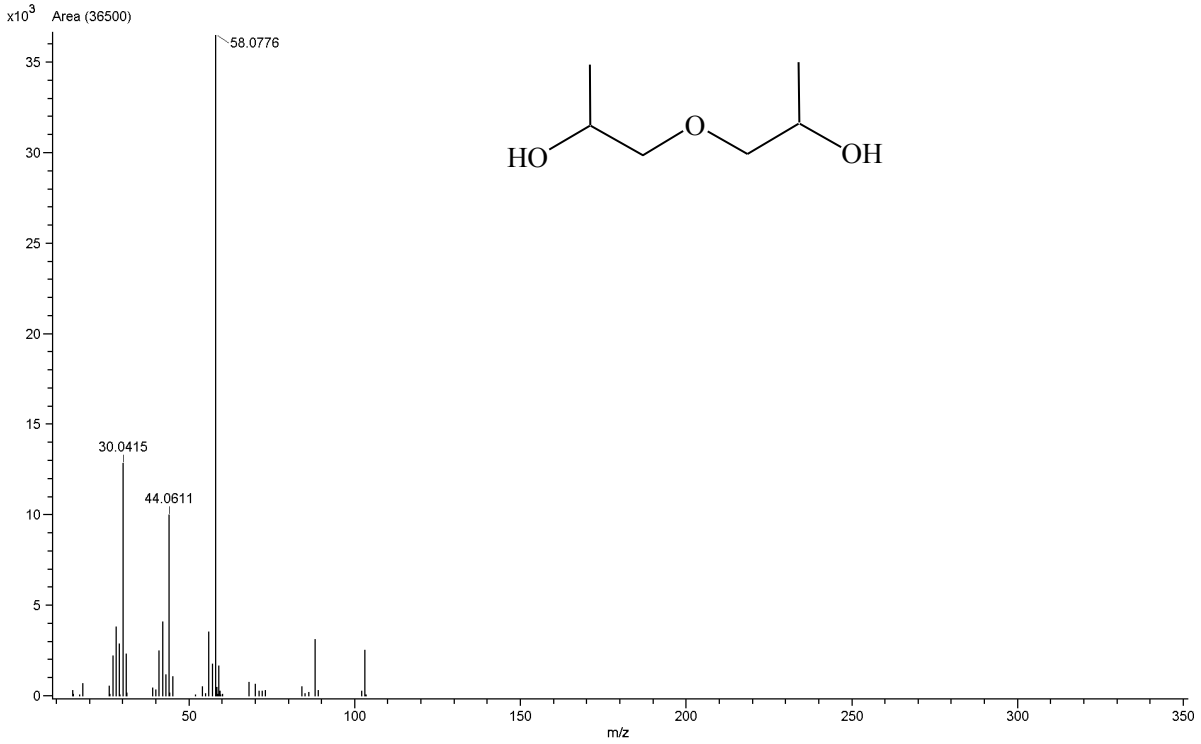


Figure B.41. 3AP1, m/z = 102 at rt 20.4 min

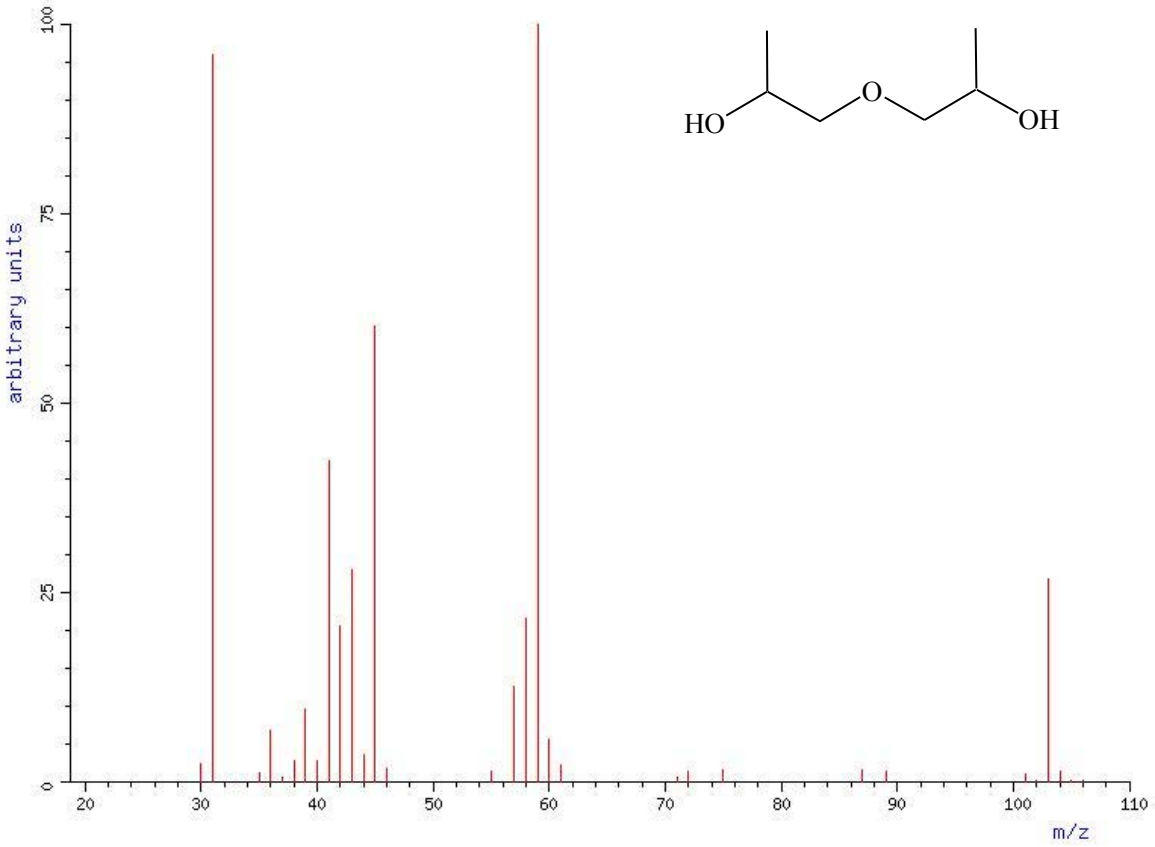


Figure B.42. DEG spectrum from database

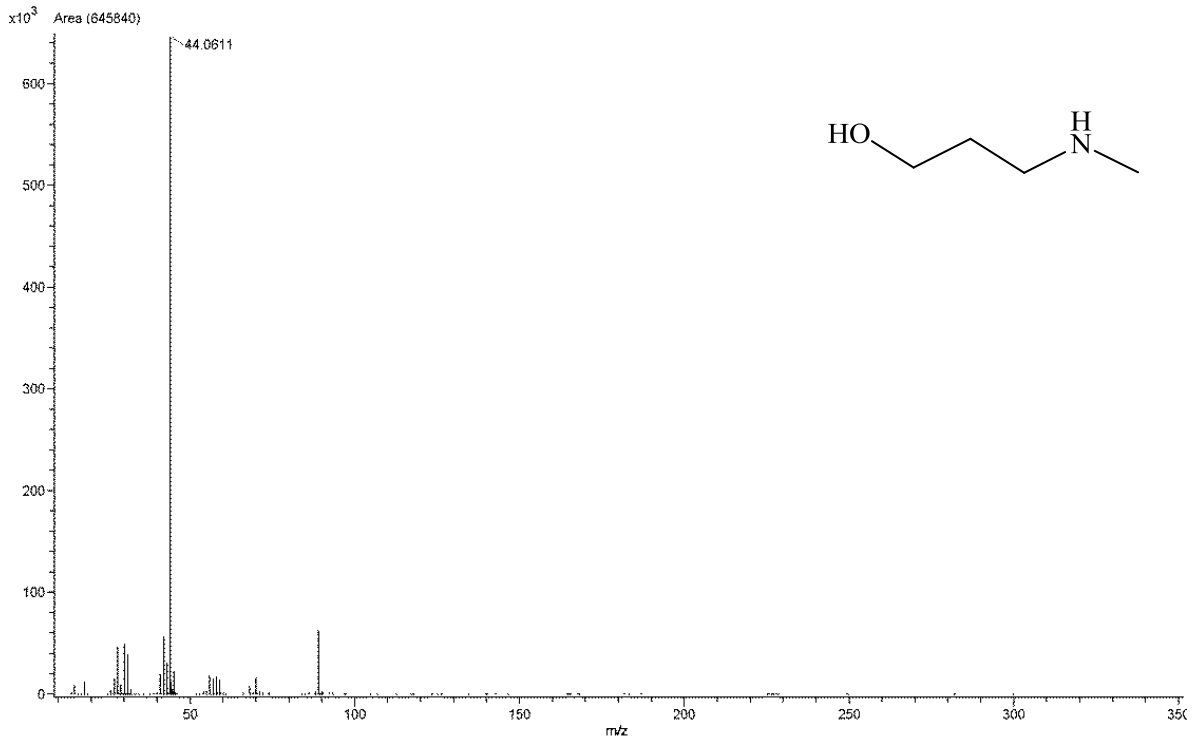


Figure B.43. 3AP1, m/z = 89 at rt = 16.7 min

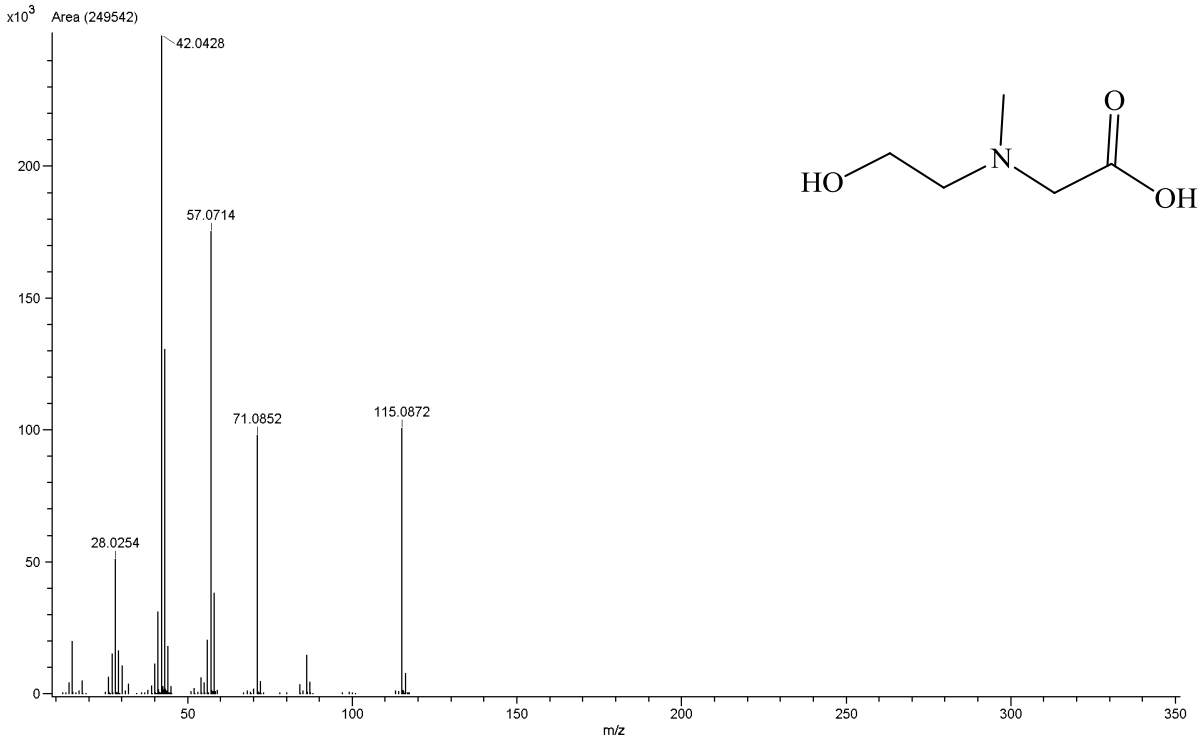


Figure B.44. MAE, m/z = 115 at rt = 28.7 min

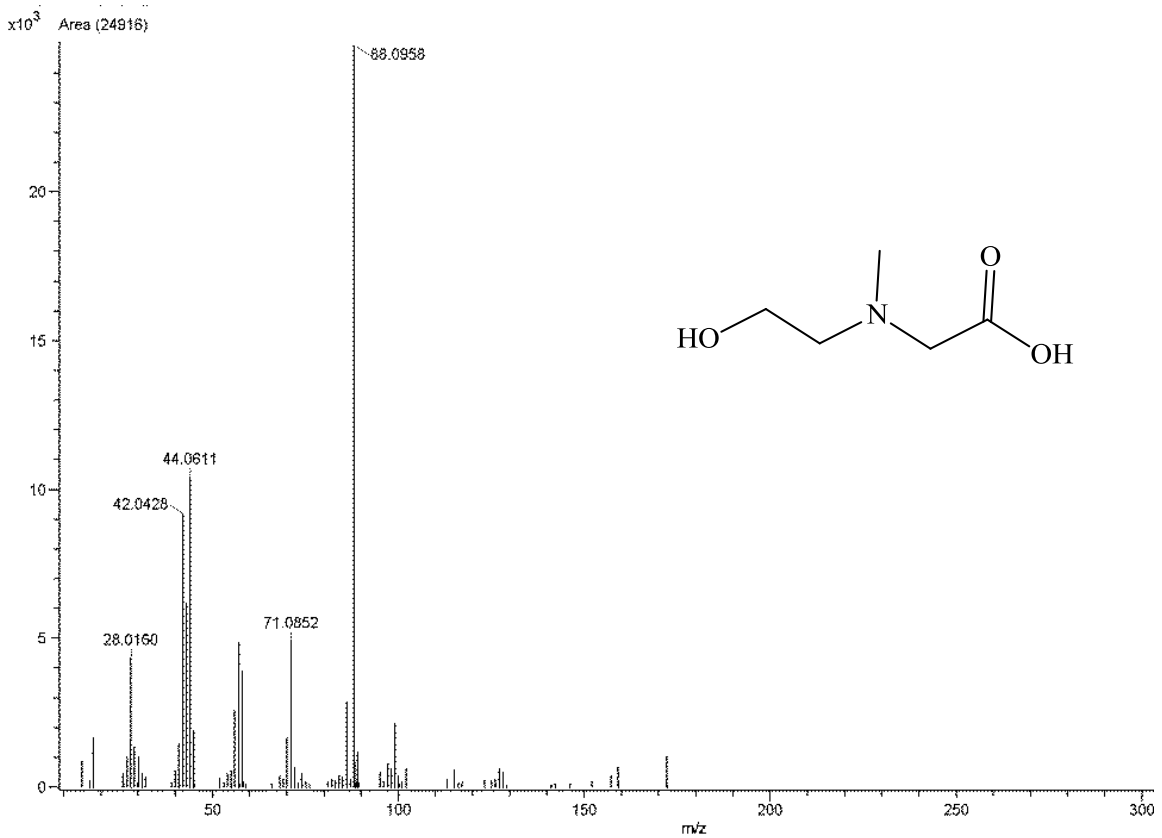


Figure B.45. MAE, m/z = 190 at rt = 56.3 min

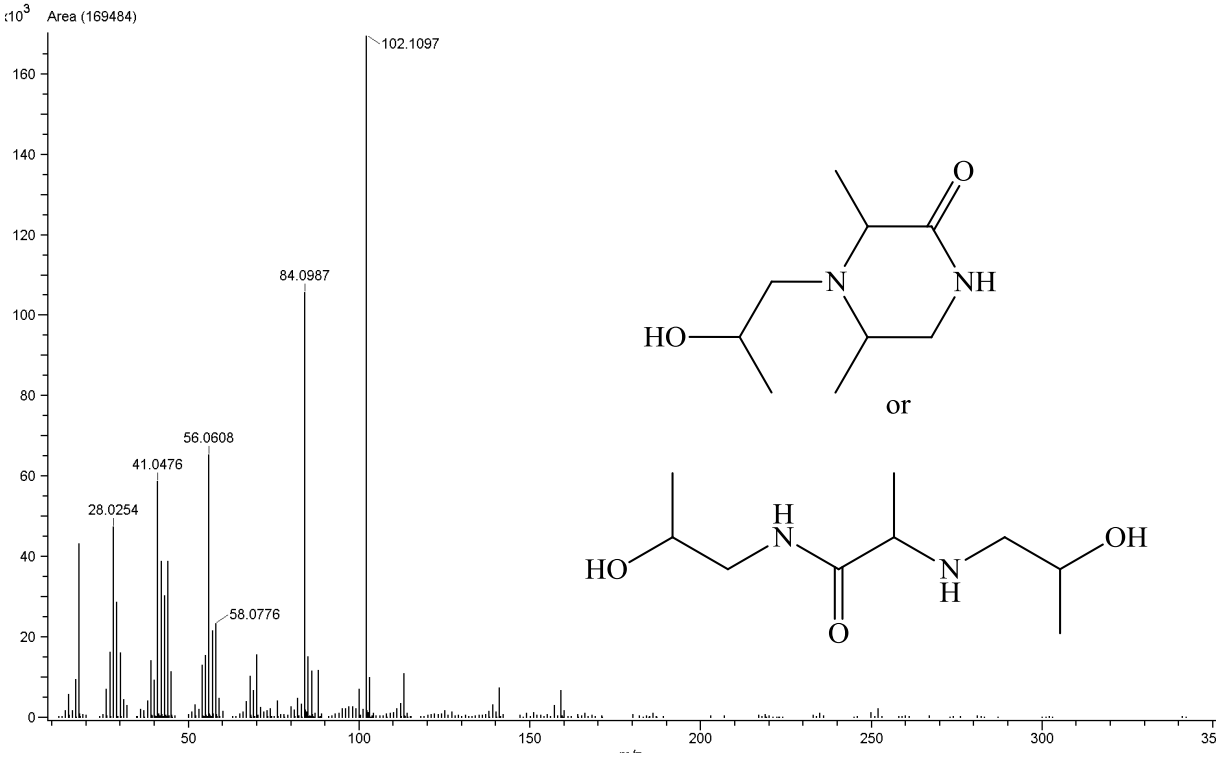


Figure B.46. 1AP2, m/z = 186 at rt = 56.9 min

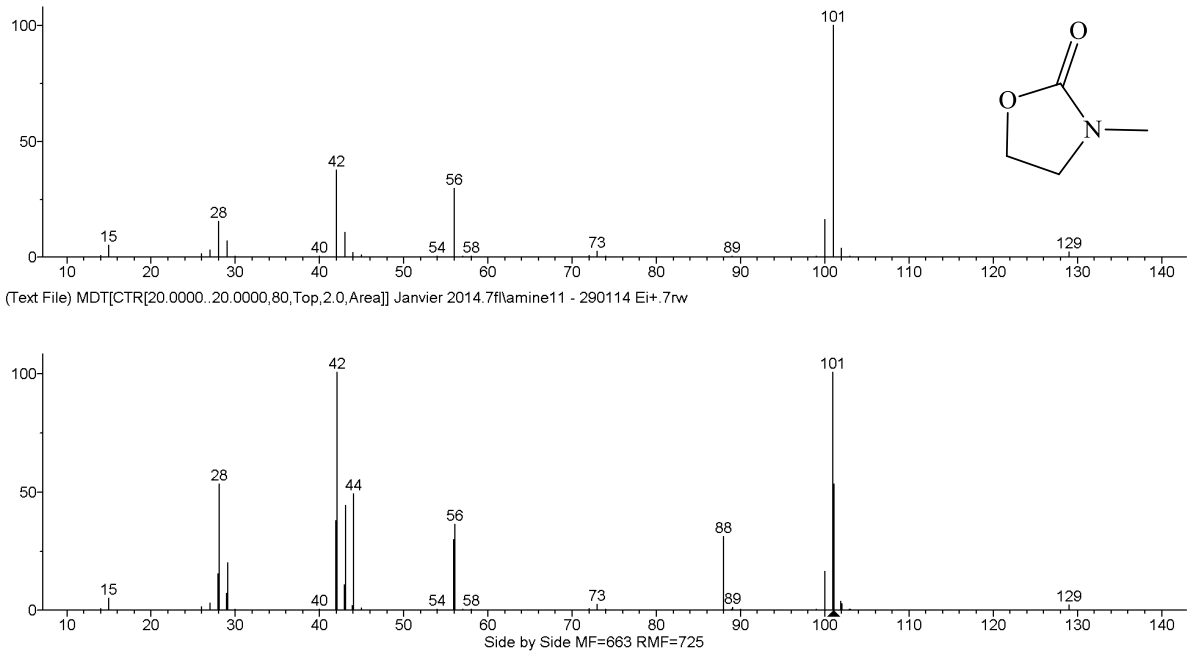


Figure B.47. Comparison mass spectra of the GC peak (MAE, m/z = 101 at rt = 29.5) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

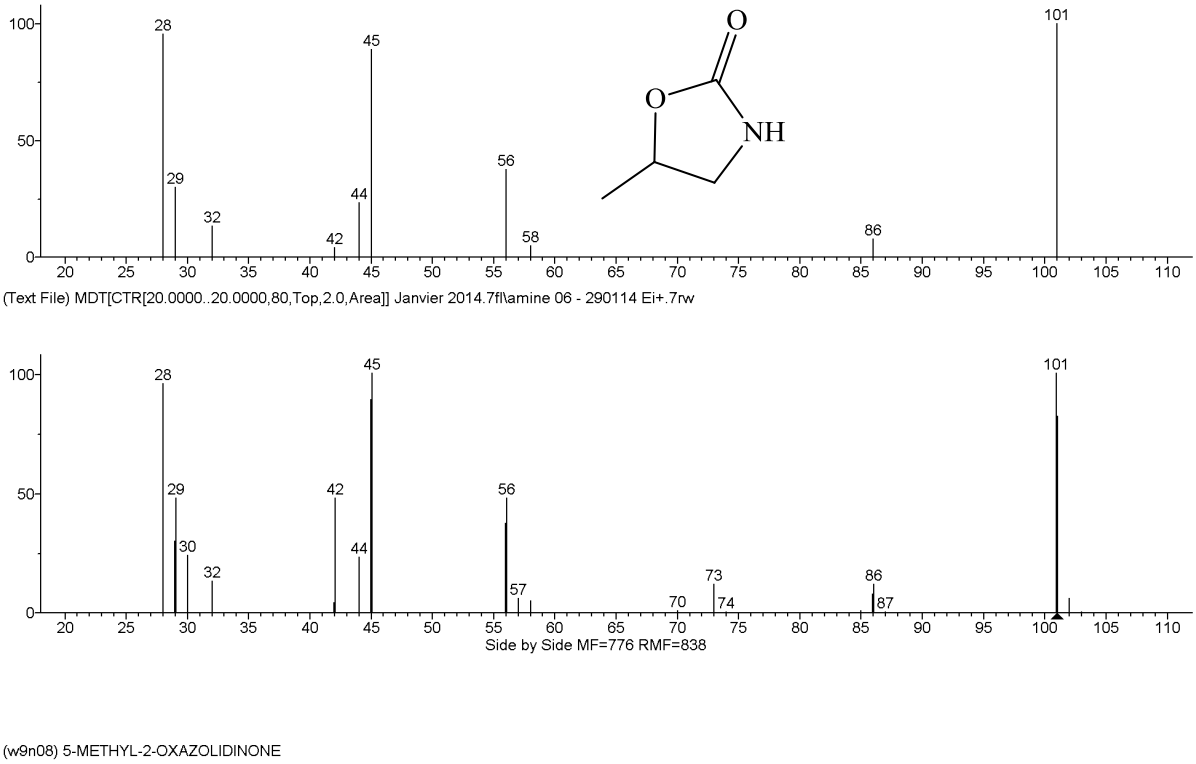


Figure B.48. Comparison mass spectra of the GC peak (1AP2, m/z = 101 at rt = 34.4) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

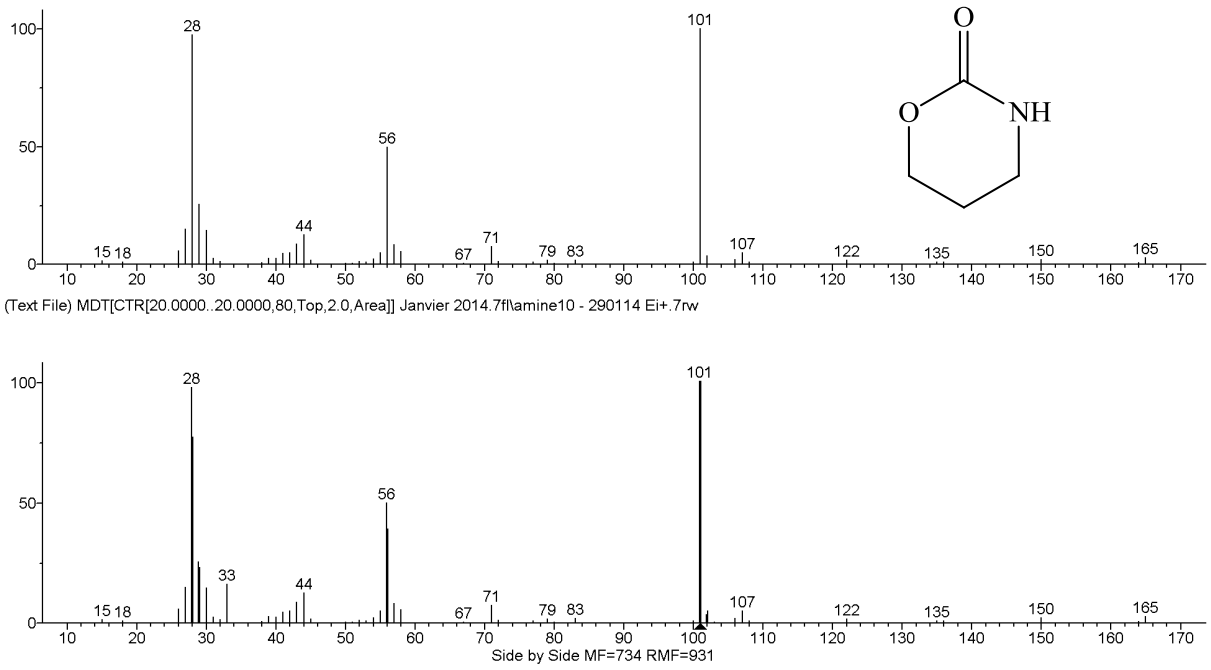


Figure B.49. Comparison mass spectra of the GC peak (3AP1, m/z = 101 at rt = 40.9) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

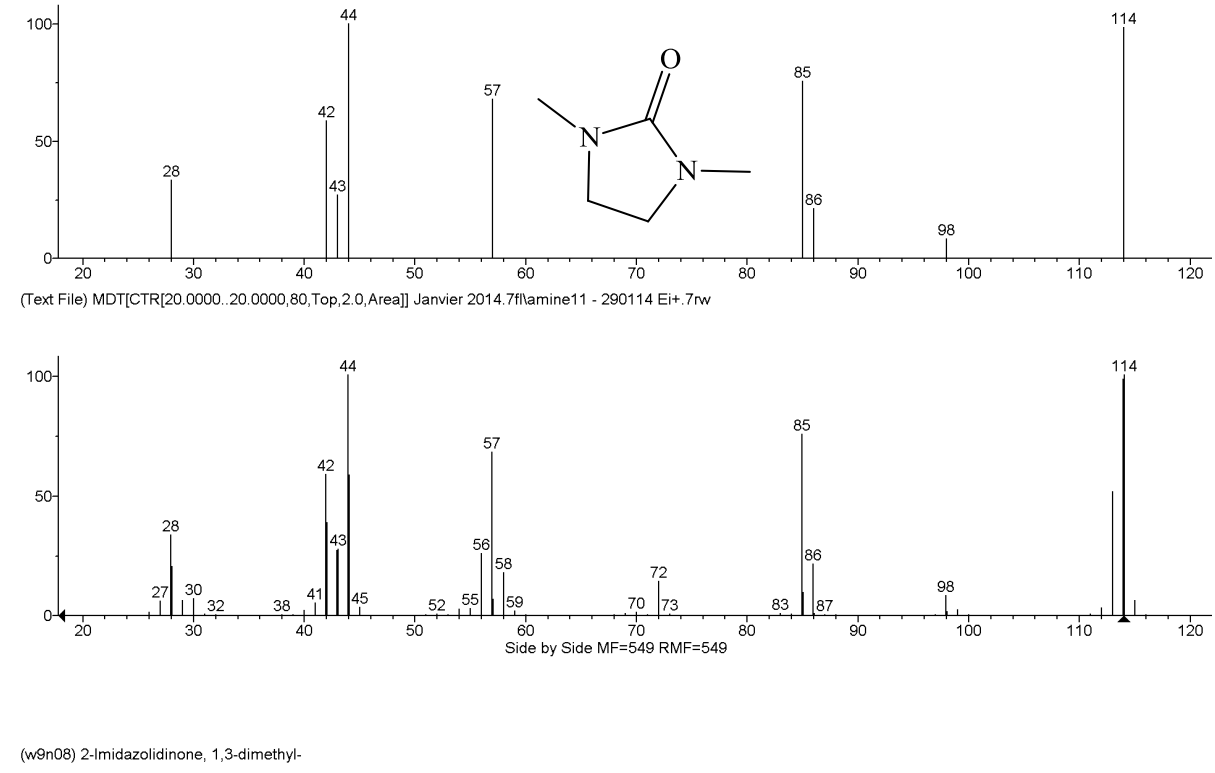


Figure B.50. Comparison mass spectra of the GC peak (MAE, m/z = 114 at rt = 37.2) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition

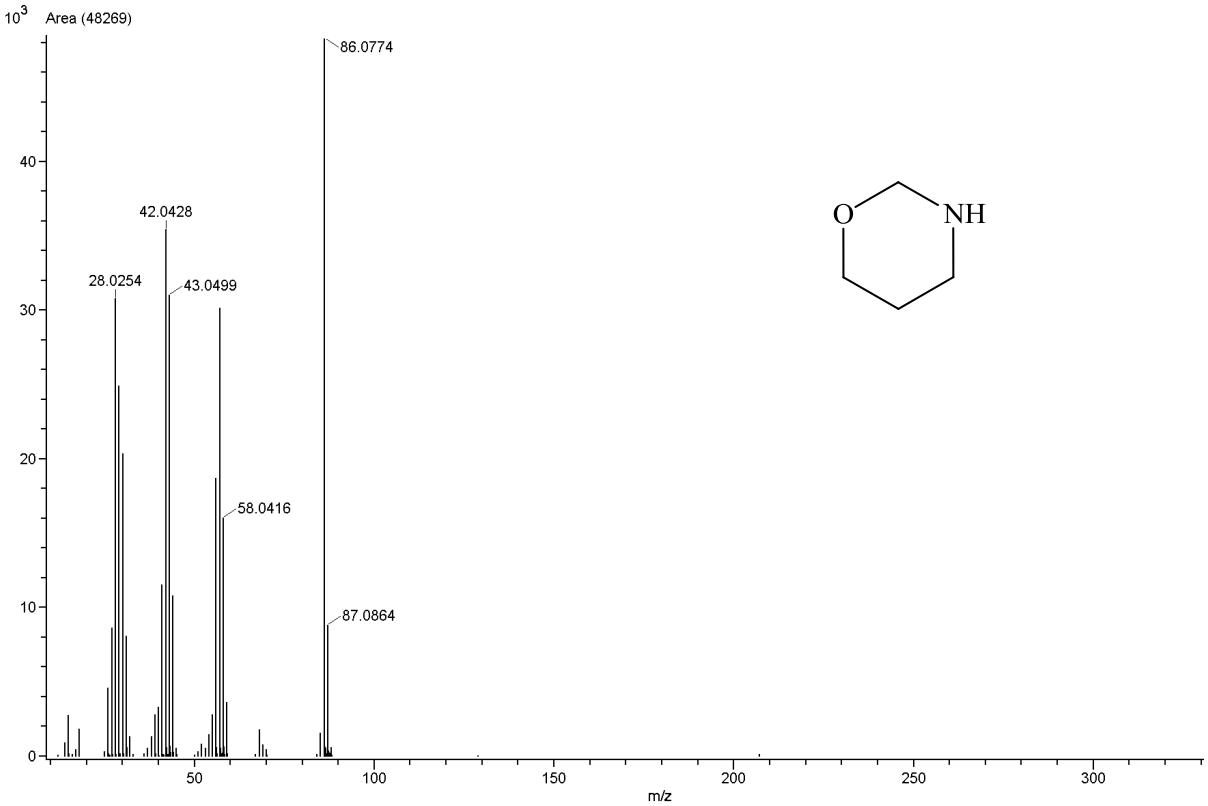


Figure B.51. 3AP1, m/z = 87 at rt = 12.4 min

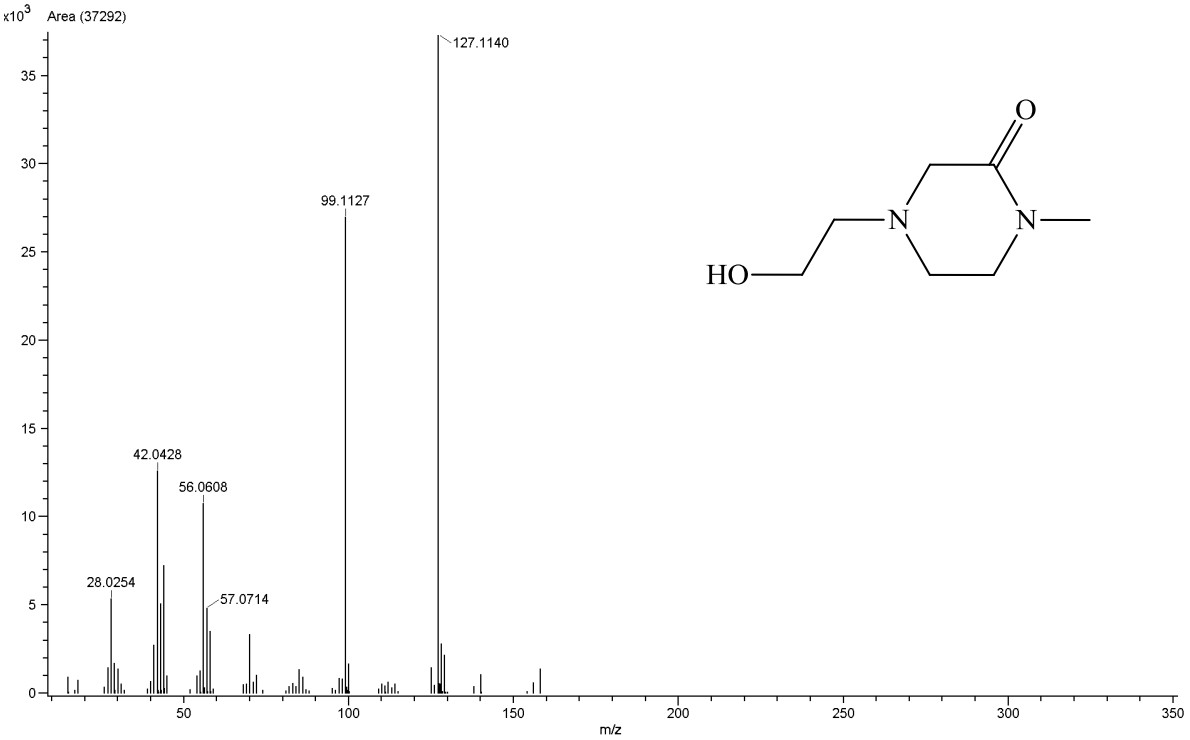


Figure B.52. MAE, m/z = 158 at rt = 51 min

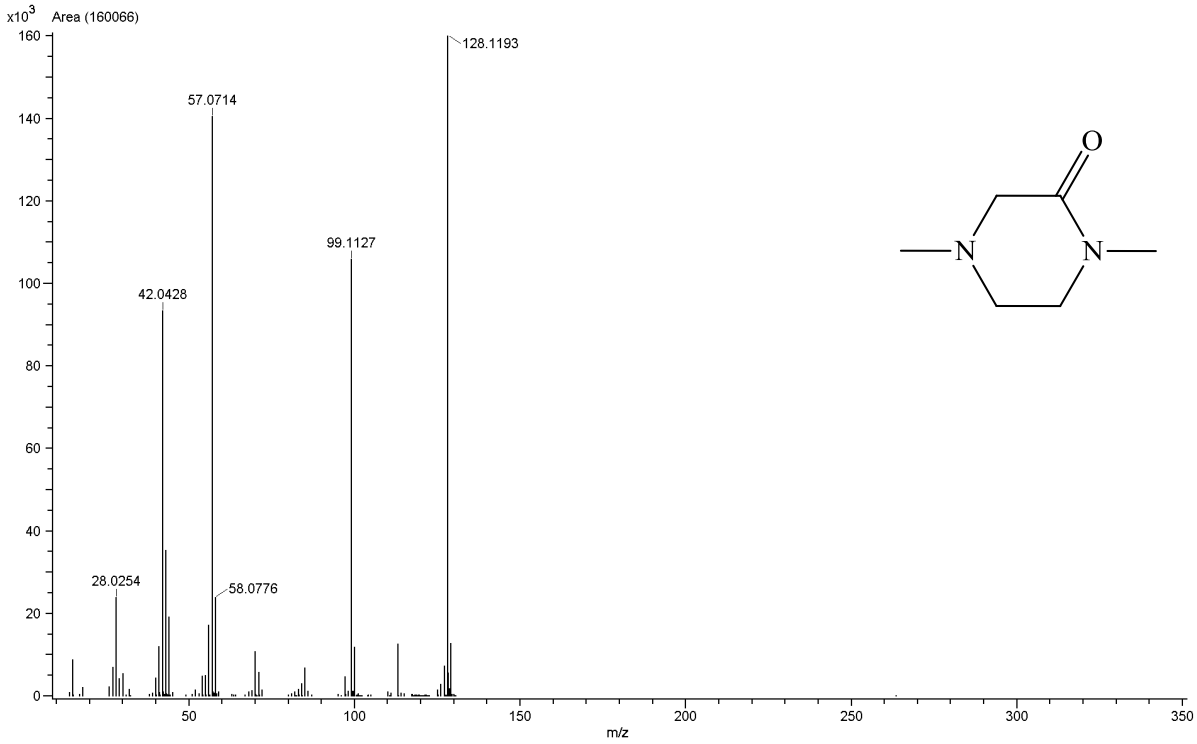


Figure B.53. M AE, m/z = 128 at rt = 35.5 min

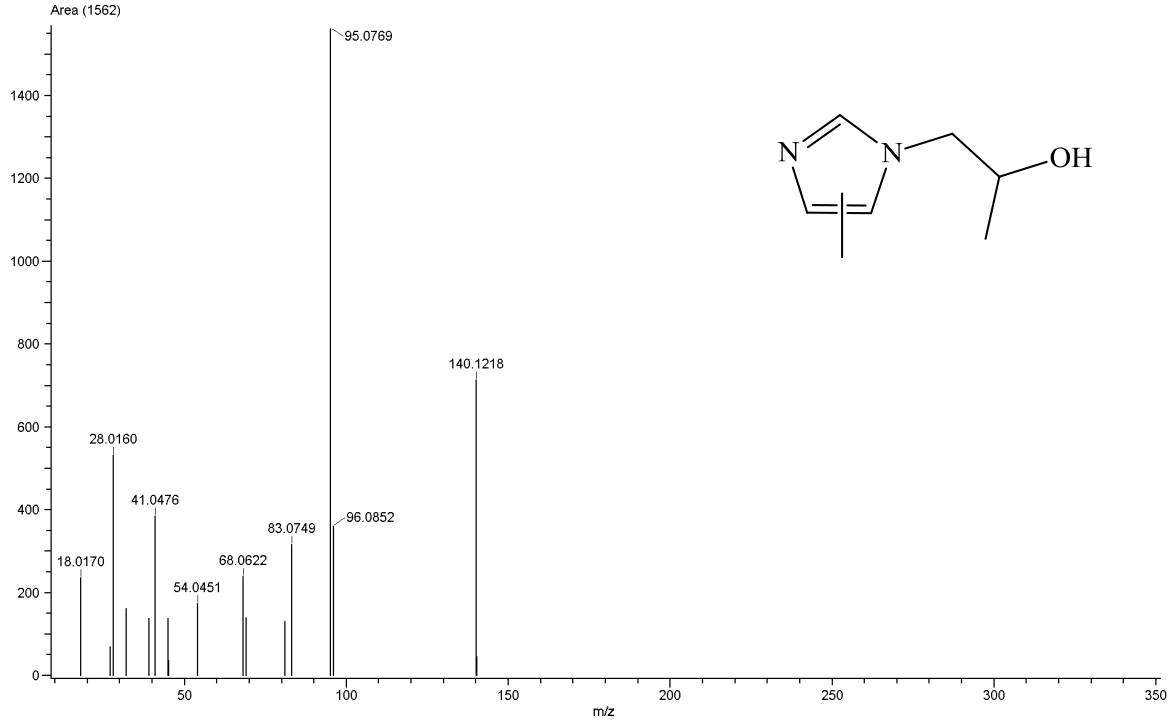


Figure B.54. 1AP2, m/z = 140 at rt = 41.3 min

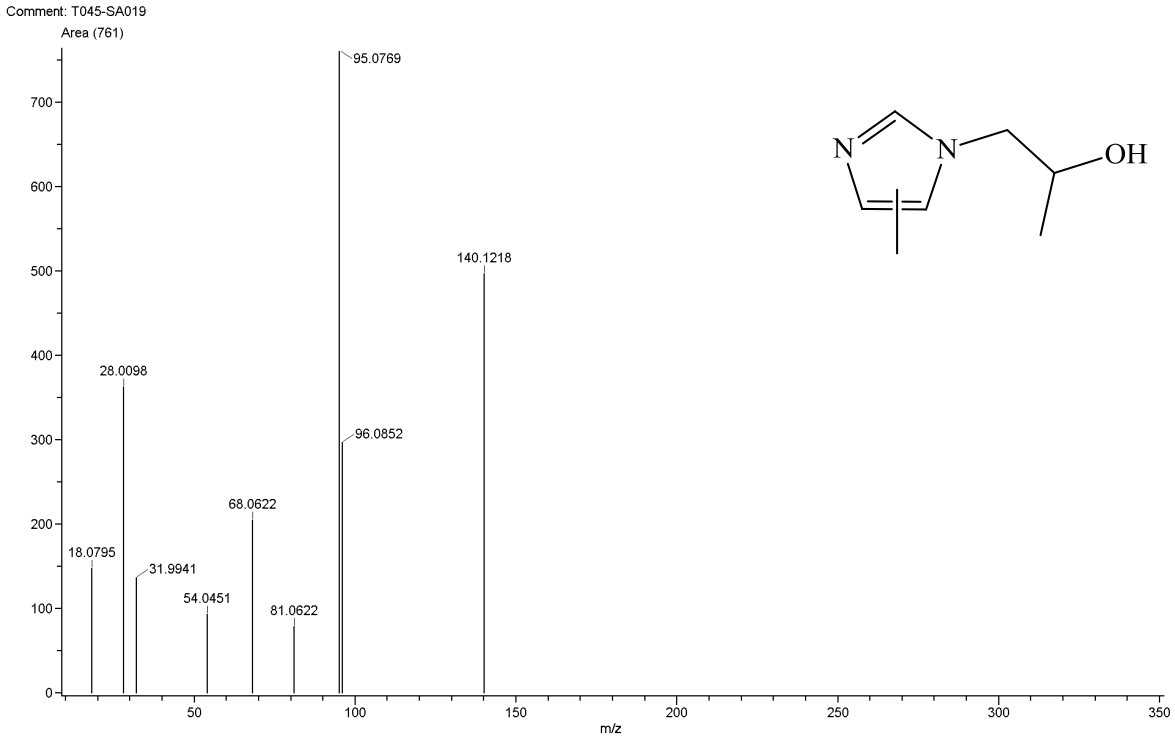


Figure B.55. 1AP2, m/z = 140 at rt = 44.5 min

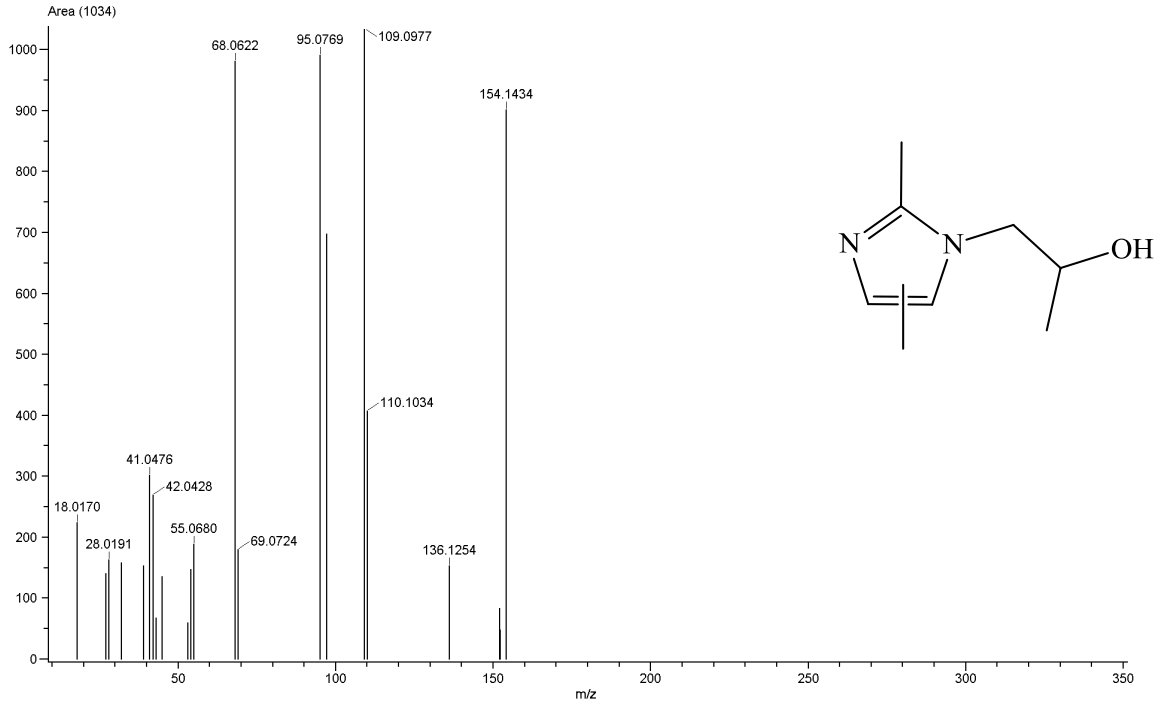


Figure B.56. 1AP2, m/z = 154 at rt = 46.6 min

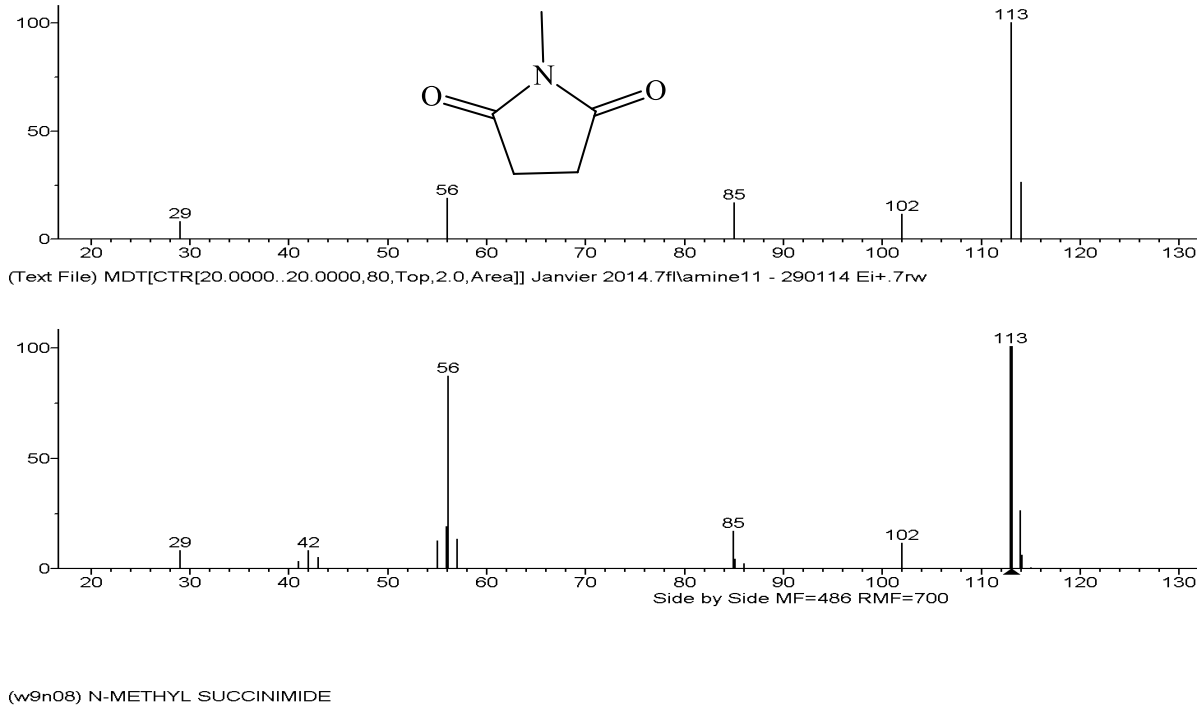


Figure B.57. Comparison mass spectra of the GC peak (MAE, m/z = 113 at rt = 45.3) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

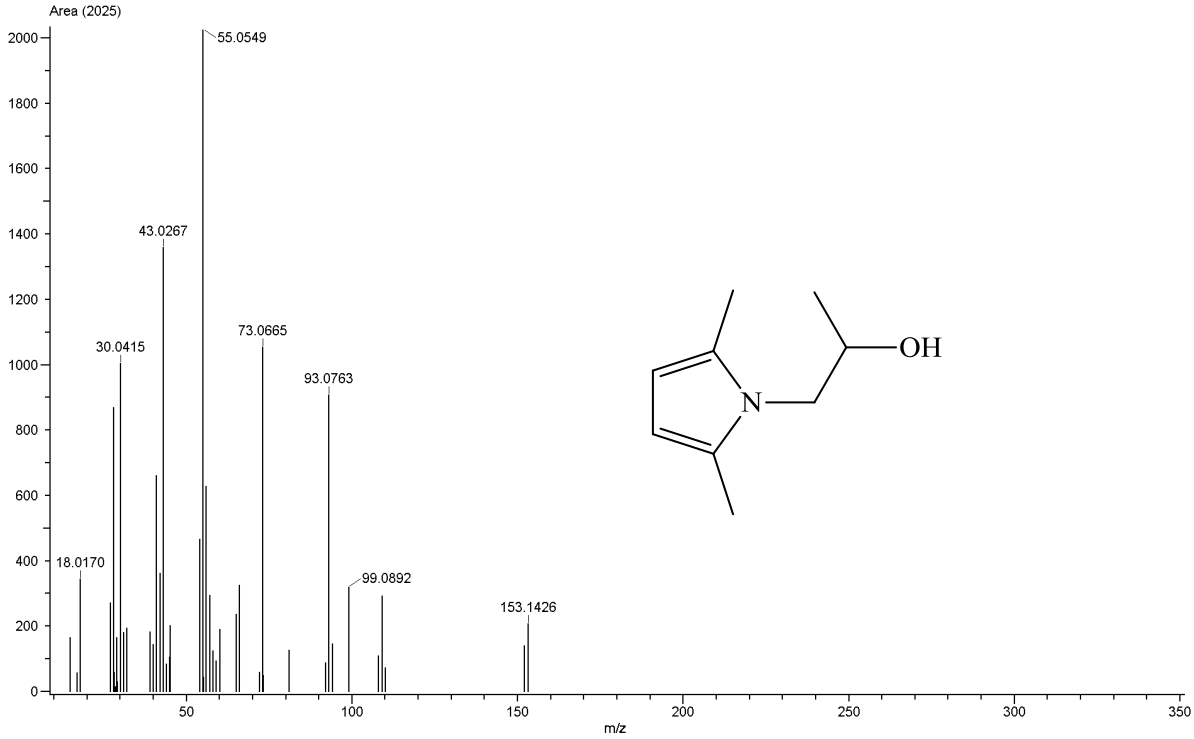


Figure B.58. 1AP2, m/z = 153, rt = 32.9 min

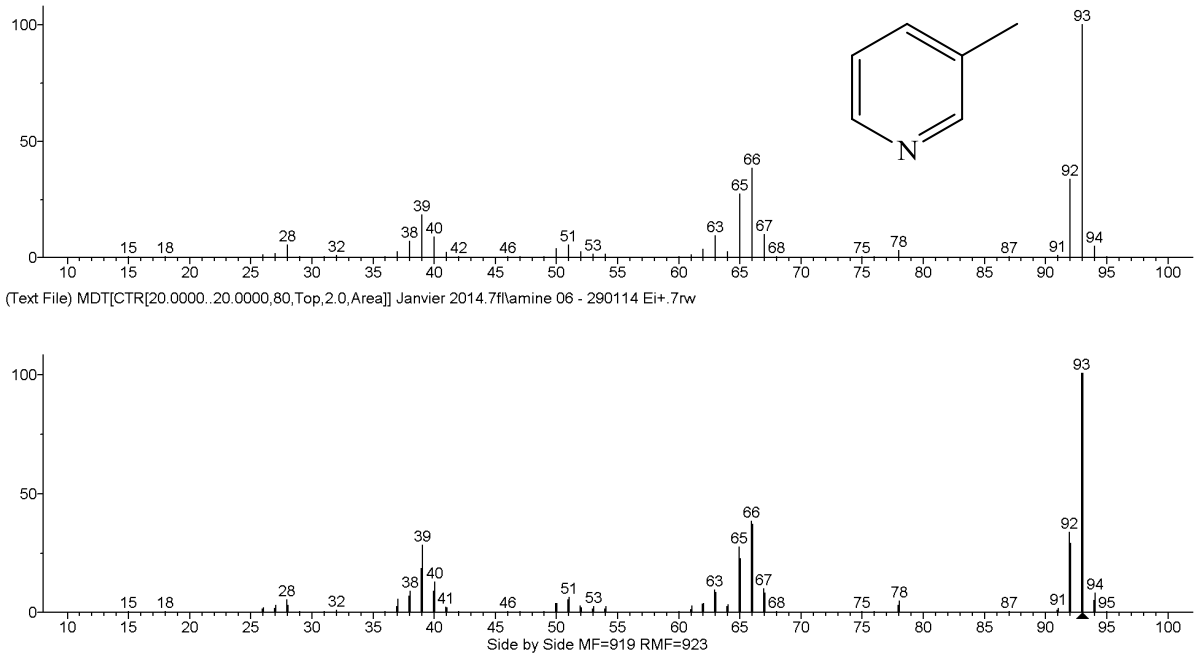


Figure B.59. Comparison mass spectra of the GC peak (1AP2, m/z = 93 at rt = 16.5) with the NIST proposal (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

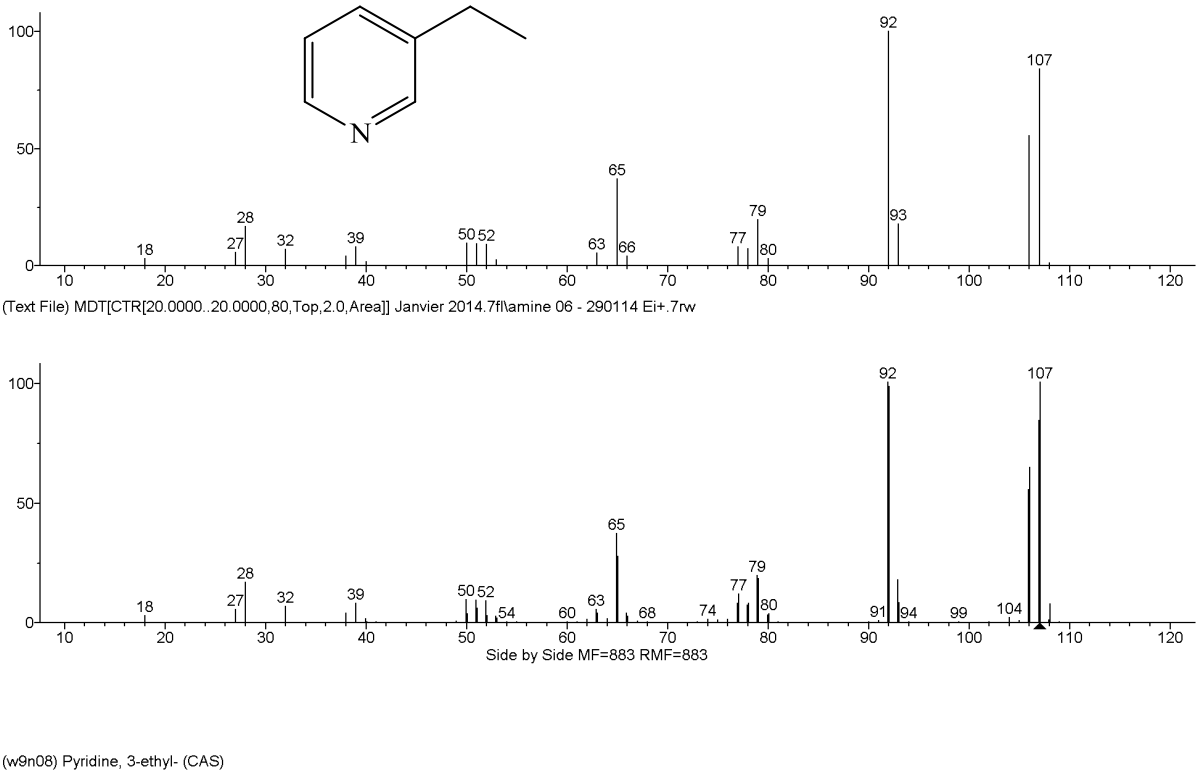


Figure B.60. Comparison mass spectra of the GC peak (1AP2, m/z = 107 at rt = 22) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

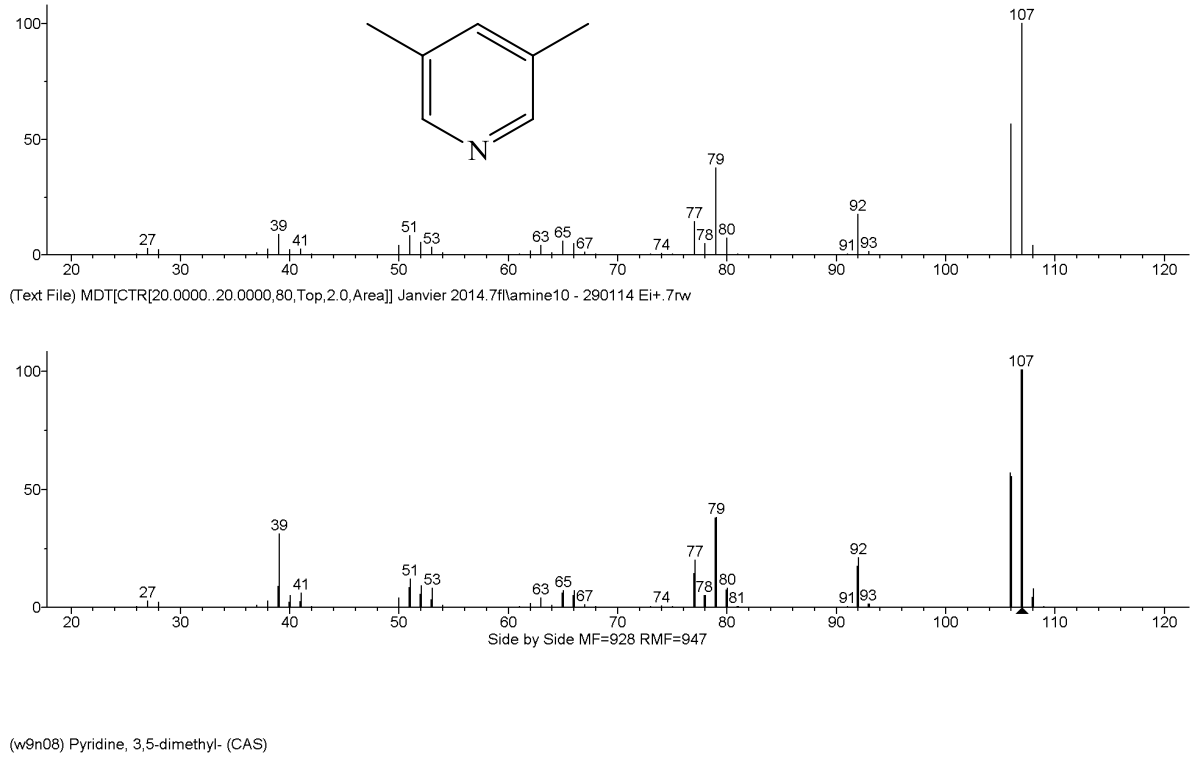


Figure B.61. Comparison mass spectra of the GC peak (3AP1, m/z = 107 at rt = 23) with the proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)

Appendix C – Publications

We would like to acknowledge Elsevier to allow us to insert our publication in this manuscript.

International Journal of Greenhouse Gas Control 10 (2012) 244–270

Contents lists available at SciVerse ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Review

Amine degradation in CO_2 capture. I. A review

C. Gouedard [a], D. Picq [a,b], F. Launay [c], P.-L. Carrette [a,*]

[a] IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France
[b] LMOPS/LEPMI, chemin du canal, 69360 Solaize, France
[c] LRS/UPMC-Paris 6, 3 rue Galilée, 94200 Ivry-sur-Seine, France

ARTICLE INFO

Article history:
Received 7 March 2012
Received in revised form 21 June 2012
Accepted 23 June 2012

Keywords:
Post-combustion CO_2 capture
Amine degradation
MEA/DEA/MDEA/PZ/AMP
SO_x and NO_x
Mechanisms

ABSTRACT

Post-combustion CO_2 capture based on CO_2 absorption by aqueous amine solutions is the most mature gas separation technology. A main problem is amine degradation due to heat, CO_2, O_2, NO_x and SO_x. This review proposes to make a critical survey of literature concerning degradation, to list degradation products and to discuss mechanisms proposed by authors. Benchmark molecule is monoethanolamine (MEA) but diethanolamine (DEA), N-methyldiethanolamine (MDEA), piperazine (PZ) and 2-amino-2-methylpropan-1-ol (AMP) are also studied. Uses of other amines and amine blends are also considered. In the case of MEA, ammonia, N-(2-hydroxyethyl)-piperazin-3-one (HEPO) and N-(2-hydroxyethyl)-2-(2-hydroxyethylamino) acetamide (HEHEAA) are the main identified degradation products in pilot plants. Among lab studies, the most cited degradation products are ammonia, carboxylic acids, N-(2-hydroxyethyl)-formamide (HEF), N-(2-hydroxyethyl)-acetamide (HEA) and N-(2-hydroxyethyl)-imidazole (HEI) for oxidative degradation, and oxazolidin-2-one (OZD), N-(2-hydroxyethyl)-ethylenediamine (HEEDA) and N-(2-hydroxyethyl)-imidazolidin-2-one (HEIA) for thermal degradation. Numerous degradation products have been identified but some are still unknown. A lot of degradation mechanisms have been proposed but some are missing or need proofs. SO_x and NO_x effects are still few examined and much work remains to be done concerning volatile degradation products potentially emitted to atmosphere: their identification and their formation mechanisms need further investigations.

© 2012 Elsevier Ltd. All rights reserved.

Contents

1. Introduction 245
2. Studied amines 245
 2.1. Monoethanolamine (MEA) 245
  2.1.1. Thermal degradation 245
  2.1.2. Oxidative degradation 247
 2.2. Diethanolamine (DEA) 252
  2.2.1. Thermal degradation 254
  2.2.2. Oxidative degradation 256
 2.3. Methyldiethanolamine (MDEA) 258
  2.3.1. Thermal degradation 258
  2.3.2. Oxidative degradation 258
 2.4. Piperazine (PZ) 258
  2.4.1. Thermal degradation 258
  2.4.2. Oxidative degradation 258

* Corresponding author at: IFP Energies nouvelles – Catalysis and Separation Division, Lyon Establishment, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France. Tel.: +33 4 37 70 27 23; fax: +33 4 37 70 20 66.
E-mail address: p-louis.carrette@ifpen.fr (P.-L. Carrette).

1750-5836/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijggc.2012.06.015

2.5. 2-Amino-2-methylpropan-1-ol (AMP) 262
2.5.1. Thermal degradation 262
2.5.2. Oxidative degradation 262
2.6. Other amines 262
2.7. Amine blends 263
3. Effect of SO_x and NO_x 263
4. Conclusion 269
References 269

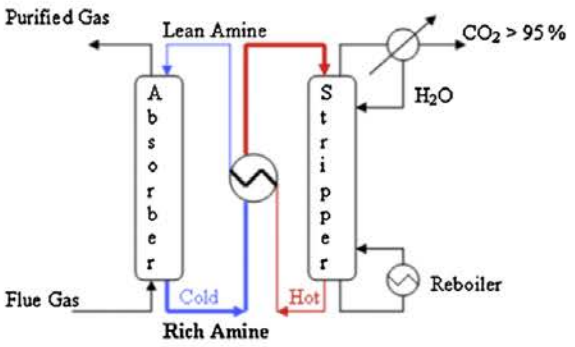
1. Introduction

CO_2 emissions have to be decreased to limit greenhouse effect. A part of the solution is post combustion CO_2 capture (EIA, 2011), which still needs a huge research development.

Most mature post-combustion CO_2 capture technology is based on CO_2 absorption by aqueous amine solutions and thus takes advantage of the strong experience of industrials in natural gas deacidification. CO_2 reacts reversibly in an absorber with amines which are regenerated by heating the solution in a stripper column (Scheme 1). Then CO_2 is compressed for transport and storage. A main problem associated with chemical absorption using amines is degradation through irreversible side reactions mainly with CO_2 and O_2 but also with NO_x and SO_x. These reactions can lead to different problems with the process: solvent loss, formation of volatile compounds potentially dangerous for environment, foaming, fouling and corrosion (Islam et al., 2011).

Alkanolamines are the most studied solvents. The benchmark molecule is monoethanolamine (MEA) (Davis and Rochelle, 2009; Lepaumier et al., 2011a; Polderman et al., 1955; Strazisar et al., 2003; Supap et al., 2011; Vevelstad et al., 2011), but some other amines were studied like diethanolamine (DEA) (Chakma and Meisen, 1986; Choy and Meisen, 1980; Holub et al., 1998), methyldiethanolamine (MDEA) (Abu-Zahra et al., 2007; Chakma and Meisen, 1988, 1997; Lawal et al., 2005a), piperazine (PZ) (Freeman et al., 2010; Freeman and Rochelle, 2011; Lensen, 2004) and 2-amino-2-methylpropan-1-ol (AMP) (Eide-Haugmo et al., 2011; Wang and Jens, 2011).

MEA has several advantages such as high CO_2 cyclic capacity and high kinetic at low CO_2 partial pressure. Moreover it has high solubility in water, low viscosity and it is cheap, but this amine has some disadvantages: one of them is degradation. Solvent degradation is around 10% of total cost of CO_2 capture (Rao and Rubin, 2002). Therefore, knowledge of amine degradation mechanisms is crucial. It is also important to list formed compounds and their ratio because some of them are volatile. Therefore, they could be emitted in atmosphere and could be unfriendly for environment like nitrosamines for instance (IARC, 1978; NTP, 2012; Thitakamol et al., 2007).



Scheme 1. Simplified CO_2 capture process.

Two main types of degradation have been studied: thermal degradation, which occurs at high temperature and high CO_2 partial pressure in the stripper (Davis, 2009; Holub et al., 1998; Lepaumier, 2008) and oxidative degradation (Lepaumier et al., 2009b; Rooney et al., 1998a; Sexton, 2008). Oxidative degradation is mainly due to the presence of a large amount of O_2 in flue gases. For instance, in the case of coal-fired power plants, flue gases typically contain 70–75% N_2, 10–15% CO_2, 8–10% H_2O and 3–4% O_2 (Bhown and Freeman, 2011). Because some traces of SO_x and NO_x are also present in flue gases, some authors reported their influence of amine degradation (Fostas et al., 2011; Jackson and Attala, 2010; Supap et al., 2009).

Generally, for lab scale experiments, researchers focus on one type of degradation. Samples coming from pilot plants were analysed too (Lepaumier et al., 2011a; Moser et al., 2011a,b; Strazisar et al., 2001, 2003). They have the advantage to take into account all types of degradation.

The aim of this review is to list degradation products and pathways of their formation described in the literature. This review is divided into eight parts. MEA, which is the most studied amine in the literature, is presented first, then other well studied amines are described: DEA, MDEA, PZ and AMP. In each part, thermal and oxidative degradations are described separately. After that, other amines and amine blends are presented. Finally influence of SO_x and NO_x is described.

2. Studied amines

2.1. Monoethanolamine (MEA)

MEA is the most studied amine. Lots of articles described degradation products and some of them proposed degradation pathways.

2.1.1. Thermal degradation

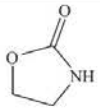
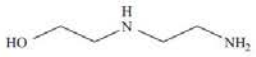
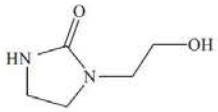
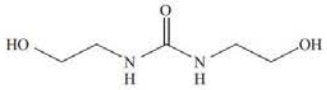
Thermal degradation takes place mainly in the stripper (Davis and Rochelle, 2009; Lepaumier et al., 2011a). Most of the studies postulate that degradation is due to high temperature in the presence of CO_2.

A fundamental study presents also degradation due to high temperature without CO_2 to understand the role of heat (Lepaumier, 2008). This type of degradation causes dealkylation, dimerisation and cyclisation but no mechanism was proposed, even if a radical pathway is highly likely to occur as for oxidative degradation (Lepaumier, 2008). In this case, most important degradation products are ammonia and N-(2-hydroxyethyl) ethylenediamine (HEEDA).

Because of high partial pressure of CO_2 and high temperature, thermal degradation of MEA leads to successive degradation compounds. The main ones are given in Table 1. Formation of these compounds has been well established. Proposed mechanisms are listed below (for MEA, $R^1 = H$ in all figures).

Firstly, MEA reacts with CO_2 to form a carbamate (Fig. 1), this reaction takes place in the absorber. Then carbamate can be transformed into oxazolidin-2-one (Fig. 2) (Holub et al., 1998; Lepaumier et al., 2009a; Polderman et al., 1955). Oxazolidin-2-one

Table 1
MEA main thermal degradation products.

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	Oxazolidin-2-one (OZD)	87	Lepaumier et al. (2009a, 2011a), Strazisar et al. (2001, 2003)
	N-(2-hydroxyethyl)ethylenediamine (HEEDA)	104	Davis and Rochelle (2009), Lepaumier et al. (2009a, 2011a), Supap et al. (2006)
	N-(2-hydroxyethyl)imidazolidin-2-one (HEIA)	130	Davis and Rochelle (2009), Lepaumier et al. (2009a, 2011a), Sexton and Rochelle (2011), Strazisar et al. (2001), Supap et al. (2006)
	N,N′-bis-(2-hydroxyethyl)urea	148	Davis and Rochelle (2009), Lepaumier (2008), Lepaumier et al. (2011a)

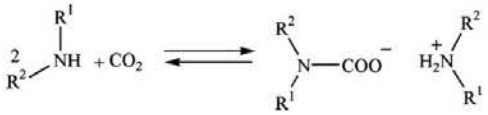


Fig. 1. Carbamate formation (R^1 = H, R^2 = CH_2CH_2OH).

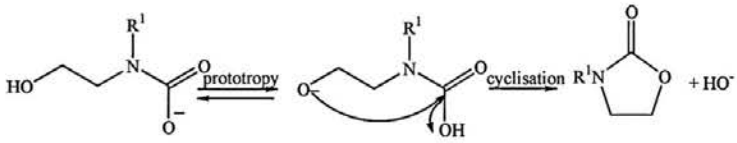


Fig. 2. Oxazolidin-2-one formation (R^1 = H).

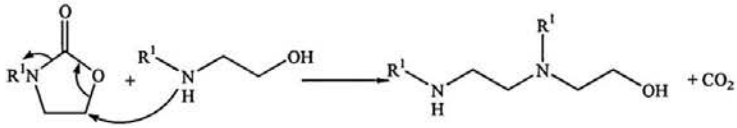


Fig. 3. Diamine formation (R^1 = H).

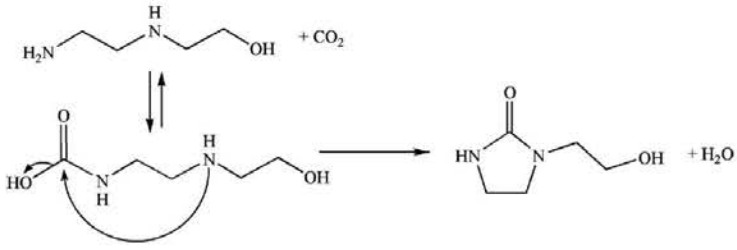


Fig. 4. Imidazolidin-2-one formation.

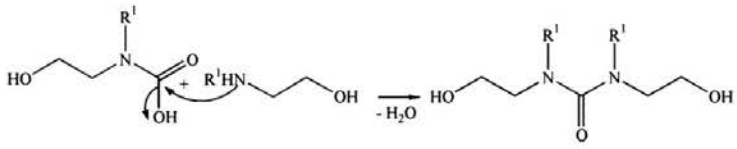


Fig. 5. Ureas formation (R^1 = H) according to Davis and Rochelle (2009).

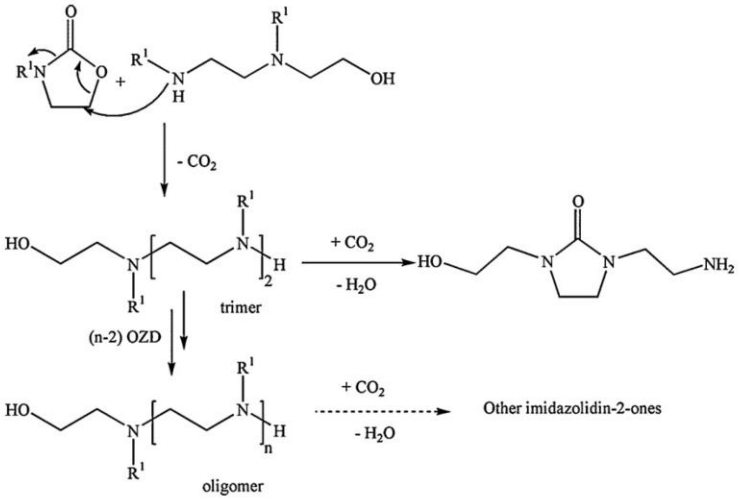


Fig. 6. Degradation products formed from HEEDA (R^1 = H).

can react with another molecule of MEA to form HEEDA (Fig. 3) (Davis and Rochelle, 2009; Holub et al., 1998; Lepaumier et al., 2009a). HEEDA can then react with CO_2 to form another carbamate, followed by intramolecular cyclisation giving HEIA (Fig. 4), which is not very reactive and can accumulate in the solution (Davis and Rochelle, 2009; Lepaumier et al., 2009a; Sexton and Rochelle, 2011).

The two last figures can be discussed. Polderman et al. (1955) described HEIA as the precursor of HEEDA but thanks to HPLC analyses, Davis and Rochelle (2009) and Lepaumier et al. (2011a) have shown that it is the opposite. Moreover, Lepaumier et al. (2009a) showed that HEIA was the major degradation product and was very stable. These results are in accordance with Fazio (1984) who described diamine syntheses with oxazolidin-2-ones as starting materials.

Similarly to imidazolidin-2-ones formation, ureas can be obtained by reaction between carbamates and amines (Fig. 5) (Davis and Rochelle, 2009; Lepaumier, 2008). This reaction is less favourable than that described in Fig. 2 (intermolecular vs intramolecular reaction). Therefore, it explains why ureas are minor degradation products.

Other degradation products are formed starting from HEEDA (Table 2). Fig. 6 (Davis, 2009; Lepaumier, 2008) shows that successive addition compound can be formed according to the mechanism described in Fig. 3 (ring opening of oxazolidin-2-one). Each addition compound can form imidazolidin-2-one derivatives as described in Fig. 4. To the best of our knowledge, no other specific thermal degradation products of MEA have been described in the literature.

2.1.2. Oxidative degradation

Oxidative degradation is mainly described in absorber conditions. Solutions are loaded with CO_2, and authors observed some similar products as for thermal degradation. Fewer reports deal with the study of oxidative degradation in the absence of CO_2 (Lepaumier et al., 2009b, 2011a).

Some authors observed the catalytic effect of dissolved metallic ions on oxidative degradation of MEA (Bello and Idem, 2006; Chi and Rochelle, 2002; Goff and Rochelle, 2004, 2006; Sexton and Rochelle, 2011). Metallic ions in solution might have been generated by corrosion or added through anticorrosion metallic salts ($CuCO_3$, $NaVO_3$).

We have firstly listed the more likely oxidative degradation products, i.e. those cited by two or more teams and which formation has been explained by realistic mechanisms. They are listed by increasing molecular weights in Table 3; main reactions are dealkylation, addition and piperazinones formation. Table 4 gives degradation products without explained mechanisms but which formation is proven or very likely to occur. Finally, we talk about some unexpected degradation products.

First of all, carboxylic acids formation and their reactions with other compounds are described. Two general mechanisms were proposed for the generation of carboxylic acids by Rooney et al. (1998b) (Fig. 7) and by Lepaumier et al. (2009b) (Fig. 8). In both of them, volatile amines like ammonia or methylamine are formed as well as aldehydes which are acids precursors. It is noteworthy that the mechanism of methylamine formation described by Rooney et al. (1998b) (Fig. 7) remains unclear. Lepaumier et al. (2009b) described the formation of ammonia and ethylene oxide which, according to Ye and Zhang (2001), was hydrolyzed into ethylene glycol leading to carboxylic acids. It is well known that aldehydes are rapidly oxidised into acids even with air only. It is the same in this case. These acids cause corrosion and fouling in pilot plants and they increase degradation ratio due to their reaction with amines affording salts commonly called HSSs "Heat Stable Salts" (Supap et al., 2011) or HSASs, "Heat Stable Amine Salts". It is important to point out that all acids are in HSSs form due to this

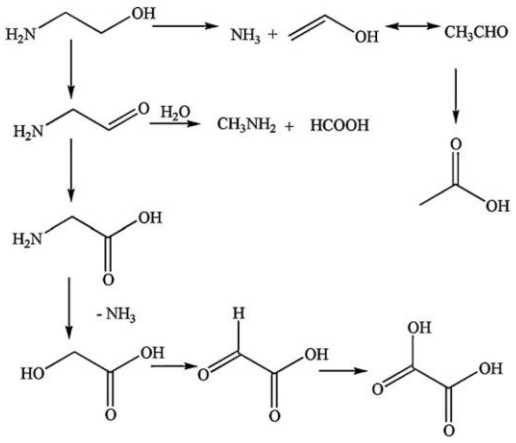
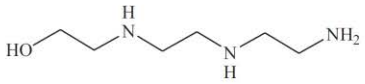
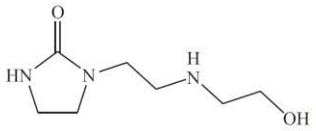
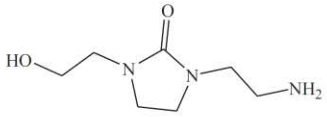
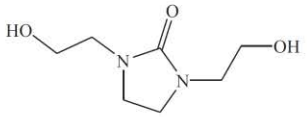
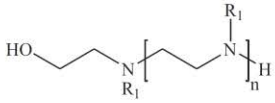


Fig. 7. Carboxylic acids formation according to Rooney et al. (1998b).

Table 2
MEA thermal degradation products formed from HEEDA.

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	N-(2-hydroxyethyl)-diethylenetriamine	147	Davis (2009)
	N-[2-[(2-hydroxyethyl)amino] ethyl] imidazolidin-2-one	173	Davis (2009)
	N-(2-aminoethyl)-N′-(2-hydroxyethyl)imidazolidin-2-one (AEHEIA)	173	Lepaumier et al. (2011a)
	N,N′-bis(2-hydroxyethyl)imidazolidin-2-one (BHEI)	174	Lepaumier et al. (2009a)
	–	–	Davis (2009)

reaction. These salts and also amides (listed in Table 3) are obtained by classical reaction (Fig. 9) between carboxylic acids and amines (Lepaumier et al., 2011a). HSSs are not regenerated in stripper conditions because carboxylic acids are more acidic than carbonic acid (Tanthapanichakoon et al., 2006; Veldman, 2000).

Some authors described in more detail oxidative fragmentation of amines with radical chemistry. Two types of radical pathways can lead to the same compounds. The first one (Fig. 10) is based on electron abstraction (Chi and Rochelle, 2002; Goff, 2005; Goff and Rochelle, 2004; Lindsay Smith and Mead, 1973; Lindsay Smith and Masheder, 1977) and the second one (Figs. 11 and 12) is based on hydrogen abstraction (Lepaumier et al., 2009b; Petryaev et al., 1984).

Electron abstraction has been proved but only for tertiary amines (Dennis et al., 1967; Hull et al., 1967, 1969; Rosenblatt et al., 1967).

Fig. 10 can be extrapolated for MEA: electron abstraction can take place on the CH_2 in α of nitrogen atom (R = H and CH_3 replaced by CH_2CH_2OH), giving ammonia and glycolic acid. Another radical pathway (Fig. 13) based on hydrogen abstraction was proposed to explain the formation of glycine (Bedell, 2009, 2011). Two molecules of glycine can react together to form N-glycylglycine (Strazisar et al., 2001; Supap et al., 2006). Among all radical mechanisms described in the literature, it remains difficult to prefer one rather another (Bedell, 2011; Chi and Rochelle, 2002; Lepaumier et al., 2009b; Lindsay Smith and Masheder, 1977; Petryaev et al., 1984).

HEEDA is obtained by oxidative or thermal degradation (Lepaumier et al., 2009b). In the case of oxidative degradation, the presence of carboxylic acids enables an ester formation with DMEA then ring cyclisation followed by a S_N2 reaction with a second MEA molecule (Fig. 14). After that HEEDA can react with ethylene oxide to form BHEEDA.

During oxidative degradation, MEA gives piperazinones in pilot plants (Strazisar et al., 2003; Lepaumier et al., 2011a) or in lab experiment (Lepaumier et al., 2009b). Two pathways are proposed:

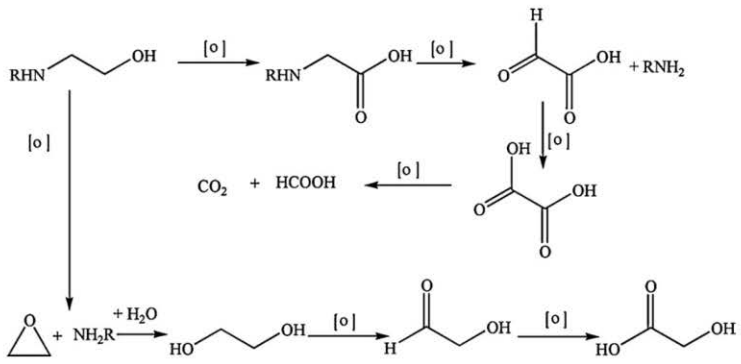


Fig. 8. Oxidations and ethylene glycol formation (R = H) according to Lepaumier (2008).

Table 3
MEA oxidative degradation products described in Figs. 7–17.

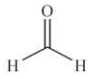
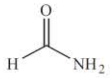
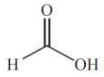
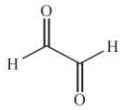
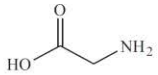
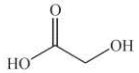
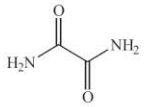
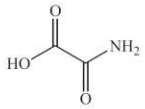
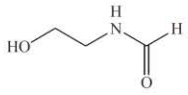
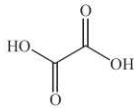
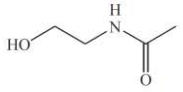
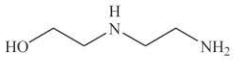
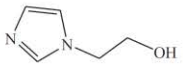
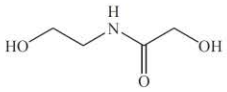
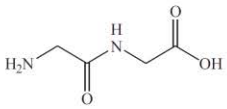
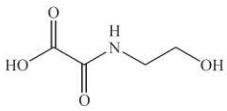
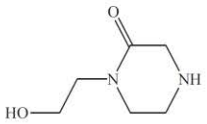
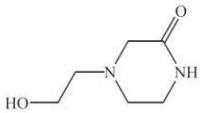
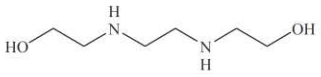
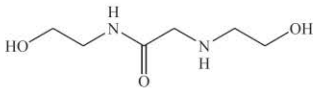
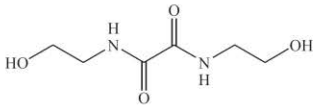
Chemical structure	Name (abbreviation)	M_w (g/mol)	References
NH_3	Ammonia	17	Goff (2005), Lepaumier et al. (2009b), Sexton and Rochelle (2011), Strazisar et al. (2003), Supap et al. (2006)
	Formaldehyde	30	Goff (2005), Lepaumier (2008), Sexton and Rochelle (2011)
	Methylamine	31	Sexton and Rochelle (2011), Strazisar et al. (2003)
	Acetaldehyde	44	Lepaumier et al. (2011a), Rooney et al. (1998b), Sexton and Rochelle (2011), Strazisar et al. (2003), Supap et al. (2006)
	Formamide	45	Lepaumier et al. (2011a), Sexton and Rochelle (2011)
	Formic acid	46	Lepaumier (2008), Lepaumier et al. (2011a), Rooney et al. (1998b), Sexton and Rochelle (2011), Strazisar et al. (2003)
	Glyoxal	58	Lepaumier (2008) Sexton and Rochelle (2011)
	Acetic acid	60	Lepaumier (2008), Lepaumier et al. (2011a), Rooney et al. (1998b), Sexton and Rochelle (2011), Strazisar et al. (2003)
	Glycine	75	Bedell (2011), Lepaumier (2008), Rooney et al. (1998b)
	Glycolic acid	76	Lepaumier et al. (2009b), Rooney et al. (1998b), Sexton and Rochelle (2011), Supap et al. (2011)
	Oxalamide, oxamide	88	Supap et al. (2011)
	Oxamic acid	89	Lepaumier (2008)
	N-(2-hydroxyethyl)formamide (HEF)	89	Lepaumier et al. (2009b, 2011a), Strazisar et al. (2003) Supap et al. (2011)
	Oxalic acid	90	Davis (2009), Rooney et al. (1998b), Sexton and Rochelle (2011), Supap et al. (2011)
	N-(2-hydroxyethyl)acetamide (HEA) (ou N-acetylethanolamine)	103	Lepaumier et al. (2009b, 2011a), Strazisar et al. (2003), Supap et al. (2006, 2011)

Table 3 (*Continued*)

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	N-(2-hydroxyethyl)ethylenediamine (HEEDA)	104	Davis and Rochelle (2009), Lepaumier et al. (2009b, 2011a), Supap et al. (2006)
	N-(2-hydroxethyl)imidazole (HEI)	112	Lepaumier et al. (2011a), Sexton and Rochelle (2011)
	2-Hydroxy-N-(2-hydroxyethyl)acetamide (HHEA)	119	Lepaumier et al. (2011a), Supap et al. (2011)
	N-glycylglycine	132	Strazisar et al. (2001), Supap et al. (2006)
	N-(2-hydroxyethyl)oxamic acid	133	Lepaumier et al. (2009b), Supap et al. (2011)
	N-(2-hydroxyethyl)piperazin-2-one	144	Lepaumier et al. (2009b, 2011a), Strazisar et al. (2003)
	N-(2-hydroxyethyl)piperazin-3-one (HEPO)	144	Lepaumier et al. (2009b, 2011a), Strazisar et al. (2003)
	N,N′-bis(2-hydroxyethyl)ethylenediamine (BHEEDA)	148	Lepaumier (2008)
	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA)	162	Lepaumier et al. (2011a), Strazisar et al. (2003)
	N,N′-bis(2-hydroxyethyl)oxalamide (BHEOX)	176	Lepaumier et al. (2011a), Supap et al. (2011)

Lepaumier et al. (2009b) explained their formation by a reaction between glycolic acid and HEEDA followed by intramolecular dehydration (Fig. 15), while Strazisar et al. (Fig. 16) proposed a radical pathway with HEHEAA as intermediate. Two isomers could be formed by these ways.

HEI is a major degradation product. There is no postulated mechanism in the literature but Arduengo et al. (2001) patented HEI and derivates syntheses (no mechanism is given); HEI was obtained by reaction between ammonium bicarbonate, formaldehyde, glyoxal and MEA (Fig. 17). Since all these compounds are present in the solution, HEI could be formed by this way.

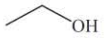
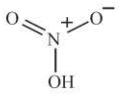
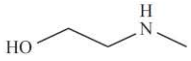
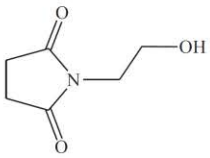
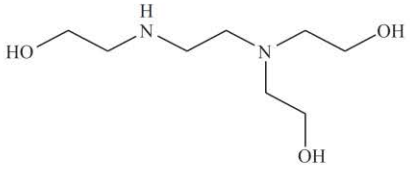
Other degradation products (Table 4) are proven or very likely but without described mechanism, therefore further investigation is needed. It is well known that nitrates and nitrites are present in the solution but, to the best of our knowledge, no mechanism was proposed. Since MAE and N-(2-hydroxyethyl)-succinimide are reported by three authors, they might be present in the solution but their formation seems difficult to explain. Ethanol and THEED are reported by one author; since they are observed as DEA degradation products, DEA might be present in initial MEA.

Moreover, 60 other degradation products are mentioned in five articles without explanation (Bello and Idem, 2005 (45 products); Lawal et al., 2005a (25 products); Lawal et al., 2005b (11 products); Strazisar et al., 2003 (8 products); Supap et al., 2006 (20 products)). Some of them are cited several times by the same group, but their formation seems very hard to explain: for example, 1-methylazetidine, pyrimidine, 1,3-dioxane, uracil, 2,6-dimethyl-4-aminopyridine and 18-crown-6.

For more details readers should refer to the five cited articles.

Under pilot plant conditions, oxidative and thermal degradation might take place. Lepaumier et al. (2011a) showed that MEA degradation is mainly due to oxidation. Lepaumier et al. (2011a) and Strazisar et al. (2003) obtained both as major degradation

Table 4
MEA degradation products without any described mechanisms.

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	Ethanol	46	Supap et al. (2006)
	Nitrous acid	47	Davis (2009), Strazisar et al. (2001)
	Nitric acid	63	Davis and Rochelle (2009), Davis (2009), Strazisar et al. (2001)
	2-(Methylamino)ethanol (MAE)	75	Davis and Rochelle (2009), Goff (2005), Rooney et al. (1998b)
	N-(2-hydroxyethyl)-succinimide	143	Lepaumier et al. (2009b), Rooney et al. (1998b), Supap et al. (2011)
	N,N,N′-tris(2-hydroxyethyl)ethylenediamine (THEED)	192	Lepaumier et al. (2009b)

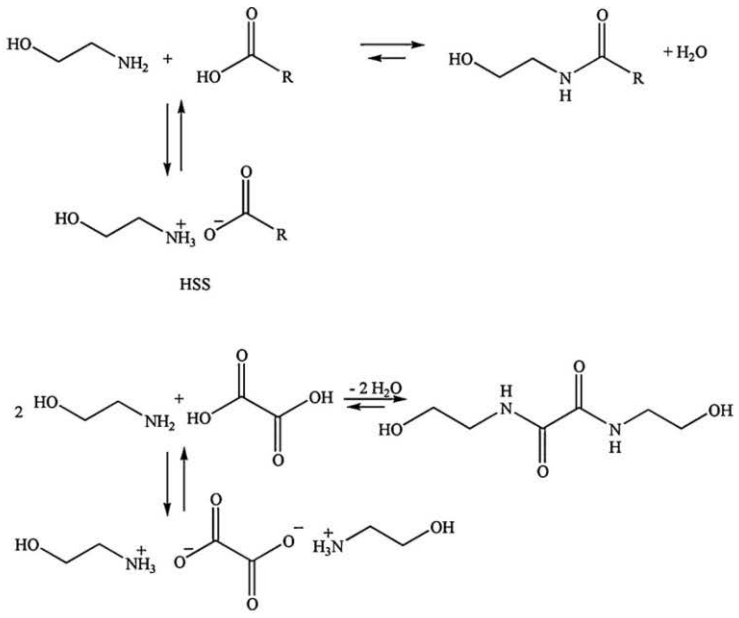


Fig. 9. Amides and HSSs formation (R = H, CH_3 or CH_2OH).

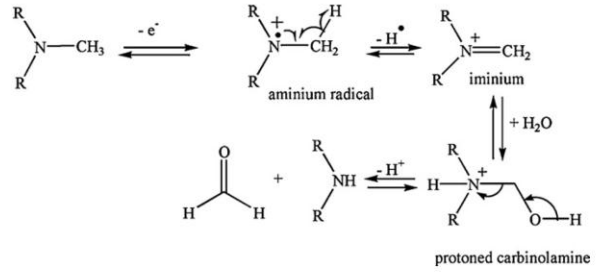


Fig. 10. Electron abstraction (R = H or alkyl) according to Lindsay Smith and Masheder (1977).

products HEPO, HEHEAA and a compound with a molecular weight of 176 g/mol. Since only Strazisar et al. (2003) identified it as N,3-bis-(2-hydroxyethyl)-propanamide it needs further investigation.

2.2. Diethanolamine (DEA)

Before its utilisation in CO_2 capture, DEA was extensively used in gas treatment, so the literature is focused on degradation due to CO_2.

Some authors (Kennard, 1983; Kennard and Meisen, 1980) reported that initial DEA solutions already contained MEA, so they found obviously degradation products coming from MEA.

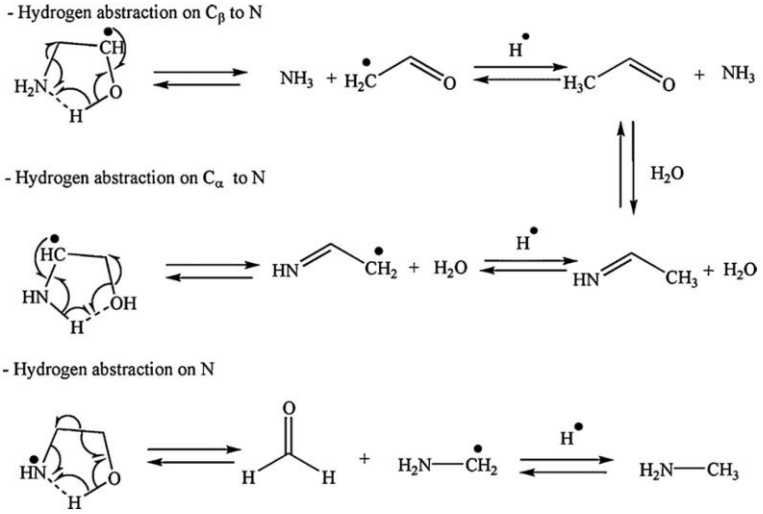


Fig. 11. Hydrogen abstraction according to Petryaev et al. (1984).

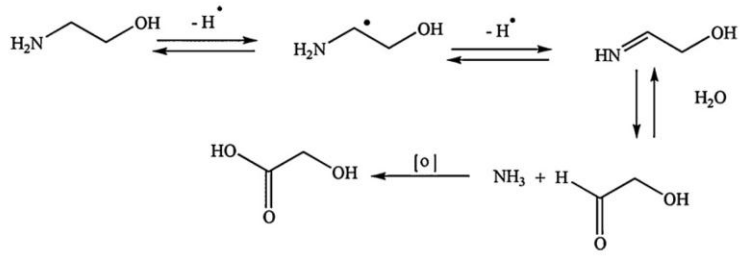


Fig. 12. Hydrogen abstraction according to Lepaumier et al. (2009b).

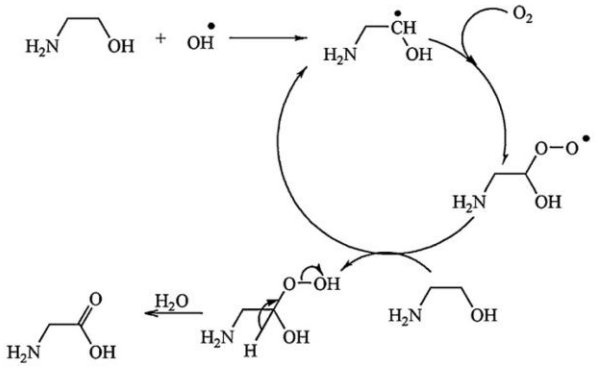


Fig. 13. Radical mechanism proposed for glycine formation according to Bedell (2009).

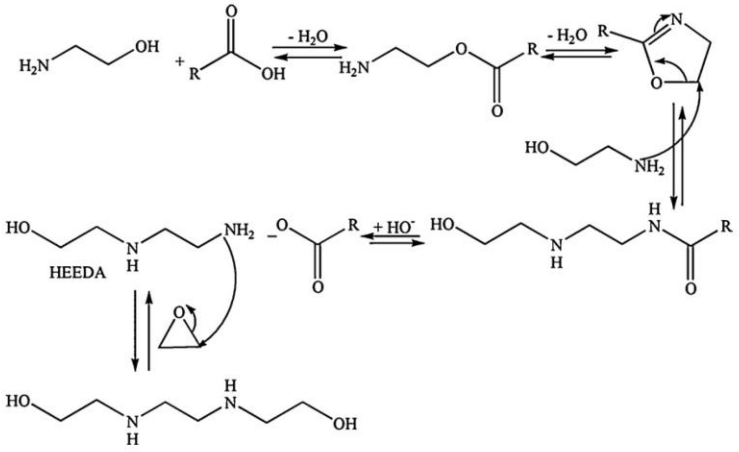


Fig. 14. HEEDA and BHEEDA formation according to Lepaumier et al. (2009b) (R = H, CH_3 or CH_2OH).

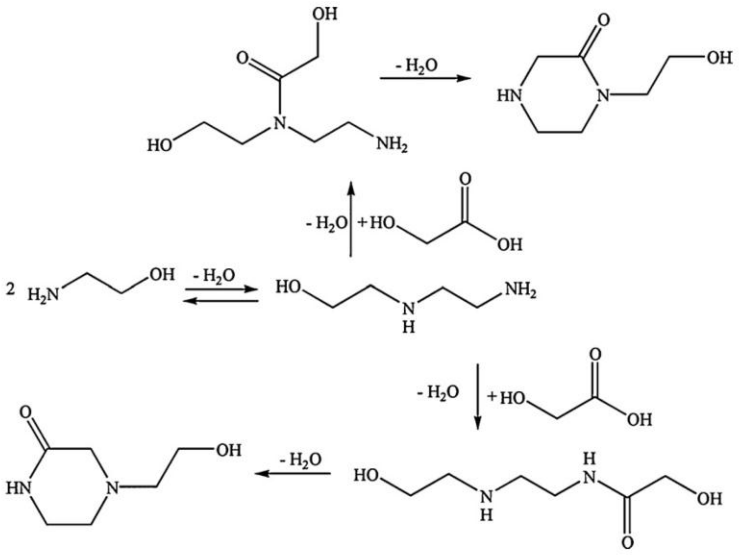


Fig. 15. Piperazinones formation according to Lepaumier et al. (2009b).

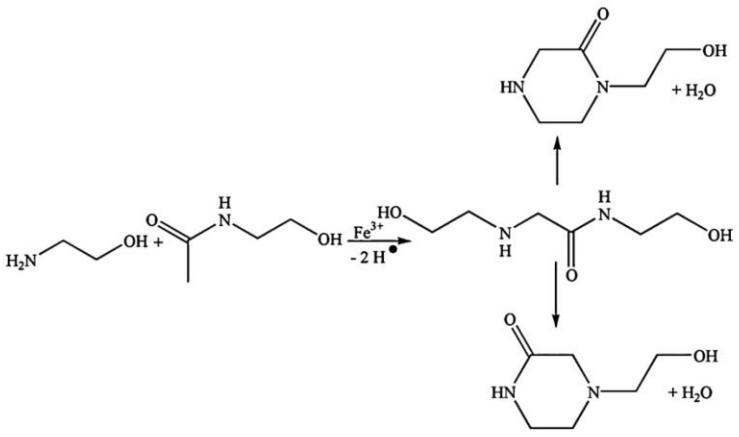


Fig. 16. Piperazinones formation according to Strazisar et al. (2003).

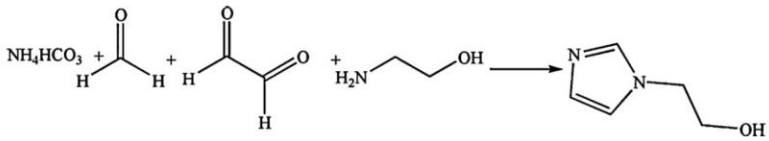


Fig. 17. HEI formation according to Arduengo et al. (2001).

Moreover DEA degrades to MEA (see Section 2.2.2), therefore all products listed in previous tables could be seen in DEA degraded solutions.

DEA was firstly studied by Polderman and Steele (1956) and then by Hakka et al. (1968). After that, between 1980 and 1996, only two groups studied DEA degradation. One is Exxon Research (Hsu and Kim, 1985; Kim and Sartori, 1984) and the other one is the University of British Columbia (Chakma and Meisen, 1986, 1987, 1988; Dawodu and Meisen, 1991, 1996a; Kennard, 1983; Kennard and Meisen, 1980, 1983, 1985; Meisen and Kennard, 1982). The last studies of DEA degradation have been done in France by IFP and LMOPS (Lepaumier, 2008; Lepaumier et al., 2009a,b).

2.2.1. Thermal degradation

DEA degradation products due to CO_2 are listed in Table 5; in this table we have only reported the most relevant reference for each team.

Lots of mechanisms described for MEA can be applied to DEA degradation.

Firstly, DEA forms carbamate with CO_2 (Fig. 1 with $R^1 = R^2 = CH_2CH_2OH$), which can lead to HEOD by intramolecular cyclisation (Fig. 2, $R^1 = CH_2CH_2OH$). Then, following Fig. 3 ($R^1 = CH_2CH_2OH$), THEED can be formed (Kim and Sartori, 1984) whereas Kennard and Meisen (1985) described THEED formation by intermolecular reaction between DEA and DEA carbamate.



Fig. 21. Alkylation/dealkylation ($R = CH_2CH_2OH$).

Lepaumier et al. (2009a) proposed another way for diamine formation through an aziridium salt as intermediate (Fig. 18).

Diamines can form piperazines by intramolecular dehydration: THEED gives by this way BHEP (Fig. 19, $R^1 = R^2 = CH_2CH_2OH$) (Kennard and Meisen, 1985; Kim and Sartori, 1984).

Polderman and Steele (1956) did not observe THEED, so they proposed a mechanism involving two HEOD molecules (Fig. 20).

DEA alkylation/dealkylation (transamination) leads to MEA and TEA (Fig. 21) according to Lepaumier (2008).

Besides these main degradation products, other compounds were identified. DEA gives an urea (TEHEU); the mechanism is given Fig. 5 with $R^1 = CH_2CH_2OH$. HEM can be formed by intramolecular dehydration of DEA. Then HEM can react with DEA to form THEED (Fig. 18, $R^1 = R^2 = R^3 = CH_2CH_2OH$, $R^4 = H$). Moreover two molecules of DEA could react together to form BHEAE (Kennard and Meisen, 1985) (Fig. 22).

Hsu and Kim (1985) cited other products: HAO is an oxazolidin-2-one formed by intramolecular cyclisation of THEED carbamate (Fig. 2 with $R^1 = CH_2CH_2N(CH_2CH_2OH)_2$). This product can react with DEA to form THEDT (Fig. 3, $R = CH_2CH_2OH$). i-THEDT is formed (Fig. 6, $R^1 = CH_2CH_2OH$) with HEOD and THEED as starting

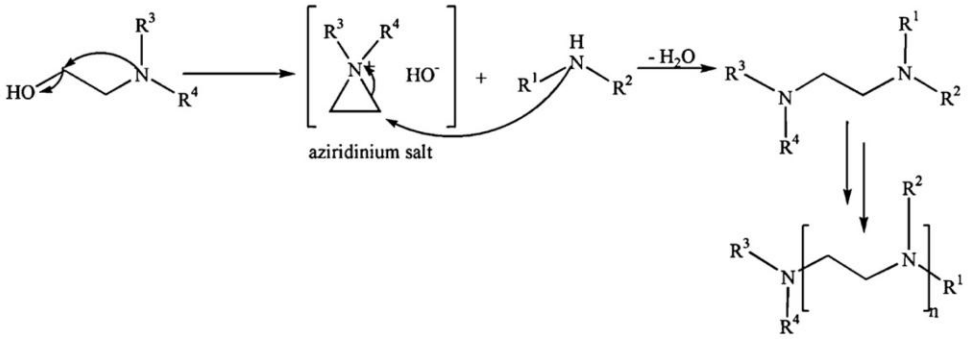


Fig. 18. Addition products formation (R^1, R^2, $R^3 = CH_2CH_2OH$ and $R^4 = H$ or CH_2CH_2OH) according to Lepaumier et al. (2009a).

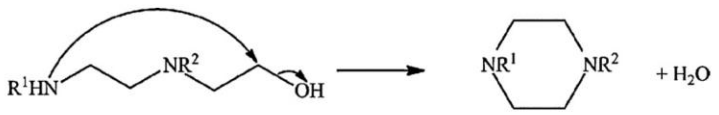


Fig. 19. Ring closure according to Lepaumier et al. (2009a).

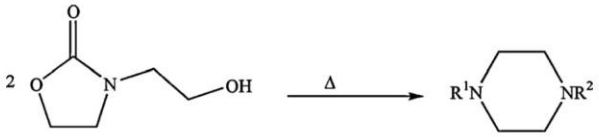


Fig. 20. BHEP formation according to Polderman and Steele (1956).

Table 5
DEA main thermal degradation products.

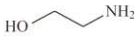
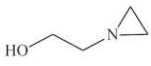
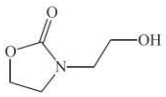
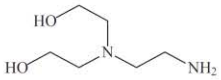
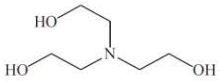
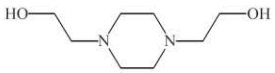
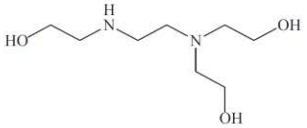
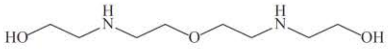
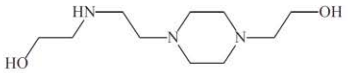
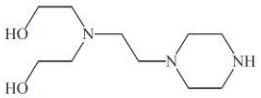
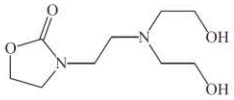
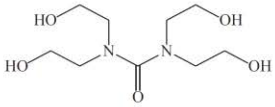
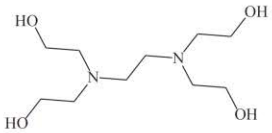
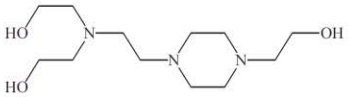
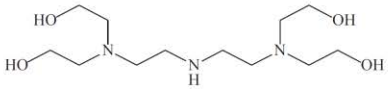
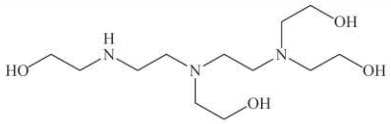
Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	Monoethanolamine (MEA)	61	Kennard (1983), Lepaumier (2008)
	N-(2-hydroxyethyl)aziridine (HEM)	87	Kennard (1983)
	N-(2-hydroxyethyl)oxazolidin-2-one (HEOD)	131	Hsu and Kim (1985), Kennard (1983), Lepaumier (2008)
	N,N-bis(2-hydroxyethyl)ethylenediamine	148	Kennard (1983)
	Triethanolamine (TEA)	149	Kennard (1983), Lepaumier (2008)
	N,N′-bis(2-hydroxyethyl)piperazine (BHEP)	174	Kennard (1983), Lepaumier (2008)
	N,N,N′-tris(2-hydroxyethyl)ethylenediamine (THEED)	192	Hsu and Kim (1985), Kennard (1983), Lepaumier (2008)
	Bis-(2-(2-hydroxyethylamino)ethyl)ether (BHEAE)	192	Kennard and Meisen (1985)
	N-(2-hydroxyethyl)-N′-(2-(2-hydroxyethylamino)ethyl)piperazine (HEAEHEP)	217	Lepaumier (2008)
	N-2-[bis(2-hydroxyethyl)-amino]ethyl-piperazine (HEAEP)	217	Lepaumier (2008)
	N-2-[bis(2-hydroxyethyl)-amino]ethyl-oxazolidin-2-one (HAO)	218	Hsu and Kim (1985)
	N,N,N′,N′-tetrakis(2-hydroxyethyl)urea (TEHEU)	236	Kennard and Meisen (1985)
	N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (TEHEED)	236	Kennard (1983)
	N-2-[bis(2-hydroxyethyl)-amino]ethyl-N′-(2-hydroxyethyl)piperazine (HAP)	261	Hsu and Kim (1985)
	N,N,N′,N′-tetrakis(2-hydroxyethyl)diethylenetriamine (THEDT)	279	Hsu and Kim (1985)

Table 5 (*Continued*)

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	N,N,N′,N″-tetrakis(2-hydroxyethyl)diethylenetriamine (i-THEDT)	279	Hsu and Kim (1985)

materials. Then THEDT and i-THEDT can lead to HAP by intramolecular dehydration (Fig. 19 with $R^1 = CH_2CH_2N(CH_2CH_2OH)_2$ and $R^2 = CH_2CH_2OH$ and vice versa).

Kennard (1983) postulated that TEHEED was formed by reaction between DEA and TEA. Fig. 18 could explain this reaction ($R^1 = R^2 = R^3 = R^4 = CH_2CH_2OH$).

MEA can react with DEA to form i-BHEEDA (Fig. 23), then this compound can react with HEOD to form a very reactive intermediate (Fig. 6), which immediately gives HEAEHEP and HEAEP by intramolecular dehydration (Fig. 19, $R^1 = CH_2CH_2NHCH_2CH_2OH$, $R^2 = CH_2CH_2OH$)

2.2.2. Oxidative degradation

Few authors studied oxidative degradation, and the same kind of mechanisms as for MEA could be applied (Hsu and Kim, 1985; Kennard and Meisen, 1983; Lepaumier, 2008; Rooney et al., 1998b). Compounds observed by oxidative degradation are listed in Table 6.

For formic, acetic and glycolic acids formation, Rooney et al. (1998b) proposed the same way as for MEA (Fig. 7). MEA is formed by oxidation of DEA (Fig. 8, $R = CH_2CH_2OH$).

MDEA could be formed by methylation of DEA but no mechanism was proposed (Lepaumier, 2008). THEED is explained (Lepaumier, 2008) by ester formation (reaction between DEA and carboxylic acids) followed by S_N2 with another molecule of DEA (Fig. 24). BHEP is formed by THEED ring closure as for thermal degradation (Fig. 19, $R^1 = R^2 = CH_2CH_2OH$). Lepaumier (2008) postulated that bicine is formed by oxidation of TEA (Fig. 25), even if TEA was not observed.

Table 6
DEA oxidative degradation products.

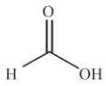
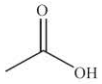
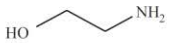
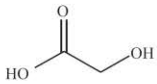
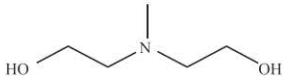
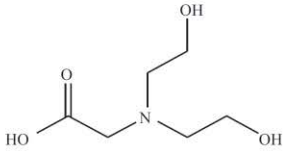
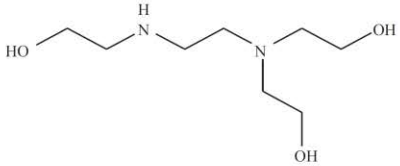
Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	Formic acid	46	Rooney et al. (1998a,b)
	Acetic acid	60	Rooney et al. (1998a,b)
	Monoethanolamine (MEA)	61	Kennard (1983), Lepaumier (2008)
	Glycolic acid	76	Rooney et al. (1998a,b)
	N-methyldiethanolamine (MDEA)	119	Lepaumier (2008)
	N-(carboxymethyl)diethanolamine (bicine)	163	Lepaumier (2008)
	N,N′-bis(2-hydroxyethyl)piperazine (BHEP)	174	Lepaumier (2008)
	N,N,N′-tris(2-hydroxyethyl)ethylenediamine (THEED)	192	Hsu and Kim (1985), Kennard (1983), Lepaumier (2008)

Table 7
MDEA main thermal degradation products.

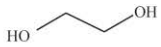
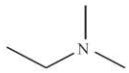
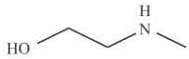
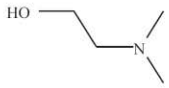
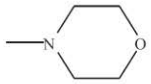
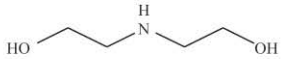
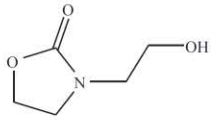
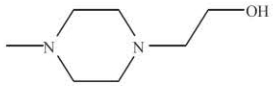
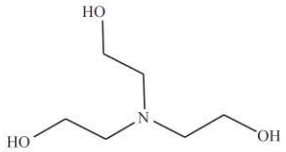
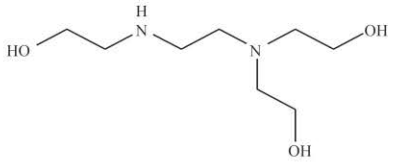
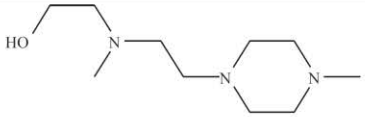
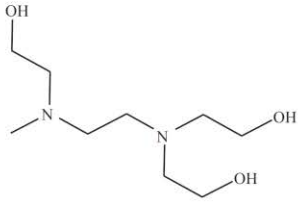
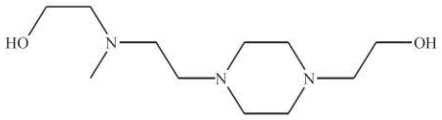
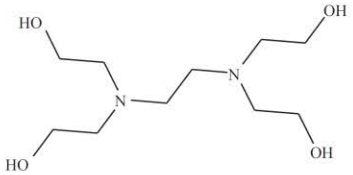
Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	Methanol	32	Chakma and Meisen (1988)
	Ethylene oxyde (EO)	44	Chakma and Meisen (1988)
	Trimethylamine (TMA)	59	Chakma and Meisen (1988)
	Ethylene glycol (EG)	62	Chakma and Meisen (1988), Lepaumier (2008)
	N,N-dimethylethylamine (DMEA)	73	Chakma and Meisen (1988)
	N-methylethanolamine (MAE)	75	Chakma and Meisen (1988)
	N,N-(dimethyl)ethanolamine (DMAE)	89	Chakma and Meisen (1988), Lepaumier (2008)
	N-methylmorpholine (MM)	101	Chakma and Meisen (1988)
	Diethanolamine (DEA)	105	Chakma and Meisen (1997), Lepaumier (2008)
	N,N′-dimethylpiperazine (DMP)	114	Chakma and Meisen (1988)
	N-(2-hydroxyethyl)oxazolidin-2-one (HEOD)	131	Chakma and Meisen (1988)
	N-(2-hydroxyethyl)-N′-methylpiperazine (HMP)	144	Chakma and Meisen (1988)
	Triethanolamine (TEA)	149	Chakma and Meisen (1988), Lepaumier (2008)
	N,N′-bis(2-hydroxyethyl)piperazine(BHEP)	174	Chakma and Meisen (1988)
	N,N,N′-tris(2-hydroxyethyl)ethylenediamine (THEED)	192	Chakma and Meisen (1988)

Table 7 (*Continued*)

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	N-[2-(2-hydroxyethylmethylamino)ethyl]-N′-methylpiperazine (HEMAEMP)	201	Dawodu and Meisen (1996a)
	N-methyl-N,N′,N′-tris(2-hydroxyethyl)ethylenediamine(MTHEED)	206	Dawodu and Meisen (1996a), Lepaumier (2008)
	N-[2-2-hydroxyethylmethylamino)ethyl]-N′-(2-hydroxyethyl)piperazine (HEMAEHEP)	231	Dawodu and Meisen (1996a)
	N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (TEHEED)	236	Chakma and Meisen (1997)

2.3. Methyldiethanolamine (MDEA)

MDEA was firstly used for natural gas desulphurisation because it is a tertiary amine and authors said that it did not react with CO_2. Actually, tertiary amines cannot form carbamate but can react with CO_2 to give hydrogenocarbonate (Fig. 26).

2.3.1. Thermal degradation

Thermal or oxidative degradation for MDEA alone was studied by some teams (Chakma and Meisen, 1988, 1997; Dawodu and Meisen, 1996a; Ye and Zhang, 2001). Degradation products due to CO_2 are listed in Table 7.

Methylation of one molecule of MDEA and demethylation of another gives DEA, which is a major degradation product (Closmann and Rochelle, 2011) and an ammonium intermediate which leads to DMAE and EO (Fig. 27) was proposed by Bedell (2009). It is disproportionation of MDEA, which leads to DMAE and TEA. MAE formation can be explained by Fig. 29 according to Dawodu and Meisen (1996a,b). After ammonium formation, dealkylation by S_NI leads to MAE and EO.

HEOD, TEA, THEED, TEHEED and BHEP can be formed from DEA as seen before.

TMA is formed following Fig. 27 ($R = CH_3$) with DMAE instead of MDEA., $R = CH_2CH_2OH$). EO can react with DEA to give triethanolamine. Another pathway (Fig. 28

N-methylmorpholine (MM) was obtained by cyclic dehydration by the same way described in Fig. 19. DMP was obtained from 2 molecules of MAE (cf. Fig. 23, $R^1 = R^2 = CH_3$) followed by cyclic dehydration.

HMP is obtained after dehydration by the same way with DEA and MAE as starting materials. Then, HMP can react with another molecule of MAE (as nucleophile) giving HEMAEMP (Fig. 23).

MTHEED can be obtained following Fig. 23 with MDEA and DEA as starting materials.

BHEP can react with MAE (as nucleophile) to give HEMAEHEP according to Fig. 23.

DMEA is reported by some authors (Chakma and Meisen, 1988; Closmann, 2011) but without any mechanism of formation.

2.3.2. Oxidative degradation

Oxidative products are listed in Table 8.

All products except morpholinones could be explained by previous figures.

N-methylmorpholin-2-one is obtained from dehydration of 2-[methyl(2-hydroxyethyl)amino]acetic acid and N-methylmorpholin-2,6-dione from the corresponding diacid according to Ye and Zhang (2001).

MDEA degradation was also studied to understand its role in blend solutions (Dupart et al., 1999; Lawal et al., 2005a,b).

2.4. Piperazine (PZ)

Piperazine is mainly used as promoter to increase CO_2 absorption kinetic, therefore only few authors studied piperazine degradation alone (Alawode, 2005; Closmann, 2011; Freeman, 2011). Closmann (2011) showed that thermal and oxidative degradations are negligible but Freeman (2011) tried to identify some degradation products.

2.4.1. Thermal degradation

Thermal degradation products are listed in Table 9.

2.4.2. Oxidative degradation

Oxidative degradation products are presented in Table 10.

A special study with chlorine dioxide (Dennis et al., 1967) showed that major oxidation products are EDA and formic acid. With EDA as starting material, some degradation products like imidazolidin-2-one can easily be explained (Fig. 4).

Table 8
MDEA main oxidative degradation products.

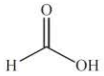
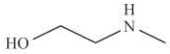
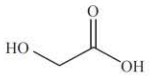
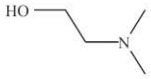
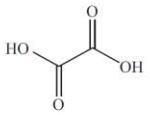
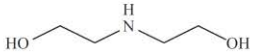
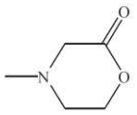
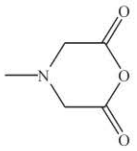
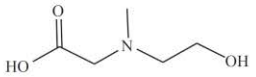
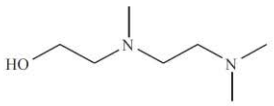
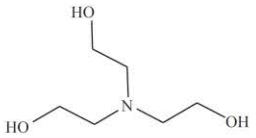
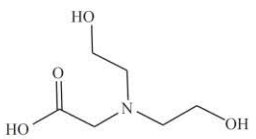
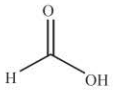
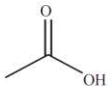
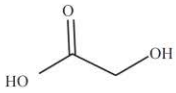
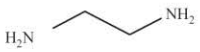
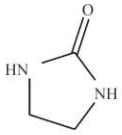
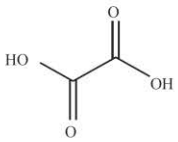
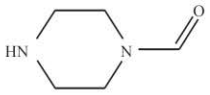
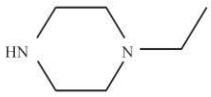
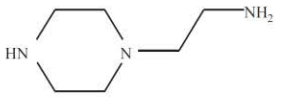
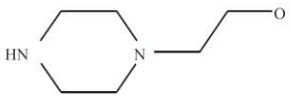
Chemical structure	Name (abbreviation)	M_w (g/mol)	Reference
	Methylamine	31	Rooney et al. (1998b)
	Ethylene oxyde (EO)	44	Chakma and Meisen (1988)
	Dimethylamine	45	Rooney et al. (1998b)
	Formic acid	46	Ye and Zhang (2001)
	Acetic acid	60	Ye and Zhang (2001)
	N-methylethanolamine (MAE)	75	Chakma and Meisen (1988)
	Glycolic acid	76	Closmann (2011)
	N,N-(dimethyl)ethanolamine (DMAE)	89	Chakma and Meisen (1988)
	Oxalic acid	90	Ye and Zhang (2001)
	Diethanolamine (DEA)	105	Chakma and Meisen (1997)
	N-methylmorpholin-2-one	115	Ye and Zhang (2001)
	N-methylmorpholin-2,6-dione	129	Ye and Zhang (2001)
	2-[Methyl(2-hydroxyethyl)amino] acetic acid	133	Closmann (2011)
	N,N,N′-trimethyl-N′-(2-hydroxyethyl)ethylenediamine	146	Lepaumier (2008)
	Triethanolamine (TEA)	149	Chakma and Meisen (1988)
	N-(carboxymethyl)diethanolamine (bicine)	163	Lepaumier (2008)

Table 9
PZ main thermal degradation products (Freeman, 2011).

Chemical structure	Name (abbreviation)	M_w (g/mol)
	Formic acid	46
	Acetic acid	60
	Glycolic acid	75
	Ethyl enediamine (EDA)	75
	Imidazolidin-2-one (2-Imid)	86
	Oxalic acid	90
	N-methylpiperazine (MPZ)	100
	N,N′-dimethylpiperazine (DMP)	114
	N-formylpiperazine (FPZ)	114
	N-ethylpiperazine (EPZ)	114
	N-(2-hydroxyethyl)-N′-methyl piperazine (HMP)	129
	N-(2-hydroxyethyl)piperazine (HEP)	130

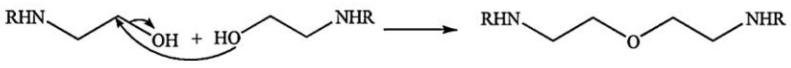


Fig. 22. BHEAE formation according to Kennard and Meisen (1985) (R = CH_2CH_2OH).

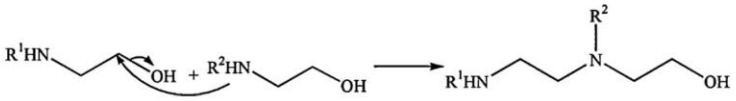


Fig. 23. i-BHEEDA formation (R^1 = H and R^2 = CH_2CH_2OH).

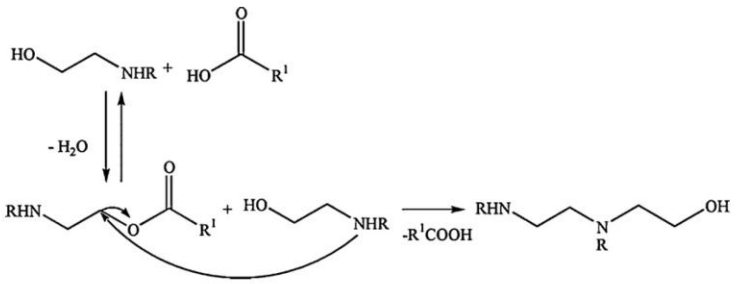


Fig. 24. THEED formation (R = CH_2CH_2OH, R^1 = H, CH_3 or CH_2OH) according to Lepaumier (2008).

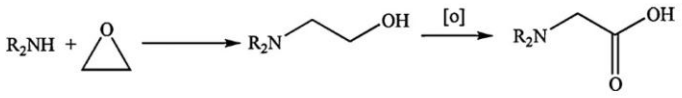


Fig. 25. Bicine formation (R = CH_2CH_2OH) according to Lepaumier (2008).

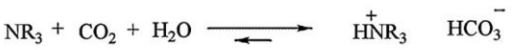


Fig. 26. Formation of carbonate.

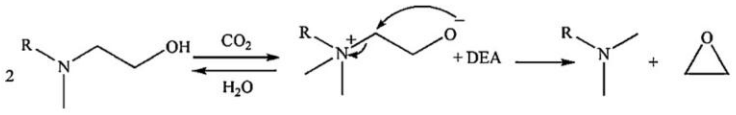


Fig. 27. Transamination according to Chakma and Meisen (1997).

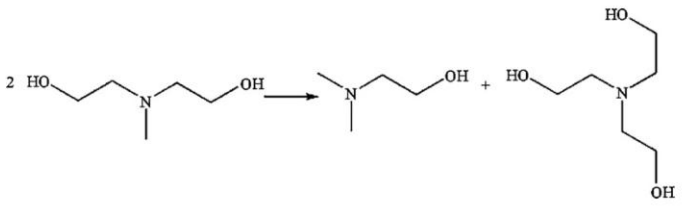


Fig. 28. Disproportionation of MDEA according to Bedell (2009).

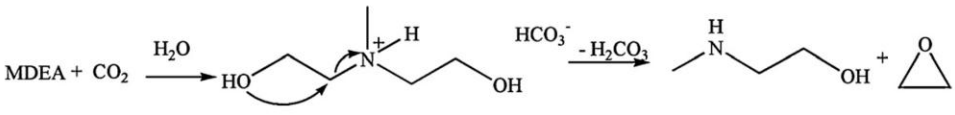
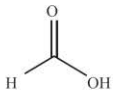
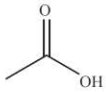
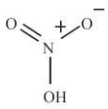
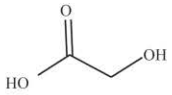
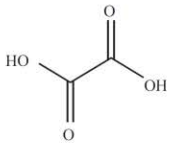
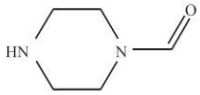


Fig. 29. Intramolecular dealkylation mechanism.

Table 10
PZ main oxidative degradation products.

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	Formic acid	46	Alawode (2005), Freeman (2011), Closmann (2011)
	Nitrous acid	47	Freeman (2011)
	Acetic acid	60	Alawode (2005), Freeman (2011)
	Nitric acid	63	Freeman (2011)
	Ethylenediamine (EDA)	75	Freeman (2011), Closmann (2011)
	Glycolic acid	76	Freeman (2011)
	Oxalic acid	90	Freeman (2011)
	N-formylpiperazine (FPZ)	114	Freeman (2011)

Freeman (2011) proposed some mechanisms but a lot of intermediates were not identified. People who are interested could report to her thesis.

2.5. 2-Amino-2-methylpropan-1-ol (AMP)

2.5.1. Thermal degradation

AMP is a sterically hindered primary amine; it suggests that it is less liable to thermal degradation than MEA. That was confirmed by Davis (2009), Eide-Haugmo et al. (2011) and Lepaumier (2008). Thermal degradation products are reported in Table 11. These products are obtained following same figures as MEA (Figs. 1–5). Limiting step will be carbamate formation because steric hindrance decreases carbamate stability. Carbamate polymerisation with oxazolidinones or imidazolidinones formation is more difficult and neither dimer nor trimer was reported.

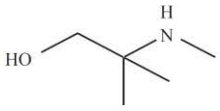
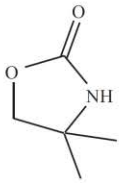
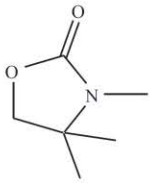
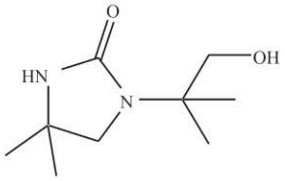
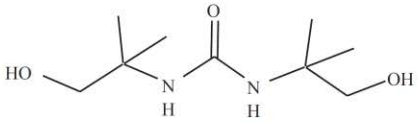
2.5.2. Oxidative degradation

In the same way, oxidative degradation will be lower than for MEA. To the best of our knowledge, only few authors studied AMP degradation and mechanisms. Oxidative degradation products are listed in Table 12. All products, except lutidine observed by Wang and Jens (2011), belong to the same previously described families. Wang and Jens (2012) proposed a mechanism to explain lutidine formation (Fig. 30). A peroxyl radical is firstly formed which gives formic acid and imine. This imine (in equilibrium with enamine) could be hydrolyzed leading to ammonia and acetone, which could react with formaldehyde to form an unsaturated ketone. This ketone could react with the enamine leading to lutidine. They observed also two trimethylpyridines but methyl positions are still unknown.

2.6. Other amines

Other amines were studied (Davis, 2009; Eide-Haugmo et al., 2011; Epp et al., 2011; Freeman, 2011; Lepaumier, 2008; Lepaumier et al., 2009a,b, 2010, 2011b). They are reported in Table 13. Previously described mechanisms could be applied for these molecules. For instance, ring closure occurs very easily in the case of linear polyamines which have two nitrogen separated by four or five atoms (Lepaumier et al., 2010). Therefore, such amines are less stable. Another mechanism based on Hofmann's degradation, can occur in the presence of CO_2 for amines having a labile proton present on β carbon atom of the nitrogen atom (Lepaumier, 2008) as shown in Fig. 31. In the case of linear amines having three carbons between the two nitrogen atoms such as N,N,N′,N′-tetramethylpropylenediamine and N,N,N′,N″,N″-pentamethyldipropylenetriamine, this is one of the main degradation mechanisms (Lepaumier et al., 2010). A very recent article described degradation and corrosion encountered

Table 11
AMP main thermal degradation products.

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
	N,2,2-trimethylethanolamine	103	Lepaumier (2008)
	4,4-Dimethyloxazolidin-2-one	115	Eide-Haugmo et al. (2011), Lepaumier (2008)
	N,4,4-trimethyloxazolidin-2-one	129	Lepaumier (2008)
	4,4-Dimethyl-1-hydroxytertiobutylimidazolidin 2-one	186	Davis (2009), Eide-Haugmo et al. (2011), Lepaumier (2008)
	l,3-Bis-(2-hydroxy-l, l-dimethylethyl)urea	204	Davis (2009)

with 22 compounds (Martin et al., 2012). This article did not describe degradation products neither their mechanism of formation because it focused on amine loss prediction.

2.7. Amine blends

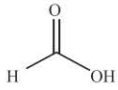
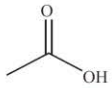
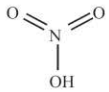
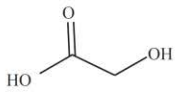
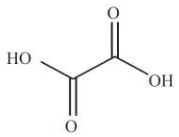
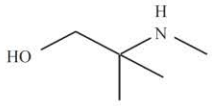
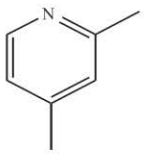
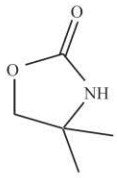
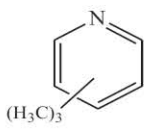
To increase solvent performance, amine blends are used and their degradations have been studied: MEA/MDEA (Dawodu and Meisen, 1996b; Lawal et al., 2005a,b); MDEA/PZ (Closmann et al., 2009; Closmann, 2011; Lensen, 2004); MDEA/DEA (Dupart et al., 1999), MEA/PZ (Davis, 2009) and MEA/AMP (Davis, 2009). More degradation products than for amines alone are generally found because of crossed reactions. For example, transaminations can occur (Figs. 21 and 22).

3. Effect of SO_x and NO_x

SO_x and NO_x are present in flue gases. Flue gases can be treated before CO_2 capture step to decrease their amount, but usually they cannot be totally removed. Consequently, it is important to know what happens in their presence, but only a few studies are presented in the literature. Bonenfant et al. (2007) showed that SO_2 decreased HEEDA capacity of CO_2 absorption because of the formation of ammonium sulphate salt. Supap et al. (2009) and Uyanga and Idem (2007) showed that SO_2 increases degradation rate. Wen and Narula (2009) proposed the formation of thioglycolic acid, when MEA reacts with SO_2. All these authors did not give more details concerning degradation products or mechanisms. A recent article (Zhou et al., 2012) dealt with thermal degradation of MEA in the presence of SO_x (Na_2SO_3, SO_2, H_2SO_4) and NO_x (HNO_3). In the presence of SO_2, authors identified sulphite, sulphate and thiosulphate ions in solution and they proposed also structures for three unidentified products based on m/z. The same team (Gao et al., 2011) has just published a pilot-scale study confirming that SO_2 increases degradation rate and decreases CO_2 absorption rate because of HSSs formation. They observed more sulphate than sulphite and pointed out that acetate dramatically decreased while glycolate strongly increased.

NO_x are known to react with secondary amines to form nitrosamines and nitramines (Challis and Challis, 1982; Loeppky and Michejda, 1994; Williams, 1988). However, this reaction can also occur with primary amines (Ridd, 1961), tertiary amines (Mirvish, 1975; Smith and Loeppky, 1967) and even with quaternary ammoniums (Fiddler et al., 1972; Kemper et al., 2010). Therefore all the amines are able to give nitrosamines. Pedersen et al. (2010) observed N-nitrosodiethanolamine (NDELA) and Fostas et al. (2011) tried to explain the effect of NO_x on MEA; they showed that NO_x react with MEA to form DEA (Fig. 30), which could react with NO_x to form NDELA. In autoclave, they observed also N-nitrosodimethylamine and N-nitrosomorpholine. Strazisar et al. (2003) observed nitrosamines in pilot plant but they did not identify species.

Table 12
AMP main oxidative degradation products.

Chemical structure	Name (abbreviation)	M_w (g/mol)	References
NH_3	Ammonia	17	Wang and Jens (2012)
	Formic acid	46	Wang and Jens (2012)
	Nitrous acid	47	Wang and Jens (2012)
	Acetone	58	Wang and Jens (2012)
	Acetic acid	60	Wang and Jens (2012)
	Nitric acid	63	Wang and Jens (2012)
	Glycolic acid	76	Wang and Jens (2012)
	Oxalic acid	90	Wang and Jens (2012)
	N,2,2-trimethylethanolamine	103	Lepaumier (2008)
	2,4-Lutidine	107	Wang and Jens (2012)
	4,4-Dimethyloxazolidin-2-one	115	Lepaumier (2008), Wang and Jens (2012)
	Trimethylpyridine	121	Wang and Jens (2012)

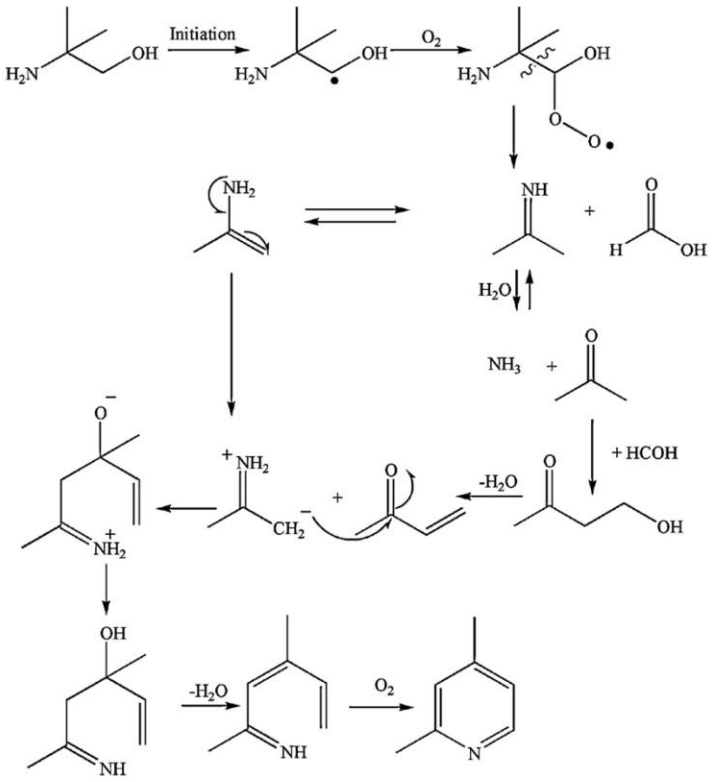


Fig. 30. 2,4-lutidine formation according to Wang and Jens (2012).

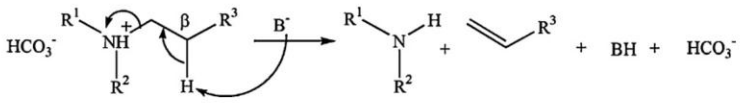


Fig. 31. Hofmann's degradation according to Lepaumier (2008).

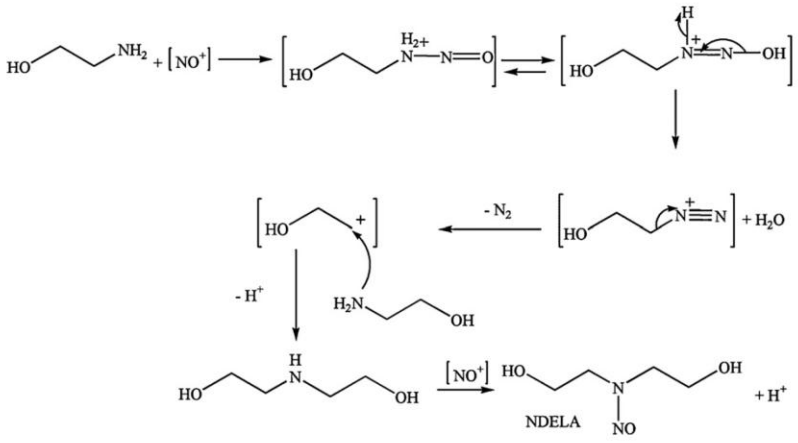


Fig. 32. Nitrosamines formation according to Ridd (1961) and Fostas et al. (2011).

Table 13
Other studied amines.

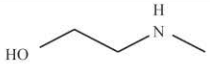
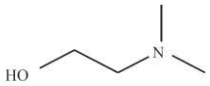
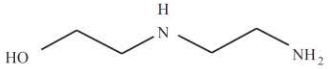
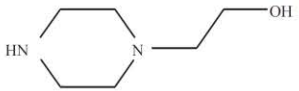
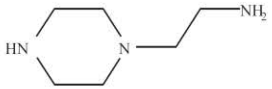
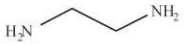
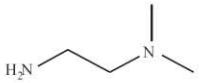
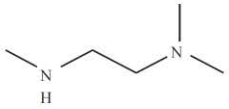
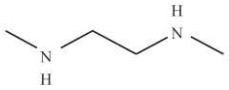
Chemical structure	Name (abbreviation)	References
	N-methylethanolamine (MAE)	Eide-Haugmo et al. (2011), Lepaumier (2008), Lepaumier et al. (2011b)
	N,N-dimethylethanolamine (DMAE)	Eide-Haugmo et al. (2011), Lepaumier (2008)
	N-(2-hydroxyethyl)ethylenediamine (HEEDA)	Davis (2009), Eide-Haugmo et al. (2011), Lepaumier (2008)
	N-(2-hydroxyethyl)piperazine (HEP)	Davis (2009)
	N,N′-dimethylpiperazine (DMP)	Lepaumier (2008), Lepaumier et al. (2010)
	N-(2-hydroxyethyl)-N′-methyl piperazine (HMP)	Davis (2009)
	Ethylenediamine (EDA)	Davis (2009), Eide-Haugmo et al. (2011), Freeman (2011)
	N,N-dimethylethylenediamine	Lepaumier (2008)
	N,N,N′-trimethylethylenediamine	Lepaumier (2008)
	N,N′-dimethylethylenediamine	Lepaumier (2008)

Table 13 (*Continued*)

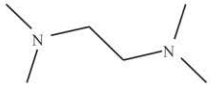
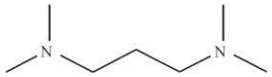
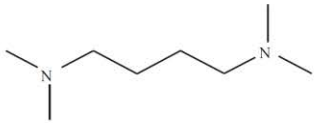
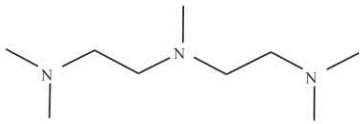
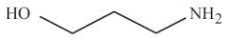
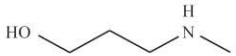
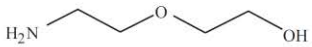
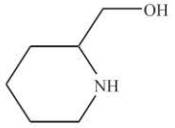
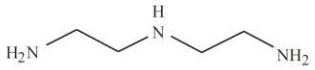
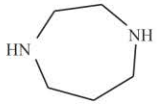
Chemical structure	Name (abbreviation)	References
	N,N,N′,N′-tetramethylethylenediamine	Lepaumier (2008), Lepaumier et al. (2010)
	N,N,N′,N′-tetramethylpropylenediamine	Lepaumier (2008), Lepaumier et al. (2010)
	N,N,N′,N′-tetramethylbutylenediamine	Lepaumier (2008), Lepaumier et al. (2010)
	N,N,N′,N″,N″-pentamethyldiethylenetriamine	Lepaumier (2008), Lepaumier et al. (2010)
	N,N,N′,N″,N″-pentamethyldipropylenetriamine	Lepaumier (2008), Lepaumier et al. (2010)
	Propanolamine (MPA)	Eide-Haugmo et al. (2011)
	N-methylpropanolamine (MAP)	Eide-Haugmo et al. (2011)
	Diglycolamine® (DGA)	Davis (2009), Epp et al. (2011)
	Morpholine	Davis (2009), Freeman (2011)
	2-Hydroxylmethylpiperidine	Davis (2009)

Table 13 (*Continued*)

Chemical structure	Name (abbreviation)	References
	Diethyl enetri amine	Davis (2009), Eide-Haugmo et al. (2011)
	Piperidine	Freeman (2011)
	Pyrrolidinone	Freeman (2011)
	Hexamethyleneimine	Freeman (2011)
	Homopiperazine	Freeman (2011)
	Hexamethylenediamine	Freeman (2011)

Saavedra (1981) studied the action of HNO_2 on MEA and AMP and observed the formation of N-nitroso-2-methyl-1,3-oxazolidine from MEA while AMP gave N-nitroso-2-isopropyl-4,4-dimethyl-1,3-oxazolidine. Even if HNO_2 cannot be present in CO_2 capture conditions, NO_x might give the same results.

This is extremely important because nitrosamines are well known as carcinogenic agents since many years (IARC, 1978; NTP, 2012) and all must be done to avoid their formation or to quickly destroy them before atmosphere emission (Fig. 32).

4. Conclusion

Amine degradation in post-combustion CO_2 capture is a main problem because of its consequences on process units and the potential impact of degradation products on environment. Therefore, amine degradation study is a key point for CO_2 capture acceptance. This is the reason why we proposed a critical survey of the literature in this field.

We presented in detail benchmark MEA and also DEA, MDEA, PZ and AMP. Other amines and amine blends were studied too. In each case, we listed degradation products and discussed mechanisms proposed by the authors. Influence of heat, CO_2, O_2, NO_x and SO_x was described.

In the case of MEA, ammonia, N-(2-hydroxyethyl)-piperazin-3-one (HEPO) and N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)-acetamide (HEHEAA) are the main identified degradation products in pilot plants. Among lab studies, the most cited degradation products are ammonia, carboxylic acids, N-(2-hydroxyethyl)-formamide (HEF), N-(2-hydroxyethyl)-acetamide (HEA) and N-(2-hydroxyethyl)-imidazole (HEI) for oxidative degradation, and oxazolidin-2-one (OZD), N-(2-hydroxyethyl)-ethylenediamine (HEEDA) and N-(2-hydroxyethyl)-imidazolidin-2-one (HEIA) for thermal degradation.

Numerous degradation products have been identified but many are still unknown. A lot of degradation mechanisms have been proposed but some are missing or need proofs. SO_x and NO_x effects are still few examined and much work remains to be done concerning volatile degradation products potentially emitted to atmosphere: their identification and their formation mechanisms need further investigations.

The conclusion is that a lot of studies have been already done but understanding of amine degradation is not completely achieved and much work remains to be done.

References

Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007. CO_2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine. International Journal of Greenhouse Gas Control 1, 37–46.

Alawode, A.O., 2005. Oxidative Degradation of Piperazine in the Absorption of Carbon Dioxide. Thesis, University of Texas at Austin.

Arduengo, A.J., Gentry, F.P., Taverkere, P.K., Simmons, H., 2001. Process for manufacture of imidazoles. US 6177575 B1, E.I.du Pont de Nemours and Compagny, Wilmington.

Bedell, S.A., 2009. Oxidative degradation mechanisms for amines in flue gas capture. Energy Procedia 1, 771–778.

Bedell, S.A., 2011. Amine autoxidation in flue gas CO_2 capture – mechanistic lessons learned from other gas treating processes. International Journal of Greenhouse Gas Control 5, 1–6.

Bello, A., Idem, R.O., 2005. Pathways for the formation of products of the oxidative degradation of CO_2-loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases. Industrial and Engineering Chemistry Research 44, 945–969.

Bello, A., Idem, R.O., 2006. Comprehensive study of the kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during CO_2 absorption from flue gases. Industrial and Engineering Chemistry Research 45, 2569–2579.

Bhown, A.S., Freeman, B.C., 2011. Analysis and status of post-combustion carbon dioxide capture technologies. Environmental Science and Technology 45, 8624–8632.

Bonenfant, D., Minleault, M., Hausler, R., 2007. Estimation of the CO_2 absorption capacities in aqueous 2-(2-aminoethylamino)ethanol and its blends with MDEA and TEA in the presence of SO_2. Industrial and Engineering Chemistry Research 46, 8968–8971.

Chakma, A., Meisen, A., 1986. Corrosivity of diethanolamine solutions and their degradation products. Industrial & Engineering Chemistry Product Research and Development 25, 627–630.

Chakma, A., Meisen, A., 1987. Degradation of aqueous DEA solutions in a heat-transfer tube. Canadian Journal of Chemical Engineering 65, 264–273.

Chakma, A., Meisen, A., 1988. Identification of methyl diethanolamine degradation products by gas-chromatography and gas-chromatography mass-spectrometry. Journal of Chromatography 457, 287–297.

Chakma, A., Meisen, A., 1997. Methyl-diethanolamine degradation – mechanism and kinetics. Canadian Journal of Chemical Engineering 75, 861–871.

Challis, B.C., Challis, J.C., 1982. 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, pp. 1151–1223.

Chi, S., Rochelle, G.T., 2002. Oxidative degradation of monoethanolamine. Industrial and Engineering Chemistry Research 41, 4178–4186.

Choy, E.T., Meisen, A., 1980. Gas-chromatographic detection of diethanolamine and its degradation products. Journal of Chromatography 187, 145–152.

Closmann, F., Nguyen, T., Rochelle, G.T., 2009. MDEA/piperazine as a solvent for CO_2 capture. Energy Procedia 1, 1351–1357.

Closmann, F., 2011. Oxidation and Thermal Degradation of Methyldiethanolamine/Piperazine in CO_2 Capture. Thesis, University of Texas at Austin.

Closmann, F., Rochelle, G.T., 2011. Degradation of aqueous methyldiethanolamine by temperature and oxygen cycling. Energy Procedia 4, 23–28.

Davis, J.D., 2009. Thermal Degradation of Aqueous Amines used for Carbon Dioxide Capture. Thesis, University of Texas at Austin.

Davis, J., Rochelle, G., 2009. Thermal degradation of monoethanolamine at stripper conditions. Energy Procedia 1, 327–333.

Dawodu, O.F., Meisen, A., 1991. Identification of products resulting from carbonyl sulfide-induced degradation of diethanolamine. Journal of Chromatography 587, 237–246.

Dawodu, O.F., Meisen, A., 1996a. Degradation of aqueous diethanolamine solutions by carbon disulfide. Gas Separation and Purification 10, 1–11.

Dawodu, O.F., Meisen, A., 1996b. Degradation of alkanolamine blends by carbon dioxide. Canadian Journal of Chemical Engineering 74, 960–966.

Dennis, W.H., Hull, L.A., Rosenblatt, D.H., 1967. Oxidations of amines. IV. Oxidative fragmentation. Journal of Organic Chemistry 32, 3783–3787.

Dupart, M.S., Rooney, P.C., Bacon, T.R., 1999. Comparing laboratory and plant data for MDEA/DEA blends. Hydrocarbon Processing 78, 81–86.

EIA, 2011. International Energy Outlook 2011., http://www.eia.gov/forecasts/ieo/index.cfm.

Eide-Haugmo, I., Lepaumier, H., da Silva, E.F., Einbu, A., Vernstad, K., Svendsen, H.F., 2011. A Study of Thermal Degradation of Different Amines and their Resulting Degradation Products., http://www.ieaghg.org/docs/General_Docs/PCCC1/Abstracts_Final/pccc1Abstract00076.pdf.

Epp, B., Fahlenkamp, H., Vogt, M., 2011. Degradation of solutions of monoethanolamine, diglycolamine and potassium glycinate in view of tail-end CO_2 absorption. Energy Procedia 4, 75–80.

Fazio, M.J., 1984. Nucleophilic ring-opening of 2-oxazolines with amines – a convenient synthesis for unsymmetrically substituted ethylenediamines. Journal of Organic Chemistry 49, 4889–4893.

Fiddler, W., Pensabene, J.W., Doerr, R.C., Wasserman, A.E., 1972. Formation of N-nitrosodimethylamine from naturally occurring quaternary ammonium compounds and tertiary amines. Nature 236, 307.

Fostas, B., Gangstad, A., Nenseter, B., Pedersen, S., Sjovoll, M., Sorensen, A.L., 2011. Effects of NO_x in the flue gas degradation of MEA. Energy Procedia 4, 1566–1573.

Freeman, S.A., Davis, J., Rochelle, G.T., 2010. Degradation of aqueous piperazine in carbon dioxide capture. International Journal of Greenhouse Gas Control 4, 756–761.

Freeman, S.A., 2011. Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture. Thesis, Universty of Texas at Austin.

Freeman, S.A., Rochelle, G.T., 2011. Thermal degradation of piperazine and its structural analogs. Energy Procedia 4, 43–50.

Gao, J., Wang, S., Zhao, B., Qi, G., Chen, C., 2011. Pilot-scale experimental study on the co_2 capture process with existing of SO_2: degradation, reaction rate, and mass transfer. Energy and Fuels 25, 5802–5809.

Goff, G.S., Rochelle, G.T., 2004. Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. Industrial and Engineering Chemistry Research 43, 6400–6408.

Goff, G.S., 2005. Oxidative Degradation of Aqueous Monoethanolamine in CO_2 Capture Processes: Iron and Copper Catalysis, Inhibition, and O_2 Mass Transfer. Thesis, University of Texas at Austin.

Goff, G.S., Rochelle, G.T., 2006. Oxidation inhibitors for copper and iron catalyzed degradation of monoethanolamine in CO_2 capture processes. Industrial and Engineering Chemistry Research 45, 2513–2521.

Hakka, L.E., Singh, K.P., Bata, G.L., Testart, A.C., Andrejchyshyn, W.N., 1968. Some Aspects of Diethanolamine Degradation in Gas Sweetening. The Canadian Natural Gas Processing Association.

Holub, P.E., Critchfield, J.E., Su, W.Y., 1998. Amine degradation chemistry in CO_2 service. In: 48th Laurance Reid Gas Cond. Conf, pp. 146–160.

Hsu, C.S., Kim, C.J., 1985. Diethanolamine (DEA) degradation under gas treating conditions. Industrial & Engineering Chemistry Product Research and Development 24, 630–635.
Hull, L.A., Davis, G.T., Rosenblatt, D.H., Williams, H.K.R., Weglein, R.C., 1967. Oxidations of amines. III. Duality of mechanism in the reaction of amines with chlorine dioxide. Journal of the American Chemical Society 89, 1163–1170.
Hull, L.A., Davis, G.T., Rosenblatt, D.H., Mann, C.K., 1969. Oxidations of amines. VII. Chemical and electrochemical correlations. Journal of Physical Chemistry 73, 2142–2146.
IARC, 1978. Monographs on the Evaluation of Carcinogenic Risks to Humans. Some N-Nitroso Compounds, vol. 17. IARC, Lyon.
Islam, M.S., Yusoff, R., ALi, B.S., Islam, M.N., Chakrabarti, M.H., 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. International Journal of Physical Sciences 6, 5883–5895.
Jackson, P., Attala, M.I., 2010. N-nitrosopipezaines form at high pH in post-combustion capture solutions containing piperazine: a low-energy collisional behaviour study. Rapid Communications in Mass Spectrometry 24, 3567–3577.
Kemper, J.M., Walse, S.S., Mitch, W.A., 2010. Quaternary amines as nitrosamine precursors: a role for consumer products? Environmental Science and Technology 44, 1224–1231.
Kennard, M.L., Meisen, A., 1980. Control DEA degradation. Hydrocarbon Processing 60, 103–106.
Kennard, M.L., 1983. Degradation of Diethanolamine (DEA) Solutions. Thesis, The University of British Columbia at Vancouver.
Kennard, M.L., Meisen, A., 1983. Gas-chromatographic technique for analyzing partially degraded diethanolamine solutions. Journal of Chromatography 267, 373–380.
Kennard, M.L., Meisen, A., 1985. Mechanisms and kinetics of diethanolamine degradation. Industrial and Engineering Chemistry Fundamentals 24, 129–140.
Kim, C.J., Sartori, G., 1984. Kinetics and mechanism of diethanolamine degradation in aqueous solutions containing carbon dioxide. International Journal of Chemical Kinetics 16, 1257–1266.
Lawal, O., Bello, A., Idem, R., 2005a. 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. Industrial and Engineering Chemistry Research 44, 1874–1896.
Lawal, O., Bello, A., Idem, R., 2005b. Pathways and reaction products for the oxidative degradation of CO_2 loaded and concentrated aqueous MEA and MEA/MDEA mixtures during CO_2 absorption from flue gases. Greenhouse Gas Control Technologies 7, 1159–1164.
Lensen, R., 2004. The Promoter Effect of Piperazine on the Removal of Carbon Dioxide., http://www.bsdfreaks.nl/files/hoofd6.pdf.
Lepaumier, H., 2008. Étude des mécanismes de dégradation des amines utilisées pour le captage du CO2 dans les fumées. Thesis, Laboratoire des matériaux organiques à propriétés spécifiques (Université de Savoie).
Lepaumier, H., Picq, D., Carrette, P.L., 2009a. New amines for CO_2 capture. I. Mechanisms of amine degradation in the presence of CO_2. Industrial and Engineering Chemistry Research 48, 9061–9067.
Lepaumier, H., Picq, D., Carrette, P.L., 2009b. New amines for CO_2 capture. II. Oxidative degradation mechanisms. Industrial and Engineering Chemistry Research 48, 9068–9075.
Lepaumier, H., Picq, D., Carrette, P.L., 2010. New amines for CO_2 capture. III. Effect of alkyl chain length between amine functions on polyamines degradation. Industrial and Engineering Chemistry Research 49, 4553–4560.
Lepaumier, H., da Silva, E.F., Einbu, A., Grimstvedt, A., Knudsen, J.N., Zahlsen, K.R., Svendsen, H.F., 2011a. Comparison of MEA degradation in pilot-scale with lab-scale experiments. Energy Procedia 4, 1652–1659.
Lepaumier, H., Grimstvedt, A., Vernstad, K., Zahlsen, K., Svendsen, H.F., 2011b. Degradation of MMEA at absorber and stripper conditions. Chemical Engineering Science 66, 3491–3498.
Lindsay Smith, J.R., Mead, L.A.V., 1973. Amine oxidation. Part VII. The effect of structure on the reactivity of alkyl tertiary amines towards alkaline potassium hexacyanoferrate(III). Journal of the Chemical Society Perkin Transactions 2, 206–210.
Lindsay Smith, J.R., Masheder, D., 1977. Amine oxidation. Part 13. Electrochemical oxidation of some substituted tertiary alkylamines. Journal of the Chemical Society Perkin Transactions 2, 1732–1736.
Loeppky, R.N., Michejda, C.J., 1994. Nitrosamines and Related N-Nitroso Compounds. ACS Symp. Ser., vol. 553.
Martin, S., Lepaumier, H., Picq, D., Kittel, J., De Bruin, T., Faraj, A., Carrette, P.L., 2012. New amines for CO_2 capture. IV. Degradation, corrosion and quantitative structure property relationship model. Industrial and Engineering Chemistry Research 51, 6283–6289.
Meisen, A., Kennard, M.L., 1982. DEA degradation mechanism. Hydrocarbon Processing 61, 105–108.
Mirvish, S., 1975. Formation of N-nitroso compounds: chemistry, kinetics, and in vivo occurrence. Toxicology and Applied Pharmacology 31, 325–351.
Moser, P., Schmidt, S., Sieder, G., Garcia, H., Stoffregen, T., 2011a. Performance of MEA in a long-term test at the post-combustion capture pilot plant in Niederaussem. International Journal of Greenhouse Gas Control 5, 620–627.
Moser, P., Schmidt, S., Stahl, K., 2011b. Investigation of trace elements in the inlet and outlet streams of a MEA-based post-combustion capture process results from the test programme at the Niederaussem pilot plant. Energy Procedia 4, 473–479.
NTP, 2012. http://ntp.niehs.nih.gov/go/roc.
Pedersen, S., Sjøvoll, M., Foastås, B.F., 2010. Flue Gas Degradation of Amines. IEA GHG workshop, Oslo.
Petryaev, E.P., Pavlov, A.V., Shadyro, O.I., 1984. Homolytic deamination of amino alcohols. Journal of Organic Chemistry of the USSR 20, 25–29.
Polderman, L.D., Dillon, C.P., Steele, A.B., 1955. Why monoethanolamine solution breaks down in gas-treating service. Oil and Gas Journal 53, 180–183.
Polderman, L.D., Steele, A.B., 1956. Degradation of diethanolamine in gas treating service. Oil and Gas Journal 54, 49–56.
Rao, A.B., Rubin, E.S., 2002. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. Environmental Science and Technology 36, 4467–4475.
Ridd, J.H., 1961. Nitrosation, diazotisation, and deamination. Quarterly Reviews of the Chemical Society 15, 418–444.
Rooney, P.C., Dupart, M.S., Bacon, T.R., 1998a. Oxygen's role in alkanolamine degradation. Hydrocarbon Processing 77, 109–113.
Rooney, P.C., Dupart, M.S., Bacon, T.R., 1998b. The role of oxygen in the degradation of MEA, DGA, DEA and MDEA. In: 48th Laurence Reid gas Cond. Conf, pp. 335–347.
Rosenblatt, D.H., Hull, L.A., De Luca, D.C., Davis, G.T., Weglein, R.C., Williams, H.K.R., 1967. Oxidations of amines. II. Substituent effects in chlorine dioxide oxidations. Journal of the American Chemical Society 89, 1158–1163.
Saavedra, J.E., 1981. Deamination of primary aminoalkanol. Formation of substituted N-nitroso-1,3-oxazolidines and N-nitroso-1,3-tetrahydrooxazines. Journal of Organic Chemistry 46, 2610–2614.
Sexton, A.J., 2008. Amine Oxidation in Carbon Dioxide Capture Processes. Thesis, University of Texas at Austin.
Sexton, A.J., Rochelle, G.T., 2011. Reaction products from the oxidative degradation of monoethanolamine. Industrial and Engineering Chemistry Research 50, 667–673.
Smith, P.A.S., Loeppky, R.N., 1967. Nitrosative cleavage of tertiary amines. Journal of the American Chemical Society 89, 1147–1157.
Strazisar, B.R., Anderson, R.R., White, C.M., 2001. Degradation of monoethanolamine used in CO_2 capture from flue gas of a coal-fired electric power generating station. Journal of Energy and Environmental Research 1, 32–39.
Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Degradation pathways for monoethanolamine in a CO_2 capture facility. Energy and Fuels 17, 1034–1039.
Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C., 2006. 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. Industrial and Engineering Chemistry Research 45, 2437–2451.
Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C., 2009. Kinetics of sulfur dioxide- and oxygen-induced degradation of aqueous monoethanolamine solution during CO_2 absorption from power plant flue gas streams. International Journal of Greenhouse Gas Control 3, 133–142.
Supap, T., Idem, R., Tontiwachwuthikul, P., 2011. Mechanism of formation of heat stable salts (HSSs) and their roles in further degradation of monoethanolamine during CO_2 capture from flue gas streams. Energy Procedia 4, 591–598.
Tanthapanichakoon, W., Veawab, A., McGarvey, B., 2006. Electrochemical investigation on the effect of heat-stable salts on corrosion in CO_2 capture plants using aqueous solution of MEA. Industrial and Engineering Chemistry Research 45, 2586–2593.
Thitakamol, B., Veawab, A., Aroonwilas, A., 2007. Environmental impacts of absorption-based CO_2 capture unit for post-combustion treatment of flue gas from coal-fired power plant. International Journal of Greenhouse Gas Control 1, 318–342.
Uyanga, I.J., Idem, R.O., 2007. Studies of SO_2- and O_2-induced degradation of aqueous MEA during CO_2 capture from power plant flue gas streams. Industrial and Engineering Chemistry Research 46, 2558–2566.
Veldman, R.R., 2000. Alkanolamine solution corrosion mechanisms and inhibition from HSS and CO_2. Corrosion/00, paper 496 (Houston, Texas, 2000).
Vevelstad, S.J., Eide-Haugmo, I., da Silva, E.F., Svendsen, H.F., 2011. Degradation of MEA; a theoretical study. Energy Procedia 4, 1608–1615.
Wang, T., Jens, K.J., 2011. Oxidative degradation of 2-amino-2-methyl-1-propanol. In: Post-combustion Capture Conference, PCC1, Abu Dhabi, UAE, 17th–19th May 2011, http://www.ieaghg.org/docs/General_Docs/PCCC1/Presentations/3_PCCC1_TL%20Wang.pdf.
Wang, T., Jens, K.J., 2012. Oxidative degradation of aqueous 2-amino-2-methyl-1-propanol solvent for postcombustion CO_2 capture. Industrial and Engineering Chemistry Research 51, 6529–6536.
Wen, H., Narula, R., 2009. Impacts of carbon capture on power plant emissions. In: 12th International Post-Combustion Capture Network, Regina, Canada.
Williams, L.H., 1988. N-Nitrosation. Cambridge University Press, Cambridge, pp. 77–112.
Ye, Q.-G., Zhang, S.-S., 2001. The methyldiethanolamine degradation products in desulphurization process for acid waste gas. Gaoxiao huaxue Gongcheng Xuebao 15, 35–39.
Zhou, S., Wang, S., Chen, C., 2012. Thermal degradation of monoethanolamine in CO_2 capture with acidic impurities in flue gas. Industrial and Engineering Chemistry Research 51, 2539–2547.

International Journal of Greenhouse Gas Control 19 (2013) 576–583

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Amine degradation in CO_2 capture. 2. New degradation products of MEA. Pyrazine and alkylpyrazines: Analysis, mechanism of formation and toxicity

A. Rey[a], C. Gouedard[b], N. Ledirac[c], M. Cohen[a], J. Dugay[a], J. Vial[a], V. Pichon[a], L. Bertomeu[c], D. Picq[b,d], D. Bontemps[e], F. Chopin[e], P.-L. Carrette[b,*]

[a] LSABM, UMR PECSA 7195, ESPCI – UPMC – CNRS, 10 rue Vauquelin, 75005 Paris, France
[b] IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France
[c] CEHTRA, 43 rue Laroque, 33560 Sainte Eulalie, France
[d] LEPMI, UMR 5279, CNRS – Grenoble INP – Université J. Fourier, 1130 rue de la Piscine, BP 75, 38402 Saint Martin d'Hères, France
[e] EDF R&D, 6, quai Watier, 78401 Chatou Cedex, France

ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form 11 October 2013
Accepted 15 October 2013

Keywords:
Post-combustion CO_2 capture
MEA degradation
Pyrazines toxicity
HS-SPME coupled with GC–MS
Mechanisms
SAR

ABSTRACT

Amine degradation in post-combustion CO_2 capture is a main problem because of its consequences on process units and the potential impact of degradation products on environment. Ethanolamine (MEA) is the benchmark amine for this application. Although MEA degradation has been intensively studied, some degradation products are still unidentified. In this article, new degradation products of MEA are reported: pyrazine and 9 alkylpyrazines. A new analytical method based on HS-SPME and GC–MS was developed to identify and quantify the 10 pyrazines present in two pilot plant samples. A mechanism for their formation was proposed. The toxicity of these molecules was assessed based on available toxicological data and, when the information was not sufficient, a computational approach was used: TOPKAT and DEREK SARs. LD_{50}, skin and eye irritancy potential, genotoxicity and reproductive effects were assessed. The study showed that the ten identified pyrazines are currently not indicating toxicological concern at the level of intake estimated at 0.2–120 μg/day in Europe.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

CO_2 capture and storage is one of the promising technologies to reduce greenhouse gas emissions. To be used, this technology needs economic but also environmental acceptance. In this process, amines are known to react with flue gas components (O_2, CO_2, NOx, SOx...) to form degradation products, and some of them could be potentially dangerous to humans or environment according to their toxicity and their concentration. These products could be discharged to the atmosphere essentially with treated flue gas. Such amine degradation causes also amine loss, therefore additional costs, and can lead to corrosion (DeHart et al., 1999; Islam et al., 2011; Martin et al., 2012), solid deposit (Chakma and Meisen, 1987) and foaming (Kohl and Riesenfeld, 1985).

Therefore it is necessary to list all the degradation products of amines used in CO_2 capture, to understand their formation and to study their toxicity.

Alkanolamines are the most studied molecules regarding degradation in the case of CO_2 capture and natural gas sweetening. The benchmark molecule is monoethanolamine (MEA) (Davis and Rochelle, 2009; Fostas et al., 2011; Lepaumier et al., 2011; Sexton, 2008; Strazisar et al., 2003; Supap et al., 2011; Vevelstad et al., 2011), but some other amines were studied: mainly diethanolamine (DEA) (Chakma and Meisen, 1986; Choy and Meisen, 1980; Holub et al., 1998), methyldiethanolamine (MDEA) (Chakma and Meisen, 1988, 1997; Lawal et al., 2005), piperazine (PZ) (Freeman et al., 2010; Freeman and Rochelle, 2011) and 2-amino-2-methylpropan-1-ol (AMP) (Wang and Jens, 2012). Some alkylamines and polyamines were studied too (Lepaumier et al., 2009a,b, 2010). The identification of amine degradation products and their mechanisms of formation were recently reviewed (Gouedard et al., 2012).

Abbreviations: DEREK, deductive estimate of risk from existing knowledge; FEMA, flavor and extract manufacturers association; GRAS, generally recognized as safe; HS, head space; MSDI, maximised survey-derived daily intakes; SAR, structure–activity relationship; SIM, single ion monitoring; SPME, solid phase micro extraction; TIC, total ion current; TOPKAT, toxicity prediction by komputer assisted technology.

* Corresponding author. Tel.: +33 437 70 27 23; fax: +33 437 70 20 66.
E-mail address: p-louis.carrette@ifpen.fr (P.-L. Carrette).

1750-5836/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijggc.2013.10.018

Although MEA is the most studied amine for CO_2 capture, some degradation products are still unidentified (da Silva et al., 2012).

In this article, ten new degradation products of MEA are reported: pyrazine and nine alkylpyrazines. They were observed in liquid samples of two pilot plants at IFP Energie nouvelles (IFPEN) and EDF R&D, respectively. They were identified and quantified thanks to the development of a new analytical method based on HS-SPME and GC–MS.

A mechanism of formation was proposed in accordance with literature.

The toxicity of these molecules was assessed based on available toxicological data and, when the information was not sufficient, a computational (*in silico*) approach was used. Predictions were generated by using two structure–activity relationship (SAR) software tools, one based on expert rules, DEREK (deductive estimate of risk from existing knowledge) and another based on statistical methodologies, TOPKAT (toxicity prediction by komputer assisted technology). LD_{50}, skin and eye irritancy potential, genotoxicity and reproductive effects were assessed.

2. Material and methods

2.1. Chemicals and SPME materials

Pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethylpyrazine, 2,3,5-trimethylpyrazine, 2-ethyl-3-methylpyrazine, a mix of isomers 2-ethyl-5-methylpyrazine and 2-ethyl-6-methylpyrazine and ethanolamine (ReagentPlus®, ≥99%) were purchased from Sigma–Aldrich (Saint Quentin Fallavier, France). Ultra pure water was produced using a Direct-Q UV 3 system (18.2 MΩ/cm) from Millipore (Molsheim, France). 75 μm Carboxen/PDMS SPME fibre were obtained from Supelco (Sigma–Aldrich, Saint Quentin Fallavier, France).

The liquid sample from IFPEN CO_2 capture pilot plant was obtained after 1000 h. The synthetic flue gas composition was CO_2 14.9% N_2 68.1% and O_2 17%. Gas flow rate was 750 NL/h and liquid flow rate was 2.5 L/h. Absorber temperature profile was 36–58 °C and bottom stripper temperature was 108 °C at atmospheric pressure. 40% weight MEA solution used for the pilot plant campaign was provided by Carlo Erba.

The liquid sample from EDF R&D lab-scale pilot plant was obtained after about 400 h (more details about the equipment will be published soon). The synthetic flue gas composition was CO_2 15% N_2 82% and air 3%. Gas flow rate was 1800 NL/h and liquid flow rate was 30 L/min. Absorber temperature was 50 °C at atmospheric pressure and stripper temperature was 120 °C at 4 bara. 30% weight MEA solution used for the pilot plant campaign was provided by Alfa Aesar.

2.2. GC–MS analysis

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer (Santa Clara, USA). The device is equipped with a MPS autosampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated HS-SPME analyses. Two columns were used to separate all the target compounds, a non-polar fused silica capillary column CP-SIL 8CB-ms (30 m × 0.25 mm with 1 μm film thickness) and a polar fused silica capillary column DB-WAX (30 m × 0.25 mm with 0.5 μm film thickness), both columns were obtained from Agilent. Two temperature gradients were used, one for each column. For the non-polar column, initial temperature was 40 °C held for 2 min then raised to 130 °C at 7 °C/min, increased to 280 °C at 13 °C/min and held for 10 min. For the polar column, oven temperature programme started at 40 °C, held for 2 min then raised to 130 °C at 7 °C/min, increased to 200 °C at 10 °C/min held for 7 min. In both cases, helium was used as carrier gas in constant flow mode at 1 mL/min. The transfer line temperature to the MS detector was set at 280 °C.

Mass spectrometer was used with the electronic ionization source (70 eV) heated at 250 °C. The acquisition was made with scan and SIM mode simultaneously. The scan range was 25–250 amu and SIM parameters are shown in Table 1.

Table 1
Pyrazine and alkylpyrazines studied standards, with the selected ion for detection in MS SIM mode and their retention times on both columns used.

Pyrazines	MW (g/mol)	*m/z*	Ret. time (min)	
			Non-polar	Polar
Pyrazine	80	80	9.28	12.38
2-methylpyrazine	94	94	11.86	13.55
2,5-dimethylpyrazine	108	108	14.27	14.72
2,6-dimethylpyrazine	108	108	14.29	14.84
2-ethylpyrazine	108	107	14.44	14.95
2,3-dimethylpyrazine	108	67	14.47	15.22
2-ethyl-6-methylpyrazine	122	121	16.38	15.92
2-ethyl-5-methylpyrazine	122	121	16.51	16.06
2,3,5-trimethylpyrazine	122	42	16.47	16.27
2-ethyl-3-methylpyrazine	122	121	16.50	16.30

2.3. HS-SPME procedures

For HS-SPME procedures, standards were prepared by spiking a solution of water/ethanolamine (70/30 v/v) to mimic a real solution used for CO_2 capture. The volume of sample introduced in the 20 mL HS vial was 5 mL both for synthetic and real samples.

The fully automated HS-SPME procedure was as follows. First, the vial was equilibrated at 70 °C during 5 min then the Carboxen/PDMS fibre was placed into the head-space of the sample for the extraction, still maintained at 70 °C for 30 min. At the end of the extraction, the fibre was desorbed directly in the injector set at 250 °C in split mode (1:5).

2.4. Toxicity analysis (DEREK and TOPKAT)

Derek Nexus version 3.0.0 (LHASA Limited, Leeds, UK) and TOPKAT DS 3.5 (Accelrys Software Inc., Discovery Studio Modelling Environment, Release 3.5, San Diego: Accelrys Software Inc., 2007) were used in this study. The individual structure of each pyrazine derivative was imported into both QSAR models and processed.

TOPKAT and DEREK were used to predict genotoxicity (AMES prediction with TOPKAT, structural alerts for mutagenicity and chromosome damage with DEREK), skin and eye irritation potential, and the sensitization effect of the molecules. TOPKAT was also used for continuous measurements for quantifiable endpoints such as LD_{50} values.

2.5. TOPKAT criteria for positivity and negativity

TOPKAT confirms if the query structure is in the model applicability domain (*i.e.* in the Optimal Predictive Space – OPS) which indicates the level of confidence in the prediction. This criterion was checked and when the submitted structure was outside the OPS, the prediction results were considered unreliable. Then, predictions with a probability values greater than or equal to 0.7 were considered positive and below 0.3 were considered negative. Results falling between 0.3 and 0.7 were considered equivocal (Snyder et al., 2004). Additional parameters provided by TOPKAT were used such as the enrichment, the Mahalanobis Distance or the Bayesian score in order to support the reliability of TOPKAT predictions. All

statistical calculations were considered together to assess the confidence in the prediction.

2.6. DEREK criteria for positivity and negativity

DEREK does not provide quantitative assessment, but checks if structural alerts in the knowledge base can be identified in the query structure. It describes the molecular substructures that have been associated with the toxicity (toxicophore) supported by literature references. The rules used are not chemical-specific but serve as broad generalizations with regard to the chemical structure. The level of confidence in the prediction is indicated, from impossible to certain. When no alert is found, 'nothing to report' is mentioned.

In this study, DEREK was used together with TOPKAT and the predictions were considered reliable when prediction results were concordant between these two SARs.

3. Results

3.1. Identification of pyrazines

Identification of target compounds was made by matching MS spectra and retention times, which are shown in Table 1. MS SIM chromatograms obtained with non-polar and polar column are shown in Figs. 1 and 2 respectively.

Best separation was obtained with the polar column that could separate all the isomers except 2-ethyl-3-methylpyrazine and 2,3,5-trimethylpyrazine but those compounds can be identified by their spectra. Nevertheless, m/z 42 used for 2,3,5-trimethylpyrazine was interfered by ethanolamine as shown on the last chromatogram in Fig. 2. Therefore this compound was preferentially analyzed with the non-polar column. The only doubt remaining was about the identification of isomers 2-ethyl-5-methylpyrazine and 2-ethyl-6-methylpyrazine: they were well separated but the only available standard was a mixture of both isomers. The definitive identification was allowed by a NMR analysis of the standard mixture.

3.2. Quantification

A semi-quantitative approach was applied to obtain an approximate content of all pyrazines identified in liquid samples from IFPEN and EDF R&D CO_2 capture pilot plants. MS SIM chromatograms were used to evaluate the amount of the target products as shown in Fig. 3. An external calibration was made with a mix of the ten pyrazines studied by spiking a solution of water/MEA at three levels of concentration. The results obtained for liquid samples are reported in Table 2. The pooled relative uncertainty on the pyrazines amount determination has been roughly estimated around 18% by using two repetitions obtained in intermediate precision conditions, *i.e.* column and day different. To be sure that pyrazines were produced by a degradation process, the water/MEA mixture originally introduced in the pilot plant was analyzed before the pilot plant experience was launched. All pyrazines could be found at traces levels, between 60 times less than in the degraded sample for 2-ethyl-3-methylpyrazine and 300 times less for 2,3-dimethylpyrazine. 10 pyrazines were observed in the case of IFPEN pilot plant and 7 among them in the case of EDF R&D pilot plant. This result can be explained by the shorter duration of EDF R&D pilot plant campaign and therefore the smaller amount of pyrazine alkylation confirmed by a higher concentration of pyrazine in this case. Pyrazine concentration was compared with some known degradation products to assess its relative abundance in the IFPEN sample: pyrazine concentration was very close to acetate and oxalate ions concentrations (55 ppm and 53 ppm, respectively). Nevertheless, identified pyrazine derivatives are less concentrated in the liquid

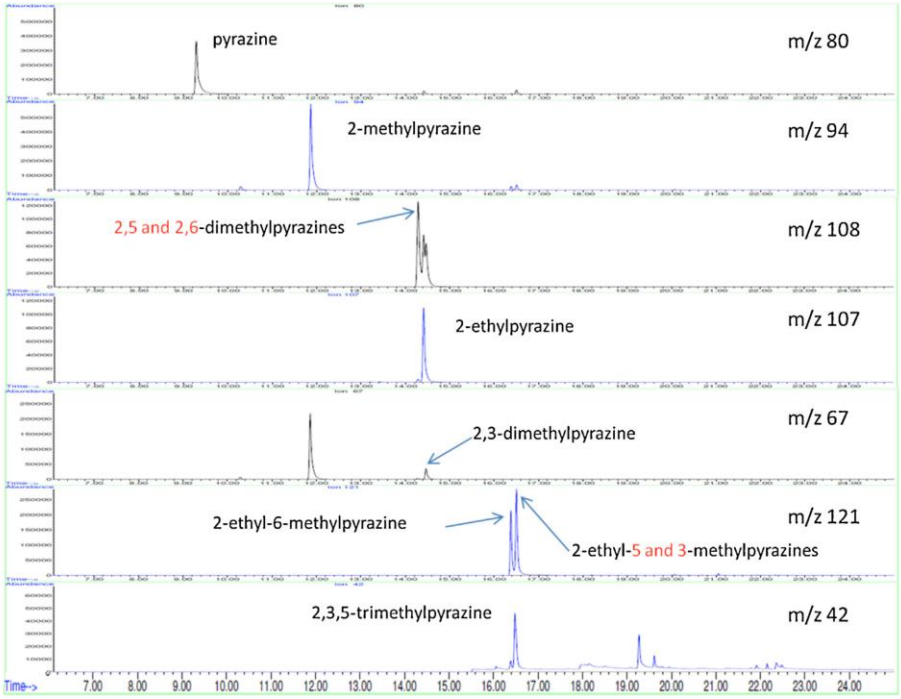


Fig. 1. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 1 mg/L, other alkylpyrazines were at 0.1 mg/L) in a water/MEA solution with the non-polar column and the associated temperature programme.

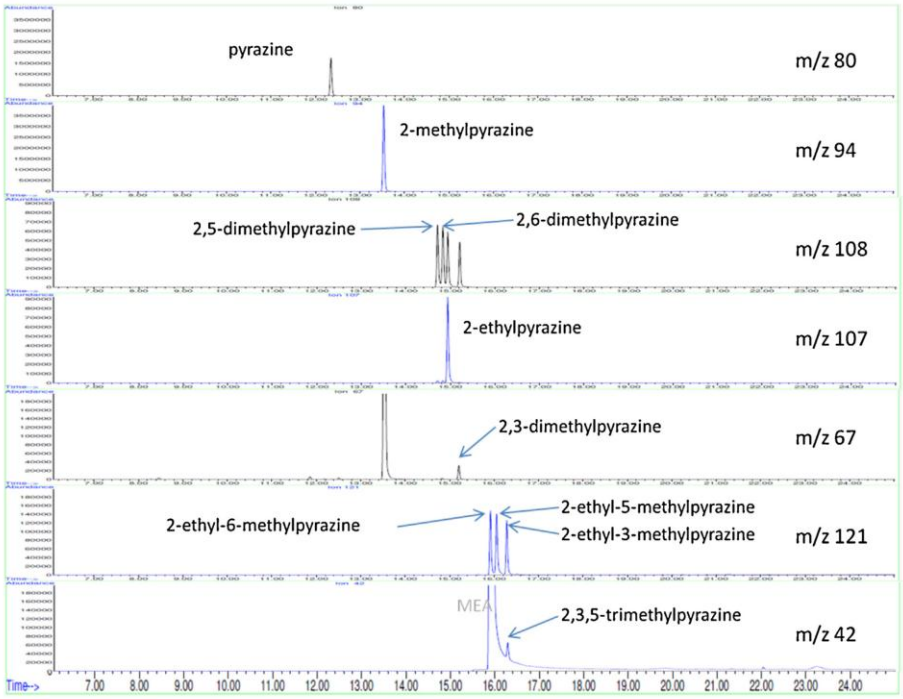


Fig. 2. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 10 mg/L, other alkylpyrazines were at 0.1 mg/L) in a water/MEA solution with the polar column and the associated temperature programme.

phase than carboxylic ions but they are more concentrated in the gas phase because of their much higher volatility. Their presence in the gas phase is proved by HS-SPME method using a temperature (70 °C) close to highest temperatures encountered in absorber conditions.

3.3. Mechanism of formation

A mechanism for the formation of pyrazine derivatives is proposed in Figs. 4 and 5. Their formation is due to the presence of 2-aminoacetaldehyde, formaldehyde and acetaldehyde. Oxidation of MEA in 2-aminoacetaldehyde is very easy in pilot plant conditions (Rooney et al., 1998), and the presence of formaldehyde and acetaldehyde was previously reported by Rooney et al. (1998) and Sexton and Rochelle (2011). The first step is a fast condensation of two 2-aminoacetaldehyde molecules followed by a dehydration leading to dihydropyrazine. This molecule is then easily oxidized in pyrazine as explained by Krems and Spoerri (1947) in a review; this oxidation was also observed by Guerra and Yaylayan (2010) during a pyrolysis at 150 °C and by Adams

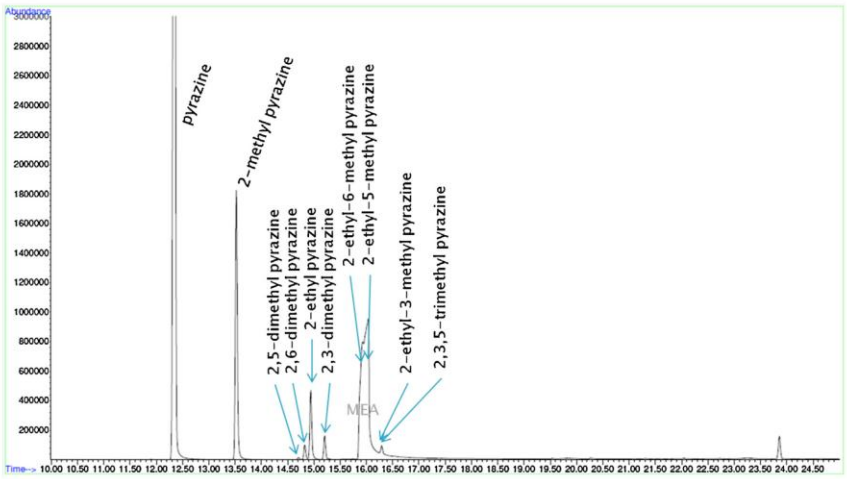


Fig. 3. Chromatogram SIM (TIC), after HS-SPME, of a liquid sample from IFPEN CO_2 capture pilot plant with the polar column and the associated temperature programme.

Table 2
Average concentrations of ten alkylpyrazines in liquid samples from IFPEN and EDF R&D CO_2 capture pilot plants.

Pyrazines	Concentrations in IFPEN pilot plant sample (mg/L)	Concentrations in EDF R&D pilot plant sample (mg/L)
Pyrazine	50	100
2-methylpyrazine	3	1
2,5-dimethylpyrazine	0.02	Traces
2,6-dimethylpyrazine	0.13	Traces
2-ethylpyrazine	0.28	Traces
2,3-dimethylpyrazine	0.20	0.03
2-ethyl-6-methylpyrazine	0.04	<LOD*
2-ethyl-5-methylpyrazine	Traces	<LOD*
2,3,5-trimethylpyrazine	0.01	Traces
2-ethyl-3-methylpyrazine	0.02	<LOD*

*Limit of detection = 0.5 ppb.

et al. (2008) during a reaction at 90 °C. Conditions used by Adams et al. (2008) can be encountered in the case of CO_2 capture. On the other hand dihydropyrazine can react with formaldehyde or acetaldehyde to form 2-methylpyrazine or 2-ethylpyrazine respectively (Adams et al., 2008; Guerra and Yaylayan, 2010). The formed alkylpyrazines can give di- or trialkylpyrazines by electrophilic addition catalyzed by a metal in presence of a base (Bramwell et al., 1971) as shown in Fig. 5. Thanks to metal, SET (single electron transfer) occurs, therefore alkylpyrazines can react with formaldehyde to form dialkylpyrazines then trialkylpyrazines.

3.4. Toxicity assessment

Pyrazine and some of its alkyl derivatives were identified in tobacco smoke as long ago as 1968 (Stedman, 1968) and have been reported to naturally occur in foods (Maarse et al., 1999; Maga, 1982; Tang et al., 1983).

These molecules are absorbed, distributed and excreted rapidly when administered orally to rats (Sjoedin et al., 1989). Acute oral toxicity effects in rats are summarized in Table 3 (LD_{50} values – Lethal Dose with 50% of mortality). They indicate a low to moderate level of toxicity with values ranging from 600 to 1800 mg/kg for seven pyrazine derivatives (Moran et al., 1980). Most of the predicted LD_{50} values obtained with TOPKAT correlate well with the experimental values (excepted for 2-methylpyrazine where the prediction is lower than the experimental value). Although no data was available for pyrazine, 2-ethylpyrazine and 2-ethyl-6-methylpyrazine, predicted LD_{50} values obtained with TOPKAT were provided (706, 959, and 592 mg/kg, respectively). Concerning other acute toxicity endpoints such as skin and eye irritation, or skin sensitization, no published literature was available. DEREK and TOPKAT predictions on irritation potency were different. DEREK did not flag any alert whereas TOPKAT predicted the substances to be moderate/severe irritant for the eyes and skin. The level of confidence for these TOPKAT predictions was considered to be low due to the poor similarity between substances of the training set and pyrazine derivatives. However classification for skin irritation and eye damage were proposed for 2,6-dimethylpyrazine and 2,3,5,6-tetramethylpyrazine, and in a lesser extend for 2-methylpyrazine (skin and eye irritation) in the classification and labelling inventory (database containing classification on substances notified under REACH regulation). These proposed classifications are based on experimental results, but the detailed results are not available. Taken together the data strongly suggests that these substances are eye and skin irritants.

The genotoxicity potential of pyrazine and pyrazine derivatives has been extensively tested. They were reported negative

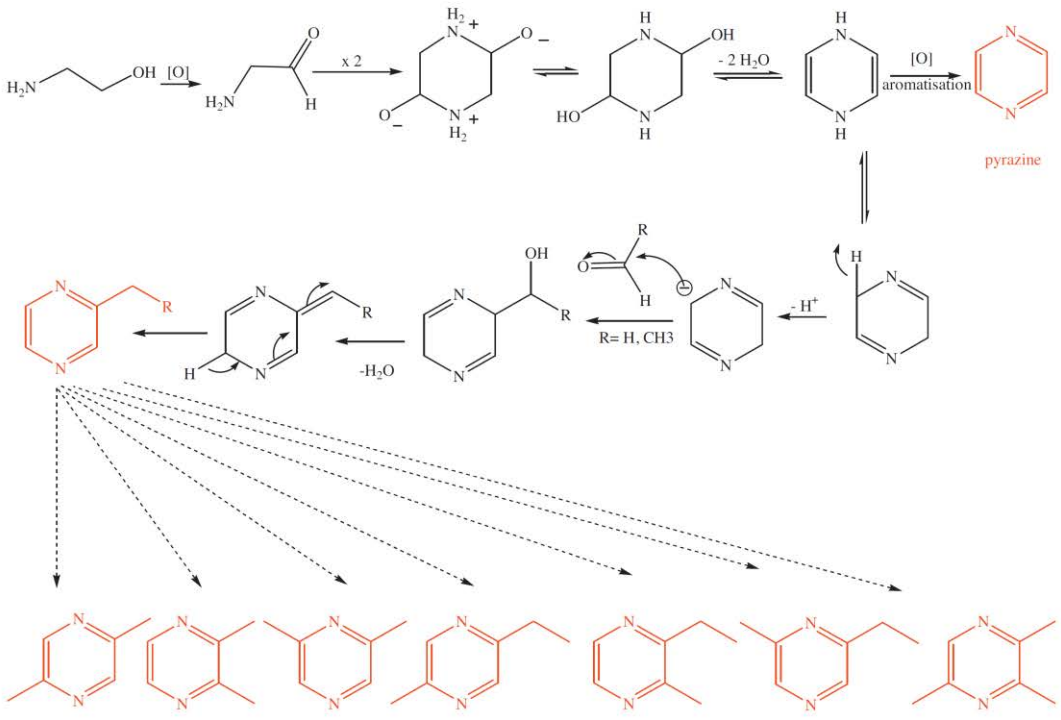


Fig. 4. Mechanism of pyrazine and alkylpyrazines formation.
Adapted from Krems and Spoerri (1947), Adams et al. (2008), and Guerra and Yaylayan (2010).

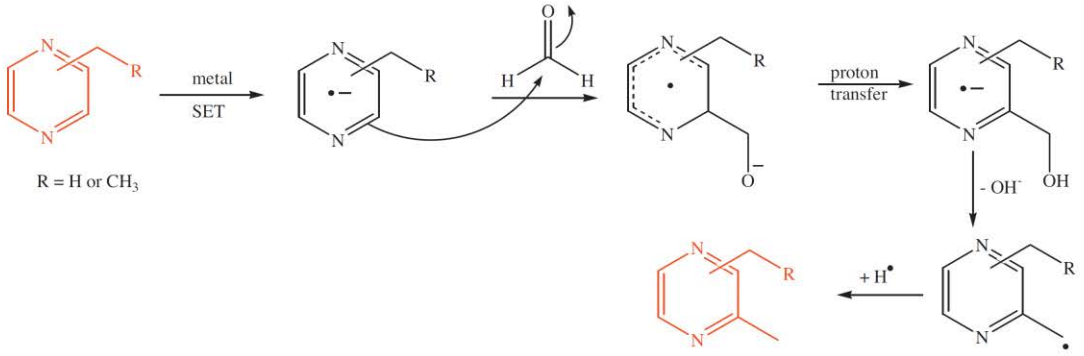


Fig. 5. Mechanism of pyrazine alkylation.

Adapted from Bramwell et al. (1971).

Table 3
Oral acute toxicity of pyrazine derivatives.

Substance	Oral LD_{50} mg/kg bw (rat)	TOPKAT prediction		Study reference
		Outside OPS (score)	Rat oral LD_{50} mg/kg bw	
2-methylpyrazine	1800	No	947	(Beckman et al., 2011; Moran et al., 1980)
2,3-dimethylpyrazine	613	No	903	
2,5-dimethylpyrazine	1020	No	1049	
2,6-dimethylpyrazine	880	No	738	
2-ethyl-3-methylpyrazine	600	No	526	
2-ethyl-5-methylpyrazine	900	No	779	
2,3,5-trimethylpyrazine	806	No	1002	
Pyrazine	ND	No	706	
2-ethylpyrazine	ND	No	959	
2-ethyl-6-methylpyrazine	ND	No	592	

ND: No data.

in mutation tests conducted in bacteria (Ames tests) (Stich et al., 1980). Experimental data was available on a large number of pyrazine derivatives including 7 molecules on the list of interest (Table 4). In the study of Stich et al. (1980), 2-methylpyrazine, 2-ethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, and pyrazine were shown to induce chromosome aberrations in Chinese Hamster Ovary (CHO) cells and to increase the mutation frequency in yeast (*Saccharomyces cerevisiae* D5). However, the increase in chromosome aberrations was found in a single report conducted with high toxic concentrations, which could have led to unspecific chromosome damage. Furthermore, pyrazine was negative in a gene mutation test conducted in mouse lymphoma cells (Mouse Lymphoma TK assay) (Fung et al., 1988) indicating no mutagenic or clastogenic activity of pyrazine. According to DEREK and TOPKAT predictions, no structural alert for mutagenic or clastogenic potential was identified among the ten molecules except for 2,6-dimethylpyrazine, which showed conflicting predictions for mutagenicity in bacteria (positive with TOPKAT and negative with DEREK). Taken together, these observations suggest that positive responses obtained by Stich et al. should be considered as

Table 4
Genotoxicity studies and computational predictions.

Substance	AMES studies[a,b,c,d]	Mutation assay *S. cerevisiae*[a]	Chromosome aberration studies[a]	TOPKAT prediction	DEREK prediction		
				AMES	AMES	Chromosome damage (*in vitro*)	Chromosome damage (*in vivo*)
Pyrazine	N	P	P	N (0.720)	N	N	N
2-methylpyrazine	N	P	P	N (0.654)	N	N	N
2,5-dimethylpyrazine	N	P	P	N (0.694)	N	N	N
2,6-dimethylpyrazine	N/P	P	P	P (0.739)[e]	N[e]	N[e]	N[e]
2,3-dimethylpyrazine	N	ND	ND	N (0.685)	N	N	N
2-ethylpyrazine	N	P	P	N (0.535)	N	N	N
2,3,5-trimethylpyrazine	N	ND	ND	N (0.681)	N	N	N
2-ethyl-3-methylpyrazine	ND	ND	ND	N (0.687)	N	N	N
2-ethyl-5-methylpyrazine	ND	ND	ND	N (0.622)	N	N	N
2-ethyl-6-methylpyrazine	ND	ND	ND	N (0.661)	N	N	N

N, negative; P, positive; ND, no data.

[a] Stich et al. (1980).
[b] Aeschbacher et al. (1989).
[c] Lee et al. (1994).
[d] Fung et al. (1988).
[e] Discordant predictions.

non-relevant for either classification or human risk assessment and that the identified pyrazines derivatives did not show genotoxic potential.

Concerning the sub-chronic toxicity of pyrazine derivatives, information on repeated dietary exposure was obtained on 2-ethyl-3-methylpyrazine, 2-ethyl-5-methylpyrazine or 2,3,5-trimethylpyrazine. In these studies rats were exposed to 5, 18 and 18 mg/kg body weight (bw)/day of the corresponding pyrazines for ninety days. No adverse effects were reported in these studies and therefore the No Observed Adverse Effect Levels (NOAELs) were set at 5 or 18 mg/kg bw/day, respectively (Oser et al., 1965; Posternak et al., 1969). No studies are available on chronic toxicity or on carcinogenicity with either pyrazine or the pyrazine derivatives identified in this study.

The effects of three dimethylpyrazine isomers were studied for effects on the reproductive organs of male and female rats after subcutaneous injection. The route of exposure is not relevant to human exposure but the effects were reported in order to highlight some potential adverse effects that would need further investigations. The 2,5-dimethylpyrazine was shown to decrease uterus weight in female rats at 100 mg/kg/day (Yamada et al., 1992). In males exposed to 2,5-dimethylpyrazine, decreases in plasma testosterone level, in prostate and seminal vesicle weights were reported at 70 mg/kg/day in juvenile but not in mature animals and these effects were no longer observed at 30 mg/kg/day (Yamada et al., 1994). At 100 mg/kg/day the 2,6-dimethylpyrazine only showed effects on seminal vesicles and no effects were reported with 2,3-dimethylpyrazine (Yamada et al., 1993). Therefore, a NOAEL for reproductive toxicity was established at 30 mg/kg bw/day based on the adverse effects of 2,5-dimethylpyrazine in juvenile male rats.

Based on their low aroma threshold and on their rapid absorption, metabolism, and excretion in humans, pyrazine derivatives were considered as safe (GRAS) by FEMA (Renberg et al., 1989). Based on the MSDI approach the estimated level of intake ranged from 0.2 to 120 μg/day in Europe (JEFCA, 2002; with estimated intake of 0.2 μg/person per day for pyrazine and 120 μg/person per day for trimethylpyrazine). Therefore, at the level of European dietary intake and according to the data provided in this study (published literature, *in silico* predictions and classifications issued from inventory data bases) the identified pyrazines are currently not indicating toxicological concerns.

4. Conclusion

Although MEA is the most studied amine, ten new degradation products were found in this work: pyrazine and nine alkyl derivatives. To do that a new analytical method based on HS-SPME and GC–MS was developed.

Pyrazines were quantified and a mechanism was proposed for their formation in accordance with literature.

Then their toxicity was assessed. Available toxicological data were used and, when information was not sufficient, a computational approach was conducted. Predictions were generated by using two SARs (structure–activity relationship) software tools: TOPKAT and DEREK.

The study showed that the ten identified pyrazines are currently not indicating toxicological concern at the level of intake estimated at 0.2–120 μg/day in Europe.

Acknowledgments

The authors would like to acknowledge financial support from French ANR (Research Project DALMATIEN).

This work is a part of the PhD thesis of C. Gouedard supported by IFPEN and hosted by MATIS LABEX.

References

Adams, A., Polizzi, V., van Boekel, M., De Kimpe, N., 2008. Formation of pyrazines and a novel pyrrole in Maillard model systems of 1,3-dihydroxyacetone and 2-oxopropanal. J. Agric. Food Chem. 56, 2147–2153.

Aeschbacher, H.U., Wolleb, U., Loliger, J., Spadone, J.C., Liardon, R., 1989. Contribution of coffee aroma constituents to the mutagenicity of coffee. Food Chem. Toxicol. 27, 227–232.

Beckman, S., Binderup, M.L., Brimer, L., Castle, L., Engel, K.H., Franz, R., Gontard, N., Gurtler, R., Husoy, T., Jany, K.D., Leclercq, C., Lhuguenot, J.C., Mennes, W., Milana, M.R., Pratt, I., Svensson, K., Toldra, F., Wolfle, D., Beltoft, V., Bursch, W., Carere, A., Frandsen, H., Hill, F., Larsen, J.C., Lund, P., Mulder, G., Norby, K., Speijers, G., Wallin, H., Nielsen, K.R., 2011. Scientific opinion on Flavouring Group Evaluation 17, Revision 3 (FGE.17Rev3): Pyrazine derivatives from chemical group 24. EFSA J. 9 (5), 66.

Bramwell, A.F., Payne, L.S., Riezebos, G., Ward, P., Wells, R.D., 1971. The nuclear alkylation of pyrazines by ketones and aldehydes. J. Chem. Soc. C, 1627–1632.

Chakma, A., Meisen, A., 1986. Corrosivity of diethanolamine solutions and their degradation products. Ind. Eng. Chem. Prod. Res. Dev. 25, 627–630.

Chakma, A., Meisen, A., 1987. Degradation of aqueous DEA solutions in a heat-transfer tube. Can. J. Chem. Eng. 65, 264–273.

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

Chakma, A., Meisen, A., 1997. Methyl-diethanolamine degradation – mechanism and kinetics. Can. J. Chem. Eng. 75, 861–871.

Choy, E.T., Meisen, A., 1980. Gas-chromatographic detection of diethanolamine and its degradation products. J. Chromatogr. 187, 145–152.

da Silva, E.F., Lepaumier, H., Grimstvedt, A., Vevelstad, S.J., Einbu, A., Vernstad, K., Svendsen, H.F., Zahlsen, K., 2012. Understanding 2-ethanolamine degradation in post combustion CO_2 capture. Ind. Eng. Chem. Res. 51, 13329–13338.

Davis, J., Rochelle, G., 2009. Thermal degradation of monoethanolamine at stripper conditions. Energy Procedia 1, 327–333.

DeHart, T.R., Hansen, D.A., Mariz, C.L., McCullough, J.G., 1999. Solving corrosion problems at the NEA Bellingham Massachussetts carbon dioxide recovery plant. In: Presented at the NACE International Conference Corrosion '99, San Antonio, TX.

Fostas, B., Gangstad, A., Nenseter, B., Pedersen, S., Sjovoll, M., Sorensen, A.L., 2011. Effects of NO_x in the flue gas degradation of MEA. Energy Procedia 4, 1566–1573.

Freeman, S.A., Davis, J., Rochelle, G.T., 2010. Degradation of aqueous piperazine in carbon dioxide capture. Int. J. Greenhouse Gas Control 4, 756–761.

Freeman, S.A., Rochelle, G.T., 2011. Thermal degradation of piperazine and its structural analogs. Energy Procedia 4, 43–50.

Fung, V.A., Cameron, T.P., Hughes, T.J., Kirby, P.E., Dunkel, V.C., 1988. Mutagenic activity of some coffee flavor ingredients. Mutat. Res. Genet. Toxicol. Test. 204, 219–228.

Gouedard, C., Picq, D., Launay, F., Carrette, P.L., 2012. Amine degradation in CO_2 capture I. A review. Int. J. Greenhouse Gas Control 10, 244–270.

Guerra, P.V., Yaylayan, V.A., 2010. Dimerization of azomethine ylides: an alternate route to pyrazine formation in the Maillard reaction. J. Agric. Food Chem. 58, 12523–12529.

Holub, P.E., Critchfield, J.E., Su, W.Y., 1998. Amine degradation chemistry in CO_2 service. In: 48th Laurance Reid Gas Conditioning Conference, pp. 146–160.

Islam, M.S., Yusoff, R., ALi, B.S., Islam, M.N., Chakrabarti, M.H., 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. Int. J. Plant Sci. 6, 5883–5895.

JEFCA, 2002. Pyrazine derivatives. JECFA Food Additives Series 48 http://www.inchem.org/documents/jecfa/jecmono/v48je12.htm#2.3.2

Kohl, A.L., Riesenfeld, F.C., 1985. Gas Purification. Gulf Publishing, Houston, TX.

Krems, I.J., Spoerri, P.E., 1947. The pyrazines. Chem. Rev. 40, 279–358.

Lawal, O., Bello, A., Idem, R., 2005. 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.

Lee, H., Bian, S.S., Chen, Y.L., 1994. Genotoxicity of 1,3-dithiane and 1,4-dithiane in the CHO/SCE assay and the Salmonella/microsomal test. Mutat. Res. Genet. Toxicol. 321, 213–218.

Lepaumier, H., da Silva, E.F., Einbu, A., Grimstvedt, A., Knudsen, J.N., Zahlsen, K.R., Svendsen, H.F., 2011. Comparison of MEA degradation in pilot-scale with lab-scale experiments. Energy Procedia 4, 1652–1659.

Lepaumier, H., Picq, D., Carrette, P.L., 2009a. New amines for CO_2 capture. I. Mechanisms of amine degradation in the presence of CO_2. Ind. Eng. Chem. Res. 48, 9061–9067.

Lepaumier, H., Picq, D., Carrette, P.L., 2009b. New amines for CO_2 capture. II. Oxidative degradation mechanisms. Ind. Eng. Chem. Res. 48, 9068–9075.

Lepaumier, H., Picq, D., Carrette, P.L., 2010. New amines for CO_2 capture. III. Effect of alkyl chain length between amine functions on polyamines degradation. Ind. Eng. Chem. Res. 49, 4553–4560.

Maarse, H., Visscher, C.A., Willemsens, L.C., Nijssen, L.M., Boelens, M.H., 1999. Volatile Components in Food, 6th ed. TNO Nutrition and food Research.

Maga, J.A., 1982. Pyrazines in foods: an update. CRC Crit. Rev. Food Sci. Nutr. 16, 1–48.

Moran, E.J., Easterday, O.D., Oser, B.L., 1980. Acute oral toxicity of selected flavor chemicals. Drug Chem. Toxicol. 3, 249–258.

Martin, S., Lepaumier, H., Picq, D., Kittel, J., De Bruin, T., Faraj, A., Carrette, P.L., 2012. New amines for CO_2 capture. IV. Degradation, corrosion and quantitative structure property relationship model. Ind. Eng. Chem. Res. 51, 6283–6289.
Oser, B.L., Carson, S., Oser, M., 1965. Toxicological tests on flavouring matters. Food Cosmet. Toxicol. 3, 563–569.
Posternak, J.M., Linder, A., Vodoz, C.A., 1969. Toxicological tests on flavouring matters. Food Cosmet. Toxicol. 7, 405–407.
Renberg, L., Simonsson, R., Hoffmann, K.J., 1989. Identification of two main urinary metabolites of [14C]omeprazole in humans. Drug Metab. Dispos. 17, 69–76.
Rooney, P.C., Dupart, M.S., Bacon, T.R., 1998. Oxygen's role in alkanolamine degradation. Hydrocarbon Process 77, 109–113.
Sexton, A.J., 2008. Amine Oxidation in Carbon Dioxide Capture Processes. University of Texas, Austin, Thesis.
Sexton, A.J., Rochelle, G.T., 2011. Reaction Products from the oxidative degradation of monoethanolamine. Ind. Eng. Chem. Res. 50, 667–673.
Sjoedin, P., Wallin, H., Alexander, J., Jaegerstad, M., 1989. Disposition and metabolism of the food mutagen 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline (MeIQx) in rats. Carcinogenesis 10, 1269–1275.
Snyder, R.D., Pearl, G.S., Mandakas, G., Choy, W.N., Goodsaid, F., Rosenblum, I.Y., 2004. Assessment of the sensitivity of the computational programs DEREK, TOPKAT, and MCASE in the prediction of the genotoxicity of pharmaceutical molecules. Environ. Mol. Mutagen. 43, 143–158.
Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Degradation pathways for monoethanolamine in a CO_2 capture facility. Energy Fuels 17, 1034–1039.
Stedman, R.L., 1968. The chemical composition of tobacco and tobacco smoke. Chem. Rev. 68, 153–207.
Stich, H.F., Stich, W., Rosin, M.P., Powrie, W.D., 1980. Mutagenic activity of pyrazine derivatives: a comparative study with *Salmonella typhimurium*, *Saccharomyces cerevisiae*, and Chinese hamster ovary cells. Food Cosmet. Toxicol. 18, 581–584.
Supap, T., Idem, R., Tontiwachwuthikul, P., 2011. Mechanism of formation of heat stable salts (HSSs) and their roles in further degradation of monoethanolamine during CO_2 capture from flue gas streams. Energy Procedia 4, 591–598.
Tang, J., Jin, Q.Z., Shen, G.H., Ho, C.T., Chang, S.S., 1983. Isolation and identification of volatile compounds from fried chicken. J. Agric. Food Chem. 31, 1287–1292.
Vevelstad, S.J., Eide-Haugmo, I., da Silva, E.F., Svendsen, H.F., 2011. Degradation of MEA: a theoretical study. Energy Procedia 4, 1608–1615.
Wang, T., Jens, K.J., 2012. Oxidative degradation of aqueous 2-Amino-2-methyl-1-propanol solvent for postcombustion CO_2 capture. Ind. Eng. Chem. Res. 51, 6529–6536.
Yamada, K., Shimizu, A., Komatsu, H., Sakata, R., Ohta, A., 1994. Effects of 2,5-dimethylpyrazine on plasma testosterone and polyamines- and acid phosphatase-levels in the rat prostate. Biol. Pharm. Bull. 17, 730–731.
Yamada, K., Shimizu, A., Ohta, A., 1993. Effects of dimethylpyrazine isomers on reproductive and accessory reproductive organs in male rats. Biol. Pharm. Bull. 16, 203–206.
Yamada, K., Takahashi, H., Ohta, A., 1992. Effects of 2,5-dimethylpyrazine on reproductive and accessory reproductive organs in female rats. Res. Commun. Chem. Pathol. Pharmacol. 75, 99–107.

The next paper will be published soon in International journal of greenhouse gas control. Revised paper was send at the end of June to the journal. This version is the revised version.

Amine degradation in CO_2 capture. 3. New degradation products of MEA in liquid phase: amides and nitrogenous heterocycles.

C. Gouedard[a] ; A. Rey[b]; V. Cuzuel[b]; J. Brunet[b]; B. Delfort[c]; D. Picq[a,d,e]; J. Dugay[b] ; J. Vial[b] ; V. Pichon[b]; F. Launay[f]; L. Assam[a]; J. Ponthus[a]; P.-L. Carrette*[a]

[a] IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

[b] LSABM, UMR CBI 8231, ESPCI – UPMC – CNRS, 10 rue Vauquelin, 75005 Paris, France

[c] IFP Energie nouvelles, 1 & 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France

[d] Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France

[e] CNRS, LEPMI, F-38000 Grenoble, France

[f] LRS/UPMC-Paris 6, 3 rue Galilée, 94200 Ivry-sur-Seine, France

Abstract

To reduce greenhouse gas emissions from fossil fuel power plants, post combustion CO_2 capture with amine-based solvent is the most mature technology. Ethanolamine (MEA), the benchmark amine, is the most studied amine but some degradation products are still unknown and for an environmental acceptance, it is important to identify them. In this work eleven amides and nitrogenous heterocycles were identified in a pilot plant liquid sample. Among them seven molecules were never reported in literature. Different analytical methods were developed especially HS-SPME coupled to GC/MS. Mechanisms of formation were proposed for each molecule and were validated in most cases.

Keywords

Post-combustion CO_2 Capture; Ethanolamine (MEA) degradation; Nitrogenous heterocycles; Amides; HS-SPME coupled with GC/MS; Mechanisms.

1. Introduction

Fossil fuels are predicted to remain as the main source of energy in the next couple of decades; therefore greenhouse gas (GHG) emissions may increase (Kenarsari et al., 2013). CO_2 is the major GHG thus carbon capture and storage (CCS) are expected to play a role to reduce GHG emissions (20 % to 28 % of the total reduction, IEA, 2010), particularly post combustion capture (PCC) with amine-based solvent, which is the most mature technology. To develop this process, it needs economic acceptance (Rao and Rubin, 2002) and also environmental acceptance (Eide-Haugmo et al., 2009). Indeed, amines are known to react with flue gas components (O_2, CO_2, NOx, SOx...) to form degradation products, and some of them could be potentially

dangerous to humans or environment according to their toxicity and their concentration. These products could be discharged to the atmosphere essentially with treated flue gas. Such amine degradation causes also amine loss, hence additional costs, and can lead to corrosion (DeHart et al., 1999; Islam et al., 2011; Martin et al., 2012), solid deposit (Chakma and Meisen, 1987) and foaming (Kohl and Riesenfeld, 1985). Therefore one important aspect of current research is to identify amine degradation products (da Silva et al., 2012; Gouedard et al., 2012, Lepaumier et al., 2009a; Lepaumier et al., 2009b; Vevelstad, 2013; Voice, 2013) and to assess their toxicity (Rey et al., 2013). Moreover to reduce amine degradation in order to limit potential degradation products emission to atmosphere, it is essential to elucidate amine degradation pathways.

MEA is the benchmark molecule. Two kinds of degradation could be observed: thermal and oxidative degradation. Studies of these degradations have been done at laboratory scale (Bedell, 2009; Chi and Rochelle, 2002; Davis and Rochelle, 2009; Sexton, 2008) and at pilot scale (Lepaumier et al., 2011; Moser et al., 2011; Reynolds et al., 2013; Strazisar et al., 2003). Even if recent publications concerning pilot plants propose new molecules (Rey et al., 2013; Reynolds et al., 2013), many degradation products are still unidentified (da Silva et al., 2012). Therefore several complementary analytical methods are required to identify as many degradation products as possible. The main analytical technique for volatile compounds is gas chromatography coupled to mass spectrometry (GC/MS). However, this technique may encounter some compound stability's issues. Moreover minor products could be hidden because of matrix effect.

In this work, headspace solid-phase micro extraction method (HS-SPME) was used to observe some minor volatile products thanks to GC/MS. This method enabled to decrease matrix effect. Different GC/MS methods using different types of columns were combined to enhance identification. ^{1}H and ^{13}C NMR were used in one case to confirm a structure. All these methods enabled to identify two amides and nine nitrogenous heterocycles in a pilot plant liquid sample. N-(2-hydroxyethyl)lactamide and N-(2-hydroxyethyl)propanamide have been already observed in literature without proposed mechanism (Strazisar et al., 2003). Oxazoline and oxazolidine have been just suspected (Reynolds et al., 2013 and Voice, 2013), therefore we confirmed their formation as well as the structure of seven new products. Commercially or synthesized standards have been used to confirm identification. For all these compounds, a mechanism of formation was proposed and, when it was possible, it was verified thanks to syntheses.

2. Material and methods

2.1. Chemicals and SPME materials

Formaldehyde (37 %), formic acid (97 %), N-(2-hydroxyethyl)acetamide (HEA) (90 %), N-(2-hydroxyethyl)formamide (HEF) (97 %), N-(2-hydroxyethyl)succinimide (95 %), 2-methyloxazoline (≥ 99 %), 3-picoline (99 %), 2-piperazinone (97 %) were purchased from Alfa Aesar. Ethanolamine (MEA) (98

%), N-(2-hydroxyethyl)lactamide, N-(2-hydroxyethyl)propanamide were purchased from Sigma Aldrich. Oxazoline (96 %) was purchased from Interchim (France). N-(2-hydroxyethyl)pyrrole (99 %) was purchased from TCI. N-(2-hydroxyethyl)glycine (HEGly) (95 %) was purchased from Enamine (Ukraine). Acetic acid (99.8 %) was purchased from Carlo Erba. Glycine (99.7 %) was purchased from Merck. Oxazolidine was purchased from Selectlab.

Ultra-pure water was produced using a Direct-Q UV 3 system (18.2 MΩ.cm) from Millipore (France). 75 µm Carboxen/ PDMS SPME fibres were obtained from Supelco.

The liquid sample from IFPEN CO_2 capture pilot plant was obtained after 1000 hours. The synthetic flue gas composition was CO_2 14.9% N_2 68.1% and O_2 17%. Gas flow rate was 750 NL/h and liquid flow rate was 2.5 L/h. Absorber temperature profile was 36-58°C and bottom stripper temperature was 108°C at atmospheric pressure. 40% weight MEA solution used for the pilot plant campaign was provided by Carlo Erba. No addition of MEA was done during this campaign.

2.2. GC/MS analyses

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer (USA). The device was equipped with a MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, France) that enabled fully automated HS-SPME analyses. Two columns (Agilent) were used to separate all the target compounds, a non-polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm with 1 µm film thickness) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm with 0.5 µm film thickness). For the non-polar column, initial temperature was 40°C held for 2 min then raised to 130°C at 7°C/min, increased to 280°C at 13°C/min and held for 10 min. For the polar column, oven temperature program started at 40°C, held for 2 min then raised to 130°C at 7°C/min, then increased to 200°C at 10°C/min and held for 7 min. In both cases, helium was used as carrier gas in constant flow mode at 1 mL/min. The transfer line temperature to the MS detector was set at 280°C. For liquid injection procedures, real samples are diluted 10 times before injecting 1µL in split mode (1:5) at 250°C.

Detection was performed with a mass spectrometer using electronic ionization (EI) or chemical ionization (CI) source. The latter was both used in positive (PCI) and negative (NCI) mode. The EI source (70 eV) was heated to 250°C, the scan range was 25 to 250 amu. As for the CI source, it was heated to 300°C for positive mode and to 150°C for negative mode, CH_4 was used as reactant gas and the scan range was 50 to 250 amu.

Some complementary analyses were also performed on a Thermo Finnigan Tempus (GC-TOF (Time of flight)/MS), which was used with CP-SIL8 CB-MS (30 m x 0.25 mm with 1 µm film thickness). Initial temperature was 35ºC then raised to 230ºC at 3°C/min and held for 50 min. Helium was used as carrier gas in constant flow mode at 0,9 mL/min. The transfer line temperature to the MS detector was set at 250°C.

Mass spectrometer was used with the EI source (70 eV) heated at 200°C. The scan range was 10 to 350 amu.

GC-TOF was used to analyse all syntheses crude mixtures.

2.3. HS-SPME procedures

For HS-SPME procedures, the volume of sample introduced in the 20 mL HS vial was 5 mL. The fully automated HS-SPME procedure was as follows. First, the vial was equilibrated at 70°C during 5 min then the Carboxen/PDMS fibre was placed into the head-space of the sample for the extraction and maintained at 70°C for 30 min. At the end of the extraction, the fibre was introduced directly in the injector set at 250°C (desorption) in split mode (1:5).

2.4. Syntheses used to demonstrate proposed mechanisms

First degradation step of MEA is oxidation forming mainly aldehydes, carboxylic acids, ammonia and glycine, commonly called first generation products. These products can then react with MEA to form second generation products (ie HEF, HEA, HEGly) (Gouedard et al., 2012). In the next described syntheses, all reactants have been observed in a pilot plant liquid sample. These reactions were done to confirm mechanism hypotheses or to confirm structure of molecules. The general procedure of these syntheses is:

Reactant 1 was diluted in water (30 % w/w), then one molar equivalent of reactant 2 was added and the solution was heated at 100°C for 15 days. Mixtures were analysed with GC/MS (TOF) without further purification to observe formed products. Reactants are given in Table 1.

Synthesis Name	Reactant 1	Reactant 2
S1	MEA	formic acid
S2	MEA	acetic acid
S3[a]	HEF	none
S4	HEA	none
S5	MEA	formaldehyde
S6[b]	MEA	acetaldehyde
S7	Glycine	OZD
S8[c]	HEGly	none

[a] 1% w/w in water at 85°C during 3 days, [b] at room temperature, [c] 3 % w/w in water.

Table 1. Syntheses description

2.5. NMR

^{1}H and ^{13}C NMR spectra was recorded in D_2O using a Bruker AMX 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) at room temperature. The HOD signal ($\delta = 4.79$ ppm) was used as internal reference for ^{1}H NMR analysis.

3. Results and discussion

Identification of MEA degradation products is still incomplete. Different analytical methods and sources of ionisation were used to enhance identification of new degradation products or to confirm the structure of some compounds reported in few papers. In most cases products were confirmed with standard comparison. Degradation products observed in a pilot plant liquid sample are reported in Table 2. None of these products was observed in fresh MEA.

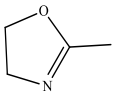
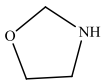
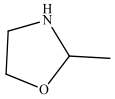
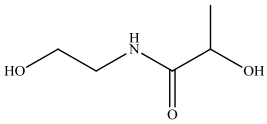
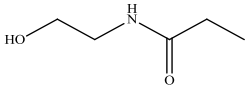
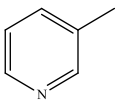
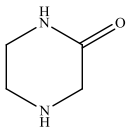
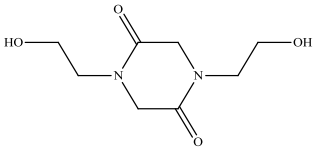
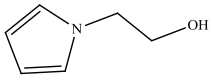
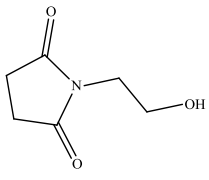
Name	Chemical structure	Analytical methods				Previously cited by
		CP-Sil	DB-WAX	SPME + CP-Sil	CP-Sil (TOF)	
oxazoline		N	Y	Y	Y	Voice, 2013*
2-methyloxazoline		N	Y	N	Y	NR
oxazolidine		N	N	N	Y	Reynolds et al., 2013* Voice, 2013*
2-methyloxazolidine[a]*		N	N	N	Y	NR
N-(2-hydroxyethyl)lactamide HEL		Y	Y	N	Y	Reynolds et al., 2013 Strazisar et al., 2003
N-(2-hydroxyethyl)propanamide HEPro		Y	Y	N	Y	NR
3-picoline		N	N	N	Y	NR
2-piperazinone		N	N	N	Y	NR
N,N'-bis(2-hydroxyethyl)-piperazin-2,5-dione* BHEPDO2,5		N	N	N	Y	NR
N-(2-hydroxyethyl)pyrrole HEPyr		Y	Y	Y	Y	NR
N-(2-hydroxyethyl)succinimide HESucc		Y	Y	Y	Y	Lepaumier et al., 2011 Reynolds et al., 2013 Strazisar et al., 2003 Supap et al., 2011

Table 2. Degradation products observed in pilot plant sample with analytical methods and previous citations.

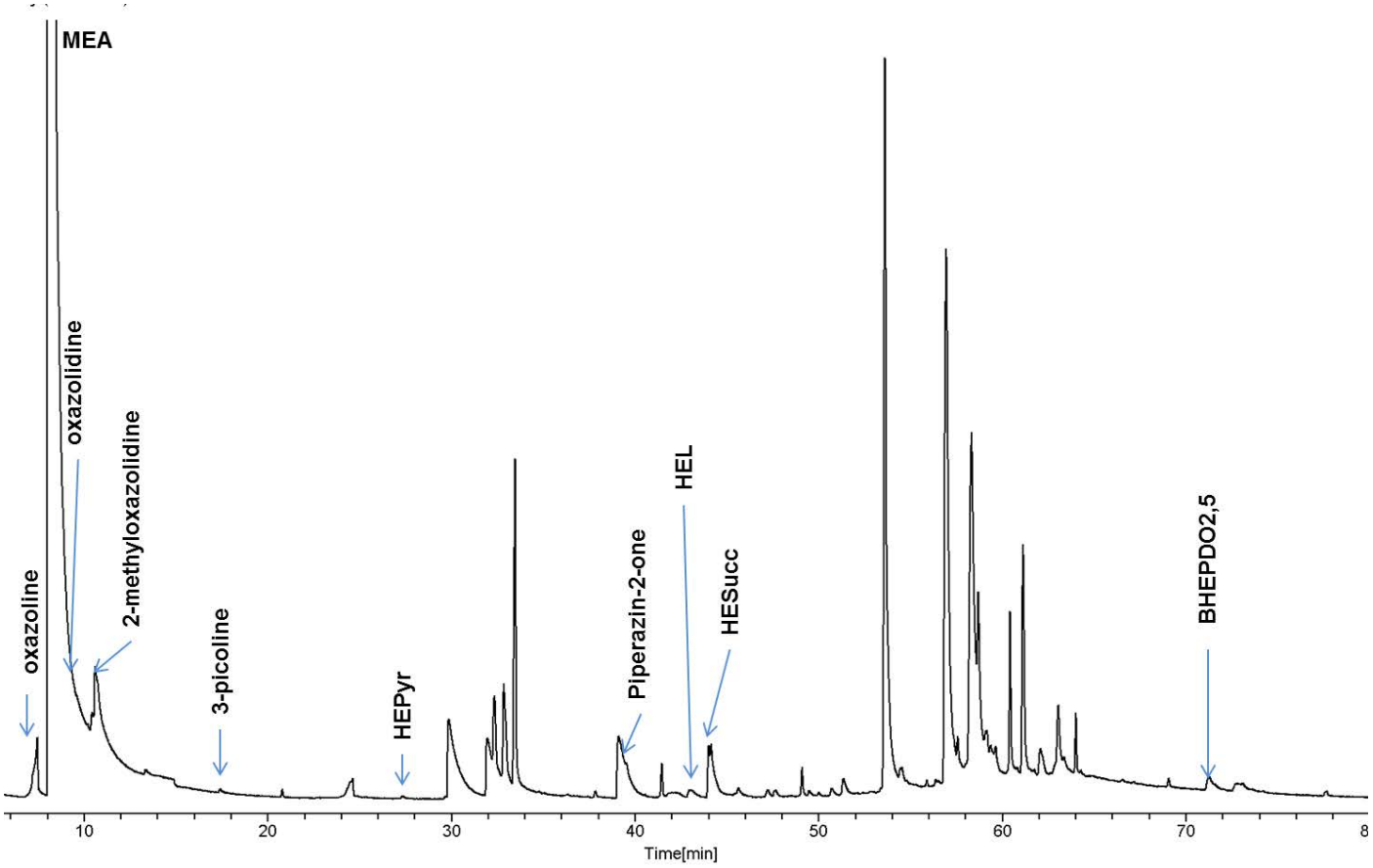


Figure 1. Chromatogram on GC/MS (TOF) of a liquid sample (dilution 1/10) from IFPEN CO_2 capture pilot plant with CP-SIL8 column

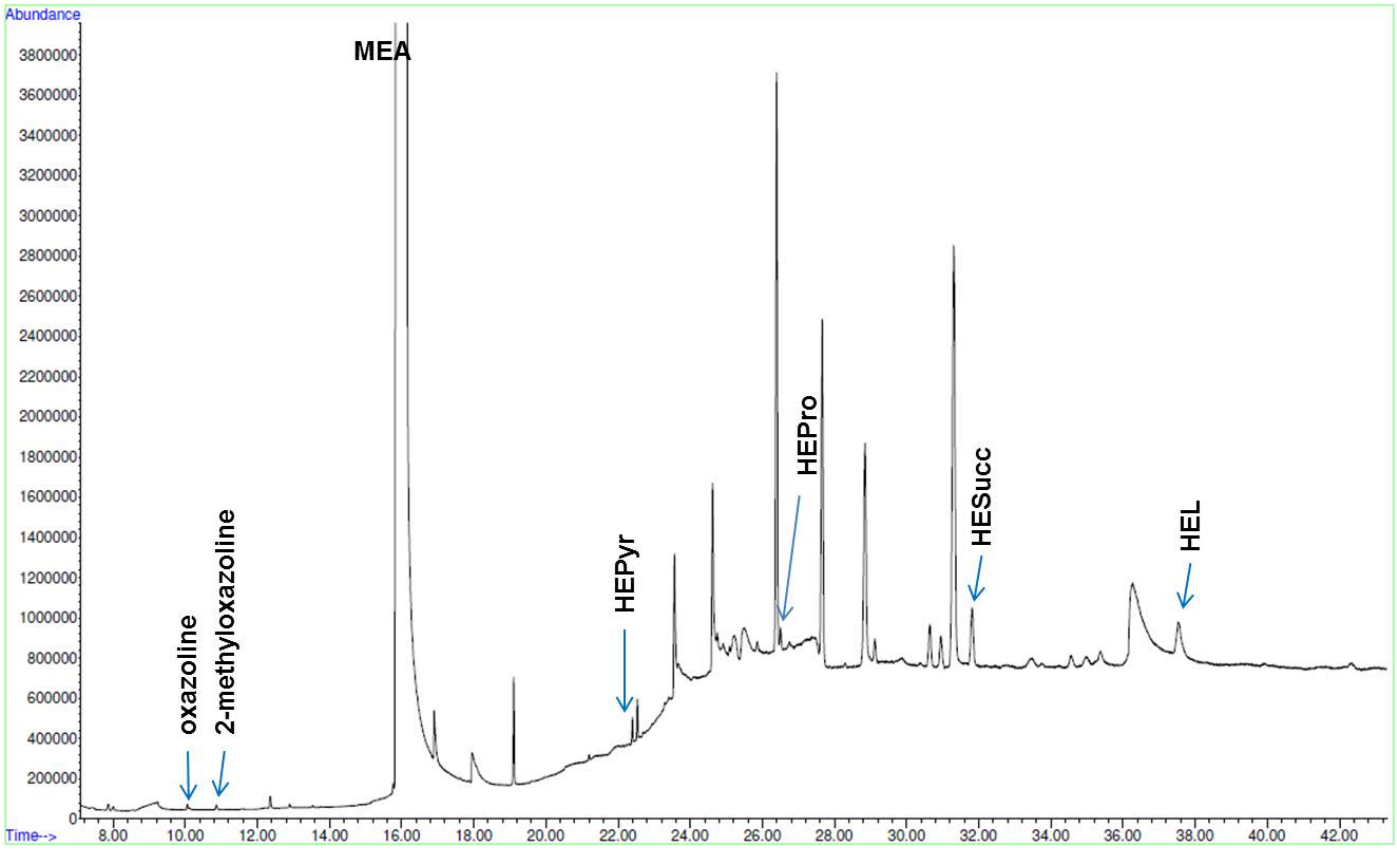


Figure 2. Chromatogram of a liquid sample (dilution 1/10) from IFPEN CO_2 capture pilot plant with DBWAX column

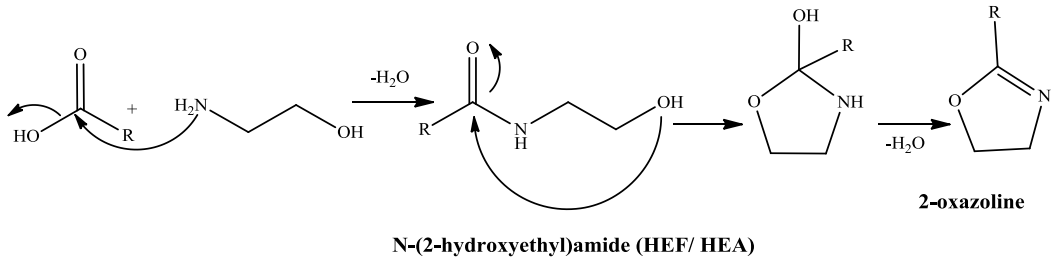
Lepaumier et al., 2011; Reynolds et al., 2013; Strazisar et al., 2003; Supap et al., 2011

These degradation products can be seen on two chromatograms (Figure 1 and Figure 2). Some major peaks were previously identified (Lepaumier et al., 2011).

A mechanism of formation is proposed for all products. When it was possible, they were confirmed by synthesis.

3.1. Oxazoline and 2-methyloxazoline

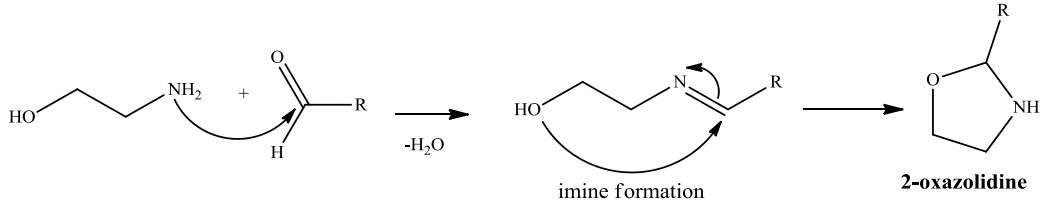
Voice, 2013 suspected oxazoline but no confirmation with standard was done. A mechanism based on literature (Ilkgul et al., 2010; Levine et al., 2008) was proposed in this work to explain oxazoline and 2-alkyloxazolines formation (Scheme 1). First step is amidification of MEA by carboxylic acid (Gouedard et al., 2012), then an intramolecular cyclisation leads to an intermediate which dehydrates to form oxazoline or 2-alkyloxazolines. Oxazoline was observed in S1 and 2-methyloxazoline in S2, confirming reaction between MEA and carboxylic acids. Amide as intermediate in this mechanism is confirmed by formation of oxazoline in S3 and 2-methyloxazoline in S4.



Scheme 1. Proposed mechanism for oxazolines (R = H, CH_3).

3.2. Oxazolidine and 2-methyloxazolidine

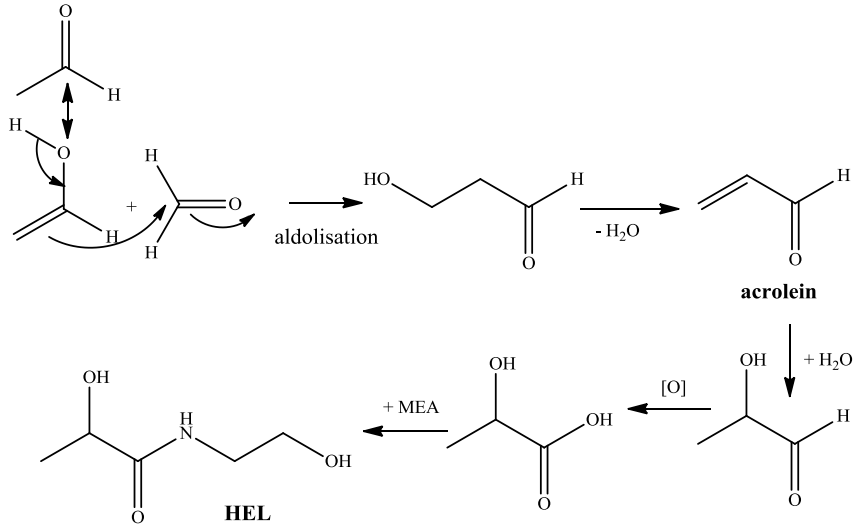
Oxazolidine was suspected by Reynolds et al., 2013 and Voice, 2013. Mechanism based on literature (Lambert and Wharry, 1982; Saavedra, 1985) was proposed in this work to explain the formation of oxazolidine and 2-alkyloxazolidines (Scheme 2). It is well known that amines and aldehydes react to form imines (first step), then MEA hydroxyl group reacts with the imine function to form 2-alkyloxazolidine (intramolecular cyclisation). This mechanism was confirmed by S5 and S6 results because oxazolidine and 2-methyloxazolidine were formed in high yield in S5 and S6 respectively.



Scheme 2. Proposed mechanism for oxazolidines (R = H, CH3).

3.3. N-(2-hydroxyethyl)lactamide

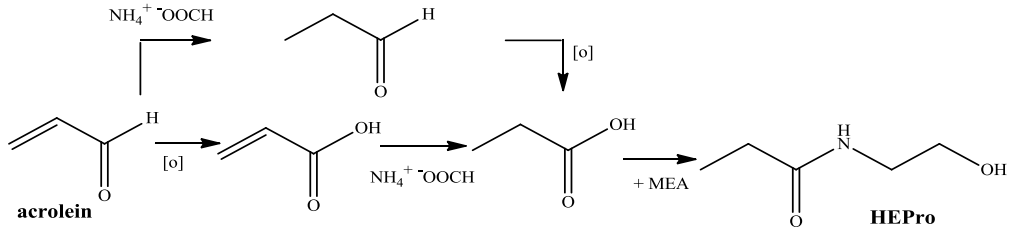
This product was already reported by Reynolds et al., 2013 and Strazisar et al., 2003. A proposed way of formation starting from MEA, acetaldehyde and formaldehyde was proposed in this work. Firstly, 3-hydroxypropanal was formed by aldolisation between formaldehyde and acetaldehyde. Secondly, it was converted to lactaldehyde. Suggested way is an OH displacement according to successive hydration-dehydration steps via acrolein intermediate, previously observed as volatile compound by Love, 2012 (Scheme 3).



Scheme 3. Proposed way of formation for N-(2-hydroxyethyl)lactamide.

3.4. N-(2-hydroxyethyl)propanamide

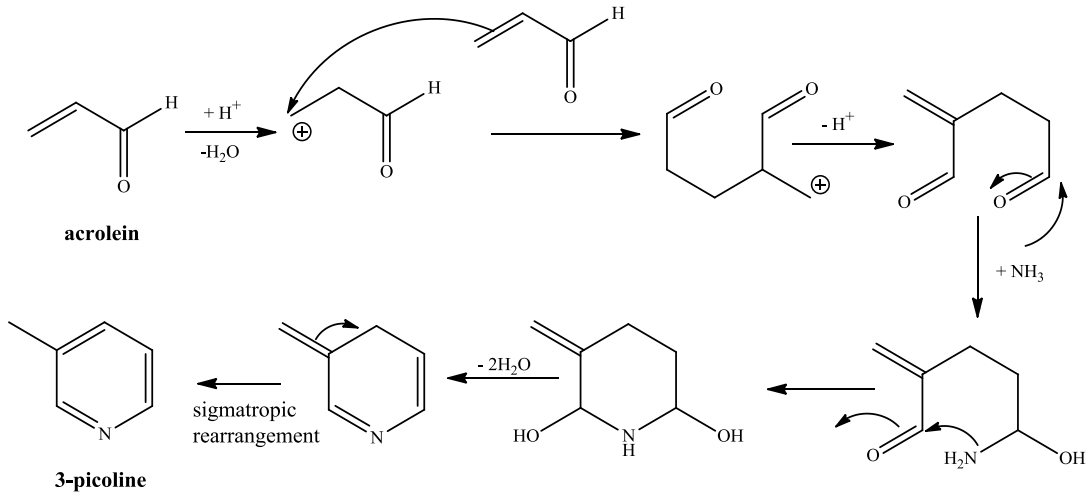
Acrolein (formed as previously explained in Scheme 3) could be either reduced by ammonium formate (very well known as a reducing agent), which is present in the solvent: reaction between ammonia and formic acid. Propanaldehyde (to be published) is then oxidized to propanoic acid, previously reported by Love, 2012. Oxidation of acrolein can also take place before double bond reduction by ammonium formate. Propanoic acid can then react with MEA to form HEPro (Scheme 4).



Scheme 4. Proposed way of formation for N-(2-hydroxyethyl)propanamide

3.5. 3-picoline

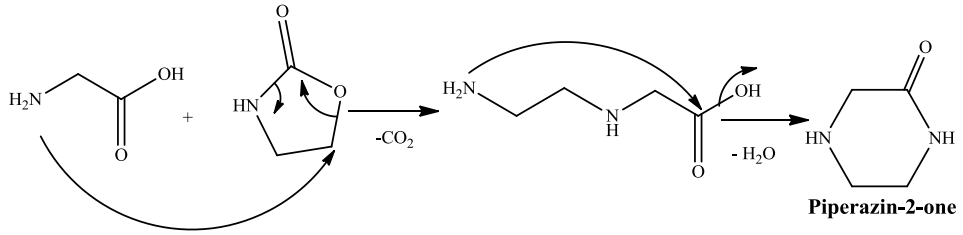
Acrolein dimerizes (Jin and Li, 2009; Singh et al., 1998) and the dialdehyde reacts twice with ammonia to form a ring (Scheme 5), which is dehydrated and aromatised (sigmatropic rearrangement) to form 3-picoline.



Scheme 517. Proposed mechanism for 3-picoline (adapted from Jin and Li, 2009; Singh et al., 1998).

3.6. Piperazin-2-one

Mechanism proposed to explain piperazin-2-one formation (Scheme 6) is based on its formation in S7. OZD (easily produced by reaction of MEA with CO_2, Davis and Rochelle, 2009) reacts with glycine then an intramolecular amidification occurs leading to piperazin-2-one.

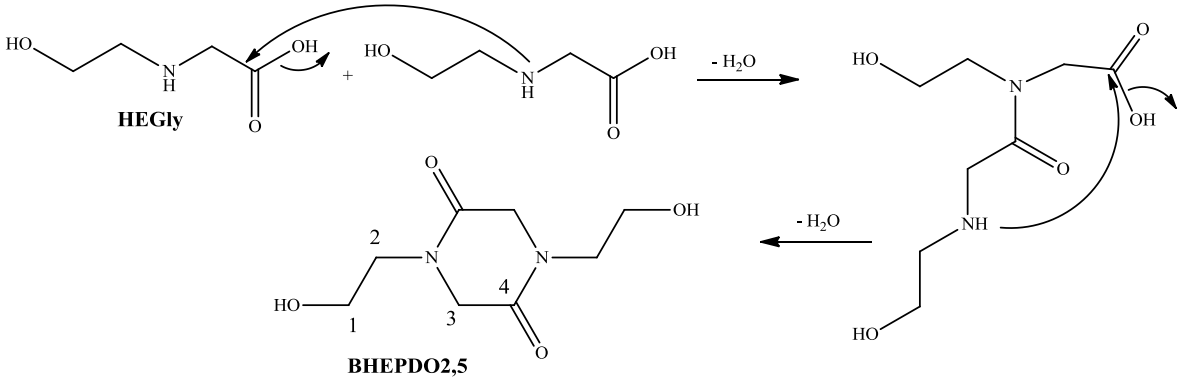


Scheme 6. Proposed mechanism for 2-piperazinone

3.7. N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione

In the pilot plant sample, a molecule with a molar mass of 202 g/mol was observed by GC/MS. This molar mass was confirmed with positive and negative chemical ionisation: for PCI, 203 is the highest peak of mass spectrum and 201 for NCI. Moreover, the major product observed in S8 had the same mass spectrum, the same retention time and the structure of this compound was determined by ^{1}H-^{13}C HSQC NMR as N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione (Figure 3). The main differences in ^{1}H NMR between HEGly, which is a precursor, and this product were the shift of the singlet from 3.65 to 4.20 ppm and of one triplet from 3.20 to 3.56 ppm, which proved the formation of amido group.

HEGly being one of the major degradation products (da Silva et al., 2012), it is highly likely that 2 molecules of HEGly react together to form this product. Firstly, amine reacts with carboxylic acid of the other molecule, then an intramolecular amidification leads to BHEPDO2,5 (Scheme 7).



Scheme 7. Proposed mechanism for N,N'-bis(2-hydroxyethyl)piperazin-2,5-dione.

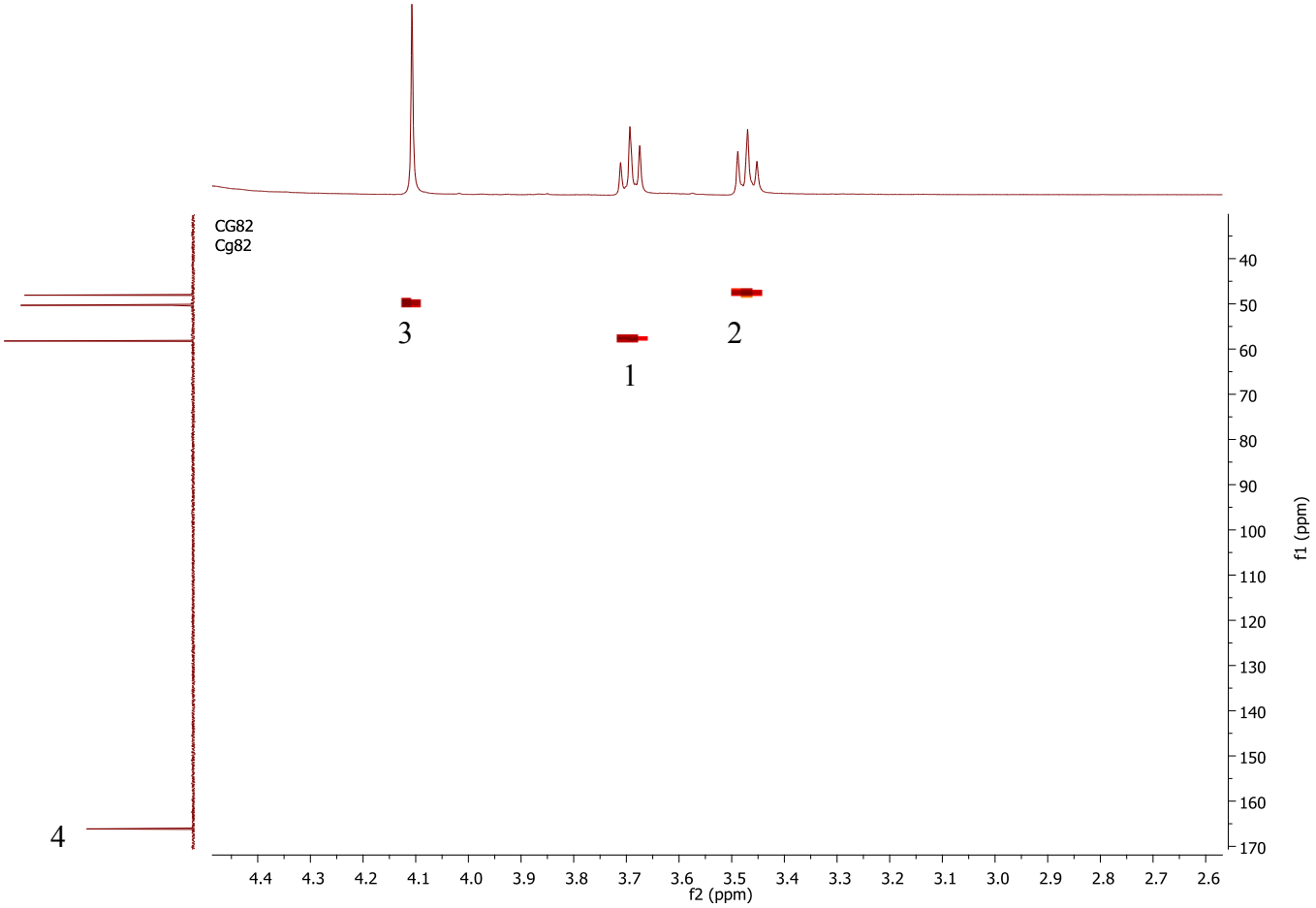
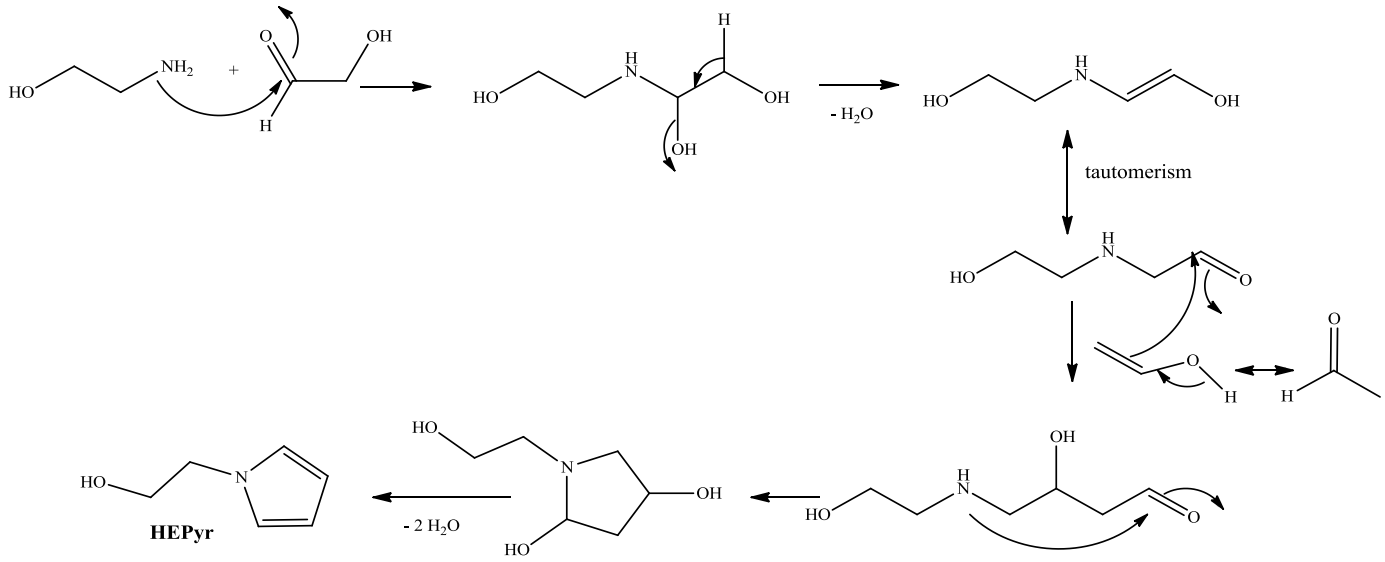


Figure 3. ^{1}H-^{13}C HSQC spectrum of S8 in D_2O.

3.8. N-(2-hydroxyethyl)pyrrole

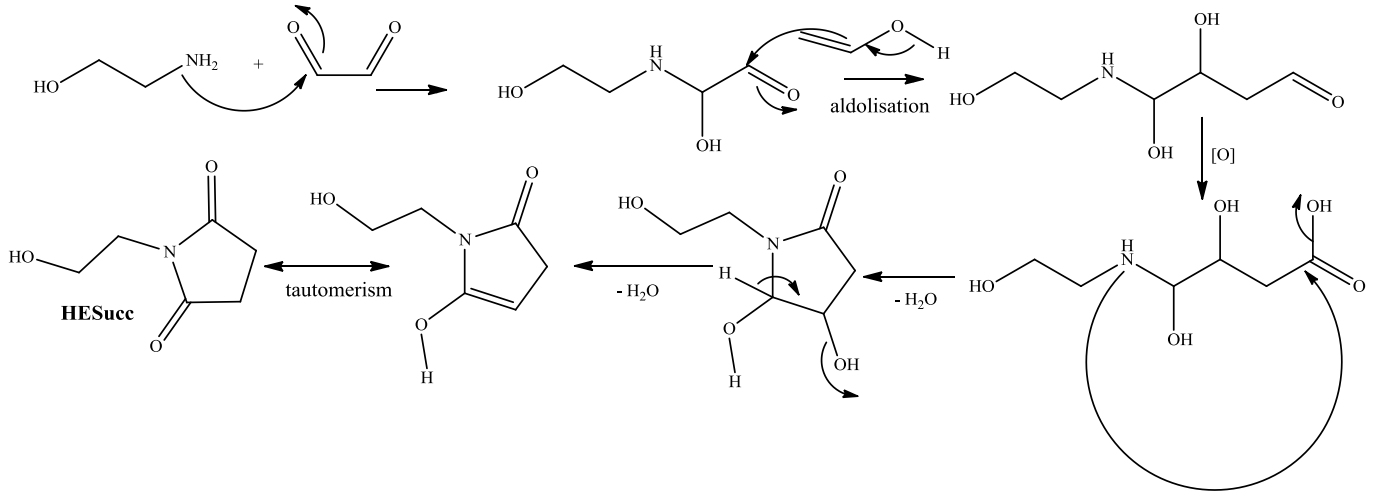
MEA reacts with glycolaldehyde, supposed as intermediate in the glycolic acid synthesis, Goff and Rochelle, 2004. The resulting cis-glycol is then dehydrated leading to an aldehyde which can react with acetaldehyde (aldolisation). An intramolecular cyclisation gives then a pyrrolidine which is dehydrated in HEPyr (Scheme 8).



Scheme 8. Proposed way of formation for N-(2-hydroxyethyl)pyrrole

3.9. N-(2-hydroxyethyl)succinimide

This product has been already reported by Lepaumier et al., 2011; Reynolds et al., 2013; Strazisar et al., 2003; Supap et al., 2011. To the best of our knowledge, no mechanism was proposed for this molecule. MEA reacts with glyoxal, then aldolisation takes place with acetaldehyde. Oxidation, intramolecular cyclisation (amidification) and dehydration leads to HESucc (Scheme 9).



Scheme 9. Proposed way of formation for N-(2-hydroxyethyl)succinimide

4. Conclusion

Because of potential impact of degradation products on environment, it is important to point up nearly all degradation products. In this work, new degradation products starting from MEA were observed thanks to analytical methods development (HS-SPME and GC/MS). Eleven amides and nitrogenous heterocycles were identified in a pilot plant liquid sample. Among them, seven were never reported in literature.

For each compound, a mechanism of formation was proposed and some of them were validated thanks to syntheses.

Some chemical reactions like amidification or aldolisation are recurrent. Aldolisation leads to carbon chain extension, therefore molecules with a chain of three, four or five carbon atoms could be observed HEPro, HEL, HESucc, HEPyr, 3-picoline).

This work showed that new degradation products of MEA can still be found thanks to analytical methods development. Understanding of chemical reactions is important to find other new degradation products and predict degradation pathways for other amines.

Acknowledgments

The authors would like to acknowledge French ANR (Research Project DALMATIEN) for financial support.

This work is a part of the PhD thesis of C. Gouedard supported by IFPEN and hosted by MATISSE LABEX.

Reference List

Bedell, S.A., 2009. Oxidative degradation mechanisms for amines in flue gas capture. Energy Procedia 1, 771-778.

Chakma, A., Meisen, A., 1987. Degradation of Aqueous DEA Solutions in a Heat-Transfer Tube. Can. J. Chem. Eng. 65, 264-273.

Chi, S., Rochelle, G.T., 2002. Oxidative degradation of monoethanolamine. Ind. Eng. Chem. Res. 41, 4178-4186.

da Silva, E.F., Lepaumier, H., Grimstvedt, A., Vevelstad, S.J., Einbu, A., Vernstad, K., Svendsen, H.F., Zahlsen, K.r., 2012. Understanding 2-Ethanolamine Degradation in Postcombustion CO_2 Capture. Ind. Eng. Chem. Res. 51, 13329-13338.

Davis, J., Rochelle, G., 2009. Thermal degradation of monoethanolamine at stripper conditions. Energy Procedia 1, 327-333.

DeHart, T.R., Hansen, D.A., Mariz, C.L., McCullough, J.G., 1999. Solving Corrosion problems at the NEA Bellingham Massachussetts carbon dioxide recovery plant. In: The NACE International Conference Corrosion '99, San Antonio, TX.

Eide-Haugmo, I., Brakstad, O.G., Hoff, K.A., Sorheim, K.R., da Silva, E.F., Svendsen, H.F., 2009. Environmental impact of amines. Energy Procedia 1, 1297-1304.

Goff, G.S., Rochelle, G.T., 2004. Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. Ind. Eng. Chem. Res. 43, 6400-6408.

Gouedard, C., Picq, D., Launay, F., Carrette, P.L., 2012. Amine degradation in CO_2 capture. I. A review. Int. J. Greenhouse Gas Control 10, 244-270.

IEA, 2010. Energy technology perspectives 2010. http://www.iea.org/publications/freepublications/publication/etp2010.pdf

Ilkgul, B., Gunes, D., Sirkecioglu, O., Bicak, N., 2010. Synthesis of 2-oxazolines via boron esters of N-(2-hydroxyethyl) amides. Tetrahedron Lett. 51, 5313-5315.

Islam, M.S., Yusoff, R., ALi, B.S., Islam, M.N., Chakrabarti, M.H., 2011. Degradation studies of amines and alkanolamines during sour gas treatment process. Int. J. Phys. Sci. 6, 5883-5895.

Jin, F., Li, Y., 2009. The Effect of H2 on Chichibabin Condensation Catalyzed by Pure ZSM-5 and Pt/ZSM-5 for Pyridine and 3-Picoline Synthesis. Catal. Lett. 131, 545-551.

Kenarsari, S.D., Yang, D., Jiang, G., Zhang, S., Wang, J., Russell, A.G., Wei, Q., Fan, M., 2013. Review of recent advances in carbon dioxide separation and capture. RSC Advances 3, 22739-22773.

Kohl, A.L., Riesenfeld, F.C., 1985. Gas purification. In: Gulf Publishing, Houston, TX.

Lambert, J.B., Wharry, S.M., 1982. Heterocyclic deformations from molecular enlargement. J. Org. Chem. 47, 3890-3893.

Lepaumier, H., da Silva, E.F., Einbu, A., Grimstvedt, A., Knudsen, J.N., Zahlsen, K.r., Svendsen, H.F., 2011. Comparison of MEA degradation in pilot-scale with lab-scale experiments. Energy Procedia 4, 1652-1659.

Lepaumier, H., Picq, D., Carrette, P.L., 2009a. New Amines for CO_2 Capture. I. Mechanisms of Amine Degradation in the Presence of CO_2. Ind. Eng. Chem. Res. 48, 9061-9067.

Lepaumier, H., Picq, D., Carrette, P.L., 2009b. New Amines for CO_2 Capture. II. Oxidative Degradation Mechanisms. Ind. Eng. Chem. Res. 48, 9068-9075.

Levine, M., Kenesky, C.S., Zheng, S., Quinn, J., Breslow, R., 2008. Synthesis and catalytic properties of diverse chiral polyamines. Tetrahedron Lett. 49, 5746-5750.

Love, D.H., 2012. Emissions of amines and their degradation products from post-combustion CO_2 capture. In: Atmospheric chemical conference, UC Davis.

Martin, S., Lepaumier, H., Picq, D., Kittel, J., de Bruin, T., Faraj, A., Carrette, P.-L., 2012. New Amines for CO_2 Capture. IV. Degradation, Corrosion, and Quantitative Structure Property Relationship Model. Ind. Eng. Chem. Res. 51, 6283-6289.

Moser, P., Schmidt, S., Stahl, K., 2011. Investigation of trace elements in the inlet and outlet streams of a MEA-based post-combustion capture process results from the test programme at the Niederaussem pilot plant. Energy Procedia 4, 473-479.

Rao, A.B., Rubin, E.S., 2002. 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.

Rey, A., Gouedard, C., Ledirac, N., Cohen, M., Dugay, J., Vial, J., Pichon, V., Bertomeu, L., Picq, D., Bontemps, D., Chopin, F., Carrette, P.L., 2013. Amine degradation in CO_2 capture. 2. New degradation products of MEA. Pyrazine and alkylpyrazines: Analysis, mechanism of formation and toxicity. Int. J. Greenhouse Gas Control 19, 576-583.

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Meuleman, E., Chaffee, A., Cottrell, A.J., Feron, P., 2013. Chemical Characterization of MEA Degradation in PCC pilot plants operating in Australia. Energy Procedia 37, 877-882.

Saavedra, J.E., 1985. Reductive alkylation of beta-alkanolamines with carbonyl compounds and sodium borohydride. J. Org. Chem. 50, 2271-2273.

Sexton, A.J., 2008. Amine oxidation in carbon dioxide capture processes. Thesis, University of Texas at Austin.

Singh, B., Roy, S.K., Sharma, K.P., Goswami, T.K., 1998. Role of acidity of pillared inter-layered clay (PILC) for the synthesis of pyridine bases. J. Chem. Technol. Biotechnol. 71, 246-252.

Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Degradation pathways for monoethanolamine in a CO_2 capture facility. Energy Fuels 17, 1034-1039.

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

Vevelstad, S.J., 2013. CO_2 absorbent degradation. Thesis, NTNU, Trondheim.

Voice, A.K., 2013. Amine Oxidation in Carbon Dioxide Capture by Aqueous Scrubbing. Thesis, The University of Texas at Austin.

Figures Captions

Figure 1.1. Scenarios to reduce CO_2 emissions to the atmosphere (IEA, 2008). 17
Figure 1.2. Simplified CO_2 capture flow sheet 18
Figure 3.1. Analytical strategy 45
Figure 3.2. ChemElut protocol 49
Figure 3.3. HS-SPME procedure 51
Figure 3.4. DNPH derivation on Sep-Pak cartridge 51
Figure 3.5. TENAX cartridge desorption and injection system 52
Figure 4.1. IFPEN pilot plant flowsheet 54
Figure 4.2. Semi-open batch reactor for representative test 55
Figure 4.3. Chromatograms comparison of pilot plant (red/up) and representative lab test samples (black/down) by GC/FID – CPSIL8 column (TEG = internal standard). 57
Figure 4.4. Chromatograms comparison of pilot plant (blue/up) and representative lab test samples (pink/down) by GC/FID- Carbowax (TEG = internal standard). 58
Figure 4.5. Ammonia and CO_2 FTIR profiles 59
Figure 5.1. Reaction mixture from MEA and oxalic acid (in pink) superposed with standards (20 ppm in black) and pilot plant sample (in blue). 66
Figure 5.2. ^{1}H-^{13}C HSQC spectrum of S8 in D_2O. 79
Figure 5.3. ^{1}H NMR spectrum of HEGly in D_2O. 79
Figure 5.4. SIM (TIC) chromatogram, after HS-SPME, of pilot plant sample using DBWAX 91
Figure 5.5. Sum up of MEA degradation 101
Figure A.1. Chromatogram (LC/MSMS) of a mix of 13 standards (1 mg/L in water) + MEA (100 mg/L) 148
Figure A.2. Chromatograms of transitions (LC-ESI-MSMS) of a mix of 13 standards (1 mg/L in water) + MEA (100 mg/L) 148
Figure B.1. Chromatogram Scan (GC/MS/TOF) of a liquid sample from pilot plant with CPSIL8 157
Figure B.2. Chromatogram Scan (GC-EI-MS) of a liquid sample from pilot plant with DBWAX. 157
Figure B.3. Chromatogram (LC/MSMS) of liquid sample from pilot plant (100-folds diluted) 158
Figure B.4. Chromatogram (HS-SPME-GC-EI-MS) of pilot plant sample with DBWAX 158
Figure B.5. TENAX Chromatogram with CPSIL8 from pilot plant (C2) after 1600 hours 159
Figure B.6. TENAX Chromatogram with CPSIL8 from pilot plant (C2) after 1000 hours 159

Figure B.7. TENAX Chromatogram with CPSIL8 from lab test 160
Figure B.8. NMR ^{1}H of S1 in D_2O 161
Figure B.9. NMR ^{13}C of S1 in D_2O 161
Figure B.10. Mass spectrum of HHEA in S1 (M = 119 $g.mol^{-1}$, rt = 45.5 min, GC/MS TOF)..... 162
Figure B.11. Mass spectrum of HHEA in pilot plant (M = 119 $g.mol^{-1}$, rt = 45.1 min GC/MS-TOF..... 162
Figure B.12. NMR ^{1}H of S2 in D_2O 163
Figure B.13. NMR ^{13}C of S2 in D_2O 163
Figure B.14. Mass spectrum of S3 at 58.06 min..... 164
Figure B.15. Mass spectrum of pilot plant at 58.22 min..... 164
Figure B.16. Mass spectrum of major peak for S8 at 71.6 min (BHEPDO2,5)..... 165
Figure B.17. Mass spectrum of pilot plant at 72.6 min..... 165
Figure B.18. Mass spectrum of S25 at 9.61 min..... 166
Figure B.19. Mass spectrum of pilot plant at 9.58 min..... 166
Figure B.20. chromatogram of S28..... 167
Figure B.21. Mass spectrum of major peak for S28 at 16.8 min 167
Figure B.22. Mass spectrum on TENAX cartridges at 16.9 min 167
Figure B.23. Mass spectrum of U4 at 32.8 min (M = 115 g/mol) 168
Figure B.24. Mass spectrum of U6 at 50.6 min (M = 158 g/mol) 168
Figure B.25. Mass spectrum of U3 at 53.6 min (M = 184 g/mol) 169
Figure B.26. Mass spectrum of U5 at 56.8 min (M = 176 g/mol) 169
Figure B.27. Mass spectrum of U8 at 58.7 min (M = 188 g/mol) 170
Figure B.28. Mass spectrum of U2 at 61.0 min (M = 202 g/mol) 170
Figure B.29. Mass spectrum of U1 at 62.1 min (M = 188 g/mol) 171
Figure B.30. Mass spectrum of U1 at 63.0 min (M = 216 g/mol) 171
Figure B.31. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 10 mg/L, other alkyl pyrazines were at 0.1 mg/L) in a water/MEA solution with CPSIL8. 172
Figure B.32. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 10 mg/L, other alkyl pyrazines were at 0.1 mg/L) in a water/MEA solution with the DBWAX. 173
Figure B.33. ^{1}H NMR spectrum of standard mixture of 2,5 and 2.6-dimethylpyrazine..... 174
Figure B.34. Comparison mass spectra of the GC peak (MAE, m/z = 61 at rt = 8,3) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition)..... 175

Figure B.35. Comparison mass spectra of the GC peak (MAE, m/z = 89 at rt = 9.9) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition). 176
Figure B.36. MAE, m/z = 103 at rt 30.3 min 176
Figure B.37. MAE, m/z = 117 at rt 33.4 min 177
Figure B.38. Comparison mass spectra of the GC peak (1AP2, m/z = 99 at rt = 32.6) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 177
Figure B.39. 1AP2, m/z = 85 at rt = 33.8 min 178
Figure B.40. 3AP1, m/z = 147 at rt = 48 min 178
Figure B.41. 3AP1, m/z = 102 at rt 20.4 min 179
Figure B.42. DEG spectrum from database 179
Figure B.43. 3AP1, m/z = 89 at rt = 16.7 min 180
Figure B.44. MAE, m/z = 115 at rt = 28.7 min 180
Figure B.45. MAE, m/z = 190 at rt = 56.3 min 181
Figure B.46. 1AP2, m/z = 186 at rt = 56.9 min 181
Figure B.47. Comparison mass spectra of the GC peak (MAE, m/z = 101 at rt = 29.5) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 182
Figure B.48. Comparison mass spectra of the GC peak (1AP2, m/z = 101 at rt = 34.4) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 182
Figure B.49. Comparison mass spectra of the GC peak (3AP1, m/z = 101 at rt = 40.9) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 183
Figure B.50. Comparison mass spectra of the GC peak (MAE, m/z = 114 at rt = 37.2) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition 183
Figure B.51. 3AP1, m/z = 87 at rt = 12.4 min 184
Figure B.52. MAE, m/z = 158 at rt = 51 min 184
Figure B.53. M AE, m/z = 128 at rt = 35.5 min 185
Figure B.54. 1AP2, m/z = 140 at rt = 41.3 min 185
Figure B.55. 1AP2, m/z = 140 at rt = 44.5 min 186
Figure B.56. 1AP2, m/z = 154 at rt = 46.6 min 186
Figure B.57. Comparison mass spectra of the GC peak (MAE, m/z = 113 at rt = 45.3) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 187
Figure B.58. 1AP2, m/z = 153, rt = 32.9 min 187
Figure B.59. Comparison mass spectra of the GC peak (1AP2, m/z = 93 at rt = 16.5) with the NIST proposal (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 188

Figure B.60. Comparison mass spectra of the GC peak (1AP2, m/z = 107 at rt = 22) with the NIST proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 188
Figure B.61. Comparison mass spectra of the GC peak (3AP1, m/z = 107 at rt = 23) with the proposition (Top = mass spectrum of peak, bottom = superposition of unknown and proposition) 189

Tables Captions

Table 2.1 MEA main thermal degradation products 22
Table 2.2. MEA thermal degradation products formed from HEEDA. 24
Table 2.3. Well-described MEA oxidative degradation products (schemes 2.9-2.23). 26
Table 2.4. Degradation products of MEA without any described mechanisms 39
Table 2.5. Nitrosamines observed in MEA degradation 42
Table 4.1. Representative test conditions. 56
Table 4.2. O_2 and CO_2 partial gas pressures. 56
Table 4.3. Comparison of IC results for lab test and pilot plant campaign C1 57
Table 4.4. Sum-up of the experiments carried out in oven. 61
Table 4.5. Sum-up of experiments carried out in stirred reactor 62
Table 5.1. Products observed in this work 63
Table 5.2. Novel products 76
Table 5.3. Products observed without identification in pilot plant sample 82
Table 5.4. Average concentrations of ten pyrazines in pilot plant samples 91
Table 6.1. Recurrent reactions for amine degradation 103
Table 6.2. Expected products from alkylation/dealkylation pathways 106
Table 6.3. Expected aldehydes/ketones and corresponding acids 107
Table 6.4. Expected products issued of aldolisation 109
Table 6.5. Expected products from amidification reaction 110
Table 6.6. Expected glycols 113
Table 6.7. Expected products from Escheweiler-Clarke reaction 114
Table 6.8. Expected amino-acids and their intermediates 116
Table 6.9. Expected products from carbamate cyclisation 118
Table 6.10. Expected imidazolidinones or six-membered rings homologues 119
Table 6.11. Expected oxazolidines and tetrahydrooxazines 121
Table 6.12. Expected piperazinones with their reactants 123
Table 6.13. Expected oxazolines and homologues 125
Table 6.14. Expected imidazoles or six-membered ring homologues 126
Table 6.15. Expected succinimides 128
Table 6.16. dicarbonyl intermediates and expected pyrroles 129

Table 6.17. Alkenal intermediate and expected pyridine..... 131
Table A.A.1. Specifications of GC/FID and GC/MS programs 146
Table A.2**.** MRM transition of target compounds..... 147
Table A.3. MRM transition of target nitrosamines..... 149
Table A.4. Lists of chemicals..... 150
Table A.5. Chemical conditions of oven experiments..... 154
Table B.1. Pyrazine and alkyl pyrazines studied standards, with the selected ion for detection in MS SIM mode and their retention times on both columns. 172

Schemes Captions

Scheme 2.1. Carbamate formation (R^1 = H, R^2 = CH_2CH_2OH) 22
Scheme 2.2. Oxazolidin-2-one formation (R^1 = H) 22
Scheme 2.3. Oxazolidin-2-one formation adapted from Patil et al., 2008 23
Scheme 2.4. Diamine formation (R^1 = H) 23
Scheme 2.5. Imidazolidin-2-one formation 23
Scheme 2.6. Ureas formation (R^1 = H) according to Davis and Rochelle 2009 24
Scheme 2.7. Degradation products formed from HEEDA (R^1 = H) 25
Scheme 2.8. Carboxylic acids formation according to. Rooney et al., 1998b 29
Scheme 2.9. Oxidations and ethyleneglycol formation (R = H) according to Lepaumier, 2008 29
Scheme 2.10. Electron abstraction (R = H or alkyl) according to Lindsay Smith and Masheder, 1977 30
Scheme 2.11. Hydrogen abstraction according to Petryaev et al., 1984 30
Scheme 2.12. Hydrogen abstraction according to Lepaumier et al., 2009b 31
Scheme 2.13. Radical mechanism proposed for glycine formation according to Bedell, 2009 31
Scheme 2.14. Amides and HSSs formation (R = H, CH_3, CH_2OH or C(O)OH) 32
Scheme 2.15. HEEDA formation adapted from Huang et al., 2014 33
Scheme 2.16. HEEDA and BHEEDA formation according to Lepaumier et al., 2009b (R = H, CH_3 or CH_2OH) 34
Scheme 2.17. Piperazinones formation according to Lepaumier et al., 2009b 35
Scheme 2.18. Piperazinones formation according to Strazisar et al., 2003 and da Silva et al., 2012 36
Scheme 2.19. HEI formation according to Arduengo et al., 2001 36
Scheme 2.20. HEI formation according to Katsuura and Washio, 2005 and Vevelstad, 2013 37
Scheme 2.21. HEGly formation by Leuckart-Wallach reaction according to Vevelstad, 2013. 37
Scheme 2.22. Methylation of amine by Eschweiler-Clarke reaction (Lepaumier, 2008) 37
Scheme 2.23. DEA formation according to Fostås et al., 2011 and Ridd, 1961 38
Scheme 2.2.24. Nitrosamines formation according to Ridd (1961) and Fostas et al. (2011) 42
Scheme 5.1. Proposed mechanism for ethyleneglycol formation 67
Scheme 5.2. Proposed mechanism for carboxylic acids and aldehydes formation 68
Scheme 5.3. Sum-up of reactions of MEA with glyoxal leading to known degradation products 69
Scheme 5.4. Proposed mechanism for HEGly formation (based on S6 results) 70
Scheme 5.5. Proposition of mechanism for MAE formation (based on S8 results) 70

Scheme 5.6. Proposed mechanism for the formation of HEI (Based on S9 results) 71
Scheme 5.7. Proposed mechanism for the formation of HEI without formaldehyde (based on S10 results) 71
Scheme 5.8. Proposed mechanism for 1HEPO and 4HEPO formation (based on S13)..... 73
Scheme 5.9. Proposed mechanism for 4HEPO formation (based on S14)..... 73
Scheme 5.10. Proposed mechanism HESucc formation (based on S15)..... 74
Scheme 5.11. Propanal and propionic acid formation via acrolein 75
Scheme 5.12. Proposed way of formation for N-(2-hydroxyethyl)lactamide..... 75
Scheme 5.13. Proposed mechanism for HEMI formation (based on HEI formation and S16)..... 78
Scheme 5.14. Sum-up of reactions for new degradation products (U1, U2, U3 unknown products see after)..... 78
Scheme 5.15. Proposed mechanism for BHEPDO2,5 formation (based on S8). 80
Scheme 5.16. Proposal for the structure and formation pathway of U1 (based on S14)..... 80
Scheme 5.17. Proposal for the structure and formation pathway of U1 (based on S14)..... 81
Scheme 5.18. Proposal for the structure and formation pathway of U3 (based on S4)..... 83
Scheme 5.19. Sum-up of proposed reactions of MEA with methylglyoxal for novel degradation products 84
Scheme 5.20. Proposal for the structure and formation pathway of U4 (based on S18)..... 85
Scheme 5.21. Proposal for the structure and formation pathway of U5 (based on S19)..... 86
Scheme 5.22. Alternative proposal for the structure and formation pathway of U5 87
Scheme 5.23. Proposal for the structure and formation pathway of U6 87
Scheme 5.24. Alternative proposal for the structure and formation pathway of U6 88
Scheme 5.25. Proposal for the structure and formation pathway of U7 88
Scheme 5.26. Proposal for the structure and formation pathway of U8 89
Scheme 5.27. Mechanism of pyrazine and alkyl pyrazines formation (adapted from Adams et al., 2008; Guerra and Yaylayan, 2010; Krems and Spoerri, 1947). 93
Scheme 5.28. Mechanism of pyrazine alkylation (adapted from Bramwell et al., 1971). 93
Scheme 5.29. Mechanism of vinylpyrazine formation. 94
Scheme 5.30. Proposed mechanism for oxazolines (R = H, CH_3). 95
Scheme 5.31. Proposed mechanism for oxazolidines formation (R = H, CH_3). 95
Scheme 5.32. Proposed mechanism for NPZ formation 96
Scheme 5.33. Proposed way of formation for HEPyr and pyrrole (R = CH_2-CH_2-OH or H) 97

Scheme 5.34. Proposed mechanism for 3- methylpyridine formation (adapted from Jin and Li, 2009; Singh et al., 1998). 98
Scheme 5.35. Proposed way of formation for N-(2-hydroxyethyl)propanamide 98
Scheme 5.36. Proposed way of formation for PO 99
Scheme 5.37. Proposed mechanism for oximes formation 99
Scheme 5.38. Proposed mechanism for glycols formation 100
Scheme 6.1. Alkylation/dealkylation mechanism 105
Scheme 6.2. Sum-up of aldehydes and carboxylic acids fornation based on Scheme 5,2 106
Scheme 6.3. Mechanism of aldolisation 108
Scheme 6.4. Mechanism of amidification 109
Scheme 6.5. Glycols formation 112
Scheme 6.6. Eschweiler-Clarke reaction 114
Scheme 6.7. General reaction for amino acids formation 115
Scheme 6.8. Ring closure of carbamates 118
Scheme 6.9. Imidazolidinone or six-membered ring homologues formation 119
Scheme 6.10. Oxazolidines and tetrahydrooxazines formation 120
Scheme 6.11. Piperazinones formation 122
Scheme 6.12. Oxazolines and homologues formation 124
Scheme 6.13. Imidazoles and homologues formation 126
Scheme 6.14. Succinimidees formation 127
Scheme 6.15. Pyrroles formation 129
Scheme 6.16. Pyridines formation 130

Abstract :

The CO_2 post-combustion capture with aqueous solutions of amines is the most mature technology to reduce greenhouse gases emissions. However chemical absorption is suffering from the degradation of amines mainly due to the presence of O_2 in flue gases. Formed products, which could be rejected to atmosphere, may be detrimental to environment and human health. The aim of this thesis was to identify as many degradation products as possible thanks to the development of different sampling and analytical methods especially for gas phase analysis. Thus more than sixty products issued from monoethanolamaine (MEA) degradation were observed in pilot plant samples. Thirty of them are novel, they often belong to the same family as pyrazines or oxazolines, or they could be characterized by the increase of carbon chain lengths (C2 between two heteroatoms to C5).
Mechanisms such as alkylation/dealkylation, aldehydes/ketones formation, amidification, aldolisation, Eschweiler Clarke, pyridines formation were proposed to explain the formation of novel products and were, most of the time, validated by mixing the reactants proposed in the mechanism. Finally, it has been shown that the transposition of these reactions to three other amines (N-methylaminoethanolamine, 1-aminopropan-2-ol, 3-aminopropan-1-ol) enabled us to predict their degradation products.

Keywords : [CO_2 Capture, amines degradation, mechanisms, monoethanolamine, N-methylaminoethanolamine, 1-aminopropan-2-ol, 3-aminopropan-1-ol]

[Nouveaux produits de dégradation de l'éthanolamine (MEA) pour le captage du CO_2 : identification, proposition de mécanismes et transposition à d'autres amines]

Résumé :

Le captage du CO_2 en postcombustion par absorption dans des solutions aqueuses d'amines est la technologie la plus mature pour réduire les émissions de gaz à effets de serre. Cependant, les amines utilisées sont susceptibles de réagir avec l'oxygène présent dans les fumées pour former de nouveaux composés qui peuvent être émis à l'atmosphère et avoir des conséquences sur l'environnement et la santé humaine.. L'objectif de cette thèse était donc d'identifier le maximum de produits de dégradation des amines grâce au développement de différentes techniques analytiques et d'échantillonnage, notamment pour l'analyse de la phase gaz. Ainsi plus de soixante produits issus de la dégradation de la monoéthanolamine (MEA) en pilote de captage du CO2 ont été identifiés. Une trentaine de ces produits sont nouveaux, ils sont souvent issus d'une même famille comme les pyrazines ou les oxazolines ou ils peuvent être caractérisés par l'allongement de la chaine carbonée (C2 entre deux hétéroatomes à C5).
Des mécanismes basés sur des réactions d'alkylation/de désalkylation, la formation d'aldéhydes ou de cétones, l'amidification, l'aldolisation, la réaction d'Eschweiler Clarke, la formation de pyridines ont été proposés pour expliquer la formation de tous les nouveaux produits de dégradation et validés, dans la plupart des cas, en mélangeant les réactifs proposés dans le mécanisme. Finalement, il a été montré que la transposition de ces schémas réactionnels à trois autres amines (N-méthylaminoéthanolamine, 1-aminopropan-2-ol, 3-aminopropan-1-ol) a permis de prédire leurs produits de dégradation.

Mots clés : [Captage du CO_2, dégradation des amines, mécanismes, monoéthanolamine, N-méthylaminoéthanolamine, 1-aminopropan-2-ol, 3-aminopropan-1-ol]