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Cuccia, L., Dugay, J., Bontemps, D., Louis-Louisy, M., Morand, T., Bellosta, V., Vial, J., Monitoring of the blend 1-methylpiperazine/piperazine/water for post-combustion CO_2 capture. Part 1: identification and quantification of degradation products. *Soumis le 8 novembre 2017 dans International Journal of Greenhouse Gas Control, en révision.*

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Communications orales

12e Congrès Francophone sur les Sciences Séparatives et les Couplages de l'AFSEP (SEP), Paris, 2017.
Présentation de type Flash Poster.
Complémentarité des Stratégies analytiques pour l'étude de la dégradation de solvants innovants pour le captage du CO_2.
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Liste des abréviations

[Bmim][BF4] : 1-Butyl-3-methylimidazolium tetrafluoroborate

1MPZ : 1-Méthylpipérazine

1,3-DAP : 1,3-Diaminopropane

14DMPZ : 1,4-Diméthylpipérazine

2MP – 2-Méthylpyrazine

AEP : 1-(2-Aminoethyl)piperazine

AEAEPZ : 1-[2-[(2-Aminoethyl)amino]ethyl]piperazine

AMP : 2-Amino-2-methylpropan-1-ol

ATIS : Adsorbent Tube Injector System

BHEOX : *N,N'*-bis(2-hydroxyethyl)oxalamide

BHE Urea : *N,N'*-bis-(2-hydroxyethyl) urea

CAR-PDMS : Carboxen-Polydimethylsiloxane

COP 21 : Conference Of the Parties (21ème conférence des parties)

CCS : Carbon Capture and Storage

CIS : Cooled Injector System (Injecteur à cryofocalisation)

CSC : Captage et Stockage du CO_2

DEA : Diéthanolamine

DEEA : 2-(Diethylamino)ethanol

DETA : Diethylenetriamine

DIPA : Bis(2-hydroxypropyl)amine

DMEA : Diméthylaminoéthanol

DMMEA : 2-Dimethylaminoethanol

DMF : Diméthylformamide

DNPH : 2,4-Dinitrophenylhydrazine

EDA : Ethylènediamine

EI : Ionisation Electronique

ELECNRTL : Electrolyte Non-Random Two Liquid

ELSD : Evaporative Light Scattering Detector

EPZ : 1-Ethylpiperazine

ESI : Electrospray Ionisation (Ionisation par Electronébulisation)

FPZ : 1-Formylpiperazine

FTIR : Fourier Transform Infrared Spectroscopy (Spectroscopie Infrarouge à transformée de Fourier)

GAP 1 : 1,5-Bis(3-aminopropyl)-1,1,3,3,5,5-hexamethyltrisiloxane

GC : Gas Chromatography (Chromatographie en phase Gazeuse)

H_{abs} : Chaleur d'absorption

HEEDA : *N*-(2-Hhydroxyethyl)ethylenediamine

HEA : *N* -(2-Hydroxyethyl)acetamide

HEF : *N* -(2-Hydroxyethyl)formamide

HEHAA : 2-Hydroxy-N-(2-hydroxyethyl)acetamide

HEI : *N* -(2-Hydroxyethyl)imidazole

HEPZ : *N* -(2-Hydroxyethyl)piperazine

HR : High Resolution (Haute Résolution)

HS-SPME : Head-Space Solid Phase Micro Extraction (Micro Extraction sur Phase Solide en Espace de Tête)

IC : Ionic Chrmatography (Chromatographie Ionique)

IEA : International Energy Agency

IS : Internal Standard (Etalon Interne)

Klif : Norwegian Climate and Pollution Agency

LC : Liquid Chromatography (Chromatographie en phase Liquide)

LEMEDES-CO2 : Laboratoire d'Etude des MEcanismes de DEgradation des Solvants utilisés pour le captage du CO_2

LLE : Liquid-Liquid Extraction (Extraction liquide-liquide)

LOD : Limite de détection

LOQ : Limite de quantification

MAPA : *N*-Methyl-1,3-diaminopropane

MDEA : Méthyldiéthanolamine

MEA : Monoéthanolamine

MMEA : 2-(Methylamino)ethanol

MS : Mass Spectrometry (Spectrométrie de Masse)

MS/MS : Spectrométrie de masse en tandem

MSA : Acide méthanesulfonique

m/z : Masse sur charge

ND : Non déterminé

NDIR : Nondispersive Infrared Sensor (Détecteur d'Infrarouges non Dispersif)

NDMA : Nitrosodiméthylamine

NOx : Oxydes d'azote

N-TBDA : *N*-Tert-butyldiethanolamine

PGC : Porous Graphitic Carbon

Ppb : Part per billion (partie par milliard)

Ppm : Part per million (partie par million)

PTR : Proton Transfer Reaction

Pts : Points

PZ : Pipérazine

RKS : Riedlich-Kwong-Soave

SOx : Oxydes de soufre

STD : Standard (Etalon)

TCM : Technology Center Mongstad (Centre Technologique de Mongstad)

TEG : Triéthylène glycol

TIC : Total Inorganic Carbon (Carbone Inorganique Total)

TDU : Thermodesorption Unit (Unité de thermodésorption)

TIC : Total Ion Current

TOF : Time Of Flight

VOC : Volatile Organic Compounds

Wt% : % Percentage weight (pourcentage massique)

Introduction générale

Le réchauffement climatique global dû aux émissions de gaz à effet de serre est aujourd'hui un sujet de préoccupation mondiale. Dans le cadre de la COP21 qui s'est tenue en 2015 à Paris, un accord a été signé entre 195 Etats avec pour ambition une réduction des émissions des gaz à effet de serre. L'objectif de cet accord est de limiter le réchauffement climatique en dessous de 2°C d'ici 2100 par rapport à la période préindustrielle [1].

68 % des émissions de gaz à effet de serre sont causées par les industries productrices d'énergie [2] et 90 % d'entre elles correspondent à des émissions de CO_2 [3]. En 2014, les deux pays les plus émetteurs de CO_2 étaient la Chine et les Etats-Unis, avec respectivement 28 % et 18 % des émissions totales mondiales annuelles, représentant 14,3 Gt de CO_2 émis. L'Europe est à l'origine de 8 % de ces émissions mondiales, avec l'Allemagne comme pays le plus émetteur [3]. Depuis l'ère préindustrielle, les émissions atmosphériques de CO_2 issues de la combustion de ressources fossiles ont augmenté d'environ 40 % [4], atteignant près de 32,4 Gt en 2014 [3]. Cette augmentation est corrélée à un rapide développement économique, impliquant des besoins énergétiques accrus passant souvent par un fort essor des centrales utilisant des combustibles fossiles (charbon, gaz, …). Malgré le développement d'énergies renouvelables issues de matières non fossiles (photovoltaïque, éolien ou centrales hydroélectriques), la proportion de ressources fossiles utilisée reste élevée. A titre d'exemple, la part mondiale des combustibles fossiles utilisés en 2014 était de 82 % contre 86 % en 1971 [3]. Les industries productrices d'énergies via l'utilisation de ressources fossiles peuvent donc jouer un rôle non négligeable dans la lutte contre les émissions de CO_2.

Parmi les scénarios proposés pour réduire les émissions de CO_2 (e.g. l'utilisation d'énergies décarbonnées (renouvelables et nucléaires)) [5], le Captage et le Stockage du CO_2 (CSC en français ou CCS en anglais) permettrait de réduire jusqu'à 20 % ces émissions [6]. Les technologies de captage du CO_2 permettraient aux centrales actuellement en fonctionnement et utilisant des ressources fossiles de continuer à fonctionner tout en participant à la réduction des émissions de CO_2.

Plusieurs étapes sont mises en œuvre au cours du captage et du stockage géologique du CO_2 : le captage à proprement parler, la compression du CO_2 suivie de son transport, et enfin son stockage géologique au sein d'aquifères salins profonds, de réservoirs de gaz ou d'huiles déplétés [7]. L'étape la plus coûteuse est celle du captage, puisqu'elle représente 80 % du coût total du processus [8]. Il existe actuellement trois filières technologiques permettant de capter le CO_2 : le captage post-combustion, le captage pré-combustion et l'oxy-combustion [9]. Le captage du CO_2 en post-combustion est aujourd'hui la technologie la plus mature, et consiste à capter le CO_2 au sein de fumées issues de la combustion de ressources fossiles telles que le charbon ou le gaz. Le processus peut être réalisé par séparation

membranaire, par séparation cryogénique (via condensation), par adsorption ou par absorption chimique [10]. Le captage du CO_2 en post-combustion par absorption chimique via l'utilisation de solvants aminés, qui permet de capter du CO_2 avec une efficacité ciblée de 90 % [11], a fait l'objet de la présente étude. Un avantage à la technologie est la possibilité d'implémentation du procédé sur des installations existantes sans avoir à mettre en œuvre d'importantes modifications. Néanmoins, deux limitations technologiques au procédé subsistent : la pénalité énergétique de l'ordre de 11 %-pts (points) sur le rendement de la centrale [12,13] et la dégradation non négligeable des solvants utilisés conduisant à un appoint de solvant frais régulier [14,15]. Cette dégradation des solvants du procédé est de surcroit responsable de la formation de produits de dégradation potentiellement toxiques pour l'Homme et l'environnement, composés pouvant être émis avec les fumées traitées émises.

Cette thèse, tripartite entre l'ADEME, l'ESPCI Paris et EDF R&D, s'inscrit dans le cadre du projet de recherche d'EDF R&D axé autour du captage, du transport, et du stockage du CO_2 émis par les centrales thermiques à flamme. Dans ce contexte, les objectifs de la thèse sont d'étudier la stabilité chimique de trois mélanges innovants d'amines, préalablement sélectionnés pour leur bon comportement thermodynamique et cinétique, ainsi que pour leurs bonnes performances de captage au cours du procédé de captage du CO_2 en post-combustion. Ces mélanges innovants ont été retenus dans l'optique de permettre un développement du procédé de captage avec une limitation de la pénalité énergétique à 10 % pts et avec un faible impact environnemental impliquant une maîtrise des émissions polluantes. Pour les trois mélanges retenus, très peu ou aucune étude n'a été réalisée concernant leur stabilité chimique dans les conditions de captage du CO_2.

Le premier objectif de ce projet est de simuler la dégradation des solvants sélectionnés. Cette dégradation a été réalisée sur un dispositif expérimental de laboratoire de captage de CO_2 construit par EDF R&D (Chatou), et représentatif des conditions industrielles. En effet, ce dispositif permet de reproduire les cycles d'absorption et de régénération vus par le solvant au cours du procédé, et ainsi mimer sa dégradation. Dans l'objectif de caractériser l'état du solvant au cours du temps, et ainsi identifier et quantifier les produits de dégradation formés, des stratégies analytiques complémentaires impliquant les chromatographies en phase liquide et gazeuse ont été développées. Cette caractérisation a été effectuée au sein de la phase liquide du solvant, mais également au sein de la phase gazeuse correspondant aux fumées traitées émises pour laquelle une technique de prélèvement originale pour le domaine a été développée. Une des difficultés a résidé dans le fait que les échantillons à analyser étaient complexes (30 à 40 % d'amines dans l'eau), et que les produits de dégradation étaient formés pour la plupart à l'état de trace. Des mécanismes réactionnels ont également été proposés dans l'objectif d'expliquer la formation de ces composés. Cette partie de l'étude a été réalisée avec l'appui

du Pr. Véronique Bellosta de l'ESPCI Paris. A terme, ce projet vise à contribuer au développement d'un modèle de dégradation à l'échelle du procédé permettant de prédire la quantité de solvant consommée par le procédé.

L'ensemble de ce travail s'articule en cinq chapitres. Le premier chapitre, bibliographique, situe le contexte de l'étude et décrit le procédé de captage du CO_2 en post-combustion, les différents solvants pouvant être utilisés et ceux retenus pour la présente étude, ainsi que les dispositifs permettant d'étudier la dégradation des différents solvants. La deuxième partie de ce chapitre, sous la forme d'une revue, présente les stratégies analytiques décrites dans la littérature pour la caractérisation de solvants utilisés pour le captage du CO_2 en post-combustion. Le second chapitre présente le dispositif expérimental de captage, ainsi que les différentes méthodes analytiques développées au cours du projet. Le chapitre 3 présente, sous la forme de deux articles, les résultats obtenus concernant l'étude d'un solvant innovant composé de 1-méthylpipérazine (1MPZ), de pipérazine (PZ) et d'eau. Le chapitre 4, sous la forme d'un article, présente l'étude du second solvant du projet, composé de méthyldiéthanolamine (MDEA), de monoéthanolamine (MEA) et d'eau. Enfin, le chapitre 5 du manuscrit présente l'étude du dernier solvant composé de diméthylaminoéthanol (DMEA), de pipérazine (PZ) et d'eau, en le comparant aux deux autres solvants du projet en termes de performances de captage et de stabilité chimique.

Chapitre 1 : Etat de l'art

Ce premier chapitre se divise en deux parties principales. La première partie a pour objectif de présenter le procédé de captage du CO_2 en post-combustion par absorption chimique, ses limitations, les solvants décrits dans la littérature et les solvants qui feront l'objet de l'étude expérimentale. La seconde partie, sous forme de revue, a pour objectif de présenter les méthodes analytiques décrites dans la littérature pour caractériser la dégradation des solvants utilisés au cours du procédé.

Partie 1 : Captage du CO_2 en post-combustion par absorption chimique

Le captage du CO_2 en post-combustion par absorption chimique à l'aide de solvants aminés est aujourd'hui la technologie la plus mature permettant de réduire les émissions de CO_2 issus de procédés industriels [16]. Cette technique a été brevetée en 1930 dans le cadre de la purification de gaz naturel (désacidification) et bénéficie d'une grande expérience industrielle depuis des décennies [17,18]. Ce procédé est reconnu pour capter jusqu'à 90 % du CO_2 contenu dans les fumées [19] et est aujourd'hui assez mature pour une utilisation à grande échelle au sein de centrales utilisant des combustibles fossiles.

1 Principe du procédé

Le procédé de captage du CO_2 par absorption chimique est basé sur l'absorption réversible du CO_2 par des solutions d'amines. Avant leur entrée au sein de l'unité de captage, les fumées à traiter sont préalablement dépoussiérées, dénitrifiées et désulfurées, ceci afin d'abaisser les teneurs en oxydes d'azote (NOx) et de soufre (SOx), dans l'objectif de réduire la dégradation du solvant [19,20]. A l'issue de ces purifications, les fumées sont composées d'environ 70-75 % de N_2, 10-15 % de CO_2, 3-4 % d'O_2, 8-10 % d'H_2O [21] et moins de 10 ppm de SOx et de NOx [10]. Les gaz sont ensuite refroidis autour de 45°C et saturés par contact direct avec de l'eau afin d'optimiser l'étape d'absorption et d'éviter les pertes de solvant par évaporation [22].

L'unité de captage est constituée de trois parties principales : une colonne appelée absorbeur, un échangeur de chaleur (également appelé économiseur), et une colonne appelée strippeur (**Figure 1**). Dans une première étape, dite d'absorption, les fumées à traiter entrent en contact à contre-courant avec la solution aqueuse aminée. Cette étape se déroule à 40-60°C et à pression atmosphérique. Le CO_2 est alors capté par ces amines via une réaction chimique réversible. Les fumées décarbonées passent alors dans une section de lavage située en tête d'absorbeur, afin de limiter les émissions dans

l'atmosphère de composés volatils comme les amines ou les produits de dégradation. Le solvant aminé riche en CO_2 est ensuite pompé puis réchauffé entre 100 et 140°C grâce à l'économiseur, avant d'être injecté en tête du strippeur. Au cours de cette seconde étape de régénération préférentiellement réalisée sous pression, le CO_2 est dissocié de l'amine et relargué en phase gaz. Après une phase de lavage et de séparation il est récupéré pur à 99,9 %. L'amine libérée est enfin redirigée vers l'économiseur pour être refroidie, puis vers l'absorbeur afin d'effectuer de nouveaux cycles de captage [8,22]. Le CO_2 capté est ensuite comprimé en vue de son stockage géologique au sein d'aquifères salins profonds, de réservoirs de gaz ou d'huiles déplétés [7]. Ce CO_2 peut également être utilisé pour l'extraction assistée de pétrole ou bien pour d'autres applications telles que l'industrie agro-alimentaire ou l'industrie chimique (production de carbonates, d'acrylates ou de polymères) [23].

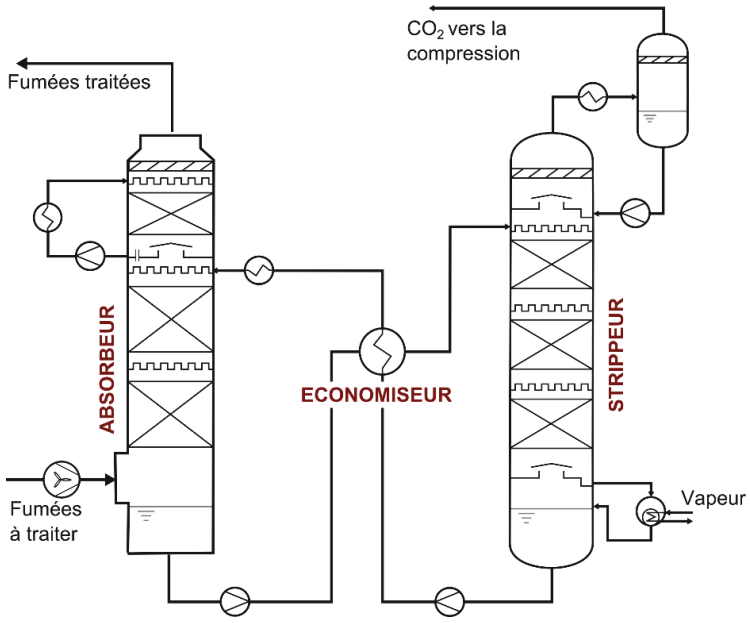


Figure 1: Procédé de captage de CO_2 en post combustion par absorption chimique (d'après document interne EDF R&D)

2 Limitations de la technologie

Les deux principales limitations du procédé de captage du CO_2 par absorption chimique sont d'une part la pénalité énergétique engendrée par le procédé, et d'autre part la dégradation des solvants aminés [12,15]. La consommation énergétique engendrée par l'étape de captage induit une pénalité énergétique non négligeable, estimée à 11 %-pts (points) pour un solvant constitué de monoéthanolamine (MEA) à 30 % en masse, solvant de référence du procédé aux amines. Ces résultats ont été observés dans le cadre du projet européen CASTOR sur le pilote industriel d'Esbjerg opéré au Danemark [13]. Cette pénalité correspond à un abaissement du rendement net de la centrale de 46,1 % sans captage à 35,1 % avec captage et compression. Elle conduit à une augmentation du coût de l'électricité de l'ordre de 30 à 70 % (en fonction du type de centrale) [24]. La principale cause de cette

pénalité énergétique est liée à la température requise lors de l'étape de régénération (100-140°C) qui est fournie par le rebouilleur [22]. Plusieurs études ont par ailleurs démontré une dégradation du solvant au cours du procédé, impliquant la formation de nombreux produits de dégradation [14,15]. Au cours des différents cycles d'absorption/régénération, les molécules aminées contenues dans le solvant de captage sont susceptibles de réagir avec l'oxygène, mais aussi avec les gaz acides résiduels (NOx et SOx) contenus dans les fumées à traiter (dégradation oxydante), entrainant la formation de produits de dégradation dont certains pouvant être toxiques pour l'Homme et l'environnement [14]. Une dégradation du solvant peut également être observée lors de l'étape de régénération (dégradation thermique), puisqu'elle est réalisée à température élevée (100-140°C) [25]. La nature et la résistance à la dégradation du solvant influent sur la température maximale atteignable pour la régénération et par conséquent sur les performances énergétiques du processus et son coût [26]. En outre, une baisse de la teneur en amine ainsi que la formation de produits de dégradation induit une consommation accrue de solvant par son renouvellement, ce qui induit un coût opératoire supplémentaire. Il s'avère par conséquent nécessaire de développer des solvants dits innovants permettant de limiter à la fois la pénalité énergétique et les impacts environnementaux liés aux phénomènes de dégradation.

3 Solvants pour le captage du CO_2 en post-combustion par absorption chimique

La pénalité énergétique du procédé de captage du CO_2 en post-combustion via l'utilisation d'amines dépend des conditions opératoires mises en œuvre (notamment de la température de l'étape de régénération) et de la dimension des équipements, eux même dépendants du solvant utilisé [10]. Plusieurs paramètres sont à prendre en compte pour le choix d'un solvant de captage du CO_2. Ces paramètres concernent ses propriétés thermodynamiques et énergétiques telles que la capacité d'absorption, la vitesse de réaction, la volatilité ou l'énergie requise pour l'étape de régénération, mais également son prix d'achat. Les autres aspects à prendre en compte sont la stabilité chimique et thermique du solvant, sa toxicité et sa résistance à la corrosion et à la précipitation [27].

Différents types de solvants ont été décrits dans la littérature pour le captage du CO_2 en post-combustion par absorption chimique. Les solvants aminés, utilisés depuis 1930 dans le cadre de la purification de gaz naturel (désacidification), bénéficient d'une grande expérience et sont aujourd'hui les plus connus dans le domaine. D'autres types de solvants dits innovants, comme les liquides ioniques ou les amino-silicones, ont été décrits dans la littérature et semblent prometteurs. Ces trois classes de solvants, candidats potentiels à la présente étude, seront présentées ci-dessous. D'autres types de solvants chimiques peuvent également être utilisés au cours du procédé de captage du CO_2, comme les

solutions ammoniacales ou les solvants démixants, mais n'ont pas été considérés dans le cas de notre étude. Ils seront néanmoins brièvement présentés dans le paragraphe 3.4.

3.1 Solvants aminés

Les solvants aqueux alkylaminés sont les plus couramment utilisés pour le captage du CO_2 en post-combustion par absorption chimique [16]. Différentes classes d'amines peuvent être utilisées : primaires, secondaires ou tertiaires. Dans le cas des amines primaires et secondaires non encombrées stériquement, le mécanisme d'absorption du CO_2 en présence d'eau implique la formation d'un carbamate stable et d'une base protonée (**Équation 1**). Sous haute température, l'hydrolyse lente du carbamate libère ensuite du bicarbonate. Dans le cas d'amines tertiaires ou d'amines encombrées stériquement, la réaction implique la formation de bicarbonate (**Équation 2**). Les amines tertiaires ou encombrées stériquement requièrent beaucoup moins d'énergie lors de la régénération de l'amine, en comparaison aux amines primaires ou secondaires, mais présentent néanmoins des taux d'absorption du CO_2 limités (**Tableau 1**)[28].

Équation 1 : Réaction d'absorption du CO_2 par des amines primaires et secondaires [28]

$$2\mathrm{R_1R_2NH} + CO_2 \longleftrightarrow R_1R_2NH_2^+ + R_1R_2NCOO^-$$

Équation 2 : Réaction globale d'absorption du CO_2 par des amines tertiaires [28]

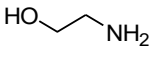
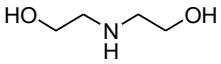
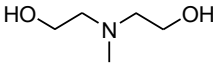
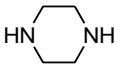
$$\mathrm{R_1R_2R_3N} + CO_2 + H_2O \longleftrightarrow R_1R_2R_3NH^+ + HCO_3^-$$

La monoéthanolamine (MEA), utilisée généralement à 30 % en masse dans l'eau, est la molécule de référence pour cette technologie [29–32]. La MEA est peu coûteuse (≈ 2,40 $/kg) comparativement à d'autres solvants utilisés pour le captage du CO_2 (e.g près de 2,4 fois moins chère que la méthyldiéthanolamine (MDEA) [18]), peu visqueuse, soluble dans l'eau et présente de bonnes propriétés thermodynamiques de captage vis-à-vis du CO_2 (capacité cyclique en CO_2 de 0,38 mol/kg [33] et chaleur d'absorption du CO_2 de l'ordre de -70 kJ/mol [34]). Les deux inconvénients majeurs à l'utilisation de MEA 30 % sont la pénalité énergétique engendrée (de l'ordre de 11 %-pts [13]) et sa dégradation au cours du procédé de captage du CO_2, conduisant à la formation de produits de dégradation potentiellement toxiques pour l'homme et l'environnement (e.g. les nitrosamines) [32].

D'autres amines ont été décrites dans la littérature, parmi lesquelles la diéthanolamine (DEA) [35], la MDEA [36,37], la 2-amino-2-methylpropan-1-ol (AMP) [38] et la pipérazine (PZ) [26,39,40]. Le **Tableau 1** donne une comparaison de quatre d'entre elles (représentatives de chacune des classes d'amines) en termes de capacité cyclique, de vitesse d'absorption, de chaleur de désorption, de dégradation, de température d'ébullition et de coûts. Comme il a été mentionné plus haut, les amines

tertiaires (e.g. la MDEA) sont caractérisées par une chaleur de désorption plus faible en comparaison à la MEA ou la DEA, ce qui est énergétiquement favorable pour l'étape de régénération. A l'inverse, les vitesses d'absorption de la MEA et de la DEA sont plus élevées que celle de la MDEA. La PZ, diamine cyclique, se caractérise par une capacité cyclique près de deux fois plus élevée [33,41] ainsi qu'une stabilité chimique dix fois plus élevée en comparaison à la MEA [26,42]. La vitesse d'absorption à 40°C du CO_2 de la PZ est par ailleurs plus de deux fois plus élevée que la MEA [40], mais la PZ se caractérise néanmoins par un coût plus élevé en comparaison à cette dernière [43].

Tableau 1 : Caractéristiques d'amines utilisées pour le captage du CO_2 en post-combustion

	Monoéthanolamine MEA 30 %	Diéthanolamine DEA 30 %	Méthyldiéthanolamine MDEA 30 %	Pipérazine PZ 30 %
Type d'amine	primaire	secondaire	tertiaire	cyclique
Structure				
Capacité cyclique (mol_{CO2}/kg_{amine})	0,38 [33]	0,56 [33]	0,74 [33]	0,79 [41]
Chaleur de désorption ($GJ.t_{CO2}^{-1}$)	1,9	1,5	1,1	Non calculé
Vitesse d'absorption à 40°C ($m^3.mol^{-1}.s^{-1}$)	10 – 15 [44]	2-6 [44]	0,1 - 0,2 [44]	51,8 à 25°C [45]
Prix €.t^{-1}	1400 [18]	1400 [18]	3200 [18]	Coûts industriels ND
Température d'ébullition (°C)	171	217	247	146
Taux de dégradation thermique à 140°C (% par semaine)	5,3 % [42]	8 % [42]	1,7 % [42]	0,35 % [26] (à 150°C)

Il a été démontré que l'utilisation de mélanges d'amines permettrait de mettre en avant les avantages individuels des amines utilisées, tout en limitant leurs inconvénients [46]. Les amines

primaires et secondaires telles que la MEA ou la DEA sont reconnues pour leur vitesse de réaction élevée mais sont limitées en termes de capacité de captage du CO_2 en comparaison aux amines tertiaires comme la MDEA (**Tableau 1**). D'un point de vu énergétique, les amines tertiaires comme la MDEA requièrent moins d'énergie pour l'étape de désorption par rapport aux amines primaires et secondaires [47]. Le développement de mélanges innovants d'amines semble donc prometteur, et permettrait d'abaisser les besoins énergétiques requis pour le procédé. Parmi les mélanges décrits dans la littérature, les mélanges à base de pipérazine et les mélanges à base d'alcanolamines seraient les plus encourageants [48–50].

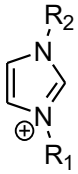
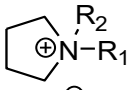
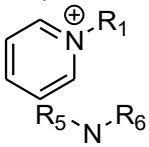
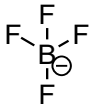
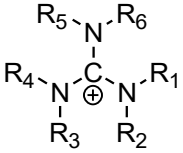
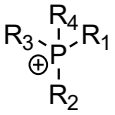
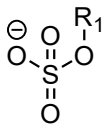
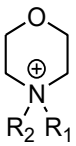
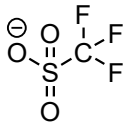
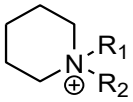
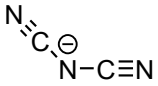
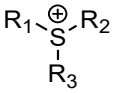
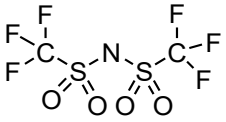
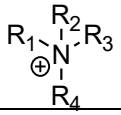
3.2 Liquides ioniques

Une alternative à l'utilisation d'amines potentiellement volatiles et sensibles à la dégradation est le développement de liquides ioniques. Les liquides ioniques sont des sels (composés d'un cation et d'un anion) dont la température de fusion est inférieure à 100°C. Ils présentent quelques avantages ; en effet, ils sont faiblement volatils, stables thermiquement, non inflammables, et offrent une solubilité élevée vis-à-vis du CO_2 [51,52]. Il existe différentes combinaisons possibles d'anions/cations constituant les liquides ioniques. Le **Tableau 2** donne quelques exemples de familles de cations et d'anions étudiés dans la littérature [51].

Une étude concernant les besoins énergétiques de ces solvants a été réalisée et a montré qu'une réduction de 24 % par rapport à la MEA 30 % pouvait être atteinte [53]. Un des inconvénients non négligeables des liquides ioniques est leur viscosité, pouvant aller jusqu'à 1000 mPa.s à 25°C contre 2,5 mPa.s dans le cas d'une solution de MEA à 30 % en masse dans l'eau [51]. La viscosité est impliquée dans le transfert de matière dans l'absorbeur et le régénérateur, ainsi que dans la vitesse apparente d'absorption du CO_2. C'est pour cela que les liquides ioniques sont fréquemment utilisés en mélange au sein de liquides ayant une faible viscosité (amines ou eau lorsque la miscibilité le permet). La composition la plus étudiée est le 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), souvent en mélange avec de l'eau et une amine comme la MEA [54] ou la MDEA [55], ou bien en mélange avec le glycinate de sodium [56]. ION Engineering a récemment étudié le comportement d'un solvant constitué de liquide ionique (composition exacte non communiquée) dans des conditions représentatives des conditions industrielles [57]. Après 72 heures d'essai, les résultats ont montré une efficacité de captage comprise entre 82 et 92 % et une réduction de l'énergie de désorption requise de l'ordre de 50 % en comparaison à la MEA. Une étude de la stabilité de liquides ioniques constitués d'imidazoliums et de *N*-methylethanolamine a par ailleurs été réalisée et comparée à la MEA, mais dans des conditions non industrielles [58]. Les résultats ont montré la formation de produits de dégradation, mais aucune information n'a été communiquée concernant les teneurs observées. Un autre

inconvénient à prendre en compte est le coût très élevé de ces solvants (1000 €/kg [51]), soit 700 fois plus élevé que la MEA. En raison de leurs coûts élevés et de leur manipulation expérimentale difficile, cette classe de solvants ne sera pas étudiée dans le cadre de cette thèse.

Tableau 2 : Anions et cations couramment utilisés pour la composition de liquides ioniques [51]

Cations		Anions	
Nom	Structure	Nom	Structure
Imidazolium		Hexafluorophosphate	
Pyrrolidinium		Chloride	Cl^-
Pyridinium		Tetrafluoroborate	
Ganidinium		Bromide	Br^-
Phosphonium		Alkylsulfate	
Morpholinium		Triflate	
Piperidinium		Dicyanamide	
Sulfonium		Bis(trifluoromethylsulfonyl)imide	
Ammonium			

3.3 Solvants amino-silicones

La troisième classe de solvants innovants pouvant être utilisée pour le captage du CO_2 en post-combustion est celle des amino-silicones. Les amino-silicones sont des oligomères synthétiques essentiellement étudiés par l'équipe de Robert J. Perry de chez GE Global Research [59–62]. Ces solvants ont de faibles pressions de vapeur, sont peu visqueux, peuvent avoir de fortes capacités de captage et peuvent être utilisés sans ajout d'eau. En comparaison à l'utilisation de MEA à 30 %, les amino-silicones permettraient une augmentation de 20 à 50 % de la capacité cyclique en CO_2 [59]. Le mécanisme de réaction d'une amino-silicone avec le CO_2 est à la fois chimique et physique, conduisant à la formation d'un carbamate (**Figure 2**) [62].

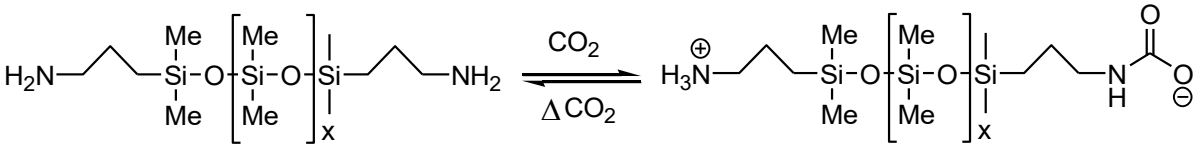


Figure 2 : Réaction entre une amino-silicone et le CO_2 [54]

Des études ont été réalisées sur différentes structures d'amino-silicones : fonctions amine primaires, secondaires, avec différents encombrements stériques et différentes longueurs de squelette principal [59,61]. Dans la majorité des cas, la formation du carbamate conduit à une forte augmentation de la viscosité du solvant, pouvant aller jusqu'à la précipitation, ce qui est limitant au niveau du procédé. Une des solutions proposées est le mélange de l'aminosilicone au triéthylène glycol (TEG), qui a la propriété de solubiliser à la fois le solvant initial mais également dans certains cas le carbamate généré. Les meilleures propriétés en termes de solubilité, viscosité et stabilité thermique ont été observées pour le mélange GAP1 (1,5-bis(3-aminopropyl)-1,1,3,3,5,5-hexamethyltrisiloxane) / TEG [62]. La dégradation thermique du mélange GAP1/TEG (60 :40) chargé en CO_2 a été étudiée au sein de réacteurs en acier inoxydable chauffés à des températures comprises entre 100°C et 175°C pendant des durées variables pouvant aller jusqu'à 60 jours [60]. Les résultats ont montré une baisse de la teneur en aminosilicone au cours du temps corrélée à une augmentation de la température du mélange. Cette baisse est d'autant plus importante que la température augmente, pouvant aller jusqu'à 80 % lorsque le solvant est chauffé à 140°C pendant 60 jours. Cette baisse a été réduite à 13 % en abaissant la température de désorption à 100°C et par l'ajout de 5 % d'eau au sein du solvant (simulant l'apport en humidité des fumées à traiter). Cette étude a par ailleurs permis l'identification d'un unique produit de dégradation dérivé de l'urée. Un des inconvénients des amino-silicones est leur coût de fabrication élevé (15 000 € pour 1 kg de solvant). A ce jour, les solvants amino-siliconés sont caractérisés par un faible niveau de développement, et très peu d'informations sont disponibles quant au comportement de ce type de solvants au sein de dispositifs similaires à celui qui sera utilisé dans la présente étude. Pour ces différentes raisons, les amino-silicones ne seront pas étudiées au cours du présent projet.

3.4 Autres solvants innovants

Parmi les solvants décrits dans la littérature pour le captage du CO_2 par absorption chimique on distingue également les solutions ammoniacales concentrées, les solvants démixants et les solutions de carbonate de potassium concentrées.

Les solutions ammoniacales concentrées sont constituées d'ammoniac et d'eau, et réagissent en présence de CO_2 pour former cinq espèces solides dont le bicarbonate d'ammonium [63]. Ces types de solvants requièrent moins d'énergie comparés aux procédés classiques utilisant des solvants aminés (près de 50 % de réduction par rapport à un procédé MEA), néanmoins, la plus grande volatilité de l'ammoniac par rapport à la MEA peut induire des pertes de ce composé lors de l'étape de régénération [8].

Les solvants à base de carbonate de potassium concentré utilisent les carbonates (CO_3^{2-}) avec formation de bicarbonates (HCO_3^-) sous forme solide. Des solvants de type K_2CO_3/PZ ont été développés et ont montré une vitesse d'absorption plus rapide de 10 à 30 % par rapport à l'utilisation de MEA [63].

L'utilisation de solvants démixants pour le captage du CO_2 est un concept breveté par l'IFPEN, impliquant un mélange de liquides susceptibles de se séparer en plusieurs fractions non-miscibles et de compositions différentes. Ce type de procédé permettrait une réduction de la consommation énergétique de près de 40 % en comparaison au procédé utilisant de la MEA 30 % [64].

Ces trois types de solvants sont prometteurs en termes de besoins énergétiques, mais nécessitent néanmoins du matériel adapté à leur étude prenant en compte les phénomènes de précipitation, de changement de phase ou de volatilisation. Dans le cas de ce projet de thèse, le matériel disponible ne permet pas leur étude.

Le choix de la composition d'un solvant pour le procédé de captage du CO_2 en post-combustion est complexe et relève du compromis. Dans le cadre de la présente étude, et en prenant en compte à la fois des critères de coûts, de performances énergétiques et de faisabilité expérimentale, des mélanges innovants constitués d'amines seront étudiés.

3.5 Solvants étudiés dans le cadre du projet

Comme nous l'avons décrit précédemment, les deux inconvénients majeurs à l'utilisation de la MEA 30 % au cours du procédé de captage du CO_2 sont d'une part la pénalité énergétique [12,13], et d'autre part la formation de produits de dégradation [14,15].

L'énergie requise par le procédé est étroitement liée aux propriétés du solvant. Le solvant optimal pour le procédé de captage du CO_2 en post-combustion doit avoir une forte capacité d'absorption du CO_2, une faible masse molaire par site actif, présenter de faibles chaleurs de

régénération, une vitesse de réaction élevée, une faible volatilité et viscosité, une stabilité chimique et thermique élevée, une bonne résistance à la corrosion, une faible toxicité pour limiter les impacts environnementaux, un faible coût, mais également une faible pénalité énergétique. Dans la présente étude, le choix des solvants a été réalisé en prenant en compte une partie de ces critères, notamment les capacités et cinétiques d'absorption, et l'énergie au rebouilleur par rapport à la MEA 30 %, énergie dépendant notamment du taux de charge du solvant, qui lui-même dépend de la teneur en amines et des proportions des différentes amines s'il s'agit d'un mélange. Le taux de charge correspond au rapport entre le nombre de moles de CO_2 capté et le nombre de moles d'amines. Deux types de taux de charges sont couramment décrits ; le taux de charge pauvre, correspondant à la fin de l'étape de régénération du CO_2, et le taux de charge riche, correspondant à la fin de l'étape d'absorption du CO_2. Plus le taux de charge pauvre est bas, plus l'énergie requise pour l'étape de régénération est élevée. Néanmoins, une augmentation du taux de charge pauvre dans l'objectif d'une réduction de cette énergie conduit à une diminution de la capacité cyclique du solvant, ce qui conduit à une augmentation du débit de solvant au sein du procédé en vue de maintenir une efficacité de captage de 90 %. Cette augmentation du débit de solvant conduit à une augmentation des besoins énergétiques. Il est par conséquent nécessaire de trouver une composition de solvant optimale prenant en compte ces différents paramètres.

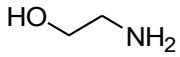
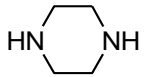
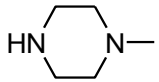
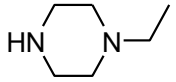
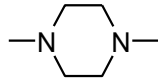
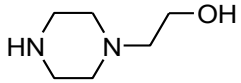
Comme nous l'avons précisé dans le paragraphe 3.1, il a été démontré que l'utilisation de mélanges d'amines permettrait de mettre en avant les avantages individuels des amines utilisées, tout en limitant leurs inconvénients [46]. Parmi les mélanges décrits dans la littérature, les mélanges à base de pipérazine et les mélanges à base d'alcanolamines seraient les plus encourageants [48–50].

Les mélanges à base de pipérazine (PZ) sont la première catégorie de mélanges prometteurs. Ces mélanges ont été étudiés dans le cadre d'une thèse en partenariat avec EDF R&D Chine et les résultats obtenus ont servi de fil conducteur à la présente étude [45]. La PZ est aujourd'hui considérée comme une des molécules les plus prometteuses puisque présentant de très bonnes cinétiques d'absorption (Tableau 1), mais aussi une bonne résistance à la dégradation [26,39,40]. La PZ est une diamine cyclique permettant de capter deux fois plus de CO_2 qu'une monoamine. De plus, à 135°C la PZ se dégrade près de dix fois moins rapidement que la MEA, et 20 fois moins rapidement que l'AMP [26,65]. D'autre part une résistance à la dégradation oxydante a été démontrée ; en présence de $Fe^{2+}/Cr^{3+}/Ni^{2+}$ et Fe^{2+}/V^{5+}, la PZ se dégrade quatre fois moins rapidement que la MEA [66]. Un des inconvénients majeurs de la PZ est sa propriété de cristalliser à température ambiante. Il est toutefois possible de s'affranchir de cette contrainte et d'utiliser la propriété activatrice de la PZ en l'associant avec d'autres amines comme la MDEA [67], la MEA [68], la *N*-(2-aminoethyl)pipérazine [69], la 2-methylpipérazine [70], ou l'AMP [71] limitant dans ces cas d'éventuels problèmes de cristallisation.

Le choix de la composition des deux premiers solvants de l'étude s'est fait en s'appuyant sur les résultats obtenus au cours de la thèse réalisée en Chine en partenariat avec EDF R&D Chine [45]. Dans le cadre de cette étude, huit amines ont été comparées pour leur propriétés thermodynamiques et cinétiques, et certaines d'entre elles ont été étudiées en mélange à la PZ [45,49]. Ces solvants ont été caractérisés en termes de capacité cyclique des amines, équilibre liquide-vapeur eau-amine et solubilité du CO_2 à différentes températures. Les propriétés thermodynamiques de ces solvants potentiels (taux de charges, capacité cyclique, chaleur d'absorption et énergies au rebouilleur) sont présentées dans le Tableau 3. L'analyse des propriétés de l'ensemble de ces amines a montré la pertinence de deux mélanges : le mélange 1-méthylpipérazine/pipérazine (1MPZ/PZ) et le mélange diméthyléthanolamine/pipérazine (DMEA/PZ). Grâces à ces données, un modèle thermodynamique, implanté sous Aspen Plus a été développé afin de simuler la courbe de performance des deux candidats i.e. la consommation de chaleur au rebouilleur en fonction du taux de charge pauvre ou du ratio liquide gaz (L/G). Aspen Plus est un logiciel de simulation pour la conception, le dimensionnement et l'optimisation des performances de masse et d'énergie de procédés pétrochimiques et énergétiques. Ce modèle a également permis de prédire la consommation énergétique des amines à différentes concentrations. Les résultats obtenus ont montré que les proportions optimales pour ces deux mélanges sont 1MPZ 30 % + PZ 10 % et DMEA 35 % + PZ 5 %.

Aucune étude n'a en revanche été réalisée concernant la stabilité chimique du mélange DMEA/PZ et quelques informations sont données dans la thèse de S. Freeman concernant le mélange 1MPZ 40 % / PZ 34 % où 4 produits de dégradation ont été identifiés sous dégradation à 150°C [72]. Dans les deux cas, aucune étude n'a été décrite concernant la stabilité chimique de ces solvants dans des conditions représentatives des conditions industrielles du procédé captage du CO_2 en post-combustion. De ce fait, dans le cadre de la thèse, nous avons choisi de travailler avec ces deux mélanges dans leurs proportions optimales calculées : 1MPZ/PZ (30/10) et DMEA/PZ (35/5).

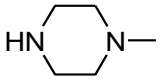
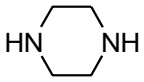
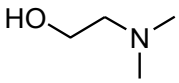
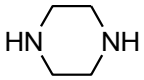
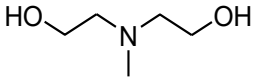
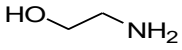
Tableau 3 : Caractéristiques thermodynamiques des amines comparées dans la thèse de Han Li (EDF R&D Chine)

Solvant	Abb	Structure	Teneur	Capacité cyclique (g/kg)	$-H_{abs}$ $kJ.mol^{-1}$	Energie au rebouilleur (MJ/kg)	Taux de charge pauvre (mol/mol)	Taux de charge riche (mol/mol)	Ref
Monoéthanolamine	MEA		30 %	45 ± 4,5	-92 ± 4,6	3,5 ± 0,53	0,31 ± 0,025	0,52 ± 0,041	[49]
Pipérazine	PZ		30 %	69 ± 6,9	-73 ± 3,7	3,5 ± 0,53	0,72 ± 0,057	0,90 ± 0,072	[49]
1-Méthylpipérazine	1MPZ		30 %	64 ± 6,4	-73 ± 3,7	2,6 ± 0,39	0,33 ± 0,026	0,82 ± 0,066	[49]
1-Ethylpipérazine	1-EPZ		30 %	44 ± 4,4	-77 ± 3,9	2,8 ± 0,42	0,44 ± 0,035	0,82 ± 0,066	[49]
1,4-Diméthylpipérazine	DMPZ		30 %	65 ± 6,5	-62 ± 3,1	1,9 ± 0,29	0,05 ± 0.004	0,61 ± 0,049	[49]
1-(2-Hydroxyéthyl)pipérazine	HEP		30 %	40 ± 4,0	-74 ± 3,7	2,8 ± 0,42	0,39 ± 0,031	0,78 ± 0,062	[49]
Triéthylènediamine	TEDA		28 %	59 ± 5,9	-51 ± 2,6	2,0 ± 0,3	0,16 ± 0,013	0,70 ± 0,056	[49]
Mélanges d'amines									
	1-MPZ+PZ		30/10	ND	ND	2.988	0,10	0,64	[50]
	DMPZ+PZ		20/10	50 ± 5,0	-70 ± 3,5	2,6 ± 0,39	0,35 ± 0,028	0,75 ± 0,060	[49]
	TEDA+PZ		20/10	51 ± 5,1	-76 ± 3,8	2,7 ± 0,41	0,43 ± 0,034	0,83 ± 0,066	[49]
	DMEA+PZ		35/5	ND	ND	2,9-3,5	0,20	0,40	[45]

En 2006, Idem et al. (2006) a comparé, dans des conditions industrielles de captage du CO_2, les performances énergétiques et la stabilité chimique de la MEA 30 % au mélange MEA/MDEA (≈ 25 % / 12 %) [48]. Les résultats obtenus ont montré qu'une baisse significative de l'énergie requise au procédé était obtenue quand le mélange MEA/MDEA était utilisé. Concernant la stabilité chimique du mélange, deux équipes ont étudié la dégradation de ce mélange au cours du temps [47,48]. La première étude a été réalisée en chauffant le mélange MDEA 40 % / MEA 5 % en présence de CO_2 à des températures comprises entre 120°C et 180°C, sans alternance entre les étapes d'absorption et de désorption [47]. Les résultats obtenus ont montré la formation de 14 produits de dégradation. Néanmoins, aucune conclusion concernant la stabilité du mélange ne peut être tirée, puisque les conditions de dégradation ne sont pas représentatives des conditions industrielles. La deuxième étude s'est penchée sur la dégradation du mélange MEA/MDEA (≈ 25 % / 12 %) dans des conditions industrielles (unité industrielle de captage de CO_2), en comparant l'influence du type de fumées à traiter (issues de la combustion du charbon ou du gaz naturel) sur la stabilité du solvant [48]. Les résultats ont montré qu'une dégradation du mélange a été observée dans le cas du traitement de fumées issues de la combustion du charbon et en présence d'un inhibiteur de la dégradation ajouté au solvant. En effet, une baisse plus importante de la teneur en amines du mélange MDEA/MEA (baisse de 2,3 mol%/jour pour la MEA et 1,5 mol%/jour pour la MDEA) a été observée en comparaison à la MEA seule (perte de 0,5 mol%/jour). Six produits de dégradation ont par ailleurs été identifiés, sans aucune information sur leur concentration au sein du solvant. Les résultats ont toutefois montré qu'aucune dégradation significative du mélange MDEA/MEA n'a été observée lorsque les fumées à traiter étaient issues de la combustion du gaz naturel, et en absence d'inhibiteur de la dégradation. Deux hypothèses ont été émises et concernent l'impact de la composition des fumées à traiter et l'effet potentiel de l'inhibiteur de la dégradation. Ces résultats sont intéressants en raison de la tendance à la diminution de la contribution du charbon au profit du gaz naturel, moins polluant, au niveau de la production d'électricité [73]. Au vu des bonnes performances énergétiques du solvant MDEA/MEA et du peu d'informations sur sa dégradation potentielle, ce mélange sera étudié dans le cadre de ce projet de thèse. Une modélisation thermodynamique implantée sous Aspen + a été développée par l'équipe d'EDF R&D Chatou afin de simuler la courbe de performance de ce mélange (chapitre 4). Ce modèle a permis de prédire la consommation énergétique des amines à différentes concentrations. Les résultats d'optimisation obtenus ont indiqué la pertinence du mélange MDEA 25 % et MEA 5 %.

Le Tableau 4 rappelle les trois mélanges qui seront étudiés au cours de ce projet de thèse et donne les caractéristiques physico chimiques principales des amines concernées comme leur température d'ébullition, pKa et masse molaire.

Tableau 4 : Mélanges sélectionnés dans le cadre de la thèse

		Proportions	Structure	M (g/mol)	pKa	Teb (°C)
1	1MPZ	30 %		100,16	pKa_1 = 9,14 ; pKa_2 = 4,63	138
	PZ	10 %		86,14	pKa_1 = 9,73 ; pKa_2 = 5,35	146
2	DMEA	35%		89,14	9,23	134
	PZ	5%		86,14	pKa_1 = 9,73 ; pKa_2 = 5,35	146
3	MDEA	25 %		119,16	8,52	243
	MEA	5 %		61,08	9,45	170

4 Méthodes de dégradation des solvants

Différentes méthodologies permettant l'étude de la dégradation de solvants dans le cadre du procédé de captage de CO_2 en post-combustion sont présentées dans la littérature. Ces méthodes se différencient par leur échelle (industrielle, laboratoire), ainsi que par le type de dégradation qu'elles étudient lorsque celle-ci est effectuée en laboratoire (oxydante, thermique ou les deux à la fois).

4.1 Unités de captage du CO_2 à échelle industrielle

Les unités de captage à échelle industrielle sont conçues à proximité de centrales électriques de manière à traiter des fumées réelles issues de la combustion du charbon ou du gaz. On distingue trois catégories d'unités de captage ; les unités commerciales, conçues pour capter du CO_2 destiné à une utilisation pour la récupération assistée de pétrole, les démonstrateurs et les pilotes, ces deux derniers ayant une visée de recherche avec pour objectif l'amélioration du procédé de captage. Les démonstrateurs sont caractérisés par une capacité de captage supérieure à 50 tonnes de CO_2 par jour, et les pilotes par une capacité de captage inférieure ou égale à 50 tonnes de CO_2 par jour [48]. Le **Tableau 5** donne une liste mondiale non exhaustive des unités industrielles de captage en post-combustion par absorption chimique.

A l'heure actuelle, seules deux unités commerciales de captage du CO_2 en post-combustion sont opérationnelles et en activité : l'unité SaskPower de Boundary Dam au Canada et l'unité NRG de Petra Nova au Texas (USA). L'unité de captage de Boundary Dam (**Figure 3**) permet le traitement de fumées issues de la combustion du charbon (1,4 x 10^4 m^3 de fumées traitées par jour) en utilisant un solvant propriétaire Cansolv à base d'amines dont la composition est confidentielle [74]. Il en est de même pour l'unité Petra Nova qui traite des fumées issues de la combustion du charbon et utilise un solvant aminé MH1-KS-1, dont la composition est confidentielle [75].

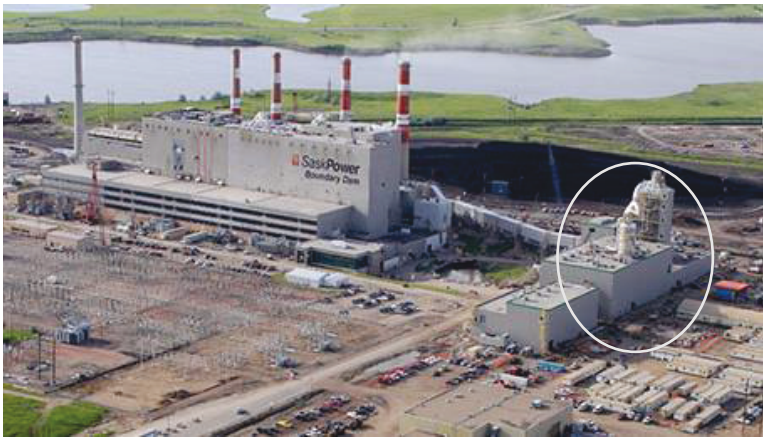


Figure 3 : Unité de captage de Boundary Dam (unité de captage entourée)

Le démonstrateur de captage du CO_2 en post-combustion le plus connu est le Centre Technologique de CO_2 de Mongstad (TCM) en Norvège. Le TCM a pour objectif l'amélioration du procédé de captage du CO_2 en post combustion afin de diminuer les pénalités énergétiques et financières, et ce, dans l'objectif d'accélérer le déploiement de la technologie à grande échelle [74,76]. Ce démonstrateur traite des fumées issues de la combustion du gaz, et a, jusqu'à aujourd'hui, expérimenté plusieurs solvants aminés comme la MEA [77], le solvant CRDMax propriétaire de Carbon Clean Solutions Ltd [78] ou encore d'autres solvants propriétaires e.g. ACC™ [79].

La dernière catégorie d'unités industrielles de captage de CO_2 est le pilote, dont la capacité de captage est inférieure à 50 tonnes de CO_2 par jour. Près de 40 pilotes ont été construits à ce jour, parmi lesquels le pilote du Havre en France construit par EDF et Alstom avec le soutien de l'ADEME [19]. Le pilote du Havre (**Figure 4**) a été implanté à proximité de la centrale à charbon EDF du Havre, et une technologie de captage développée par Alstom et DOW Chemical a été testée ainsi qu'une nouvelle formulation de solvant (solvant UCARSOL™ FGC-3000) propriétaire de DOW Chemical. Ce pilote a été conçu pour capter 25 tonnes de CO_2 par jour.

Figure 4 : Pilote de Captage du CO_2 en post-combustion du Havre

Ces unités de captage permettent l'étude des performances énergétiques de différents procédés, ainsi que la stabilité chimique de différents solvants dans des conditions caractéristiques des conditions industrielles. Dans l'objectif d'étudier à l'échelle du laboratoire le comportement physico-chimiques des solvants, des réacteurs permettant de simuler les étapes d'absorption et/ou de régénération du procédé ont été développés.

Tableau 5 : Unités commerciales, démonstrateurs et pilotes de captage du CO_2 en post-combustion [22,74,80,81]

Projet	Type de fumées	Industriel	Statut	Localisation	Solvant de captage	Taux de captage
Unités commerciales						
Boundary Dam	Charbon	SaskPower	En cours	Canada	Cansolv	4 t/jour
WA Parish Petra Nova	Charbon	NRG	En cours	USA	MH1-KS-1	3800 t/jour
China Resources Power Integrated carbon capture	-	-	A venir (2020)	Chine	-	-
Korea CCS-1	-	-	A venir (2020)	Corée du sud	-	-
Sinopec Shengli Power Plant	-	-	A venir (2020)	Chine	-	-
Caledonia Clean Energy	-	-	A venir (2024)	Royaume Uni	-	-
Démonstrateurs						
Technology Center Mongstad	Gaz	Statoil	En cours	Norvège	MEA, solvants propriétaires aminés	270 t/jour
Brindisi Power Plant	Charbon	IFPEN/EnEL	Fin du projet	Italie	Amines dont MEA	54 t/jour
Wilhelmshaven	Charbon	E.ON	Fin du projet	Allemagne	Fluor's Econamine FG Plus ^{SM}	3,5 ou 70 t/jour
Plant Barry	Charbon	Southern Energy/MHI, AL	Fin du projet	USA	KS-1 (amines)	500 t/jour
Ferrybridge Carbon Capture Pilot	Charbon		Fin du projet	Royaume-Uni	MEA et solvant RS-2^{TM}	100 t/jour
Boryeong	Charbon	KEPCO	Fin du projet	Corée du sud	Amines KEPCO	500 t/jour
Pilotes						
CESAR/CASTOR	Charbon	Dong Energy	Fin du projet	Danemark	30 % MEA, solvant confidentiels	24 t/jour
Separation Research Program	-	Université du Texas	En cours	USA	MEA & PZ + K_2CO_3	3 t/jour
CO2CRC	Charbon	International Power	En cours	Australie	BASF PuraTreat & nouveaux solvants confidentiels	50 t/jour
EnBW CHP Plant	Charbon	EnBW	Fin du projet	Allemagne	Amines (MEA)	7,2 t/jour
KoSol Process	Charbon		Fin du projet	Corée du Sud	KoSol.4	2 t/jour

Brindisi Capture Pilot Plant	Charbon	Enel	Fin du projet	Italie	MEA (20 % ; 30 % ; 40 %)	60 t/jour
Aberthaw Pilot Carbon Capture Facility	Charbon	Shell	Fin du projet	Royaume-Uni	Solvants Cansolv	50 t/jour
Pilote du Havre – C2A2 Field Pilot	Charbon	Alstom/EDF/ADEME/DOW	Fin du projet	France	Ucarsol^{TM} FGC 3000	25 t/jour
Karlshamn Field Pilot	Gaz	Alstom/E.ON Thermal Power	Fin du projet	Suède	Solution ammoniacale concentrée	60 t/jour
Pleasant prairie	Charbon	Alstom/EPRI	Fin du projet	USA	Solution ammoniacale concentrée	48 t/jour

4.2 Pilotes de captage du CO_2 à échelle laboratoire

Afin d'étudier la dégradation de solvants aminés utilisés, ou potentiellement utilisables, au cours du procédé de captage du CO_2 en post-combustion, de nombreuses équipes ont développé des méthodes de dégradation à l'échelle du laboratoire. Ces méthodes permettent d'étudier la stabilité du solvant sur des durées et conditions opératoires variables (températures, pression, débit et composition de gaz), tout en utilisant de faibles masses de solvant. La quasi-totalité de ces études considère de manière séparée les deux types de dégradations impliquées, dégradation oxydante (ayant lieu au cours de l'étape d'absorption) et thermique (ayant lieu au cours de la régénération), et utilisent des réacteurs batch (réacteurs fermés) ou semi-batch (réacteurs semi fermés).

Les études de dégradation oxydante impliquant l'utilisation de réacteurs semi-batch sont réalisées en introduisant des débits plus ou moins importants (de 100 mL/min à 7,5 L/min) de mélanges de gaz contenant du CO_2 et du dioxygène [14,30]. Certaines équipes [65,82] utilisent des mélanges de CO_2(2%)/O_2(98%) au sein de réacteurs à pression atmosphérique et chauffés à 55°C, qui est la température moyenne de l'étape d'absorption du CO_2. D'autres équipes [65,83] introduisent des mélanges composés de CO_2(2%)/O_2(15%)/N_2(83%) afin de se rapprocher de la composition des fumées industrielles à traiter. Les réacteurs batch, ont également été utilisés dans de nombreuses études de dégradation oxydante [29,30,84–86]. Ces types de réacteurs permettent d'avoir un contrôle précis des conditions expérimentales, notamment la pression. Afin d'étudier l'impact de SOx ou de NOx présents dans les fumées à traiter, certaines équipes introduisent au sein de leur gaz synthétique du SO_2 (jusqu'à 200 ppm) [84] ou du NO et NO_2 [87]. Des exemples de réacteurs décrits dans la littérature sont donnés en **Figure 5**. Ces dégradations à l'échelle du laboratoire permettent également d'étudier l'impact de métaux comme le Fer, le Chrome ou le Nickel sur la dégradation oxydante des amines. Dans ce cas, différentes quantités d'ions métalliques (Fe^{2+}, Cr^{3+} ou Ni^{2+}) sont ajoutées au sein du réacteur au moment des essais de dégradation [66].

Les études de dégradation thermiques sont le plus souvent réalisées au sein de réacteurs batch contenant le solvant, et chauffés à des températures allant de 100°C [37,65,72,88] à 200°C [37,89], bien que les températures les plus étudiées sont comprises entre 135°C et 140°C afin de se rapprocher des conditions de régénération [30,85,86].

a) b)

Figure 5 : Réacteurs semi-batch (a) et batch (b) décrits par Vevelstad [75]

L'ensemble des méthodes décrites permettent de simuler une dégradation oxydante ou thermique des solvants de manière rapide, simple à mettre en place et peu coûteuse. Néanmoins, aucune des études décrites à l'échelle laboratoire ne permet une alternance des étapes d'absorption et de régénération afin de prendre en compte à la fois les phénomènes de dégradation oxydante mais également de dégradation thermique, représentatives des conditions industrielles. A ce jour et à notre connaissance, un seul dispositif à l'échelle laboratoire a été conçu dans l'objectif d'étudier la dégradation de la MEA dans des conditions représentatives des conditions industrielles [90]. Ce dispositif, construit au sein du laboratoire LEMEDES-CO2, permet de traiter des fumées synthétiques au sein d'un réacteur contenant 1,5 L de solvant, en alternant entre des étapes d'absorption et de régénération. Au cours de notre projet, les études expérimentales de dégradation seront réalisées sur ce dispositif, et permettront de prendre en compte les deux principaux facteurs de dégradation : la composition des gaz à traiter et la température des différentes étapes. Une description plus détaillée de ce dispositif expérimental sera donnée dans le Chapitre 2.

5 Etat de l'art sur la dégradation des solvants du projet

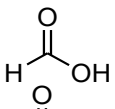
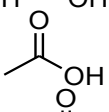
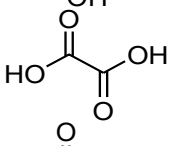
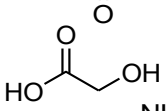
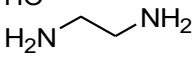
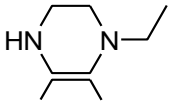
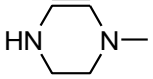
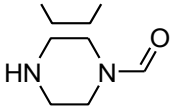
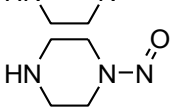
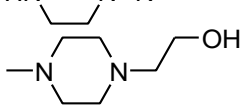
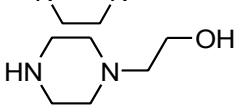
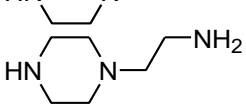
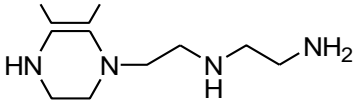
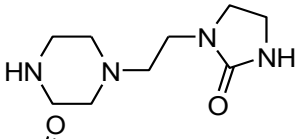
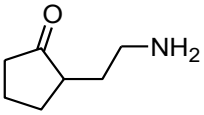
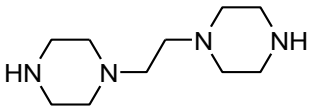
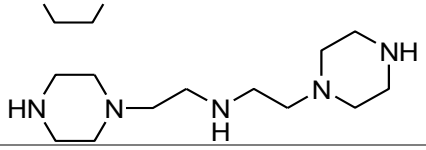
5.1 Etude de la dégradation des solvants 1MPZ/PZ et DMEA/PZ

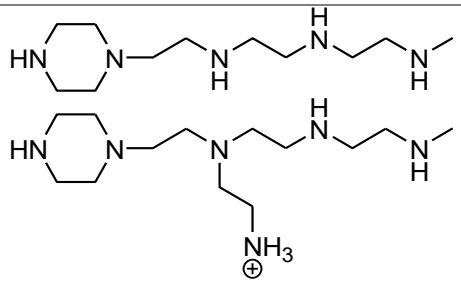
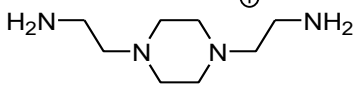
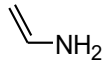
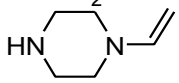
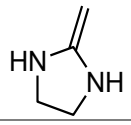
Dans le cadre de sa thèse, Stephanie Anne Freeman a étudié en détail les dégradations thermique et oxydante de la pipérazine au cours desquelles près de 20 produits de dégradation ont pu être identifiés (Tableau 6) [72]. Parmi ces composés, ont été répertoriés des acides organiques, une amine aliphatique et des dérivés de la pipérazine. Une sous partie de sa thèse décrit brièvement et de manière non détaillée la dégradation à 150°C du mélange 1MPZ 40% / PZ 34 %. Quatre produits de dégradation ont pu être identifiés : l'acide formique, l'éthylènediamine, la formylamide et la 1,4-diméthylpipérazine, composés déjà identifiés dans le cadre de la dégradation de la PZ. Il semblerait néanmoins que les analyses effectuées sur ce mélange ne soient pas aussi approfondies que dans le cas de l'étude de la PZ où différentes méthodes analytiques complémentaires (impliquant à la fois les chromatographies liquide et gazeuse) ont été développées. Les conditions de dégradation mises en œuvre ne sont par ailleurs pas représentatives des conditions industrielles et plus de la moitié des échantillons de solvant dégradé (correspondant aux deux derniers tiers de la durée de dégradation) a été perdue et non présentée dans son travail. En ce qui concerne le mélange DMEA/PZ, aucune étude de dégradation n'a été réalisée à notre connaissance.

Au vu du peu d'informations disponibles sur ces deux mélanges, les études réalisées par Stephanie Freeman concernant la PZ seront dans le cadre de ce projet utilisées à titre comparatif [65,66,72,91,92]. Il est en effet très probable que certains des produits déjà identifiés dans la littérature soient également identifiés dans la présente étude.

Pour certains des composés identifiés, des schémas réactionnels ont été proposés [72,91,93], et seront utilisés pour notre étude afin de suggérer des mécanismes pouvant expliquer la formation des composés observés. Parmi les schémas réactionnels proposés dans ces études sont décrits des oxydations de la PZ par voie radicalaire, et des réactions d'additions d'acides organiques sur la PZ [91,93].

Tableau 6 : Produits de dégradation de la pipérazine

Composés	Structure	Type de dégradation impliquée	Réf.
Ammoniac	NH_3	Oxydante & Thermique	[72]
Acide formique		Oxydante & Thermique	[72]
Acide acétique		Oxydante & Thermique	[72]
Acide oxalique		Oxydante & Thermique	[72]
Acide glycolique		Oxydante & Thermique	[72]
Ethylènediamine		Oxydante & Thermique	[72]
1-Ethylpipérazine		Thermique	[72]
1-Méthylpipérazine		Thermique	[72]
N-Formylpipérazine		Oxydante & Thermique	[72]
1-Nitrosopipérazine		Oxydante	[94]
N-(2-hydroxyéthyl)-N'-méthylpipérazine		Thermique	[72]
N-(2-hydroxyethyl)pipérazine		Thermique	[72]
N-(2-aminoéthyl)pipérazine		Thermique	[72]
1-[2-[(2-aminoéthyl)amino]ethyl]pipérazine		Thermique	[91]
1-[2-(piperazinyl)ethyl]2-imidazolidinone		Thermique	[91]
1-(2-aminoéthyl)imidazolidone		Thermique	[91]
1,1'-(1,2-ethanediyl)bis-pipérazine		Thermique	[91]
N,N'-(2-aminoéthyl)pipérazine		Thermique	[72]

PZ dérivés hexamines		Thermique	[72]
N,N-di(2- aminoethyl)pipérazine		Thermique	[72]
Ethenamine		Thermique	[72]
Vinylpipérazine		Thermique	[72]
Imidazolidin-2-one		Thermique	[72]

5.2 Etude de la dégradation du solvant MDEA/MEA

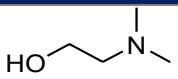
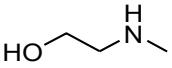
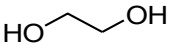
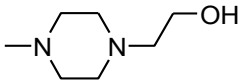
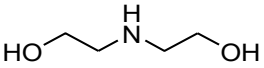
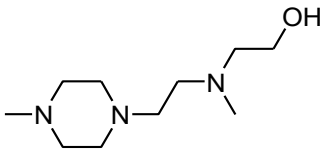
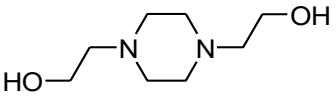
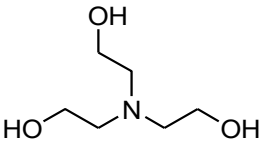
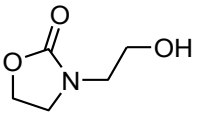
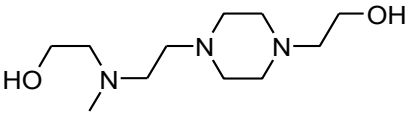
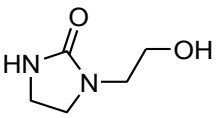
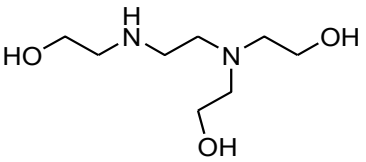
A notre connaissance, seules deux études ont été réalisées concernant la dégradation du solvant MDEA/MEA [47,48]. En 1996, Dawodu et al. [47] a étudié la dégradation thermique du mélange MDEA 40 % / MEA 5 % à des températures comprises entre 120 et 180°C et a identifié 14 produits de dégradation. Ces produits sont listés dans le Tableau 7.

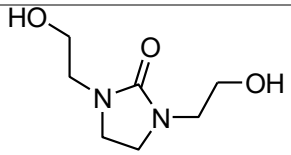
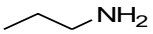
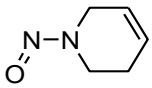
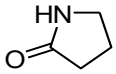
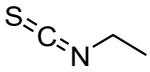
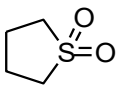
Parmi eux, 11 ont déjà été identifiés comme produits de dégradation de la MDEA (les composés 1,2,3,4,5,6,7,9,10,11,13) et 4 comme produits de dégradation de la MEA (les composés 2,5,12,14) [15,32]. Néanmoins, les conditions mises en œuvre pour cette dégradation ne sont pas représentatives des conditions industrielles, puisqu'il n'y a pas d'alternance entre les conditions typiques de l'étape d'absorption (40°C et présence de CO_2) et de régénération (120°C). La deuxième étude effectuée sur le mélange (MEA 15 % / MDEA 12 %), a en revanche été réalisée dans des conditions industrielles en comparant le traitement de fumées issues de la combustion du charbon et du gaz naturel [48]. Comme il a été décrit dans le paragraphe 3.5, 6 produits de dégradation ont été identifiés lorsque les essais ont été réalisés avec des fumées issues de la combustion du charbon (Tableau 7). Aucune information n'a néanmoins été donnée sur les concentrations de ces composés, ni sur la composition des fumées traitées issues du procédé. Dans le cas du traitement de fumées issues de la combustion du gaz naturel, cette dégradation s'est avérée être non significative avec la détection de 4 produits de dégradation, dont deux présents à l'état de trace.

Dans le cadre de la présente étude, des schémas réactionnels seront proposés dans l'objectif d'expliquer la formation des potentiels produits de dégradation formés. De nombreux schémas

réactionnels ont déjà été décrits concernant la dégradation de la MDEA et MEA seules dans l'eau, e.g. déalkylations, additions ou mécanismes radicalaires, et ont fait l'objet d'une revue [15]. De ce fait, pour les composés déjà identifiés dans la littérature, les mécanismes réactionnels décrits seront utilisés comme base de travail.

Tableau 7 : Composés issus de la dégradation du mélange MDEA/MEA

	Composé	Structure	Ref
1	Diméthylaminoéthanol		[47]
2	Méthylaminoéthanol		[47]
3	Ethylène glycol		[47,48]
4	N-(2-hydroxyethyl)-N'-methylpiperazine		[47]
5	Diéthanolamine		[47]
6	N-[2-(2-hydroxyethylmethylamino)ethyl]-N'-methylpiperazine		[47]
7	N,N'-bis(2-hydroxyethyl)piperazine		[47]
8	Hydroxyethyl-methyl-imidazolidinone		[47]
9	Triéthanolamine		[47]
10	N-(2-hydroxyethyl)oxazolidin-2-one		[47]
11	N-[2-2-hydroxyethylethylmethylamino)ethyl]-N'-(2-hydroxyethyl)piperazine		[47]
12	N-(2-hydroxyethyl)imidazolidin-2-one		[47]
13	N,N,N'-tris(2-hydroxyethyl)ethylenediamine		[47]

14	N,N'-bis-(2-hydroxyethyl)imidazolidin-2-one		[47]
15	1-propanamine		[48]
16	1,2,3,6-tetrahydro-1-nitrosopyridine		[48]
17	2-pyrrolidinone		[48]
18	Isothiocyanatoethane		[48]
19	1,1-dioxide-tetrahydrothiophene		[48]

Partie 2 : Méthodes analytiques permettant la caractérisation de la dégradation des solvants

Cette partie se présente sous la forme d'une revue, et a pour objectif de présenter les différentes stratégies analytiques décrites dans la littérature permettant la caractérisation de la dégradation des solvants aminés utilisés au cours du procédé de captage du CO_2 en post-combustion.

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Analytical methods for the monitoring of post-combustion CO_2 capture process using amine solvents: A review

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ABSTRACT

Post-combustion CO_2 capture is considered to be the most promising technology to limit the CO_2 emissions from existing fossil fuel power plants. One of the main problems associated with the CO_2 capture process is the degradation of amine solvents, which can negatively impact both human health and the environment. Degradation products are formed in the liquid phase of the solvent, but can also be emitted with the gaseous effluents, increasing the need for monitoring strategies. The present review proposes a critical analysis of the literature concerning the analytical strategies developed in the field of post-combustion capture to identify and quantify the main classes of degradation products formed; specifically amines, amides, aldehydes, nitrosamines and organic acids. Regarding the liquid phase, the principal analytical methods involved are Liquid Chromatography (LC) and Gas Chromatography (GC) for the analysis of amines and Ionic Chromatography (IC) for the analysis of organic and inorganic acids. Concerning aldehydes, the most described method is derivatization of the compounds with 2,4-dinitrophenylhydrazine prior to LC analysis. In order to monitor the gaseous effluents, four methods have been described: FTIR, implementation of impingers, online MS analysis and sampling on solid sorbents.

1 Introduction

In 2015, the average concentration of CO_2 was 40% higher compared to the pre-industrial period, with an average increase of 2 parts per million (ppm)/year in the last ten years [3]. Twenty-five percent of these emissions originated from electricity and energy production associated with the combustion of fossil fuels [95]. To mitigate future climate change due to CO_2 emissions, the International Energy Agency (IEA) proposes CO_2 capture as one of the key technologies to be developed and utilized [96]. In the power production sector, three technologies of CO_2 capture can mitigate this increase: post-combustion CO_2 capture, pre-combustion CO_2 capture and oxy-fuel combustion [9]. Currently, post-combustion CO_2 capture by amines-based chemical absorption is the most mature technology to reduce CO_2 emissions [16,41,97]. The process is based on the reversible absorption of CO_2 at low temperature (40-70°C) and atmospheric pressure by the amine through the formation of a carbamate when using primary and secondary amines (Figure 6). In the case of sterically hindered amines (e.g. 2-amino-2-methylpropan-1-ol, AMP) or tertiary amines (e.g. *N*-methyldiethanolamine, MDEA), the reaction with CO_2 will lead to the formation of the protonated amine and the bicarbonate ion [98,99]. The amine is then regenerated at high temperature (100-150°C) and pressure (between 1 and 5 bars) to emit pure CO_2 expected for storage [16,25].

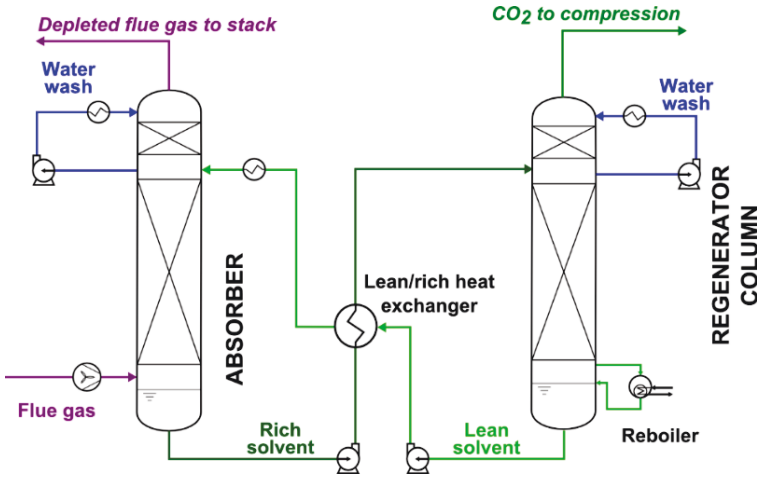

Figure 6: Conventional scheme of the CO_2 capture process

Post-combustion CO_2 capture process using amines has been extensively studied due to its possible application on existing CO_2 sources and can recover up to 99% of CO_2 present. The main drawbacks of the capture process are the high energy penalty (around 20% of the power plant efficiency) and the irreversible degradation of the amine [5,15] which is responsible of around 10% of the total CO_2 capture cost [10]. In addition to reacting with CO_2 and O_2, amines also react with NOx and

SOx which are likely to be present in the flue gas. Indeed, even after gas purification (particulate removal, denitrification and desulfurization), NOx and SOx can still be present in the ppm range [20]. The high temperature used during the regeneration step is also involved in the thermal degradation of the solvent [14,25]. The benchmark amine of the process is monoethanolamine (MEA). MEA has many advantages including high water solubility, low viscosity, low cost, and high CO_2 cyclic capacity. However, MEA's degradation is not negligible and results in the formation of several toxic degradation products such as nitrosamines [32]. Those degradation products (present at trace level), are formed in the liquid phase of the solvent and can be emitted with the treated flue gas [100]. The degradation of MEA has been studied by many researchers and industries [30–32,101–105] and permitted the identification of numerous degradation compounds. Reactional mechanisms have been proposed to explain their formation during the CO_2-capture process [15]. With the aim to find a performant and resistant solvent, other amines have also been studied e.g. diethanolamine (DEA) [106,107], methyldiethanolamine (MDEA) [108], 2-amino-2-methylpropan-1-ol (AMP) [85] or piperazine (PZ) [72]. PZ seemed to be resistant to both oxidative and thermal degradation and was frequently blended with other amines to limit crystallization and improve energy performance [49,67,109]. However, PZ can also degrade resulting in the formation of nitrosamines, a class of carcinogenic compounds [94,110,111].

Various methods have been utilized to mimic amine solvent degradation. The most representative method is the cycling of solvents in demonstration pilot plants which enable both thermal and oxidative degradation [112–117]. The treatment of real flue gas derived from coal power plants containing traces of NOx, SOx but also fly ash, leads to representative degradation conditions. Most of the studies performed thus far have been lab-scale, and consider oxidative [107,118–120] or the thermal degradation [72,88,89] of amines or amine blends separately. Thermal degradation is frequently conducted in stainless steel cylinders heated to high temperature [88,92] while oxidative degradation is conducted within reactors supplied with CO_2 and O_2 [120]. These studies are of high interest to the understanding of each factor on the degradation, however, some degradation products due to both factors may be missing. Recently, a lab-scale CO_2 capture pilot plant named LEMEDES-CO2 [90] has been developed to study the combined effect of both factors and is to our knowledge the only lab-scale pilot plant that is able to investigate oxidative and thermal degradations.

Characterization of the amine solvent degradation is essential to improve the energetic performance of the process, the process operation, the solvents formulation and safety assessment. This is the case even for advanced solvents where degradation is not as problematic as in the case of pure MEA [78]. Indeed, even if results showed low degradation, it is still necessary to use accurate methods to confirm the results. Currently, there is no general agreement or validated methods can be used to assess the good efficiency of the process. The aim of this review is to perform a critical survey

of the analytical methods described in the literature for the determination and characterization of degradation products formed during post combustion CO_2 capture (PCCC) using amine solvents. The main solvents considered in this study are MEA and PZ. The present review is divided in two sections: first we present the analytical methods used for the characterization of the liquid phase of the solvent for each class of degradation compounds (amines, acids, aldehydes, amides, nitrosamines), then we describe the current methods used for monitoring gaseous effluents i.e. the treated flue gas.

2 Analysis of degradation products in the liquid phase of the solvent

Analysis of degradation products present at trace level in the solvent is challenging due to the high amine content, usually of 5M for MEA (30% wt.) and between 5 and 8 M for PZ (30-40% wt.). Degradation products can be classified in five major chemical classes: amines derivatives (alkylamines, alkanolamines, cyclic amines), acids (organic and inorganic), aldehydes, amides and nitrosamines.

2.1 Analysis of amine derivatives

Analysis of low-molecular weight amines is difficult because of their physicochemical properties, i.e., high volatility and polarity, viscosity, and basic character. Most of the studies regarding amine analysis referred to water matrix, and their application on amine solvents for Post-Combustion CO_2 Capture (PCCC) is difficult.

2.1.1 Monitoring of the starting amines

The main focus of studies involving amine solvent degradation for post combustion CO_2 capture is the monitoring of the stability of the major amine (i.e. MEA, AMP, MDEA, PZ). Knowing the amount of amine over time is essential to anticipate any addition of fresh amine and to conclude about the solvent's overall resistance. The quantification of the solvent has to be fast, simple and accurate. Two strategies have been described for the monitoring of the main amine concentration: total alkalinity measurement and chromatographic analysis. Total alkalinity measurements are based on pH titrations performed with an acidic solution to reach the equivalence point [39,40,66,72,101,120–122]. This method is very easy to use, fast, low cost and can be implemented directly on site. Chromatographic strategies have also been developed to quantify the constituent amine of the solvent. The high amine content in the solvent makes a direct analysis difficult regardless of the chosen chromatographic method. A dilution of the solvent is therefore needed before any quantitative analysis. The dilution factors are in the range 25 [123] to 10000 [30] and in the latter case prevent the analytical column or the detector from damages. Both Gas Chromatography (GC) [32,124] and Liquid Chromatography (LC)

[30,120] were used for the quantitative analysis. Nearly two thirds of published work use Ionic Chromatography with suppressed conductivity [82,92,122,125,126] for the quantification of starting amines. Ionic chromatography associated with suppressed conductivity is one of the cheaper chromatographic methods and involves minimal maintenance compared to other methods e.g. LC/MS. The chosen column in these studies was Ion Pac CS17 (carboxylate-functionalized) analytical column with an Ion Pac CG17 guard column with a methanesulfonic acid (MSA) eluent delivered in gradient mode. The validation step is essential in order to assess the reliability of the method. To the best of our knowledge, only two studies performed validation of quantitative methods for amine monitoring [127,128]. In the study of Fytianos et al. (2015), an Ion Pac CS19 (carboxylate-functionalized) analytical column associated with a CG19 guard column were used, and different methods were compared in terms of elution mode (gradient or isocratic). The isocratic mode was preferred because of a shorter analysis time. However, a gradient separation may be needed in the case of a complex matrix, or unresolved peaks. To our knowledge, only one study gave precisions regarding the accuracy of the method [127]: an accuracy close to 100% was obtained for MEA. No information was provided about accuracies in other studies, even if these information are essential in order to assess the reliability of the analytical method and the obtained results. Very poor information is also given about any replicate sample analysis.

The two described methods, specifically total alkalinity measurements and chromatography, are complementary as they provide similar results without the same precision. Alkalinity measurement is a first approach to rapidly evaluate the stability of the total amine concentration whereas chromatography enables the direct quantification of the individual amine(s) within the solvent.

2.1.2 Identification and quantification of amine degradation products

The second aim of these studies was the identification of degradation compounds along with their amine derivatives. Table 8 gives a non-exhaustive list of the main amine degradation products associated with the sample treatment and the analytical method used (a more exhaustive list can be found in Annexe 1). In this case, unknown compounds are present at trace level in a concentrated amine matrix making their identification difficult. Therefore, dilution prior to analysis has to be as low as possible, and is in the range of 10 [32] to 10000 [129], to avoid damage of the separation column or saturation of the detector. Two analytical methods were used for the characterization of the degradation products: gas chromatography (GC) [32,93,107] and liquid chromatography [32,120] (LC) including ionic chromatography [72,83,93,130] (IC). These different methods were used equally and permitted to identify and quantify the degradation products formed. GC was often used in association with mass spectrometry (MS) or Flame Ionization Detector (FID). Different capillary columns were used

for the separation i.e. CP-SIL-8CB (base deactivated 5% phenyl polydimethylsiloxane) [30,32,86,90,107], Carbowax amines (base modified poly(ethylene glycol) [32,107] or DB-5MS ((5%-phenyl)-methylpolysiloxane) [93]. Separation was always performed with temperature gradient with an analysis time between 25 min [90] and 37 min [93]. An example of a chromatogram obtained after the analysis of degraded MEA samples is provided in **Figure 7** [30], where 11 degradation products were identified. Regarding quantitative analysis, no information was available about the accuracy of the methods, the LOD and LOQ, or about any matrix effects on the method response. In the field of water analysis, other methods including sample preparation steps such as preconcentration followed by derivatization or solid phase microextraction (SPME) associated with GC-MS analysis were proposed [131–133]. However, the complex composition of samples makes derivatization difficult [134].

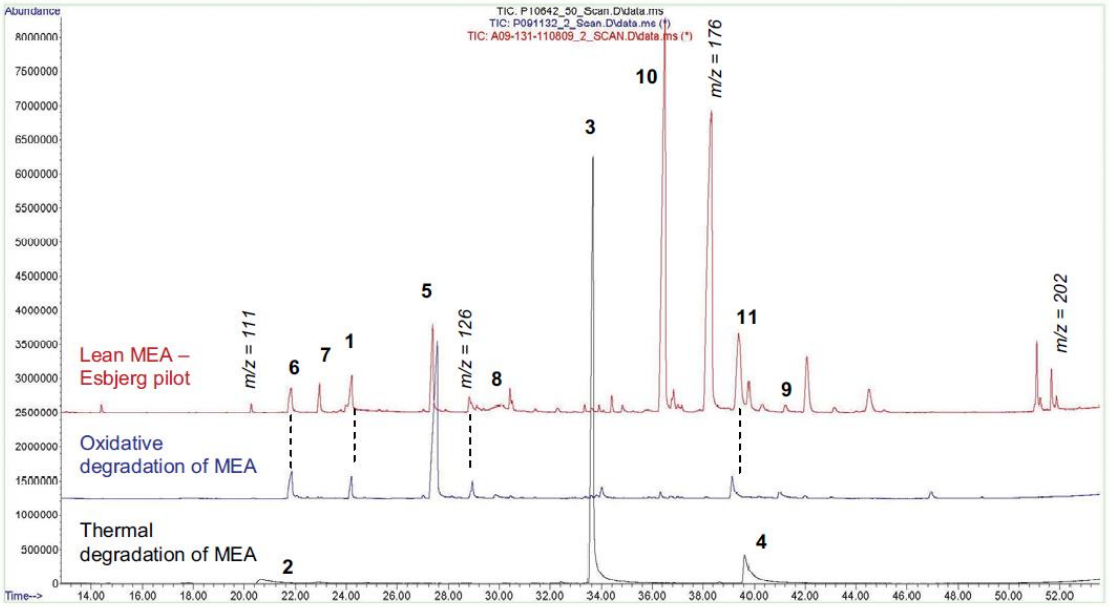

Figure 7 : Example of chromatogram obtained after the GC-MS analysis (CP-SIL-8 CB Amines column) of degraded MEA solutions from two lab-experiments in comparison to a lean MEA solution obtained from the Esbjerg plant. Reprinted with permission from (Lepaumier et al., 2011). 1: 2-oxazolidinone (OZD); 2: N-(2-hydroxyethyl)ethylenediamine (HEEDA); 3: N-(2-hydroxyethyl)imidazolidinone (HEIA); 4: N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidinone (AEHEIA); 5: N-(2-hydroxyethyl)imidazole (HEI); 6: N-(2-hydroxyethyl)formamide (HEF); 7: N-(2-hydroxyethyl)acetamide (HEA); 8: 2-hydroxy-N-(2-hydroxyethyl)acetamide (HHEA); 9: N,N'-bis(2-hydroxyethyl)oxalamide (BHEOX); 10: 4-(2-hydroxyethyl)piperazin-2-one (HEPO); 11: N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA).

LC-MS, mainly LC-MS/MS, was also used for both qualitative and quantitative analysis of degradation products. In addition, two studies also reported the use of High Resolution Mass Spectrometry (Time Of Flight) for the analysis of amines derivatives [103,135]. Tandem mass spectrometry or High-Resolution Mass Spectrometry are very specialized methods that provide accurate results. However, these devices are costly and more sensitive to contaminations in the CO_2

capture solvents samples. Moreover, their infrequent presence on site puts forward the question about the stability and the preservation of the samples. Only one study has reported the validation of a quantitative method for 5 degradation products, specifically, diethanolamine (DEA), N,N'-bis-(2-hydroxyethyl) urea (BHE Urea), Bicine, N-(2-hydroxyethyl)glycine and N-glycylglycine with the use of two deuterated internal standards [136]. IC associated with conductimetric detection also allows to identify and quantify degradation products. This method is cheaper than LC-MS/MS and requires less maintenance. In most of the studies [39,91,92,122,125,126,130] an IonPac CS17 associated with an IonPac CG17 was used for the separation and MSA was used as eluent. Figure 8 gives an example of a chromatogram obtained after the analysis of a thermally degraded PZ sample [72], where 4 degradation products were identified. Quantitative analysis has been described for many compounds e.g. *N*-(2-hydroxyethyl)ethylenediamine (HEEDA), PZ, *N*-formylpiperazine (FPZ), ethylenediamine (EDA), *N*-(2-hydroxyethyl)piperazine (HEPZ), 1-ethylpiperazine (EPZ), 1-(2-aminoethyl)piperazine (AEP), 1-[2-[(2-aminoethyl)amino]ethyl]piperazine (AEAEPZ) and ammonia. More recently, Fytianos et al., (2015) described the use of a IonPac CS19 column, and validated a IC quantitative method for 14 compounds, namely MEA, MDEA, *N*-methyl-1,3-diaminopropane (MAPA), DEA, AMP, diethylenetriamine (DETA), 2-(diethylamino)ethanol (DEEA), bis(2-hydroxypropyl)amine (DIPA), PZ, 1,3-diaminopropane (1,3-DAP), 2-dimethylaminoethanol (DMMEA), *N*-tert-butyldiethanolamine (N-TBDA), 2-(Methylamino)ethanol (MMEA) and HEEDA. An ion pair-based – HPLC method was also developed to separate 6 amines with a C18 based Hypersil gold aq column [137].

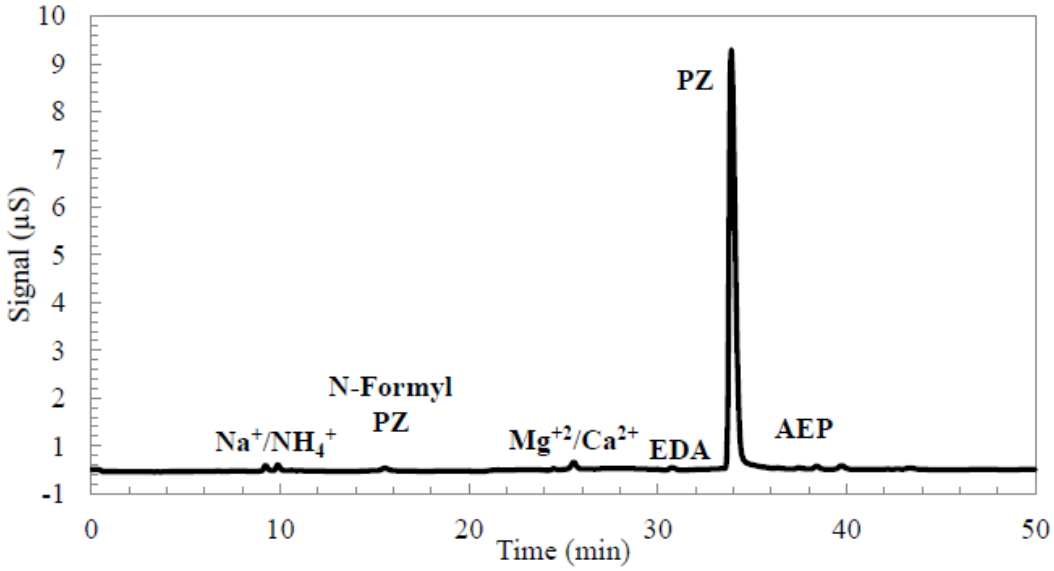

Figure 8: Example of chromatogram obtained after the analyses of a thermally degraded PZ sample. Reprinted with permission from (Freeman, 2011).

Regarding the different detectors used, mass spectrometry associated with GC enables the comparison of experimental mass spectra against a spectra database, leading to putative compound identification. These putative compound identifications were often confirmed by the analysis of commercial standards [82,93,130]. The use of other types of detection like FID or conductimetric detection makes the identification more difficult as compounds have to be proposed for unidentified peaks, and confirmed according to comparison of retention times with those of commercial standards. Either way, confirmation with purchased corresponding commercial standards or the fall due synthesized compounds is a necessary task, and should be specified in the published studies [82,138].

Table 8: Analytical methods used for the analysis of amine and degradation products in CO_2 capture solvents

Compounds	Solvent composition	Sample treatment	Dilution matrix	Dilution factor	Method	References
1H-pyrrole	MEA	HS-SPME	-	-	GC-MS	[32]
1-(2-hydroxyethyl)piperazin-2-one	MEA	dilution	methanol	10	GC-MS	[32]
1,4-dimethylpiperazine	MEA	dilution	methanol	10	GC-MS	[32]
	MEA	-	-	-	GC-MS	[107]
	PZ	dilution	-	-	IC	[125]
1-methylpiperazine	PZ	dilution	-	-	IC	[39,125]
2-oxopiperazine	PZ & AMP/PZ	-	-	-	GC-MS	[93]
2,5-piperazinedione	PZ & AMP/PZ	-	-	-	GC-MS	[93]
2-(dimethylamino)ethanol	MEA	dilution	water	100	LC-MS/MS	[139]
2-amino-2-methylpropan-1-ol (AMP)	AMP	-	-	-	GC-MS	[107]
	PZ blend	dilution	water	2000 to 10000	IC	[130]
2-methylpiperazine	MEA	dilution	methanol	10	GC-MS	[32]
	PZ	dilution	-	-	IC	[39]
2-oxazolidinone	MEA	HS-SPME	-	-	GC-MS	[32]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	10000	LC-MS/MS	[129,139,140]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	water	10 to 100	GC-MS	[30]
	MEA	dilution	methanol	10	GC-MS	[90]
4-(2-hydoxyethyl)piperazin-2-one	MEA	dilution	water	10000	LC-MS/MS	[129,140]
	MEA	dilution	water	2	GC-FID	[141]

	MEA	dilution	methanol	10	GC-MS	[32,90]
ammonium	MEA	-	-	-	IC	[83,126]
	MEA	dilution	water	100	LC-MS/MS	[140]
bicine	MEA	dilution	water	1000	LC-MS/MS	[32]
	MEA	-	-	-	NMR	[124]
Diethanolamine (DEA)	MEA	dilution	water	1000	LC-MS/MS	[32]
	MEA	-	-	-	LC-MS	[87]
	MEA	dilution	water	100	LC-MS/MS	[129]
	MEA	-	-	-	NMR	[124]
	DEA	-	-	-	GC-MS	[107]
ethylenediamine	PZ	dilution	-	-	IC	[72]
	PZ	dilution	water	1000	IC	[122]
	PZ; AMP/PZ	-	-	-	GC-MS	[93]
	PZ; AMP/PZ	dilution	ethanol	100 to 150	GC-MS	[142]
glycine	MEA	dilution	water	1000	LC-MS/MS	[32]
hexamethyleneimine	PZ	dilution	-	-	IC	[72]
homopiperazine	PZ	dilution	-	-	IC	[72]
Methyldiethanolamine (MDEA)	PZ blend	dilution	water	2000 to 10000	IC	[130]
monoethanolamine	MEA	-	-	-	GC-FID	[32]
	MEA	-	-	-	GC-MS	[107]
	MEA/PZ	-	-	-	GC-MS	[143]
	MEA	dilution	water	10000	LC-MS/MS	[30]

	MEA	dilution	-	1000000	LC-MS/MS	[144]
	MEA	dilution	water	10000	LC-MS/MS	[139,140]
	MEA	dilution in 0.1% ammonium hydroxide			GC-FID	[31,124]
	MEA	dilution	water	-	IC	[127]
	MEA	-	-	-	IC	[83]
	MEA	-	-	-	IC	[126]
	MEA	dilution	water	50	LC-RID	[123]
	MEA	dilution	acetonitrile/water 50:50	10	LC-RID	[141]
	MEA	dilution	water	40	LC-RID	[84]
	MEA	dilution	water	60	LC-RID	[145]
morpholine	PZ	dilution	-	-	IC	[72]
N-(2-((2-aminoethyl)amino)ethyl)-piperazine	PZ	dilution	water	1000	IC	[122]
N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidinone	MEA	dilution	water	10 to 100	GC-MS	[30]
N-(2-aminoethyl)piperazine	PZ	dilution	water	1000	IC	[122]
N-(2-hydroxyethyl)pyrrole	MEA	HS-SPME	-	-	GC-MS	[32]
N-(2-hydoxyethyl)ethylenediamine	MEA	dilution	methanol	10	GC-MS	[32]
	MEA	dilution	(water + 0,01% formic acid) / methanol : 9:1	500	LC-HR-MS	[135]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	10 to 100	GC-MS	[30,107]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	water	-	IC	[127]
	MEA	dilution	water	1000	LC-MS/MS	[32]

N-(2-hydoxyethyl)glycine	MEA	dilution	methanol	10	GC-MS	[32,90]
	MEA	dilution	water	10000	LC-MS/MS	[129]
	MEA	dilution	water	1000	LC-MS/MS	[32]
N-(2-hydroxyethyl)imidazole	MEA	dilution	methanol	10	GC-MS	[32,90]
	MEA	dilution	water	10 to 100	GC-MS	[30]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	(water + 0,01% formic acid) / methanol : 9:1	500	LC-HR-MS	[135]
	MEA	dilution	water	10000	LC-MS/MS	[129,140]
	MEA	-	-	-	NMR	[124]
	MEA	-	-	-	LC-ELSD	[82,83]
N-(2-hydroxyethyl)imidazolidin-2-one	MEA	dilution	water	10000	LC-MS/MS	[32]
	MEA	dilution	(water + 0,01% formic acid) / methanol : 9:1	500	LC-HR-MS	[135]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	water	10 to 100	GC-MS	[30]
	MEA	-	-	-	NMR	[124]
N-(2-hydroxyethyl)piperazine	PZ	dilution	water	1000	IC	[122]
N,N'-Bis-(2-hydroxyethyl)urea	MEA	dilution	water	1000	LC-MS/MS	[32]
N,N'-bis(2-hydroxyethyl)ethylenediamine	MEA	dilution	water	1000	LC-MS/MS	[32]
N-ethylpiperazine	PZ	dilution	water	1000	IC	[122]
N-formylpiperazine	PZ	dilution	water	1000	IC	[122]

	PZ & AMP/PZ	-	-	-	GC-MS	[93]
oxazolidine	MEA	HS-SPME	-	-	GC-MS	[32]
	MEA	dilution	water	1000	LC-MS/MS	[32]
oxazoline	MEA	HS-SPME	-	-	GC-MS	[32]
piperazine	MEA/PZ	-	-	-	GC-MS	[143]
	PZ	dilution	water	25	HPLC-RID	[123]
	PZ	dilution	water	2000	IC	[93]
	PZ	dilution	-	-	IC	[72]
	PZ	dilution	-	10000	IC	[122]
	PZ	dilution			IC	[127]
piperidine	PZ	dilution	-	-	IC	[72]
N-(2-aminoethyl)piperazine	PZ	dilution	ethanol	10 to 150	GC-MS	[142]
pyrrolidine	PZ	dilution	-	-	IC	[72]
pyrazine	MEA	dilution	methanol	10	GC-MS	[32]

2.2 Analysis of acids

Organic and inorganic acids are present as degradation products in most degraded solvents, largely due to oxidative degradation [82]. In the field of CO_2 capture studies, the main technique employed for their analysis is Ionic Chromatography (IC) associated with conductimetric detection without any sample pretreatment except dilution in water, making its application easy and inexpensive compared to other systems i.e. LC/MS (**Table 10**). The most commonly used separation column is IonPac AS15 (alkanol quaternary ammonium ion) associated with an IonPac AG15 guard column [32,39,82,85,91,120,122,126,130,135,146]. Elution was performed with potassium hydroxide in gradient mode starting at low concentrations (from 2 to 10 mM) [82,85] and raising at up to 60 mM [32,85,120], with a running time between 36 [146] and 60 min [32]. An example chromatogram obtained using this process is given in **Figure 9**. A conductimetric detector was frequently used and associated with suppression in order to decrease the background eluent conductivity and to increase the analytes conductivity. One drawback of this detector is the difficulty in identifying unknown peaks, which is only based on matching their retention time with standards [130]. An alternative to this method is capillary electrophoresis (CE) which has been described, in our knowledge, in only one article where the formation of heat stable salts and their roles in MEA degradation was studied [147]. CE has been used to analyze acetic, formic, oxalic and glycolic acids in other matrixes e.g. wine, silage or biodiesels [148–155]. This method reduces the volume of injected sample and therefore waste generation. However, CE is known for its poor repeatability especially when using real samples.

Quantification of acids at different stages of the degradation was mostly realized by IC, and the most frequently targeted compounds were formate, oxalate, glycolate, acetate, thiosulfate, sulfate, nitrite and nitrate [32,82,91,122,126,126]. Very little information was provided about the accuracy of the described methods. LOD and LOQ have only been reported in the study of Thompson [146] for eight compounds, namely glycolate, acetate, formate, nitrite, nitrate, sulfate, oxalate and thiosulfate. LOD were in the range of 2 µg/L and 30 µg/L, respectively, for glycolate and thiosulfate. LOQ were in the range of 1 mg/L and 16 mg/L, respectively, for glycolate and thiosulfate. The quantitative results varied according to pilot plant scale, operating conditions i.e. duration, temperature or composition of the flue gas to treat. In the case of MEA degradation, formate formation varied from 0.195 [32] to 11.8 g/kg [156] (**Table 9**).

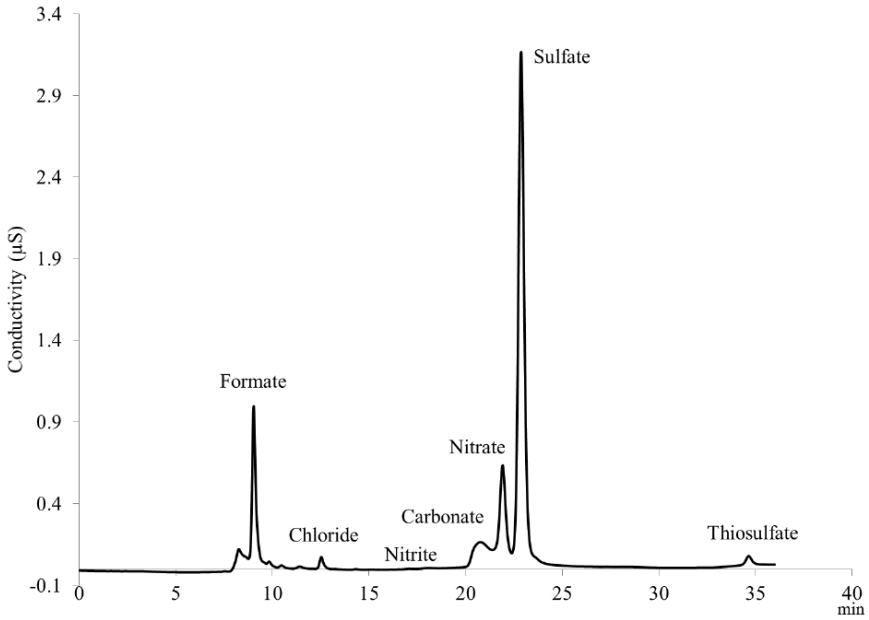

Figure 9: Example of chromatogram obtained after the analysis of a 100h degraded MEA 30% wt. sample. Reprinted with permission from (Thompson et al., 2014)

Table 9: Comparison of anion concentrations during 30% wt. MEA degradation in different pilot plants facilities

Compounds	Chahen et al. [32]	Thompson et al. [146]	Reynolds et al. [156]
Time of degradation	1700 hours	100 hours	≈ 4200 hours
Formate	195 mg/kg	≈ 3400 ppm	11.8 g/kg
Glycolate	100 mg/kg	NR	NR
Oxalate	39 mg/kg	NR	3.1 g/kg
Acetate	NR	NR	5.10 g/kg

Table 10: Analytical methods associated to the analysis of acids degradation compounds

Compound	Solvent composition	Pre treatment	Matrix dilution	Dilution factor	Analysis	Reference
Acetic acid	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72,91]
		-	-	-	IC	[122]
	MEA	dilution	water	500	IC	[135,146]
	MEA	dilution	water	-	IC	[120]
	AMP	dilution	-	-	CE-DAD	[147]
	AMP	dilution	water	50 to 200	IC	[85,93,138]
Formic acid	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72,91]
		-	-	-	IC	[122]
	AMP	dilution	-	-	CE-DAD	[147]
	MEA	dilution	water	-	IC	[82,83,120,126]
		dilution	water	500	IC	[135,146]
	AMP	dilution	water	50 to 200	IC	[85,93,138]
Propanoic acid	AMP	dilution	-	-	CE-DAD	[147]
	MEA	dilution	water	-	IC	[157]
Glycolic acid	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72,91]
	AMP	dilution	-	-	CE-DAD	[147]
	MEA	dilution	water	-	IC	[82,83,120,126]
		dilution	water	500	IC	[135,146]
	AMP	dilution	water	50 to 200	IC	[85,93,138]
Oxalic acid	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72,91]

		-	-	-	IC	[122]
	MEA	dilution	water	-	IC	[82,83,120,126]
		dilution	water	500	IC	[135,146]
	AMP	dilution	water	50 to 200	IC	[80,89,134]
	AMP	dilution	-	-	CE-DAD	[147]
Nitrite	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72]
		-	-	-	IC	[122]
	PZ	dilution	water	20 to 50	LC-UV (240 nm)	[94]
	MEA	dilution	water	-	IC	[82,83,120,126]
		dilution	water	500	IC	[103,135,146]
	AMP	dilution	water	50 to 200	IC	[85,138]
Nitrate	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72]
		-	-	-	IC	[122]
	MEA	dilution	water	-	IC	[82,83,120,126]
		dilution	water	500	IC	[135,146]
	AMP	dilution	water	50 to 200	IC	[85,138]
Sulfate	MEA	dilution and/or addition of HNO_3 69%	water	-	IC	[32]
	PZ	dilution	-	-	IC	[72]
		-	-	-	IC	[122]
	MEA	dilution	water	-	IC	[126]
		dilution	water	500	IC	[103,135,146]

2.3 Analysis of amides

One of the most described methods for the analysis of the total amide content is amide hydrolysis (often with sodium hydroxide) followed by chromatography analysis of the generated organic acids [66,83]. This method is complementary to the quantitative method enabling the analysis of organic acids, as the acid surplus is associated with the corresponding amide. This method is easy to use, but can only be used when the amide of interest and the associated acid have been identified and quantified. Moreover, there is a need to know the recovery and the accuracy of this pre-treatment step which can lead to a large variability to the results. To our knowledge, none of the studies performed thus far provide any validation of this method. Regarding more specific amide identification, both gas and liquid chromatography have been utilized (**Table 11**). GC-MS has been described for the detection of N-(2-hydroxyethyl)formamide (HEF) and N-(2-hydroxyethyl)acetamide (HEA). The sample was firstly diluted by a factor 10 and the separation was achieved with a CP-SIL-5 CB Amines or CP-SIL-5 CB ms column [30,32,90]. LC-ELSD (Evaporative Light Scattering Detector) and LC-MS/MS have also been described for the identification of N-(2-hydroxyethyl)imidazole (HEI), N-(2-hydroxyethyl)formamide (HEF), *N*,N'-bis(2-hydroxyethyl)oxalamide (BHEOX), N-(2-hydroxyethyl)acetamide (HEA), 2-hydroxy-N-(2-hydroxyethyl)acetamide (HEHAA) [83,129]. Quantification was determined in the study of Lepaumier et al. [30] and Chahen et al., [32] without information regarding any validation of the analytical method.

Table 11: Analytical methods associated to the analysis of amides degradation compounds

Compounds	Solvent composition	sample treatment	dilution matrix	dilution factor	method	reference
2-hydroxy-N-(2-hydroxyethyl)acetamide	MEA	dilution	water	10 to 100	GC-MS	[30]
N-(2-hydroxyethyl)acetamide	MEA	dilution	water	10000	LC-MS/MS	[129,140]
	MEA	dilution	methanol	10	GC-MS	[32,90,158]
	MEA	-	-	-	GC-MS	[147]
N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	MEA	dilution	water	10000	LC-MS/MS	[129]
	MEA	dilution	water	2	GC-FID	[141]
N-(2-hydroxyethyl)formamide	MEA	dilution	water	10000	LC-MS-MS	[129,140]
	MEA	dilution	methanol	10	GC-MS	[32,90,158]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	-	-	-	GC-MS	[147]
	AMP	-	-	-	GC-MS	[138]
	MEA	-	-	-	LC-ELSD	[82,83]
N-(2-hydroxyethyl)succinimide	MEA	-	-	-	GC-MS	[147]
	MEA	dilution	methanol	10	GC-MS	[90,158]
	MEA	dilution	D2O	0,7	NMR	[124]
N,N'-(Bishydroxyethyl)oxalamide	MEA	dilution	methanol	10	GC-MS	[32]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	10000	LC-MS-MS	[129,140]
N'-bis(2-hydroxyethyl)oxamide	MEA	-	-	-	GC-MS	[147]
Formamide	AMP	-	-	-	GC-MS	[138]
Acetamide	AMP	-	-	-	GC-MS	[138]

2.4 Analysis of nitrosamines

Nitrosamines are, to our present knowledge, the most harmful degradation products formed during the PCCC process [94] that can also be emitted with the gaseous effluents. These compounds are formed after the reaction of amine solvents with NOx, specifically NO and NO_2 contained in the flue gas to treat. NO_2 is likely to be absorbed in the solution as nitrite [94].

In order to monitor their formation in the solvent, various analytical strategies have been proposed (Table 12). This part of the review will only focus on the analysis of the solvent itself. The analysis of the nitrosamine content in the gaseous effluents will be mentioned in section 3. The most described method related to the quantitation of the total nitrosamine content, where a reaction of nitrosamines with hydrobromic acid in acetic acid was performed [159,160]. This reaction led to the formation of one mole of nitric oxide (NO) gas for every mole of nitrosamine. The analysis of the NO formed was performed with a NOx analyzer. In the study of Strazisar [160], where MEA degradation in the IMC Chemical Facility in Trina, California was studied, a concentration of nitrosamines of 2.91 µmol/mL was determined. This method is cheap and easy to apply, but does not provide accurate results due to reaction efficiency variability. Moreover, this method does not permit the identification of each nitrosamine present in the sample. Methods described in the literature for the individual analysis of nitrosamines mainly involved LC-MS/MS [32,161,162] and LC-UV with a wavelength of 240 nm [94,163–165]. One of the drawbacks of using mass spectrometry with real samples from CO_2 capture pilot plants is the possible pollutions of the apparatus, leading to frequent maintenance. Various analytical columns have been reported for the separation of nitrosamines. For example, N-nitrosodiethanolamine was analyzed with a Polar Advantage 2 (polar embedded stationary phase) column in the study of Fine et al. [159], with a Ascentis Express RP-Amide by Sorensen et al. [162] and with a Thermo Hypercarb PGC (Porous Graphitic Carbon) by Chahen et al. [32]. N-nitrosopiperazine was analyzed with a Polar Advantage 2 (reversed phase) by Goldman et al. and Fine et al. [94,111] and with a Discovery HS F5 (bonded fluoro (pentafluorophenyl)) by Sorensen et al. [162]. LOD and LOQ were rarely mentioned and in the study of Fine et al. were respectively for N,N'-dinitrosopiperazine of 0.1 ppm and 0.4 ppm. GC-MS has therefore been reported for the analysis of nitrosamines [32,163] but less than LC. In the study of Chahen et al. [32] nitrosodimethylamine (NDMA) concentration was determined by GC-HRMS. After 1400 hours of degradation of MEA, the NDMA concentration was close to 500 µg/kg (541 µg/kg in the lean amine, and 446 µg/kg in the rich amine). Regarding sample pre-treatment, most of the studies diluted samples from 20X to 50X in water [94,111]. Other studies involved liquid-liquid extraction [32,166].

Table 12: Analytical methods associated to the analysis of nitrosamines degradation compounds

Compounds	Matrix	Sample treatment	Dilution matrix	Dilution factor	Extraction	Method	References
nitrosodiethanolamine	MEA	dilution	-	1000	-	LC-MS/MS	[32]
	MEA	-	-	-	-	LC-MS	[87,167]
	CCS solvent	-	-	-	-	LC-MS/MS	[162]
	CCS solvent	dilution	water	20 to 50	-	LC-UV (240 nm)	[159]
	CCS solvent	Dilution	water	20 to 100	-	IC-MS/MS	[161]
Nitrosomethylethylamine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
Nitrosopyrrolidine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
Nitrosodiethylamine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
Nitrosopiperidine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
Nitrosodi-n-propylamine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
Nitrosodi-n-butylamine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
Nitrosodiphenylamine	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]

Nitroso-(2-hydroxyethyl)glycine	PZ	dilution	water	20 to 50	-	LC-UV (240 nm)	[159]
nitrosodimethylamine	MEA	-	-	-	-	LC-MS	[87,167]
	CCS solvent	-	-	-	-	LC-MS/MS	[162]
	MEA	Extraction	-	-	Orbo 60 tubes	GC-HRMS	[32]
Nitrosopiperazine	CCS solvent	Dilution				GC-MS	[93]
	Solvent	-	-	-	-	LC-MS/MS	[161]
	PZ	Dilution				LC-UV	[94,111,159,168–170]
	CCS solvent	-	-	-	-	LC-MS/MS	[162]
Dinitrosopiperazine	CCS solvent	-	-	-	-	LC-MS/MS	[162]
	PZ	Dilution	water	40	-	LC-UV (240 nm)	[111]
N-nitrosomorpholine	MEA	Extraction	-	-	-	GC-HRMS	[32]
	Morpholine	-	-	-	-	LC-UV (254 nm)	[164,171]
	CCS solvent	-	-	-	-	LC-MS/MS	[162]
	CCS solvent	Dilution + Extraction	water	≈ 7	Hydrophilic-Lipophilic Balance Sorbent	LC-MS/MS	[161]
N-nitroso-1-(2-hydroxyethyl)-ethylenediamine	CCS solvent	-	-	-	-	LC-UV (240 nm)	[170]

2.5 Analysis of aldehydes

Aldehydes are one of the major classes of degradation products formed during the CO_2 capture process. In the field of MEA degradation, the main aldehydes reported were formaldehyde [82,120], acetaldehyde [82,120] and glyoxal [82]. Very little information is given about the analysis of aldehydes in the field of CO_2 capture solvent analysis. Analysis of aldehydes is difficult, and often require a derivatization step. This derivatization generally involved the use of 2,4-dinitrophenylhydrazine (DNPH) prior to reverse phase chromatography method [122,135,159]. Some information about the accuracy of the method can be found in US EPA Method [172].

3 Analysis of the treated flue gas

Amine-based post combustion CO_2 capture processes are likely to emit degradation products with the treated flue gas [100,173]. Those emissions are dependent on the composition of flue gas and the nature of the solvent. In 2011, the Norwegian Climate and Pollution Agency (Klif) implemented some emission limits for ammonia, amines and aldehydes for the Technology Centre Mongstad (TCM) facility with a capacity of 100 000 ton/year [174]. The total amine emissions should not exceed 2800 kg/year. Knowledge of the composition of atmospheric emissions was therefore essential to assess the innocuousness of the process with the used amines [175]. Szulejko at al.(2014) reviewed the sampling methods for the analysis of airborne amines [176]. However, in the case of effluents from pilot plant CO_2 capture (PCC), the sampling of the matrix was challenging due to its low temperature and high moisture content. Currently, only a few analytical methods have been developed and applied in order to monitor the composition of the gaseous effluents. The most commonly used methods are FTIR, online MS analysis, implementation of impingers and sampling on solid sorbents. These methods are listed in Table 13.

Table 13: Analytical methods associated to the analysis of the treated flue gas

Method	Monitored compounds	References
FTIR	CO_2	[32,77,177]
	NO	[32,77,82,113,177]
	NO_2	[32,77,82,113,177]
	SO_2	[32,77]
	CO	[82,177]
	Ammonia	[77,82,87,113,119,177–180]
	Piperazine	[113,177,180,181]
	methylamine	[82,87]
	MEA	[82,87,119,175,177]
	2-amino-2-methyl-1-propanol	[177]
	Formic acid	[180]
	Formaldehyde	[82,177]

	Acetaldehyde	[82,177]
	Chlorhydric acid	[177]
Impingers trains	Acetaldehyde	[177]
	Formaldehyde	[177]
	Ammonia	[77,177,182]
	MEA	[77,182]
	Nitrosamines	[182,183]
On-line MS	Acetaldehyde	[184]
	Ammonia	[184]
	MEA	[184]
	nitrosodimethylamine	[87]
	nitrosomorpholine	[87]
	Formaldehyde	[184]
	Formamide	[184]

3.1 On-line FTIR monitoring

The most used method for the analysis of stable emitted compounds (CO_2, CO, NOx, SOx …) is Fourier Transform Infrared Spectroscopy (FT-IR). Measurements are performed using the absorption spectra of each compound present in the database. This analyzer enabled simultaneous analysis of up to 50 components. This technique has been applied on lab-scale pilot plants [32,87,119,141], and on demonstration pilot plants i.e. the TCM [77], the PCCC pilot plant of Esbjerg in Denmark [177], Maasvlakte in Netherlands [179,182] or Tarong in Australia [113,168]. FT-IR enabled the detection and quantification of many target compounds like amines (MEA, PZ, and ammonia), NOx, SOx or aldehydes (formaldehyde, acetaldehyde). To avoid any condensation due to the high humidity of the effluent, the entire system including the probes, filter and sampling lines are heated up to 180°C [185,186]. This method seems to be essential to monitor the main predictable emissions with a detection limit close to 1 ppm. However, the method does not provide any pre-concentration step or measurement of unknown compounds. Indeed, reference spectra of expected compounds must be registered in the database for their measurements on the effluents. Moreover, fluctuations of the sampling temperature induces a response variation of up to 4% per degree C temperature [187]. This can be problematic when these kind of analysis are realized directly on-site. Another drawback of the method is the lack of sensitivity at low concentrations which makes this technique unsuitable for trace analysis.

3.2 On-line MS analysis

In order to identify compounds emitted at parts per billion (ppb) level, online MS systems have been tested [87,188]. Zhu at al., (2013) used a Proton Transfer Reaction time-of-flight mass spectrometry (PTR-ToF-MS) method for a real time measurement to identify and quantify emissions from industrial scale carbon capture pilot plants [184]. This method was applied in the TCM in Norway.

In this study, the emitted flue gas was diluted from 1:20 to 1:10 with bottled zero air because of interferences with water, ammonia and CO_2. The main emissions were due to MEA, ammonia and acetaldehyde. This method also enabled the first identification of pyrazine as degradation products in the gas phase. This method is more sensitive than FTIR but does not provide any preconcentration steps in order to identify degradation products present at trace level. Indeed, the possible high amine content of the treated flue gas can be responsible of a matrix effect, which can modify or suppress the ionization of trace compounds.

3.3 Sampling on impingers followed by chromatographic analysis

The second most used method for the characterization of the emitted flue gas, is the implementation of impinger trains. This method has several advantages including low price, ease of use, and large gas sampling volume. In this case, the emitted gas phase was sampled through an impinger train containing absorption liquids (**Figure 10**) [135,182,183,189,190]. Before passing through these liquids, the gas phase was condensed and collected for analysis. The nature of the absorbent liquids varied according to the nature of compounds to sample. Ammonia and amine derivatives were frequently absorbed in 0.05 M sulphuric acid or ultrapure water [186,191], whereas nitrosamines and nitramines were sampled in 0.1 wt% sulfamic acid [135]. A second concentration step can be achieved using solid phase extraction cartridges [135]. Aldehydes among which acetaldehyde and formaldehyde could be sampled in impingers filled with 2,4-dinitrophenylhydrazine [135,177]. Analysis of the obtained solutions was often realized by LC-MS, GC-MS or IC-ECD [127,182,183]. Recently, Fraboulet et al., [183] set up Round Robin tests in order to evaluate the capability of the analytical methods to give accurate and reliable results. The aim of the tested methods was to quantify 9 nitrosamines in atmospheric samples collected in sulfamic acid solutions. The involved methods were LC-MS, LC-MS/MS, GC-MS/MS, GC-HRMS, GC-TEA and UPLC-MS which sometimes included a pre-concentration step (LLE, SPE). The results showed good compliance with the different laboratories, and reinforced the usefulness of this sampling method for the quantification of nitrosamines. However, because of the specificity of the impingers approach to nitrosamines or aldehydes, other sampling methods are needed in order to monitor other classes of compounds.

Figure 10: Impinger trains, reprinted with permission from (Broutin et al., 2014)

3.4 Sampling on solid sorbents

Another promising but less common method used for the analysis of CO_2 capture pilot plant gaseous effluents was sampling on solid sorbents [180,192,193]. This method was used for the identification of degradation products emitted after the photo-oxidation of MEA on the European Photochemical Reactor (EUPHORE, Valencia, Spain). 2,4-dinitrophenylhydrazine (2,4-DNPH) sorbents permitted the selective analysis of carbonyl compounds like aldehydes and ketones which reacted with the acidified 2,4-DNPH to form hydrazine species. In order to identify Volatile Organic Compounds (VOC), Tenax® TA absorption tubes were also used [32,192,193]. This method permitted the identification of 21 compounds emitted at trace level (in the range of the µg/m^3), as the sampling enabled a pre-concentration of the gas phase. As mentioned previously, the high moisture content of the effluent makes its sampling on solid sorbents difficult. Actually, the thermodesorption step preceding the GC-MS analysis does not allow any condensation on the solid sorbents. In this case, a condensation of the emitted flue gas moisture has to be performed before the sampling step [32]. This method also allows the quantification of emitted compounds trapped on the solid sorbent. In order to get accurate results and take into account both the adsorption and extraction efficiencies of each analytes, the developed methods must be validated. Recently, a quantification method on Tenax® TA sorbents for five targeted compounds (pyrazine, nitrosodimethylamine, 2-methylpyrazine, dimethylformamide and pyrrole) was developed and validated with an acceptance limit of 30% [192]. This method has been applied to treated flue gas from IFPEN pilot plant, and concentrations were determined to be less than 300 µg/m^3 [32,192]. When compared to impingers, solid sorbents are more expensive but reusable after regeneration with high temperature. Moreover, different sorbents are commercially available (Tenax® TA, Tenax® GR and Carbopack™ B/Carbopack™ X, …) even if Tenax® TA seemed to cover a large range of compounds [32].

4 Conclusion

Amine degradation during post-combustion CO_2 capture process is one of the problems associated with current technology. The degradation products formed in the liquid phase of the solvent are likely to be emitted with the treated flues gas. Analytical strategies are a powerful tool which can provide reliable information about the identity and the amount of products formed. This enables to explain the mechanism of formation of these compounds with the objective to reduce their formation. In this review we presented a critical survey of analytical methods described in the literature in the field of post-combustion CO_2 capture. The most used methods for the monitoring of the main class of compounds (amines, acids, amides and nitrosamines) are gas and liquid chromatography among which ionic chromatography. These methods are even used for quantitative monitoring. Regarding the gaseous effluents analysis, four methods have been described: FTIR, implementation of impingers, online MS analysis and sampling on solid sorbents. Among all the methods described, very little information was provided about the accuracy of the supplied results. Indeed, chromatographic methods can be sensitive to matrix effect, a question non broached to this date in the field of CO_2 capture.

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Chapitre 2 : Matériels et méthodes

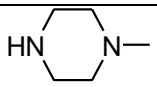
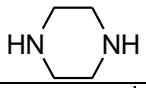
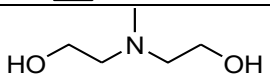
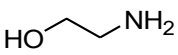
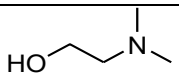
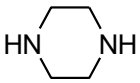
Dans ce chapitre sont présentés le dispositif expérimental permettant de simuler la dégradation des différents solvants de l'étude, les solvants d'intérêt, ainsi que les méthodes analytiques permettant la caractérisation des solvants et leur suivi au cours du temps.

1 Dégradation des solvants

1.1 Préparation des solvants

Tous les solvants étudiés au cours du projet de thèse sont préparés par pesée à l'aide de produits commerciaux et d'eau déminéralisée (18,2 MΩ) alimentant le réseau du site EDF R&D de Chatou. Le **Tableau 14** donne la composition des différents solvants ainsi que les fournisseurs de chacune des amines. La pipérazine (PZ) ayant une faible solubilité dans l'eau (env. 0,9 g/L à 20°C [194]), une étape de chauffage préalable (à près de 90°C) a été nécessaire pour la préparation des solvants 1 et 3 afin d'avoir un mélange homogène.

Tableau 14 : Fournisseurs des amines utilisées pour la préparation des 3 mélanges

	Composition	Structure	Fournisseur	Pureté
Solvant 1	1MPZ (30% wt.)		Sigma Aldrich	99%
	PZ (10% wt.)		Merck	≥99%
Solvant 2	MDEA (25% wt.)		Alfa Aesar	98%
	MEA (5% wt.)		Alfa Aesar	99%
Solvant 3	DMEA (35% wt.)		Afla Aesar	≥99%
	PZ (5% wt.)		Merck	≥99%

1.2 Dispositif expérimental de captage : LEMEDES CO2

Le laboratoire LEMEDES-CO2 (Laboratoire d'Etude des MEcanismes de DEgradation des Solvants utilisés pour le captage du CO_2) a été conçu afin d'évaluer les performances de différents solvants, d'étudier leur comportement et les mécanismes de dégradation. Les trois solvants du projet ont été dégradés à l'aide de ce dispositif.

Le dispositif expérimental du laboratoire est dimensionné pour reproduire les cycles d'absorption et de désorption subis par le solvant lors de son cyclage entre l'absorbeur et le régénérateur [90]. Il s'agit d'un montage innovant permettant de prendre en compte simultanément les phénomènes de dégradation oxydante et thermique pouvant avoir lieu au cours d'un processus industriel. La majorité des études présentées dans la littérature s'intéressent à ces deux voies de dégradation de manière séparée, sans passer par les étapes d'absorption et de régénération cyclique. Ce dispositif a été initialement conçu pour l'étude de la dégradation de la MEA 30 %, solvant modèle du procédé. Il est par conséquent adapté pour fonctionner à des températures (T) et pressions (P) du même ordre de grandeur que celles appliquées lors de l'étude de la MEA (40°C<T<123°C et 1 bar<$P_{absolue}$<4 bar). Au-delà de ces températures et pressions, le dispositif n'est plus dans des conditions de sécurité optimales. Une représentation schématique du montage ainsi qu'une photo sont présentées dans la **Figure 11**.

Le dispositif est construit autour d'un réacteur semi batch en verre pouvant contenir jusqu'à 1,5 L de solvant. Les gaz à traiter sont constitués d'un mélange de N_2 (≥99,995 %, Air Liquide, Mitry-Mory, France), de CO_2 (≥99,7 %, Air Liquide, Mitry-Mory, France) et d'air (20,9 % de dioxygène) issu du réseau EDF R&D de Chatou. L'entrée des gaz à traiter est régulée par trois débitmètres massiques et se fait par le bas du réacteur. Avant leur entrée au sein du réacteur, les gaz sont humidifiés à une température régulée, sensiblement égale à leur température en sortie du condenseur, et ce, afin de compenser la perte en eau. Les conditions de température, pression et la composition des gaz définissent les cycles d'absorption et de désorption. Le **Tableau 15** donne les caractéristiques de ces paramètres au cours de ces deux étapes. Les durées des deux étapes du procédé varient en fonction du solvant utilisé, et sont optimisées avant l'étude de tout nouveau solvant afin d'obtenir un taux de charge optimal. Pour cela, des prélèvements sont effectués à différents temps d'absorption et de désorption, et des déterminations de taux de charge sont réalisées pour chacun d'entre eux.

Tableau 15 : Paramètres gouvernant les étapes d'absorption et de désorption

	Gaz entrants	Température	Pression absolue
Absorption	82 % de N_2 à 21,7 L/min 3 % d'O_2 à 4 L/min 15 % de CO_2 à 4,25 L/min	42°C	1 bar
Désorption	100 % de N_2 pendant 1 min à 30 L/min Puis 100 % de N_2 à 4,5 L/min	123°C	4 bars

L'échangeur de chaleur fonctionne à l'aide d'une huile minérale permettant un rapide chauffage (via le groupe chaud) et refroidissement du solvant (via le groupe froid). La circulation du solvant au sein du dispositif est assurée par une pompe de circulation dont le débit est de 3 L/min. En sortie du réacteur, un condenseur permet de condenser la vapeur d'eau ainsi que d'éventuelles espèces volatiles émises au cours du procédé. Les condensats obtenus sont réinjectés dans le réacteur afin de maintenir constante la quantité de solvant. Deux analyseurs sont montés en parallèle en sortie du condenseur afin de suivre en temps réel la composition en CO_2 et O_2 des gaz sortants. Après lavage au sein du laveur, les gaz sont relargués en sortie du dispositif et aspirés par une hotte. Toutes les tubulures sont constituées d'hastelloy ce qui permet d'atténuer les phénomènes de corrosion. Le dispositif est piloté via un logiciel en fonctionnement continu (24h/24) permettant un suivi de la composition des gaz, de la température et de la pression en continu. Chaque campagne de dégradation dure environ 900 heures.

Des prélèvements des phases liquide et gazeuse sont réalisés chaque semaine en vue de leur analyse. Les échantillons sont ensuite conservés à 4°C au sein de flacons ambrés pour les prélèvements liquides.

Une caractérisation de l'écoulement du liquide et du transfert de matière au sein du réacteur a par ailleurs été réalisée et est présentée en **Annexe 2**.

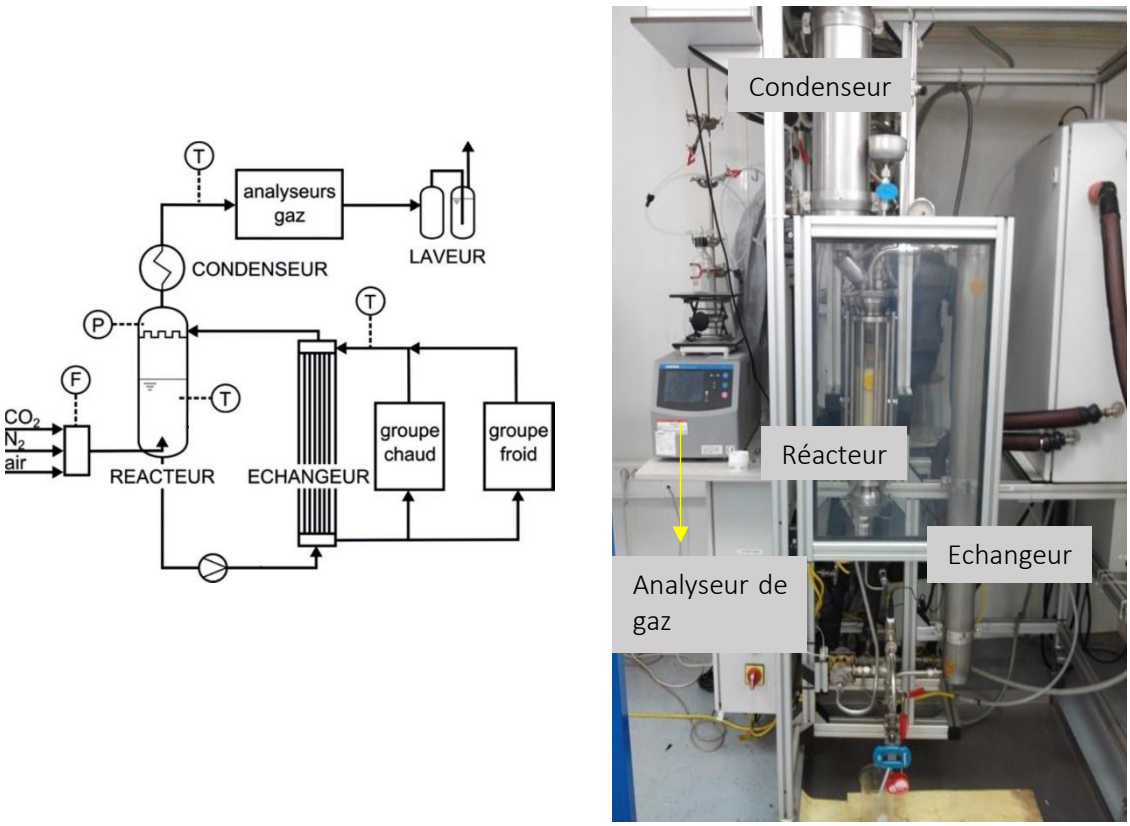


Figure 11 : Représentation schématique et photo du banc d'essai LEMEDES-CO2 [90] (T : sonde de température ; P : sonde de pression ; F : débitmètre)

Ce dispositif a été utilisé dans le cadre d'une étude préliminaire à cette thèse pour l'étude de la dégradation de la MEA, solvant modèle du procédé [158]. Les résultats obtenus ont été tout à fait en accord avec la littérature (taux de charge obtenus, produits de dégradation) [32], ce qui valide une représentativité du dispositif proche des conditions industrielle.

2 Suivi de routine des campagnes de dégradation

Afin de s'assurer du bon déroulement d'une campagne de dégradation, différents paramètres sont à contrôler régulièrement : la teneur en eau, la teneur en amines et le taux de charge du solvant de captage.

2.1 Mesure de la teneur en eau

Afin d'effectuer au cours du temps un suivi de la composition du solvant, des mesures bihebdomadaires de la teneur en eau sont effectuées à l'aide d'un titreur V20 Karl Fisher (Mettler, Viroflay, France). Les réactifs utilisés pour la titration sont l'Hydranal-Composite 5K (Sigma Aldrich, Saint-Quentin-Fallavier, France) et le Méthanol dry (Sigma Aldrich, Saint-Quentin-Fallavier, France). L'hydranal Composite 5K est composé d'imidazole, de 2-méthylimidazole, de iodine, de monohydriodide-1H-imidazole, et de dioxyde de soufre (SO_2), réactifs nécessaires à la titration. Quelques gouttes de solvant non dilué sont introduites dans le flacon titreur (soit environ 0,03 g). La réaction permettant la titration de l'eau est donnée en **Équation 3.** La réaction se poursuit jusqu'à ce que l'eau soit entièrement consommée et que l'iode libre soit détecté, la solution passant du brun jaune (en raison de la présence d'iode) à l'incolore (l'iode passant sous sa forme iodure). Le point final du titrage est déterminé à l'aide de l'indication bivoltamétrique (électrode bivoltamétrique à deux fils de platine). Le résultat fourni par le titreur est donné en pourcentage. L'incertitude de la méthode a été estimée par la répétabilité des mesures et vaut ± 5 %.

Équation 3 : Réaction à l'origine de la méthode de titrage avec la base imidazole notée RN

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN \longrightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

2.2 Mesure de la teneur en amines totale

Afin d'effectuer au cours du temps un suivi de la composition du solvant, des mesures bihebdomadaires de la teneur en amine sont effectuées à l'aide d'un titreur T50 Karl Fisher (Mettler). Les mesures sont effectuées via une titration pHmétrique, en utilisant une électrode DGi114-SC (Mettler), et l'acide chlorhydrique 0,2 N en tant que réactif titrant. L'échantillon à titrer (entre 0,4 et 0,6 g) est tout d'abord dilué par 100 avec de l'eau déminéralisée. Chacune des amines de l'étude étant

caractérisée par un voire deux pKa (**Tableau 4**), le titrage s'effectue ensuite en ajoutant progressivement l'acide chlorhydrique jusqu'à atteindre le point d'équivalence. Au point d'équivalence, la quantité d'acide ajoutée est égale à la quantité d'amine initialement présente en solution, ce qui permet d'avoir accès à la quantité d'amines (en mol/kg) présente dans l'échantillon. L'incertitude de la méthode a été estimée par la répétabilité des mesures et vaut ± 5 %.

2.3 Mesure de la teneur en carbone inorganique total

La concentration en CO_2 dissous au sein du solvant de captage reflète l'efficacité de captage du solvant étudié. Cette détermination se fait via la mesure de la teneur en Carbone Inorganique Total, réalisée par l'intermédiaire d'un TOC-L CSH (Shimadzu). Cette méthode permet la quantification du CO_2, des carbonates (CO_3^{2-}), bicarbonates (HCO_3^-) et carbamates (e.g. $PZCOO^-$; $PZ(COO^-)_2$ dans le cas de la PZ) dissous en solution. L'échantillon à analyser est tout d'abord dilué par 50 dans de l'eau déminéralisée, et 50 µL de la solution obtenue sont injectés. Le dispositif permet une acidification de l'échantillon via l'ajout d'acide phosphorique qui, par réaction avec les carbonates et bicarbonates conduit à un dégagement gazeux de CO_2. Le CO_2 est ensuite détecté et quantifié par l'intermédiaire d'un Détecteur Infra Rouge Non Dispersif (NDIR). Un étalonnage du dispositif est réalisé avant chaque campagne de vieillissement en utilisant un étalon TIC à 1000 mg/L (Fluka) dilué pour s'adapter aux teneurs attendues. Les résultats obtenus sont donnés en mg/L. L'incertitude de la méthode a été estimée par la répétabilité des mesures et vaut ± 5 %.

2.4 Détermination du taux de charge

Le taux de charge est un paramètre important pour le suivi d'une campagne de vieillissement. Il permet de conclure quant à l'efficacité de captage du solvant en question. Le taux de charge se définit par le rapport entre le nombre de moles de CO_2 et le nombre de moles d'amines (**Équation 4**), grandeurs déterminées expérimentalement.

Équation 4 : Détermination du taux de charge

$$\tau = \frac{nombre\ de\ moles\ de\ CO_2}{nombre\ de\ moles\ d'amines}$$

3 Méthodes analytiques permettant la caractérisation de la dégradation des solvants

Dans le cadre de ce projet, différentes méthodes analytiques ont été développées afin d'effectuer un bilan aussi exhaustif que possible des différents produits formés au cours du temps. Ces méthodes permettent l'étude de la phase liquide du solvant, mais également la caractérisation de la composition des fumées émises traitées. La **Figure 12** donne un bilan des méthodes développées au cours du projet. Ces méthodes concernent la GC-MS pour l'identification et la quantification des produits de dégradation volatils, la MicroExtraction sur Phase Solide en espace de tête (HS-SPME) couplée à la GC-MS pour l'analyse d'alkylpyrazines, la chromatographie ionique (CI) pour la quantification des amines majoritaires ainsi que l'identification et la quantification de produits de dégradation (amines et acides organiques), la LC-MS pour l'identification de composés non détectés en GC-MS et en IC, et enfin le piégeage sur phase solide couplée à une thermodésorption (TDU-CIS) et analyse en GC-MS pour l'étude de composés émis avec les fumées traitées.

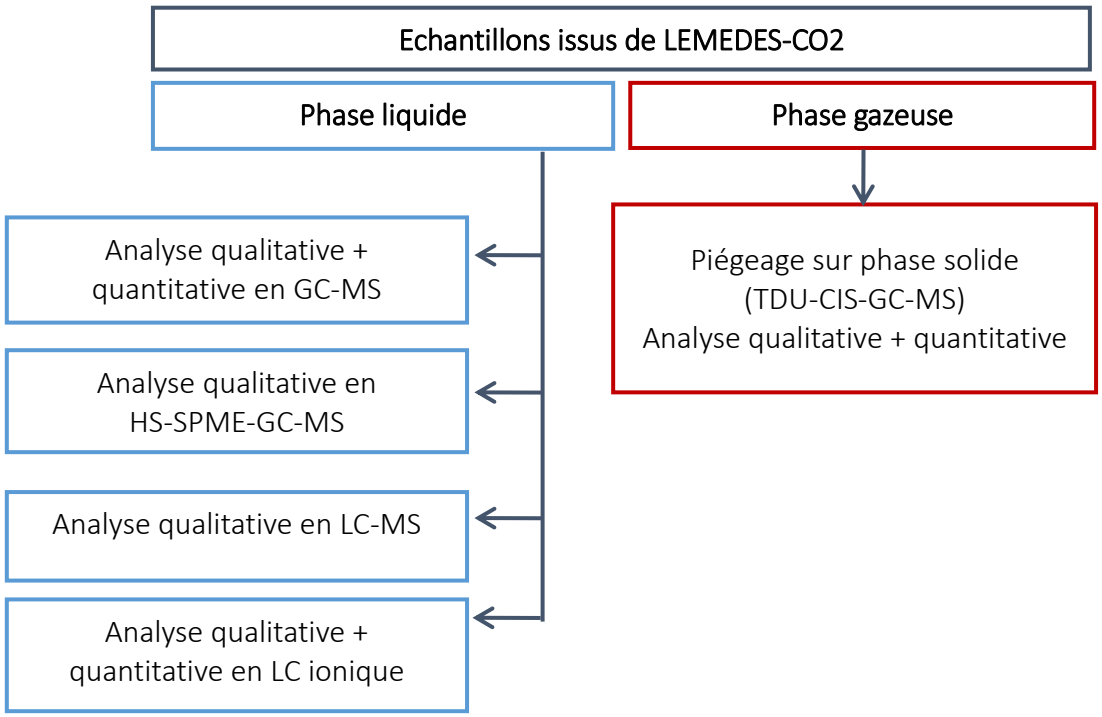


Figure 12 : Bilan des méthodes analytiques développées. GC : Chromatographie en phase Gazeuse ; MS : Spectrométrie de Masse ; LC : Chromatographie en phase Liquide ; HS-SPME : Micro Extraction sur Phase Solide en Espace de Tête ; TDU-CIS : Thermodésorption couplé à injecteur à cryofocalisation

3.1 Méthodes permettant l'analyse de la phase liquide

3.1.1 Analyse qualitative et quantitative en GC-MS

L'analyse en GC-MS par injection liquide permet l'identification de produits de dégradation volatils présents au sein du solvant dégradé. Cette méthode ne nécessite aucune technique préalable de traitement de l'échantillon, qui est simplement dilué par 10 dans le méthanol avant injection. Un GC-MS à simple quadrupôle est disponible sur chaque site du projet : ESPCI Paris et EDF R&D Chatou.

Le GC-MS présent sur le site de l'ESPCI (GC Agilent 7890A, MS Agilent 5975 inert XL MSD, source EI) possède un système totalement automatisé de gestion des échantillons (Gerstel), permettant de traiter l'échantillon avant analyse (Micro Extraction sur Phase Solide, Espace de tête Dynamique, Extraction sur barreau aimanté et Thermodésorption). Le GC-MS présent sur le site EDF R&D de Chatou (GC Agilent 7890A, MS Jeol JMS-Q1000GC-MkII Ultraquad) permet uniquement d'injecter l'échantillon sous forme liquide. Deux colonnes de polarités différentes ont été utilisées au cours des analyses afin d'avoir accès au maximum de composés. Les conditions des méthodes analytiques que nous avons développées sont données dans les **Tableau 16**, **Tableau 17** et **Tableau 18**.

Tableau 16 : Conditions analytiques utilisées en GC-MS

Volume d'injection	1 µL
Injection	Split (5 :1)
Gaz vecteur	Hélium à 1 mL/min
Température de l'injecteur	280°C
Température ligne de transfert MS	280°C

Tableau 17 : Gradient de température utilisé pour la séparation sur la colonne polaire DBWax (Agilent)

Colonne polaire DBWax		
Caractéristiques		
30 m x 0,250 mm x 0,50 µm		
Polyéthylène glycol		
Gradient de température		
Rampe (°C/min)	Température (°C)	Temps pallier (min)
	40	2
7	130	0
13	240	20

Tableau 18 : Gradient de température utilisé pour la séparation via la colonne apolaire CPSil 8 cb ms (Agilent)

Colonne apolaire CPSil 8 cb ms		
Caractéristiques		
30 m x 0,250 mm x 1,00 µm		
Film apolaire polysiloxane 95% méthyl-5% phényl		
Gradient de température		
Rampe (°C/min)	**Température (°C)**	**Temps pallier (min)**
	40	2
7	130	0
13	280	10

L'attribution des différents pics d'élution observés sur les chromatogrammes est réalisée dans un premier temps à l'aide de la base de données NIST. L'identification finale de ces composés est confirmée par injection d'étalons commerciaux.

Une méthode d'analyse quantitative a ensuite été développée pour 3 composés cibles majoritaires (1-formylpipérazine, pyrazine et 1,4-diméthylpipérazine). Cette méthode sera décrite dans le chapitre 3.

3.1.2 Analyse qualitative en HS-SPME-GC-MS

La HS-SPME (Micro Extraction sur Phase Solide en Espace de Tête) couplée à la GC-MS a été utilisée pour l'identification d'une famille de composés volatils présents en solution : les alkylpyrazines. Cette méthode a été développée dans le cadre d'un projet antérieur (ANR Dalmatien) et a fait l'objet d'une publication [195]. Elle a permis pour la première fois l'identification de cette classe de composés dans les solvants aminés issus du captage du CO_2. Les mêmes paramètres que ceux décrits dans cet article seront appliqués dans le cadre de notre projet. Le système chromatographique utilisé est le même que celui décrit en **3.1.1**. La fibre utilisée est une fibre de type Carboxen-Polydimethylsiloxane (CAR-PDMS) 75 µm (Supelco). L'échantillonnage se fait en introduisant 5 mL d'échantillon dans un flacon de 20 mL. Dans une première étape d'incubation, l'échantillon est chauffé à 70°C pendant 5 min. L'extraction est ensuite effectuée en plaçant la fibre dans l'espace de tête du flacon pendant 30 min à 70°C. La désorption s'effectue en introduisant la fibre dans l'injecteur chauffé à 280°C pendant 20 min. L'analyse en GC-MS est ensuite réalisée selon les mêmes paramètres que ceux présentés en **3.1.1**. La **Figure 13** présente de manière schématique la méthode.

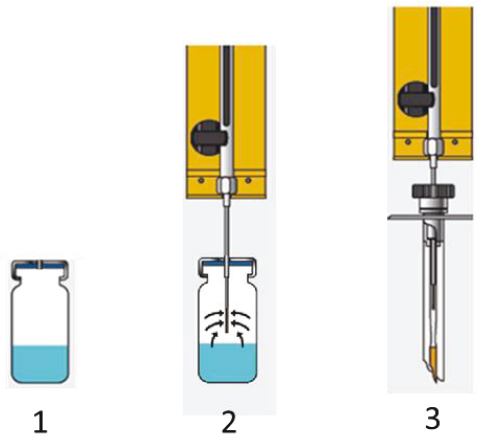


Figure 13 : Principe de la HS-SPME-GC-MS. 1 : incubation ; 2 : extraction ; 3 : désorption

3.1.3 Analyse qualitative en LC-MS

La LC-MS a été utilisée pour la caractérisation de composés non volatils sur un système LC Agilent 1100 couplé à un spectromètre de masse MS Waters micromass ZQ 4000 équipé d'une source ESI en mode positif chauffée à 120°C. Les séparations chromatographiques ont été réalisées sur une colonne Thermo Hypercarb (150 mm x 3 mm, 5µm). La phase mobile était composée de (A) eau + NH_3 (pH 10,8) et (B) Methanol + acide formique à un débit de 350 µL/min. 5 µL d'échantillons préalablement dilués par 100 dans la phase mobile A ont été injectés. Le gradient de phase mobile débutait à 100 % de A pendant 10 min avant d'atteindre le ratio 80:20 (A:B v:v) en 8 min. Ces proportions ont été maintenues pendant 12 min.

3.1.4 Analyse qualitative et quantitative en chromatographie ionique

Dans le cadre du projet, la chromatographie ionique a été utilisée pour l'analyse qualitative et quantitative des anions et des cations présents en solution.

3.1.4.1 Chromatographie ionique échangeuse de cations

La chromatographie ionique (CI) échangeuse de cations est utilisée pour l'analyse quantitative des amines majoritaires constituant le solvant, ainsi que pour l'identification des éventuelles amines formées au cours des campagnes de dégradation. Les analyses sont réalisées sur un système Dionex ICS-1100 (Thermo Scientific). Le détecteur utilisé est un conductimètre DS6 avec un suppresseur chimique auto-régénérant CERS/AERS 500 (4 mm). La précolonne (IonPac™ CG19 RFIC™ (4 x 50 mm)) et la colonne (IonPac™ CS19 RFIC™ (4 x 250 mm)) sont constituées d'une matrice résine polymérique de styrène/divinylbenzène (granulométrie 5,5 µm), sur laquelle sont greffés des groupements sulfonates ($-SO_3^-$, H^+). L'éluant est une solution aqueuse d'acide méthanesulfonique (MSA) générée par

un générateur d'éluant RFC-30. Un passeur d'échantillon Dionex AS40 permet l'injection automatisée des échantillons, et l'acquisition des données est réalisée via le logiciel Chromeleon 7. La colonne ainsi que le détecteur sont thermostatés à 35°C. Le volume d'injection est de 25 µL. Les autres paramètres ont été optimisés en fonction des composés d'intérêt (facteur de dilution de l'échantillon, gradient d'élution, débit, courant) et seront présentés dans chacun des chapitres correspondants aux différents solvants de l'étude.

3.1.4.2 Chromatographie ionique échangeuse d'anions

La chromatographie ionique échangeuse d'anions est utilisée pour l'identification d'acides organiques et inorganiques formés au cours de la dégradation des solvants étudiés, ainsi que pour le suivi quantitatif de certains acides organiques majoritaires. Les analyses sont réalisées sur un système Dionex ICS-1100 (Thermo Scientific). Le détecteur utilisé est un conductimètre DS6 avec un suppresseur chimique auto-régénérant CERS/AERS 500 (4 mm). La précolonne (IonPac™ AG11 RFIC™ (4 x 50 mm)) et la colonne (IonPac™ AS11 RFIC™ (4 x 250 mm)) sont constituées d'une matrice résine polymérique de styrène/divinylbenzène (granulométrie 13 µm), sur laquelle sont greffés des groupements amines quaternaires ($-NR_4^+$, OH^-). L'éluant est une solution aqueuse d'hydroxyde de potassium générée par un générateur d'éluant RFC-30. Un passeur d'échantillon Dionex AS40 permet l'injection automatisée des échantillons, et l'acquisition des données est réalisée via le logiciel Chromeleon 7. La colonne ainsi que le détecteur sont thermostatés à 35°C. Le volume d'injection est de 25 µL. Les autres paramètres ont été optimisés en fonction des composés d'intérêt (facteur de dilution de l'échantillon, gradient d'élution, débit, courant) et seront présentés dans chacun des chapitres correspondants aux différents solvants de l'étude.

3.2 Méthodes permettant l'analyse des fumées traitées

L'analyse des fumées traitées émises a été réalisée à l'aide d'une technique de piégeage sur phase solide couplée à une thermodésorption et une analyse en GC-MS. Une méthode d'analyse quantitative pour 5 produits de dégradation de la MEA 30 % a été développée, validée et a fait l'objet d'une publication. Cette méthode a été appliquée tout au long du projet de thèse pour l'identification et la quantification des produits de dégradation émis avec les fumées traitées.

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Novel approach for the quantitative analysis of MEA degradation products present in gas effluent of CO_2 capture process by thermal desorption–gas chromatography–mass spectrometry: Development and validation

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ABSTRACT

Post combustion CO_2 capture using amine-based solvents is currently a very attractive technology for the treatment of flue gases produced in existing power plants. One of the main drawbacks of the process is a degradation of the solvent resulting in the formation of degradation products. Those degradation products, which are potentially detrimental to humans and environment can be emitted in the treated flue gas. The aim of this study was to develop a Thermodesorption–Gas Chromatography–Mass Spectrometry method for the simultaneous quantification in gaseous phase of a wide variety of products. A selection of five MEA degradation products is presented in this work: pyrazine, nitrosodimethylamine, 2-methylpyrazine, dimethylformamide and pyrrole. This method was validated using the accuracy profile concept with acceptance limits of 30%. The method involved active sampling on solid sorbents followed by thermal desorption and GC–MS analysis. The calibration was realized with an Adsorbent Tube Injector System at a temperature of 140 °C during 3 min. This method was applied to samples from an IFPEN CO_2 capture pilot plant: the concentration in the absorber gas effluent of each targeted compound was lower than 300 µg/m³ for nitrosodimethylamine and pyrazine, and lower than 30 µg/m³ for pyrrole, dimethylformamide and 2-methylpyrazine.

3.2.1 Introduction

In the perspective of reducing greenhouse gas emission, post-combustion capture by chemical absorption of amines seems to be the most promising method for CO_2 capture [16,22,196,197]. Amine-based CO_2 capture systems are based on chemical reactions between CO_2 and an aqueous amine solution at low temperature and atmospheric pressure during the absorption step, and the release of the amine to emit pure CO_2 at high temperature during the desorption step. Monoethanolamine (MEA) is the benchmark molecule because it is a cheap molecule highly soluble in water which absorbs a large amount of CO_2 at low CO_2 partial pressure. But MEA, like several other amines, is degraded in the presence of O_2 [15,86], NOx [87] and SOx [126] contained in the flue gas and also in the presence of CO_2 in stripper conditions [107]. Degradation products can be found in the liquid phase [120,136,198,199], i.e. the solvent, and in the gaseous phase, i.e. the treated fumes. Currently, most studies focused on the identification of MEA degradation products present in the liquid phase. Regarding treated fumes, the most commonly applied qualitative and quantitative method is the use of impingers [77]. Despite its advantages, this technique does not permit to identify compounds at trace level and concerns a limited number of compounds, mainly nitrosamines. Monitoring of the emissions can also be done using FTIR [177] but this technique do not permit to identify new degradation products, and quantification can only be done on a limited number of major compounds.

In the field of air sampling and analysis, several methods have been described in the literature. Air sample can be collected in a container, canister or plastic bags; these sampling methods permit to analyze several times the same sample by GC [200]. This method is easy to use but an instability of the compounds over time (24 hours) can be observed [201], and a preconcentration step is often needed [202]. Air samples can also be collected using impinger devices[203–205], however this method can only be applied to a specific family of compounds. The most promising method is sorbent-based sampling followed by thermal desorption (TD) and GC analysis [201,206–208,208–210]. A defined volume of air is actively sampled with a pump through a solid phase enclosed in a glass tube. This method has the advantage of being easy to use, minimizing the solvents consumption, and of being automatable. This method has already been used to identify products from the atmospheric degradation of Piperazine [180]. Moreover, the calibration can be done by spiking tubes with a small volume of solution [211,212], or by using a spiking device like a Calibration Solution Loading Rig [213] or an Adsorbent Tube Injector System (ATIS) [214]. ATIS is a device that permits the vaporization of a small volume of liquid sample into a heated chamber crossed by an inert gas flow on a sorbent tube attached to the device. In opposition to Calibration Solution Loading Rig, the ATIS volatilization chamber can be heated up to 150°C. This high temperature permits to simulate the temperature conditions of volatilization in a CO_2 capture plant, where absorption is often realized at around 120°C. To our

knowledge, the use of a sorbent-based sampling approach for the quantitative analysis of the gas phase in CO_2 capture process has never been reported in the literature. So we could propose an analytical strategy complementary to the use of impingers, both for identification and quantification purposes.

The present study aims at developing and validating by the accuracy profile approach a Thermodesorption Unit – Cooled Injection System – Gas Chromatography – Mass Spectrometry (TDU-CIS-GC-MS) method for the quantification of five targeted degradation products of amine solutions in the gas phase. The development of the method concerned both the selection of a suitable adsorbent and the choice of appropriate calibration parameters. In a recent work [32] 38 degradation products were identified in the treated fumes from IFPEN pilot plant. Among them, 5 were chosen for the development and the validation of a quantitative analysis method: pyrazine, nitrosodimethylamine, pyrrole, dimethylformamide and 2-methylpyrazine. The rationale for selecting the investigated amines was their toxicity and their regular presence during the degradation campaigns on two pilot plants: the IFPEN [32] and the EDF pilot plants [90]. Regarding EDF pilot plant, results were unpublished. The relevance of using an Internal Standard (IS), the nitrosodimethylamine-d_6, was also evaluated based on the characteristics of the accuracy profiles obtained. Finally results on samples from IFPEN pilot plant are presented. The present work is complementary to Chahen et al., 2016 [32]. In Chahen et al., 2016, only the final results of quantification were presented, whereas in our study the method is exposed in details and characterization about the trueness of the results was realized.

3.2.2 Experimental and methods

3.2.2.1 Chemicals and reagents

Pyrazine (≥99 %), Nitrosodimethylamine (NDMA) (5000 µg/mL in methanol), Nitrosodimethylamine-D6 (NDMA-D6) (98 atom % D), Pyrrole (98%), Dimethylformamide (DMF) (99.8 %) and 2-methylpyrazine (2MP) (≥99 %) were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France). Methanol was purchased from Carlo Erba Reagents (Fontenay-sous-bois, France). Ultra-pure water was produced using a Direct-Q UV 3 system (18.2 MΩ.cm) from Millipore (Molsheim, France).

3.2.2.2 Sorbent and sampling material

Sampling tubes (Tenax® TA, Tenax® GR and Carbopack™ B/Carbopack™ X) were purchased from Chromoptic (Villejust, France). Each tube has a dimension of 6mm x 60mm. Tenax TA is based on 2,6-diphenylene oxide polymer. Tenax® GR is a composite material composed of 30% graphite carbon and 70% Tenax® TA. Carbopack™ B/Carbopack™ X is a mix of two graphitized carbon blacks. Tenax® TA has a specific area of 35 m²/g and a particle size of 60/80 mesh. Carbopack™ B has a particle size of 20/40 mesh and a specific surface area of 100 m²/g. Carbopack™ X has a particle size of 60/80 mesh and a

specific area of 240 m²/g. All tubes can be heated at 300°C during desorption, except for Carbopack™ B/Carbopack™ X which can be used at up to 330°C. Active sampling was realized with a pump from Sigma Aldrich (Saint Quentin Fallavier, France). Water matrix was sampled using a reflux apparatus heated with water. Air exiting the condenser is sampled actively on Tenax TA tube. ATIS (Adsorption Tube Injector System) was purchased from Sigma Aldrich (Saint Quentin Fallavier, France).

3.2.2.3 Samples from IFPEN pilot plant

The IFPEN pilot plant is described in details in Chahen at al., 2016 [32]. It consists of two columns of around 1 meter each. The first one is used as an absorber where the MEA solvent (30 % wt of MEA in water) is loaded in CO_2. The second column is used as a stripper where the solvent is regenerated and the CO_2 is released. Each column is equipped with high performance packings for ensuring good gas/liquid mass transfer. The absorber contains DX packing and the stripper contains BX packing. Synthetic flue gas contained 80.74% of N_2, 14.12% of CO_2, 5.13% of O_2, 97 ppm of NO, 9 ppm of SO_2 and 5 ppm of NO_2. The gas flow was 1000 NL/h at 40°C and the solvent flow was 2 L/h. The total volume of solvent was 20 liters. Absorber outlet gas was directed to a heat exchanger to condensate water. Condensates was separated from gas phase in a separator. Heat exchanger followed by separator may be considered as a low efficiency water wash section: heat exchanger cooling liquid temperature is 4°C and its outlet gas temperature is 15°C avoiding condensation in the sampling tubes placed after separator. Samples from IFPEN were collected at the outlet of the absorber during one hour and the gas flow rate was regulated with a flow meter at 6 NL/h (**Figure 14**). Sampling tubes were connected with polyvinyl chloride (PVC) tubes at ambient temperature, and to avoid any biased results coming from any eventual adsorption on them, flue gas was firstly pumped during 10 min before connecting the sampling tubes. Three consecutive Tenax TA tubes were used to limit breakthrough phenomenon.

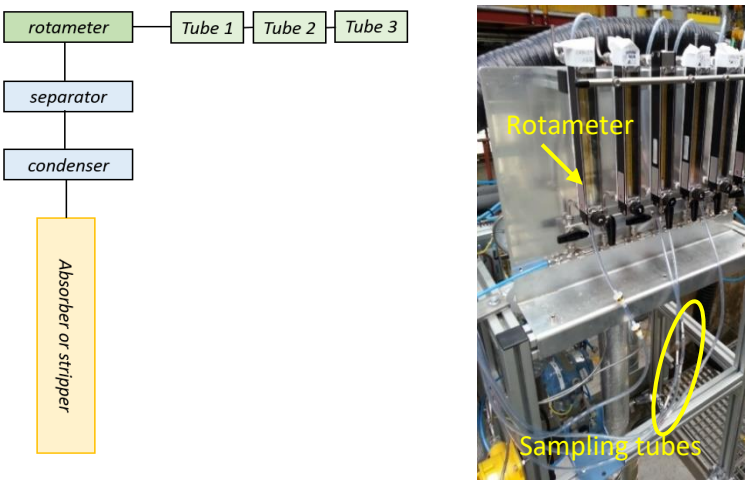


Figure 14 : Diagram and picture of the sampling system

3.2.2.4 Sample preparation for method validation

Two types of samples were prepared for the validation of the method: Tenax TA calibration tube and Tenax TA level validation tube. Five levels of concentration for the calibration and four levels of concentration for the validation were chosen (**Table 19**). All mixes were prepared in methanol with various concentration of the five compounds. Loading of the tubes was realized using ATIS. An experimental protocol was chosen after testing different temperatures and sampling times. The chamber was heated at 140°C, the N_2 flow was held at 50 mL/min and monitored with a flowmeter. 1 µL of sample was then injected in the chamber and the tube was held during 3 minutes. To mimic real samples, Tenax TA validation tubes were previously sampled with water vapor trough reflux and then spiked with validation mixes using ATIS. It is true that the representativeness of this sample can be questioned but to our knowledge, no equivalent approach to evaluate the accuracy of the impingers approach has ever been carried out. Every day, five tubes were loaded with the five standard calibration mixes and for each validation level three tubes were loaded with water matrix and then spiked with validation mix standards; one tube was only spiked with the simulated matrix to perform a blank. Each day of validation corresponds to the analysis of 18 tubes. In parallel, a second set of 18 tubes was also prepared and spiked with 1 µL of a 500 mg/L in methanol NDMA-d_6 solution (internal standard) with ATIS. Experiments were performed on 4 different days.

Table 19: Composition of the samples prepared for loading Tenax TA tubes (concentration given in mg/L)

Calibration	Pyrazine	NDMA	DMF	Pyrrole	2-MP
Mix 1	100	100	10	10	20
Mix 2	250	250	25	25	50
Mix 3	500	500	50	50	100
Mix 4	800	800	80	80	160
Mix 5	1000	1000	100	100	200
Validation	**Pyrazine**	**NDMA**	**DMF**	**Pyrrole**	**2-MP**
Level A	180	180	18	18	34
Level B	360	360	36	36	68
Level C	720	720	72	72	136
Level D	900	900	90	90	170

3.2.2.5 Analysis by thermal desorption – cryofocalisation – gas chromatography – mass spectrometry (TDU-CIS-GC-MS)

Analyses were performed using an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer (Agilent Technologies, Les Ulis, France). The device was equipped with an MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, Saint-Priest, France) that

enabled fully automated TDU-CIS analyses. The GC was equipped with a Thermal Desorption Unit (TDU) and a Cooled Injection System (CIS) packed with a Tenax TA sorbent. The tubes were desorbed with TDU with a gas flow rate of helium of 40 mL/min. 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 compounds were then cryofocussed on the CIS cooled at -40°C with liquid CO_2. At the end of desorption, CIS temperature was raised to 300°C at 720°C/min to inject the molecules in the column. The non-polar column we used (methyl 95%-phenyl 5%), was a CP-SIL-8CB ms (30m x 0.25mm x 1µm) from Agilent Technologies (Les Ulis, France). The initial temperature of 40°C was 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. Helium was used as carrier gas at 1 mL/min. Detection was performed with a mass spectrometer. The transfer line temperature to the MS detector was set at 280°C. The electronic ionization (EI) source (70 eV) was heated at 280°C, and the scan range was 25-250 amu (atomic mass unit).

3.2.2.6 Validation strategy

Validation was achieved using the total error concept and the accuracy profile [136,215–217]. This concept involves the evaluation of the trueness and the intermediate precision. Validation aims at establishing, based on experimental results, if the performances of the method are compliant with its requirements. The combination of the trueness and precision is called total error. The method permits to ensure that a proportion (β) of future measurements obtained with the analytical method is included in the acceptance limit, and therefore to know if the performance of the method is in agreement with the expectations. In the case of delicate analysis with complex matrices an acceptance limit higher than 20% is often chosen. In the study of Mompelat et al.[218], the acceptance limit was set at +/- 60%. In this study an acceptance limit of 30% has been chosen. The method will be validated only if 7 measurements out of 10 are included in the acceptance interval, in other words with β = 70%.

This statistical approach was successfully applied in various contexts. For example, methods for the detection and the quantification of neurotoxic β-*N*-methylamino-L-alanine (BMAA) in complex matrices were validated using this kind of approach [219]. In the field of CO_2 capture, a quantification method for 6 degradation compounds found in MEA solvent used for post combustion capture has also been validated using this concept [136].

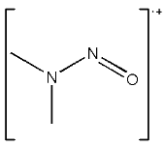
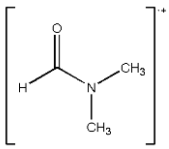
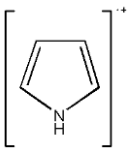
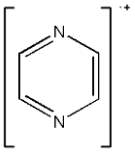
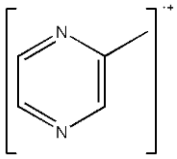
In the present study, Tenax TA tubes for calibration and validation were prepared daily. The concentrations of target compounds in the validation tubes were determined using the calibration, and were used to determine trueness and precision of the measurements. The effect of adding an internal standard on the validation results was also evaluated

3.2.3 Results

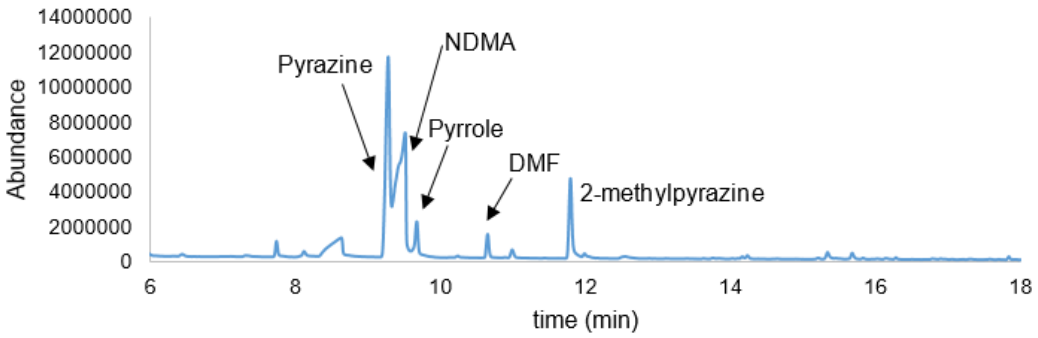
3.2.3.1 Chromatographic separation

The aim of the developed method is to estimate the amount of compounds emitted from CCS pilot plant in the gas phase. In a previous study a qualitative method that permitted to identify close to 25 compounds exiting the absorber was developed [32]. The same separation conditions were used here to quantify the 5 compounds. Because of coelutions, the peaks were systematically integrated after ion extraction, with a specific m/z fragment chosen for each compound at a specific retention time (**Table 20**). The 5 compounds were separated in 12 min (**Figure 15**).

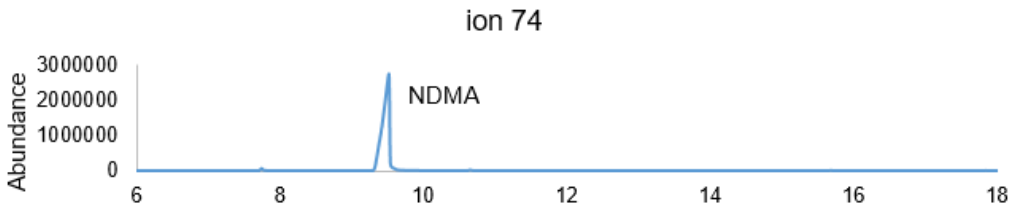
Table 20: m/z fragments selected for the ion extraction

	NDMA	DMF	Pyrrole	Pyrazine	2-MP
m/z	74	73	67	80	94
structure					

1a)



1b)



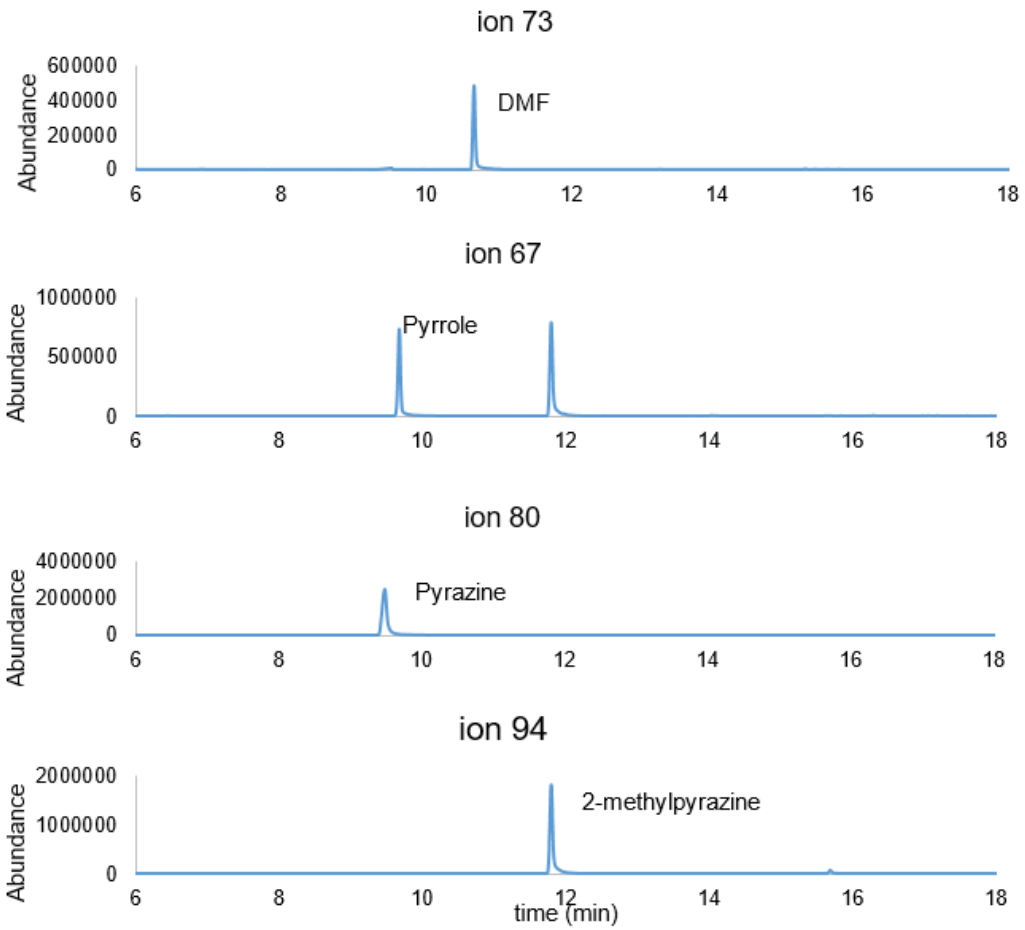


Figure 15: Chromatogram obtained after analysis by TDU-CIS-GC-MS of a Tenax tube spiked with the mix 2 by ATIS (1a: TIC; 1b: ion extraction).

3.2.3.2 Generation of gaseous standard with ATIS

Different parameters were to be optimized to ensure an optimal loading of the compounds with the ATIS: nature of the solid phase, temperature of the chamber, sampling duration, gas flow rate and injected volume. A flow rate of 50 mL/min of nitrogen was recommended by the constructor [220]. An injected volume of 1µL was chosen. Different types of sorbents are commercially available. Three of them were tested for their retentive properties on 4 compounds of interest (pyrazine, pyrrole, DMF and 2MP): Tenax® TA, Tenax® GR and Carbopack™ B/Carbopack™ X. 1µL of a standard solution of the 4 compounds was injected in the glass chamber heated at 100°C during 5 minutes. Results based on the comparison of the areas for each phase show the best performances for Tenax® TA for all the 4 compounds. **Figure 16** shows results obtained for pyrazine and pyrrole.

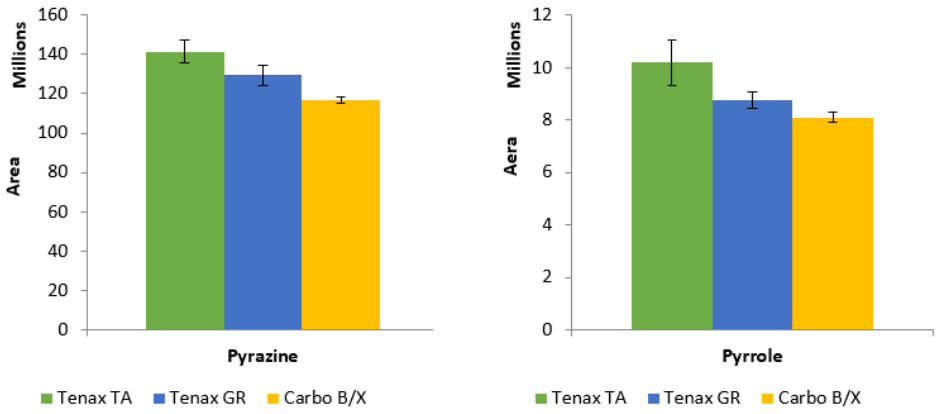


Figure 16 : Comparison of the sorbent nature on the adsorption of Pyrazine and Pyrrole (n=3)

Temperatures from 60 to 140°C were tested in this study (60; 100; 120 and 140). The best results (in terms of area of peaks) were obtained from 100°C, and no significant differences (<10%) were observed between 100, 120 and 140. The final choice was made according to the operational conditions used for CO_2 capture. Generally, the regeneration step was performed at a temperature higher than 120°C. Temperature of the glass chamber was set at 140°C. The boiling point of the studied degradation compounds will not affect the application of this method which only aims at the quantification in the gas phase. The amount of the product in the gas phase depend not only on the temperature but also on the phase ratio, and in our conditions the phase ratio guarantee the volatilization even below the boiling temperature.

Concerning the sampling time (corresponding to the duration between the injection and the removal of the tube), 4 durations were tested: 1; 2.5; 5 and 10 minutes. No significant differences (<12%) were found between the different tests. Finally, the sampling time was set at 3 minutes to ensure the rapidity of the method. The optimized parameters are presented in **Table 21**. These parameters were then applied on NDMA, for whom chemical properties were in the same range as the four other compounds, with good results.

Table 21: Optimized parameters for the generation of gaseous standards with ATIS

Nature of the solid phase	Tenax® TA
Nature of gas flow	Nitrogen at 50 mL/min
Temperature of the chamber	140°C
Sampling duration	3 min

Finally, breakthrough phenomena were studied. In order to check that compounds did not passed through the solid sorbent, three tubes were placed in series and the sampling was done according to the optimized conditions (**Table 21**); the results show no breakthrough (**Figure 17**). Less

than 1% of our compounds were found on the second and the third sampling tubes whereas usual standards using adsorbing tubes specify that the breakthrough rate must be less than 5% [221].

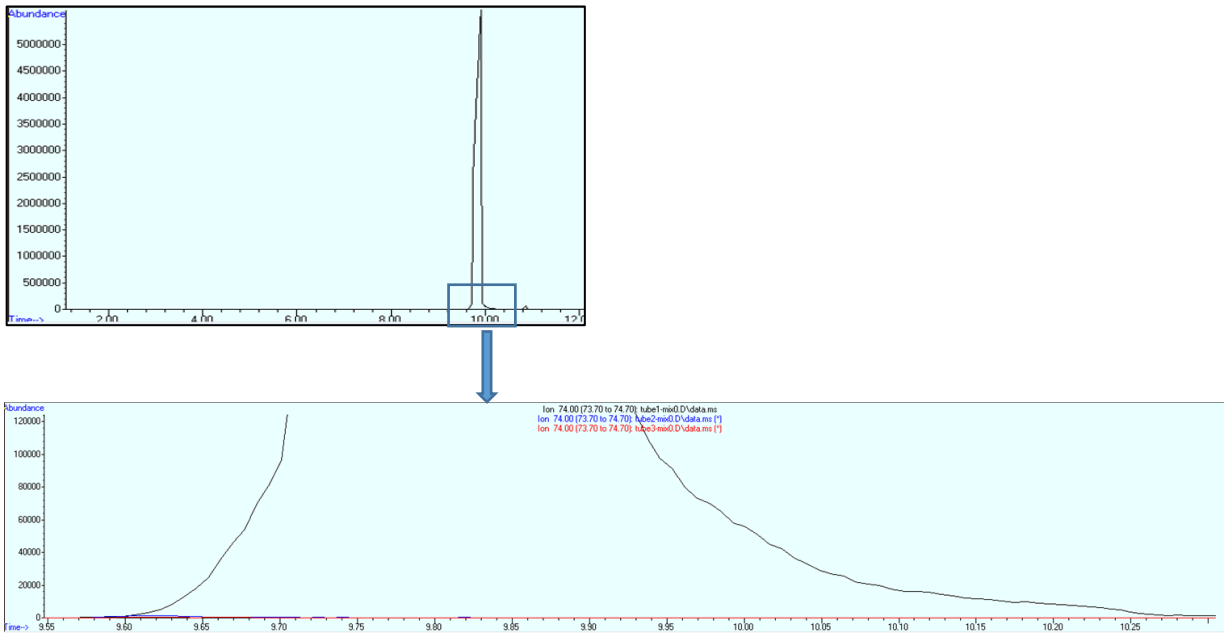


Figure 17: overlay of 3 chromatograms (NDMA m/z 74) from 3 tubes sampled in serial (1: black, 2: blue, and 3: red)

3.2.3.3 Validation of the quantitative method

The accuracy profiles of each compound were plotted according to three different calibration models: affine (two points straight line calibration), linear (straight line forced by zero) and quadratic. The results are summarized in **Table 22** and **Figure 18** gives the 3 profiles obtained for NDMA and DMF.

Table 22: Comparison of the three models for the validation of the method

	Validation		
Compounds	Affine model	Quadratic model	Linear model
NDMA	✓ +/- 30%	✓ +/- 30%	✓ +/- 30%
DMF	✓ +/- 30%	x	x
Pyrrole	✓ +/- 30%	✓ +/- 30%	x
Pyrazine	✓ +/- 30%	✓ +/- 30%	✓ +/- 30%
2MP	✓ +/- 30%	✓ +/- 30%	✓ +/- 30%

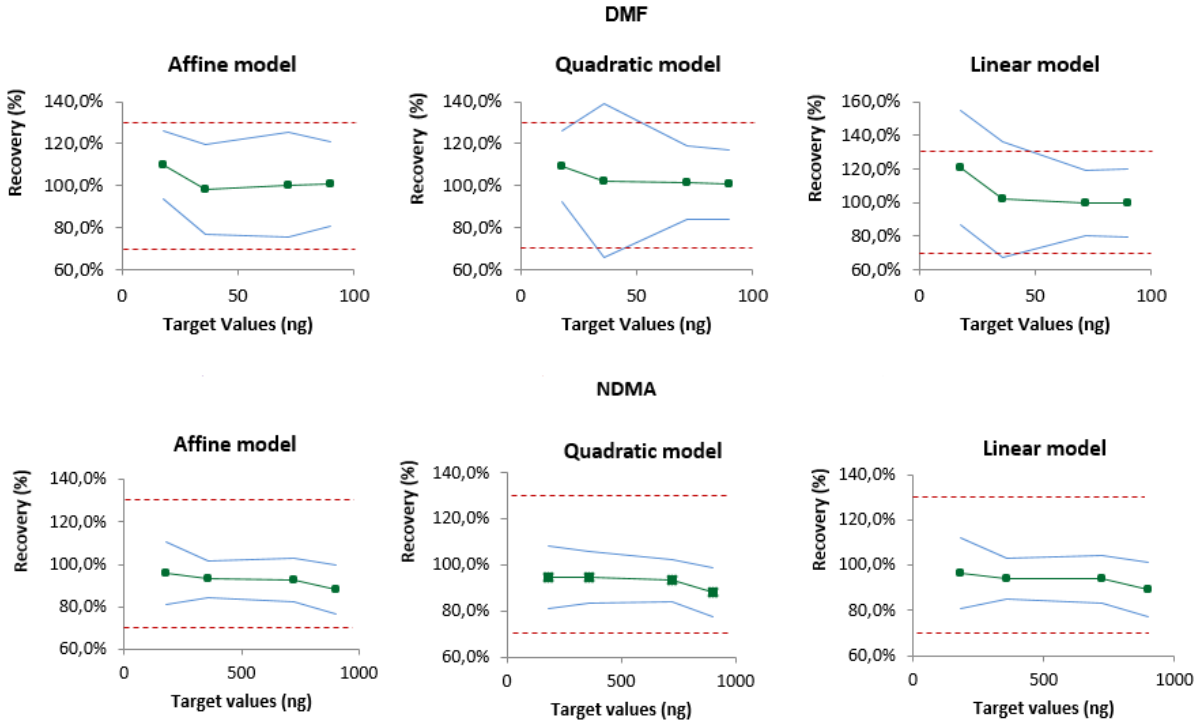


Figure 18: Accuracy profiles obtained for affine, quadratic and linear model for DMF and NDMA

For NDMA, 2MP and Pyrazine, the three models permitted a validation of the method with an accuracy of 30%. In the case of pyrrole, the linear model led to a validation on a restricted interval, which is not suitable. Concerning DMF, only the affine model led to a validation with an accuracy of 30%. Affine model has been chosen for the rest of the study. The results are shown on Figure 19. The data used to obtain these accuracy profile are presented in Annexe 3. For all the compounds except DMF, the bias tends to be negative at high concentrations, which is unusual. Concerning accuracy, all profiles have the same shape. The highest tolerance interval is observed for DMF. This can be explained by the size of the peak, which is smaller compared to the others.

The results we obtained show that the method was validated with an accuracy of 30%, and can be used in routine to quantify the emissions of the 5 compounds in the gas phase exiting a CO_2 capture pilot plant. This method has also been applied to two other compounds identified in a work to be published: ethylene glycol and diethylene glycol. For both compounds, the method cannot be validated with an accuracy of 30%.

The use of a deuterated internal standard can be a solution to compensate for the bias and improve the results. This is the purpose of the second part of this study.

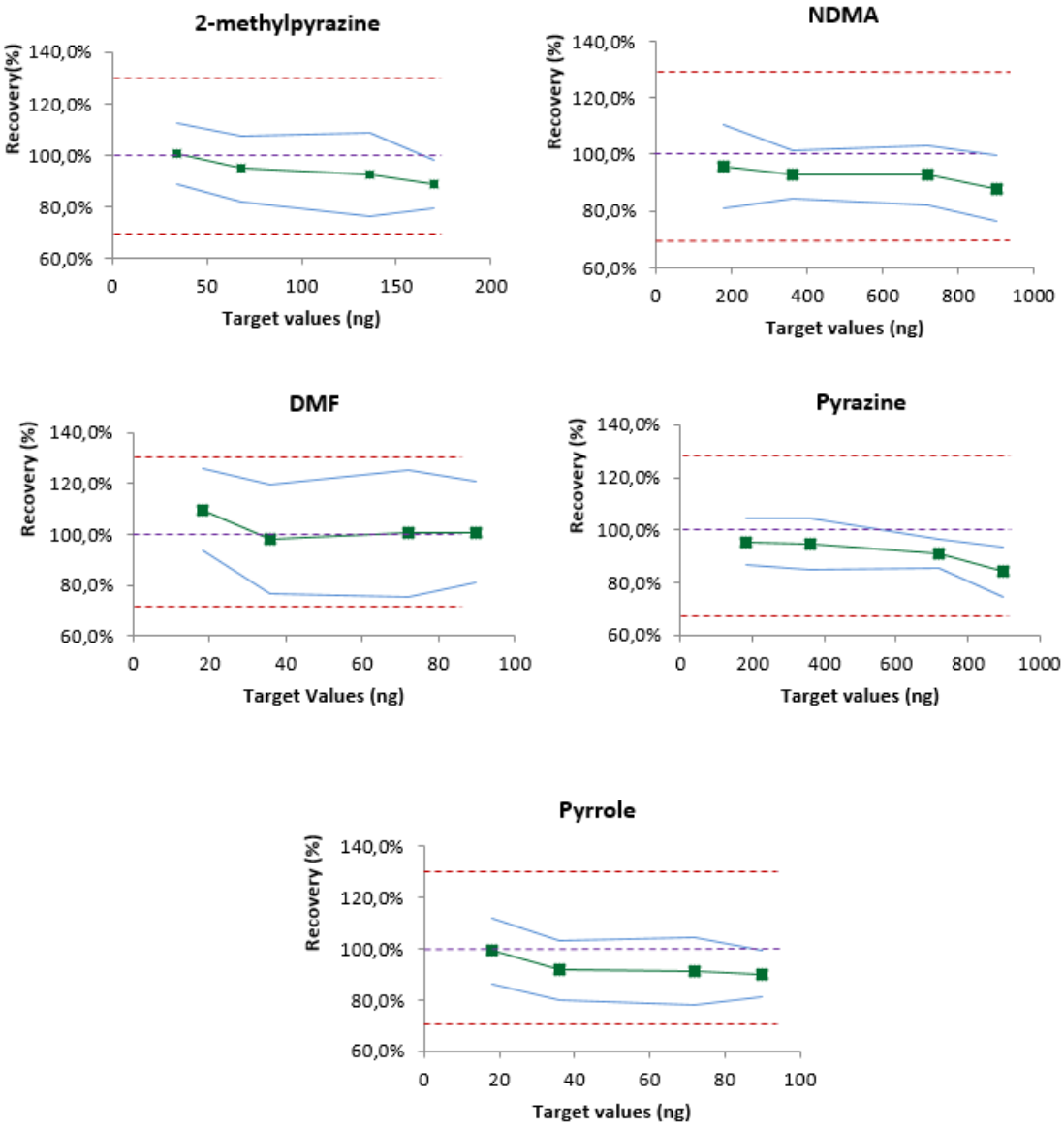


Figure 19: Accuracy profiles obtained with the affine model for the 5 compounds

3.2.3.4 Interest of using an internal standard

Generally an internal standard is known to dramatically increase the performances of a quantitative method. In the present study the impact of an internal standard on accuracy profiles was evaluated. In a first step, the interest of using a deuterated derivative of NDMA (NDMA-d_6) was

evaluated, with the objective to reach an acceptance limit of 20% or even less. The results obtained for the quantification of NDMA are shown on Figure 20.

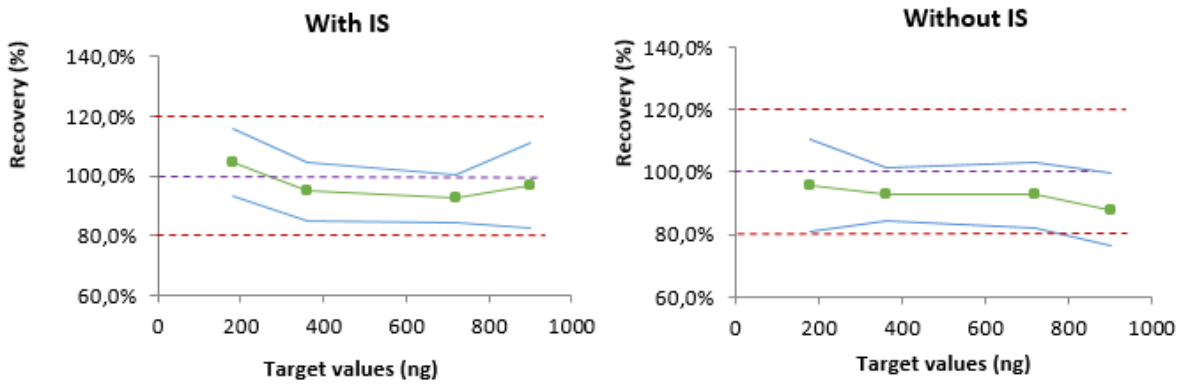


Figure 20: Evaluation of the interest of using NDMA-d6 as internal standard

As expected, the use of an internal standard compensate for the bias at high concentrations for NDMA. Moreover, it permitted to reach an accuracy of 20% on the entire range. The same approach was applied to the other compounds, using NDMA-d_6 as internal standard (Figure 21).

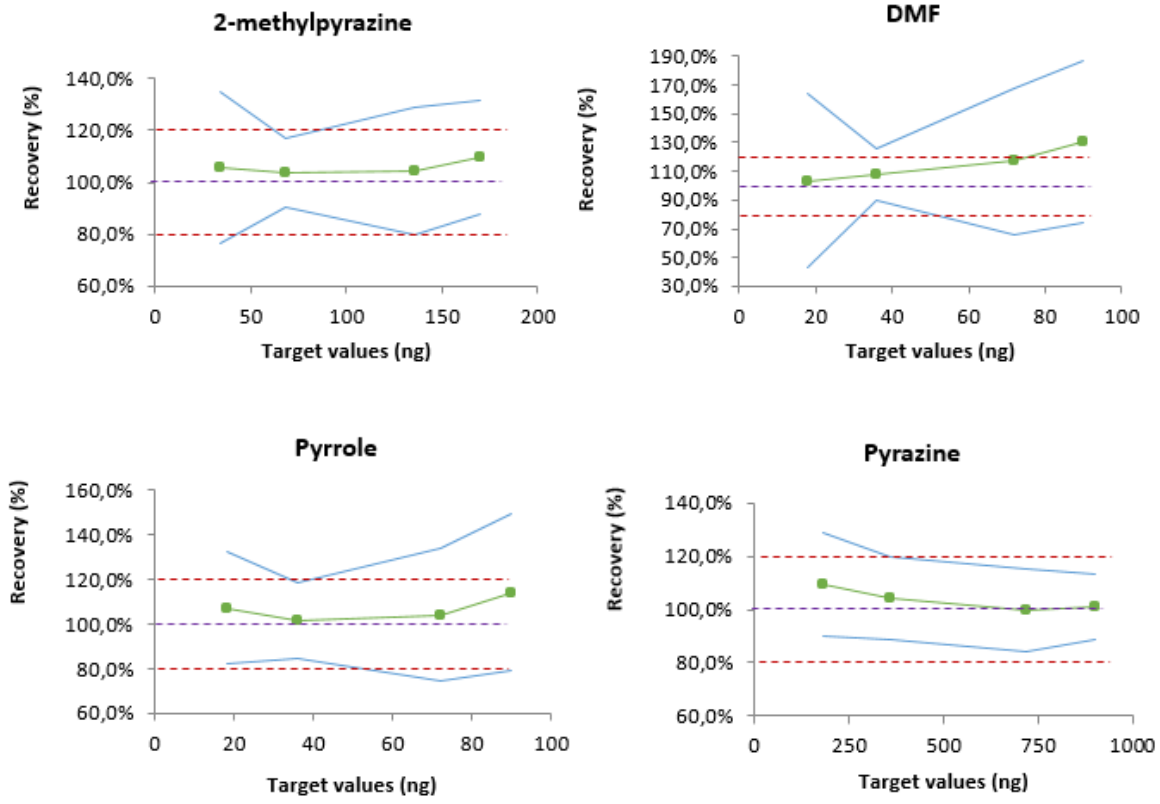


Figure 21: Accuracy profiles obtained with internal standard

The results did not meet our expectations; for the four compounds the method could not be validated with an accuracy of 20%. The bias tended to be positive at high concentrations, but with an increase of variability when comparing with results obtained without IS (Table 23).

Table 23: Mean of bias in the presence and absence of internal standard

	Without IS	With IS
NDMA	92.4%	97.1%
DMF	102.3%	114.7%
Pyrrole	93.1%	106.7%
Pyrazine	91.3%	103.6%
2MP	94.2%	105.8%

To conclude about the interest of an internal standard, it appears that in order to improve the performances, the internal standard needs to be a deuterated homologous of the compounds. Otherwise a degradation of the quantitative performances is observed rather than an improvement. Moreover, even when using a deuterated homologous compound, the improvement is rather moderate as it enables to decrease the acceptance limits from 30 % to 20 % only. This is the reason why in the present study the systematic use of internal standard is not considered compulsory.

3.2.3.5 Application on IFPEN pilot plant samples

This method has been applied to the analysis of samples from the IFPEN pilot plant. As expected, condensation never occurred on the sampled tubes during and after the sampling step. The results of the quantification are shown in Table 24.

Table 24: Results obtained from samples from IFPEN pilot plant

Weight (ng)	Tube 1	Tube 2	Tube 3	Total	Concentration in gas (µg/m^3)
Pyrrole	60	16	8	84	14
DMF	69	17	23	109	18
NDMA	1000	397	187	1584	264
Pyrazine	850	203	53	1106	184
2MP	149	0	0	149	25

The breakthrough phenomenon was negligible in the case of 2MP, pyrazine and pyrrole. Therefore, it is suspicious in the case of DMF and NDMA. Both of them are formed from dimethylamine. It is likely that reactions with dimethylamine were still going on in the gas phase. It is possible that the presence of degradation products in the matrix (like DMA) induced the formation of NDMA or DMF in the IFPEN sampling tubes. In the case of real samples, matrix is likely to be more constraining regarding breakthrough phenomena. This is the reason why three tubes have been placed in serial for the sampling. The total amount was obtained by summing the results of the three tubes. Therefore,

concentrations of DMF and NDMA might have been over evaluated, in particular for NDMA which concentration was determined at lower values by other techniques during the same pilot plant campaign.

3.2.4 Conclusion

To the best of our knowledge, this study is the first concerning the validation by accuracy profiles of a quantitative method for compounds in gas exiting CO_2 post-combustion capture pilot plants using amines. The method involved active sampling on solid phase (Tenax® TA tubes) followed by thermal desorption using TDU-CIS-GC-MS. The quantitative method was developed by spiking tubes with standard solutions with ATIS. The method showed good results and enabled the quantification of five compounds with an acceptance limit of 30%. This method was successfully applied to gas samples from an IFPEN pilot plant representative of industrial conditions, showing that the concentrations of these five compounds was lower than 300 µg/m^3. Concentrations of degradation products might be much lower in industrial conditions thanks to a more efficient water wash section than in IFPEN pilot plant. Atmospheric dispersion should be also taken into account.

This quantitative method was developed for five compounds but may be applied after development to most of the other degradation products adsorbed on Tenax tubes. Thus, this method enables the simultaneous quantification of numerous degradation products belonging to a large variety of chemical families usually not even detected by other methods. This is a real asset to characterize the gas effluents of CO_2 capture plants and to develop countermeasures limiting the emissions of amine degradation products into the atmosphere.

Acknowledgments

We would like to acknowledge the financial supports from French ANR (Agence Nationale de la Recherche) (Research Project DALMATIEN: Degradation of Amines in Liquid Matrix and Analysis: Toxicity or Innocuousness for ENvironment?) and ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie). We would like to thank Aïcha El Khamlichi (ADEME engineer) for the monitoring of this doctoral project.

Chapitre 3 : Etude du solvant 1MPZ/PZ/Eau

Ce troisième chapitre du manuscrit, composé de deux articles, présente l'étude du premier solvant innovant du projet : le mélange 1-méthylpipérazine, pipérazine et eau. Il s'agit à notre connaissance de la première étude réalisée sur ce solvant dans des conditions proches des conditions industrielles de captage du CO_2 en post-combustion.

Au total, trois campagnes de dégradation ayant duré entre 800 et 1000 heures ont été réalisées sur le dispositif expérimental du laboratoire LEMEDES-CO2. Les deux premiers essais ont été réalisés dans des conditions « idéales » (sans impuretés), en présence de fumées synthétiques uniquement constituées de N_2, de CO_2 et d'O_2. Le troisième essai a été réalisé dans l'objectif d'étudier l'impact d'impuretés (NOx et SOx) présentes dans les fumées à traiter. Pour cela, deux impuretés, les acides sulfureux (H_2SO_3) et nitrique (HNO_3) ont été sélectionnées et ajoutés sous forme liquide périodiquement au sein du réacteur.

Le premier article, soumis le 8 novembre 2017, présente les résultats des campagnes de dégradation réalisées en termes de stabilité chimique des amines constituantes du solvant, de performances de captage, et de produits de dégradation formés. Les différentes méthodes analytiques, impliquant les chromatographies en phase liquide et gazeuse, ont permis l'identification de 27 produits de dégradation. Parmi eux, 23 ont été détectés dans la phase liquide du solvant dégradé, et 14 avec les fumées traitées émises. Des méthodes de quantification ont été développées pour le suivi quantitatif des composés majoritaires présents en phase liquide et en phase gazeuse.

Le second article a pour objectif de proposer des schémas réactionnels permettant d'expliquer la formation des produits de dégradation identifiés dans le premier article. Ce travail a été réalisé avec l'appui du Pr. Véronique Bellosta de l'ESPCI Paris. Pour près de dix composés, des mécanismes de formation ont déjà été décrits dans la littérature dans le domaine de la dégradation de la PZ 40 %. Pour les autres composés, des mécanismes ont été proposés et impliquent principalement des réactions d'addition ou d'oxydation par voie radicalaire.

Monitoring of the blend 1-methylpiperazine/piperazine/water for post-combustion CO_2 capture. Part 1: identification and quantification of degradation products.

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Abstract

Post-combustion CO_2 capture process using amine solvents is limited by the high energy penalty and the irreversible degradation of amines. The present work aimed at studying the degradation of the innovative blend 1-methylpiperazine/piperazine (1MPZ/PZ: 30/10 %wt.) in a lab-scale pilot plant, LEMEDES-CO2, with conditions representative of post-combustion CO_2 capture for power generation. Degradation of the solvent was realized two times during 800 and 955 hours. Addition of acidic impurities (H_2SO_3 and HNO_3) in the second campaign was performed in order to study their impact on the solvents degradation. CO_2 loadings were determined and showed an average value of 0.28 for the lean solvent and 0.63 for the rich one. In order to identify and quantify degradation products formed, complementary analytical strategies were developed involving LC-MS, ionic chromatography and GC-MS. In order to monitor the gaseous effluents, a sampling on solid sorbents (Tenax® TA) was performed followed by a thermodesorption and GC-MS analysis. This study permitted the identification of 23 degradation products in the liquid phase of the solvent, and 14 emitted with the treated flue gas. Among them were found piperazine derivatives, alkylpyrazines and organic acids. Quantification was performed on both liquid and gaseous phases on 10 selected compounds.

1 Introduction

In 2010, 25% of the CO_2 emissions were caused by electricity and energy production [95]. Nowadays, post-combustion CO_2 capture by chemical absorption of amines is the most mature technology to reduce those emissions [16]. The process is based on the reversible absorption of CO_2 at low temperature (40-70°C) and atmospheric pressure by the amine through the formation of a carbamate. The amine is then regenerated at high temperature (100-150°C) and pressure (between 1 and 5 bars) to emit pure CO_2 intended for storage [16,25]. The main drawbacks of the capture process are the high energy penalty (around 20%) and the irreversible degradation of the amine [5,15]. Amine reacts with CO_2, O_2 but also with NOx and SOx present in the flue gas to treat (oxidative degradation). The high temperature during the regeneration step can also be involved in the thermal degradation of the solvent [25]. The benchmark amine of the process is monoethanolamine (MEA). MEA has many advantages like high solubility in water, low viscosity, low cost, but also high CO_2 cyclic capacity. However, degradation of MEA is not negligible, causing the formation of several degradation products, among them toxic compounds like nitrosamines. Those degradation products are formed in the liquid phase of the solvent, but can also be emitted with the treated flue gas [32]. Most of the studies focused today on innovative solvents with good capture capacities, but also with high resistance to degradation. Mixed amines are known to provide the advantages of individual amines without the disadvantages of each one [46]. Alkanolamines blends and piperazine blends seem to be promising in term of energy needed for the process [48,50]. PZ can be used at up to 150°C and is resistant to oxidative degradation. However, in absence of appropriate CO_2 loading, concentrated PZ can precipitate [40,222]. An alternative is the use of PZ as an activator in amine blends, like methyldiethanolamine/PZ [67], 2-methylpiperazine/PZ [70], 2-amino-2-methylpropan-1-ol/PZ [34] or *N*-(2-aminoethyl)piperazine/PZ [69], without any precipitation problems. Li et al. [49] studied the solubility and the energy for CO_2 absorption in piperazine derivatives and their mixture. The results showed that one of the most promising blend is composed of 1-methylpiperazine (1MPZ) and PZ [50]. However, no information was available about the degradation of this solvent. In the present study carried out on a lab scale pilot plant with conditions representative of post-combustion CO_2 capture during 900 hours, the blend 1-methylpiperazine/piperazine/water (30/10/60 w/w/w) was monitored in terms of stability, capture performance and degradation products formed.

2 Materials and methods

2.1 Solvent preparation

Preparation of the blend 1MPZ/PZ was realized gravimetrically by mixing and heating until dissolution commercial PZ (≥99% assay, Merck, Fontenay-sous-Bois, France) and 1MPZ (99% assay, Sigma-Aldrich, Saint-Quentin-Fallavier, France) with distilled water (18.2 MΩ).

2.2 Chemicals

Ethylenediamine (99%) was purchased from Alfa Aesar (Schiltigheim, France). Ammonia 32% extra pure was purchased from Merck (Lyon, France). Pyrazine (≥99%), 1-methyl-1H-pyrrole (99%), 2-methylpyrazine (≥99%), 1,4-dimethylpiperazine (98%), 1-methylpiperazine (99%), piperazine (reagent plus, 99%), 2,6-dimethylpyrazine (≥98%), 2,3-dimethylpyrazine (≥95%), 2-ethylpyrazine (≥98%), 1,2,4-trimethylpiperazine, 2-ethyl-3-methylpyrazine (≥98%), 2,3,5-trimethylpyrazine (≥99%), 2-ethylhexanol, 2-acetylpyrazine (≥99%), 1-piperazineethanamine (99%), 1,4-diformylpiperazine (98%), 1-piperazinecarboxaldehyde (≥90%), 2,2'-bipyrazine (97%), 2-piperazinone 97%, acetaldehyde (anhydrous, ≥99.5%), methylamine (40 % wt. in H_2O), 1,2-diaminopropane (99%), *N*-methylethylenediamine (95%), sodium lactate (98%), propanoic acid (99.5%) were purchased from Sigma Aldrich (Saint-Quentin-Fallavier, France). Oxalic acid (99.8%) was purchased from VWR (Fontenay-sous-Bois, France). Formic acid (99%) was purchased from Carlo Erba (Val-de-Reuil, France).

2.3 Pilot plant description

The blend 1MPZ/PZ/Water (30/10/60 w/w/w) was degraded on the LEMEDES-CO2 lab-scale equipment [90,158] from EDF R&D (Figure 22). LEMEDES-CO2 lab-scale apparatus has been designed to reproduce the dynamic cycling of the solvent between the absorber and the stripper columns. The technical features of this original lab-scale apparatus were based on the chemical absorption principle with short cycles of absorption and stripping, fast heating up and cooling down of the solvent and an important gas flow rate (1800 NL/h). It was designed with a single semi-batch glass reactor acting both as an absorber and a stripper. The reactor was around 350 mm in height with a diameter of 60 mm. All piping was made of hastelloy in order to uncouple oxidation and corrosion phenomenon. LEMEDES-CO2 lab-scale equipment has firstly been designed to study the MEA degradation; it is therefore adapted to operate with temperatures and pressures in the same range as those used for MEA degradation [32,82,87,147,178,223]. The MEA experimental protocol, more particularly the absorption and stripping temperatures, was used as a basis to this amine blend, in order to compare its stability with MEA's.

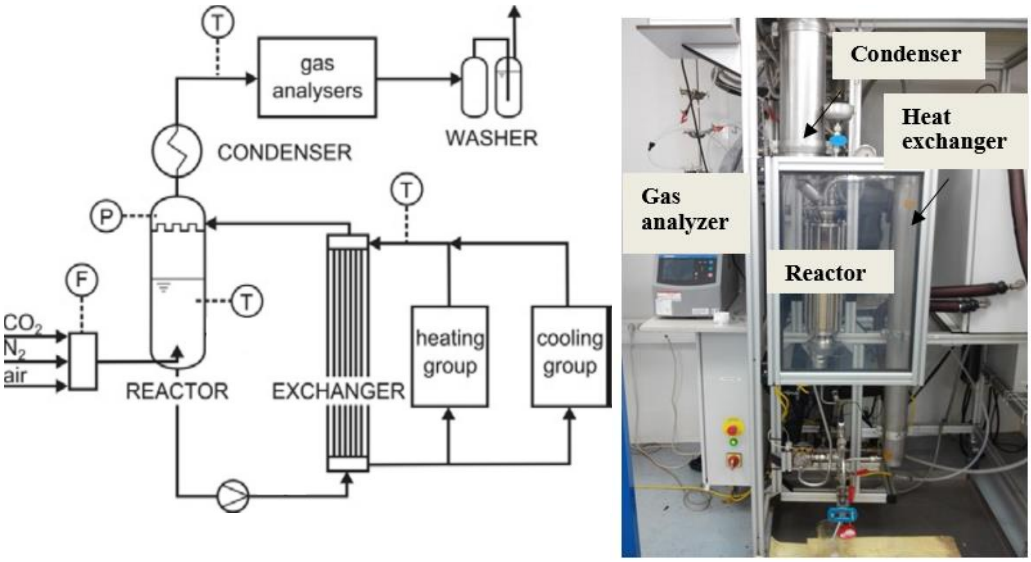

Figure 22: LEMEDES-CO2 lab-scale equipment (F: flowmeter; T: temperature probe; P: pressure sensor).

Two campaigns lasted around 900 h (400 cycles). A gas blender on the test bed controlled flow rates and composition of the synthetic flue gas. It contained 15% CO_2 (≥99.7%, Air Liquide, Mitry-Mory, France), 82% N_2 (≥99.995%, Air Liquide, Mitry-Mory, France) and 3% air (composed of 20.9% of dioxygen). Total absolute pressure during absorption was 1.0 bar. The gas flow rate was 1800 NL/h at 42°C and the solvent flow rate was 3L/min. The total volume of solvent was 1.5 L. Gas flow was injected in the bottom of the reactor after bubbling in a humidifier and a separator. The solvent was brought into contact with the synthetic flue gas (in a counter current way) and circulated in a heat exchanger supplied with mineral oil enabling a rapid heating and cooling of the solvent. Condensates were separated from gas phase in a condenser up to the reactor. Condenser was supplied with water temperature < 10°C. A fraction of gas was analysed with gas analyser, for monitoring of CO_2 and O_2 at high and low contents, and after wash the rest exhausted through outlet piping. For the desorption step a pressure of 4 bar in the reactor was first applied with N_2 as entering flue gas during 1 min. Then the solvent was heated up to 123°C and maintained during 6 seconds which enabled the regeneration of the amine and the release of CO_2. Released CO_2 was exhausted.

The control system followed many parameters such as temperature, pressure and gas composition and operated continuously and automatically (24h/24 and 7d/7). Samples were taken from the liquid and gas phase and analysed at regular intervals. Solvent sampling was done one time a week at the bottom of the reactor for the CO_2 rich amine and the CO_2 lean amine. All samples were stored in brown flaks at 4°C.

The parameters of each campaign are given in Table 25. The first campaign was repeated in order to confirm the robustness of the degradation method; the same results were obtained in terms of CO_2

loadings and degradation products formed. The aim of the second campaign was to study the impact of acidic impurities i.e. sulphurous acid (H_2SO_3) and nitric acid (HNO_3).

Table 25: Characteristics of the two degradation campaigns

Campaign		A	B
Composition (1MPZ/PZ % wt.)		30/10	
Absorption	Temperature	42°C	
	Gas composition	15% CO_2 / 82% N_2 / 3% Air	
	Pressure	1 bar	
	Duration	80 min	
Desorption	Temperature	123°C	
	Gas composition	15% CO_2 / 82% N_2 / 3% Air	
	Pressure	4 bar	
	Duration	30 min (including heating and cooling times)	
Duration		800 h	955 h
Number of cycles		400	478
Impurity additives		-	H_2SO_3 (4.8 g / week) HNO_3 (3.9 g / week)

2.4 Water content measurement

Water content of the amine blend was measured using a V20 Karl Fisher from Mettler (Viroflay, France). The reagent used for the titration was Hydranal-Composite 5K and Methanol dry from Sigma Aldrich (Saint-Quentin-Fallavier, France). Uncertainty of measurements corresponding to the repeatability of the results was ± 5%.

2.5 Amine titration

Total amine concentration was measured by acidic titration using a T50 Karl Fisher from Mettler (Viroflay, France) titrator with automatic equivalence point detection. 0.4 to 0.6 g of sample were added to 50 mL of deionized water, and placed on the device. The solution was then titrated with 0.2 M HCl to reach a pH of 2. The amount of acid needed to reach the second equivalence point was used to calculate the total amine concentration. Uncertainty of measurements corresponding to the repeatability of the results was ± 5%.

2.6 Total Inorganic Carbon measurement (TIC)

A TOC-L CSH from Shimadzu (Marne-la-Vallée, France) was used to determine the total inorganic carbon content of the solvent. The 50X diluted sample was acidified in 30 wt% phosphoric acid causing inorganic carbon to be evolved as gaseous CO_2. The CO_2 emitted was then measured with an infrared analyzer. Previous calibration of the dispositive (using a 1000 ppm standard) permitted to calculate the

amount of inorganic carbon contained in the solution. CO_2 loading was then calculated using the amount of inorganic carbon in mol/kg divided by the total amine concentration in mol/kg. Uncertainty of measurements corresponding to the repeatability of the results was ± 5%.

2.7 Ionic chromatography (IC)

2.7.1 Cation ionic chromatography

PZ and 1MPZ were individually quantified using ionic chromatography (IC). An ICS 1000 equipped with an autosampler from Thermo Fisher (Villebon-sur-Yvette, France) was used. Samples were diluted 20000 times with water, and then 25 µL were injected for the separation. A guard column (IonPacT^{M} CG19RFIC^{TM} 4 x 50 mm) was placed before the analytical column (IonPacT^{M} CS19RFIC^{TM} 4 x 250 mm) to prevent the analytical column from contaminations. An eluent generator permitted the delivery of adjustable concentrations of methanesulfonic acid (MSA). The system was equipped with a 4-mm anionic Suppressor. Detection was performed with a conductimetric cell. Both columns and conductimetric detectors were thermostated at 35°C. The separation was realized in isocratic mode with 25 mM of MSA and permitted the separation of the two amines in 10 min. A quantification method has been developed and validated with the total error concept and the accuracy profile [136,192] with an acceptance limit of 10% in the range of interest. The same device was also used to track degradation products formed in the liquid phase of the solvent. In this case, the solvent was diluted 1000 times in water before injection. The initial MSA concentration was 2mM, raised at 35 mM from 35 to 135 min. The other parameters were the same as previously described.

2.7.2 Anion ionic chromatography

Anionic species were identified and quantified using ionic chromatography (IC). The same device as previously described was used. A guard column (IonPac AG11 4 x 50 mm) was placed before the analytical column (IonPac AS11 4 x 250 mm) to prevent the analytical column from contaminations. The system was equipped with a 4-mm cationic suppressor. Detection was performed with a conductimetric cell. Both columns and conductimetric detectors were thermostated at 35°C. The separation was realized with an elution gradient of KOH starting from 0.5 mM from 0 to 30 min then raised to 40 mM in 30 min then decreased at 0.5 mM from 80 to 120 min. The flow rate was 1.5 mL/min and the applied current of 149 mA. The columns and the detector were thermostated at 35°C. A quantification method was developed and validated using the accuracy profile concept for formic and oxalic acids with acceptance limits of 20%.

2.8 Gas chromatography-Mass Spectrometry (GC-MS)

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer from Agilent Technologies (Massy, France). The device was equipped with a MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated liquid injections, HS-SPME and thermodesorption (TDU) analyses. Two columns (Chromoptic, Villejust, France) were used to separate the compounds; a non-polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm, 1 µm) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm, 0.5 µm). 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. Detection was performed with a mass spectrometer using electronic ionization (EI) source (70 eV) heated to 250°C. The scan range was 25 to 250 amu. NIST spectra data base was used for the peaks identification. Identification proposals were confirmed by the injection of commercial standards when available.

2.8.1 Direct liquid injections

For liquid injection procedures, real samples were diluted 10 times in methanol before injecting 1µL in split mode (1:5) at 280°C. Quantification of 3 compounds namely pyrazine, *N*-formylpiperazine (FPZ) and 1,4-dimethylpiperazine (14DMPZ) was realized according to the standard addition method for pyrazine and FPZ (Annexe 4), and using external calibration for 14DMPZ. Standard addition method has been used for two compounds in order to avoid a highlighted matrix effect. Both calibrations were performed using an internal standard: 1,3-dimethyltetrahydro-3,4,5,6,-tetrahydropyrimidinone.

2.8.2 Headspace Solid Phase MicroExtraction – GC-MS (HS-SPME-GC-MS)

For Head Space – Solid Phase MicroExtraction (HS-SPME) procedures, the volume of sample introduced in the 20 mL HS vial was 5 mL. A 75µm Carboxen/PDMS SPME fibre obtained from Supelco (Sigma Aldrich, Saint-Quentin-Fallavier, France) was used. The fully automated HS-SPME procedure was the same as described by Rey et al., 2013 [199]. This method was initially developed for the identification and the quantification of alkylpyrazines. It was applied here to the identification of other degradation products present in the liquid phase.

2.9 LC-MS

Analysis were performed on a LC Agilent 1100 coupled with a MS Waters micromass ZQ 4000 with ESI source. It was used in positive mode with a source temperature of 120°C. The chromatographic separation was realized with a Thermo Hypercarb column (150 mm x 3 mm, 5 µm-particles). The mobile phase was composed of (A) water + ammonia to reach a pH of 10.8 and (B) Methanol + 0.1% formic acid at a flow rate of 350 µL/min. 5 µL of sample previously diluted by 100 in mobile phase A were injected. The solvent gradient started at 100% of A for 10 min before reaching a ratio of 80:20 (A:B v:v) in 8 min. This ratio was maintained for 12 min.

2.10 Gas phase sampling

Gas sampling was performed in order to identify degradation products emitted in the gas phase during the process. The same method as described in our previous study [192] was applied here. A Tenax TA® tube (Gerstel, Saint-Priest, France) was placed after the condenser to avoid any humidity problems, and a flow of 200 mL/min during 60 min was pumped through the solid phase. Samplings for quantitative analyses were realized using three Tenax TA® tubes placed in serial with a sampling flow of 100 mL/min during 60 min. Flow rate was controlled with a rotameter, and air was pumped with an ambient air sampler from Supelco (Sigma Aldrich, Saint Quentin Fallavier, France).

2.11 Analysis of the gas phase by TDU-CIS-GC-MS

For thermodesorption of tubes, gas flow rate of helium 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 cryofocused in the injector at -40°C with liquid CO_2. Then temperature increased from -40°C to 300°C at 12°C/s and the molecules were injected in the column in splitless mode. The same GC/MS method as for liquid samples was used with a CP-SIL8 CB-MS column. Quantitative monitoring was realized on 5 compounds (14DMPZ, pyrazine, 1MPZ, 2-methylpyrazine and 2-acetylpyrazine) using the method described in Cuccia et al. [192]. Calibration of the five compounds was realized with ATIS (Adsorbent Tube Injector System).

3 Results

3.1 Monitoring of the degradation campaign

The monitoring consisted in the analysis of water content, total amine concentration, and Total Inorganic Carbon for the determination of the CO_2 loading. The **Figure 23** and **Figure 24** present the results obtained during the campaigns. Variations of the water content can be seen during time and can be explained because of the difficult equilibrium between water loss during cycles and the gas entering humidity. These results are in agreement with the total amine content, following the increase and decrease of the water content. The CO_2 loading results showed an average value of 0.28 for the lean solvent and 0.63 for the rich one. These values are in full agreement with those predicted in the literature [34] and are quite stable during time.

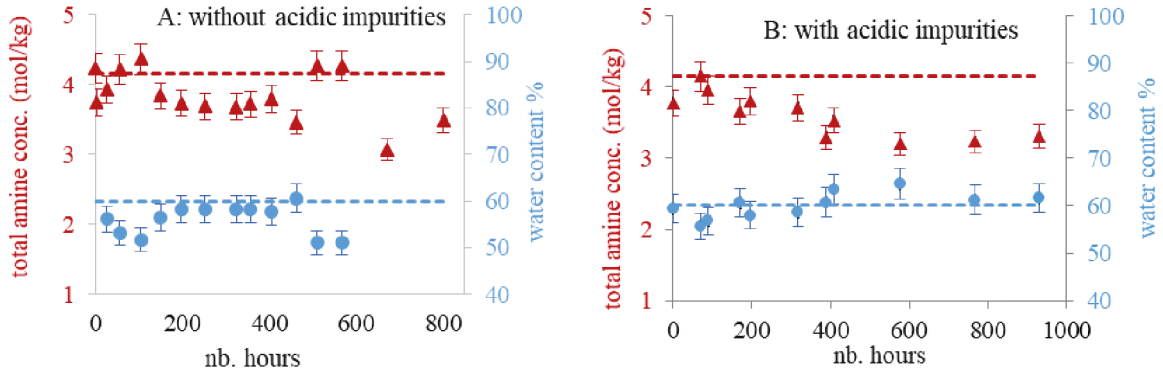

Figure 23: Monitoring of the water and amine concentrations during the degradation campaigns. Error bars correspond to uncertainty of 5% of the method.

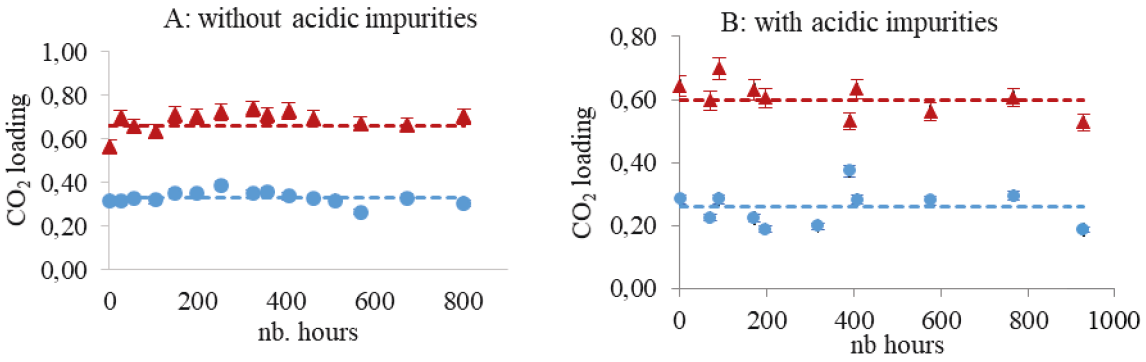

Figure 24: Monitoring of the CO_2 loading. Error bars correspond to uncertainty of 5% of the method.

In order to have more information regarding the stability of the amines in solution, samples were analyzed by IC for their content in 1MPZ and PZ. Results are shown in the **Figure 25**. A slow decrease of the constituent amines of the solvent can be seen over time. This decrease is significant in the campaign performed without acidic impurities and is in the range of 0.2 and 0.06 points per day respectively for 1MPZ and PZ. The campaign realized with acidic impurities did not show any significant degradation. This result can be explained by the dispersive nature of the points in the last case. The next step of this study is the identification of potential degradation products formed during the process.

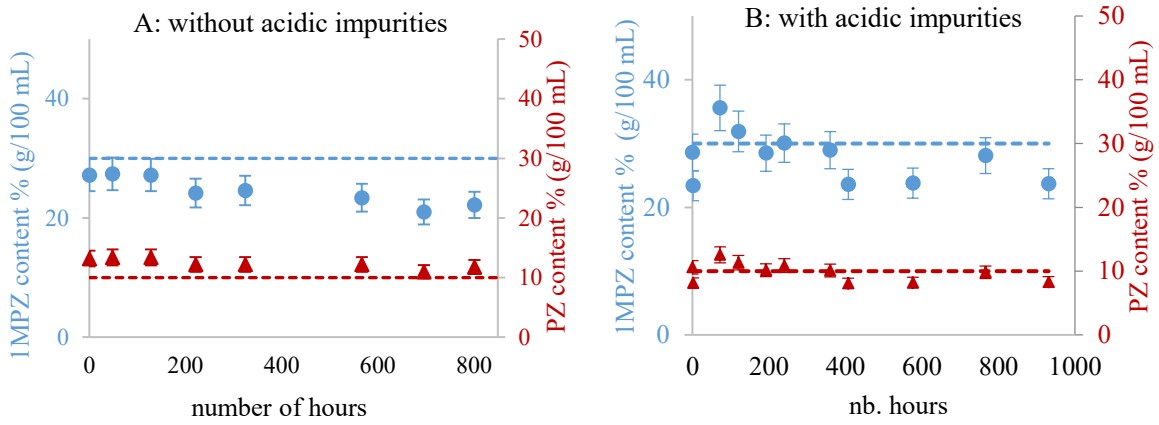

Figure 25: Monitoring of the concentration of 1MPZ and PZ during the degradation campaign. The error bar correspond to the acceptance limit of 10% of the quantification method.

3.2 Degradation products in the liquid phase of the solvent

3.2.1 Identification of degradation products

In order to identify degradation products formed in the liquid phase of the solvent, complementary analytical strategies involving GC-MS, LC-MS and IC were developed. 23 compounds were listed during the two degradation campaigns (**Table 26**). Identification was confirmed with the injection of commercial standards, and by comparing their retention time and mass spectra with real samples when mass spectrometry is the detector. Otherwise, real samples were spiked with known amounts of the standard compounds in order to confirm the presence of the target compounds by an increase of the peak of interest. The addition of acidic impurities in campaign B had no impact on the nature of the identified compounds.

Table 26: Degradation compounds identified in the liquid phase of the solvent

	compound	CAS	Analysis methods			
			GC-MS	HS-SPME-GC-MS	IC	LC-MS
Alkylpyrazines	Pyrazine	290-37-9	X	X		X
	2,6-Dimethylpyrazine	105-50-9		X		
	2,3-Dimethylpyrazine	5910-89-4		X		
	2-Ethylpyrazine	13925-00-3		X		
	2-Methylpyrazine	109-08-0	X	X		
	2-Ethyl-3-methylpyrazine	15707-23-0		X		
	2,3,5-Trimethylpyrazine	14667-55-1	X			
	2,2'-Bipyrazine	10199005	X	X		
Piperazine derivatives	1,4-Dimethylpiperazine	106-58-1	X	X	X	
	1,2,4-Trimethylpiperazine	120-85-4	X	X		
	1,4-Diformylpiperazine	4164-39-0	X	X		
	1-Formylpiperazine	7755922	X	X	X	X
	2-Piperazinone	5625-67-2	X			
Aliphatic amines	Ethylenediamine	107-15-3			X	
	Ammonia	1336-21-6			X	
	Methylamine	74-89-5			X	X
	1,2-Diaminopropane	78-90-0			X	
	N-Methyl-ethylenediamine	109-81-9			X	
Organic acids	Oxalic acid	144-62-7			X	
	Lactic acid	79-33-4			X	
	Formic acid	64-18-6			X	
	Propionic acid	79-09-4			X	
	Acetaldehyde	75-07-0				X

The main classes of identified compounds were piperazine derivatives, alkylpyrazines, organic acids and aliphatic amines. Among them, four had already been listed as thermal degradation products of concentrated piperazine [91,122] namely, ethylenediamine, formic acid, *N*-formylpiperazine and

ammonia. Eight alkylpyrazines have been identified, mainly by HS-SPME-GC-MS except for 2,3,5-trimethylpyrazine which has been identified by direct liquid injection GC-MS. Piperazine derivatives have been identified by GC-MS, and aliphatic amines by IC. Regarding organic acids, their analysis has exclusively been realized by IC. Oxalic, formic, lactic and propionic acids are heat stable salts formed because of oxidative degradation. Acetic and glycolic acids were suspected to be present, however the two compounds eluted at the same retention time even after many optimizations of the separation method. A peak at 18 min corresponding to the two compounds is present in the chromatogram corresponding to the 800 h degraded solvent.

This list is not exhaustive as other degradation products present at concentration under limits of detection may be present in the solvent. Two examples of chromatograms obtained for the analysis of degraded samples by GC-MS and IC are given in Figure 26 and Figure 27.

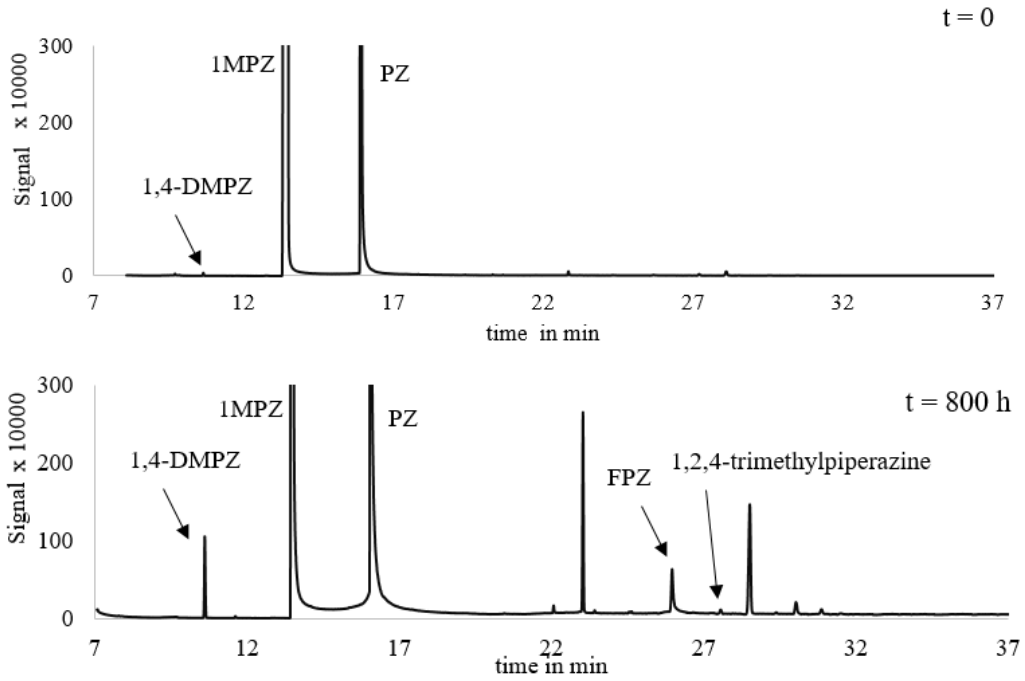

Figure 26: Chromatogram obtained after the analysis by GC-MS (DBWAX column) of a sample from campaign A (without acidic impurities) at 800 hours of degradation.

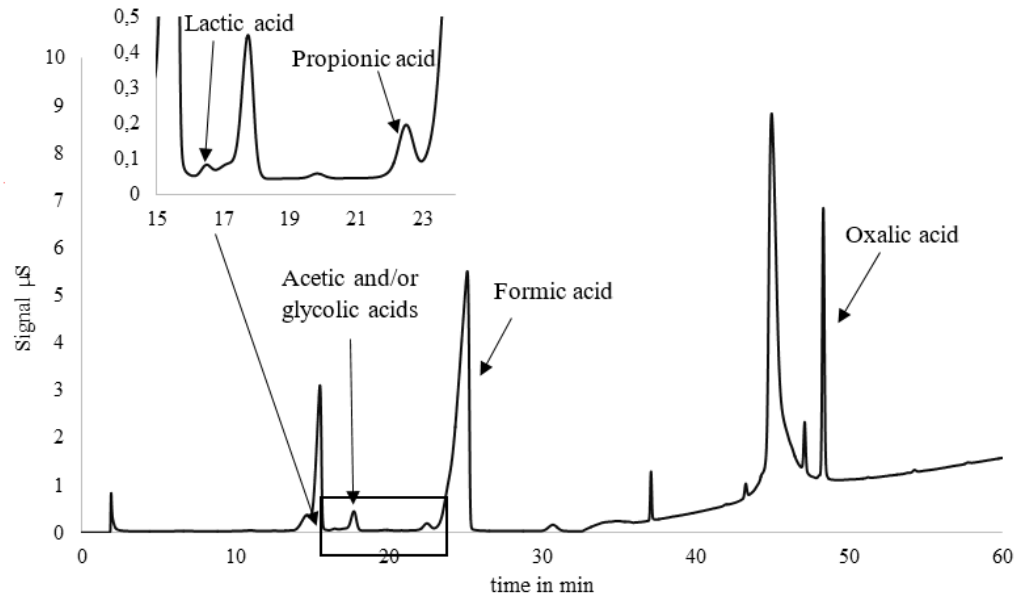

Figure 27: Chromatogram obtained after the analysis by IC of a sample from campaign A (without acidic impurities) at 567 hours of degradation.

Among the identified compounds, seven were selected for the development of quantitative methods: formic, oxalic, lactic and propionic acids by IC, and pyrazine, 1,4-dimethylpyrazine and *N*-formylpiperazine by GC-MS.

3.2.2 Quantification of targeted compounds

Figure 28 shows the evolution of the concentrations of formic and oxalic acid in the campaigns A and B. The results show an increase of the formic acid content during time reaching 3260 mg/L and 1733 mg/L respectively for the campaigns A and B. Oxalic acid's behavior was quite the same with a maximum concentration of 1230 mg/L and 563 mg/L respectively for the campaigns A and B. A ratio close to two could be seen between the two campaigns. The only difference between both campaigns was the presence of sulfurous and nitric acid in the last one, which could be the reason for these different concentrations. Lactic acid concentration was close to 5 mg/L at the end of the degradations campaigns A and B. Propionic acid concentration was lower than 60 mg/L for the campaign A and lower than 13 mg/L for the campaign B.

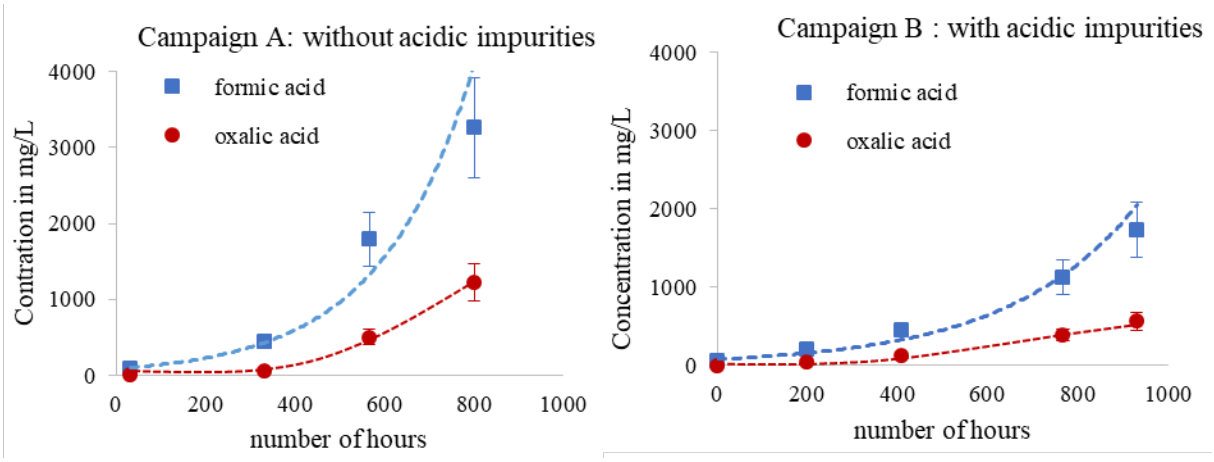

Figure 28: Evolution of the formic and oxalic acids concentration in the campaigns A and B. The error bar correspond to the acceptance limit of 20% of the quantification method.

The evolution of the concentration of pyrazine, 1,4-DMPZ and FPZ is given in **Figure 29** both for campaigns A and B. Quantitation has been done with standard addition method for pyrazine and FPZ because of a major matrix effect. This method has for consequence a highest uncertainty of the measured values [224]. Pyrazine is present in the initial solvent as impurity and its concentration remains stable during the entire campaign at concentrations close to 20 and 80 mg/L respectively for campaigns A and B. These different values can be explained by the accuracy of the method (acceptance limits of 50%), and by the difference of commercial batches used for the two campaigns. FPZ and 1.4DMPZ content increases during time to reach a concentration of 2000 and 1500 mg/L (+/-50%) for both campaigns respectively for the two compounds. No significant differences can be seen for those two compounds between the two campaigns.

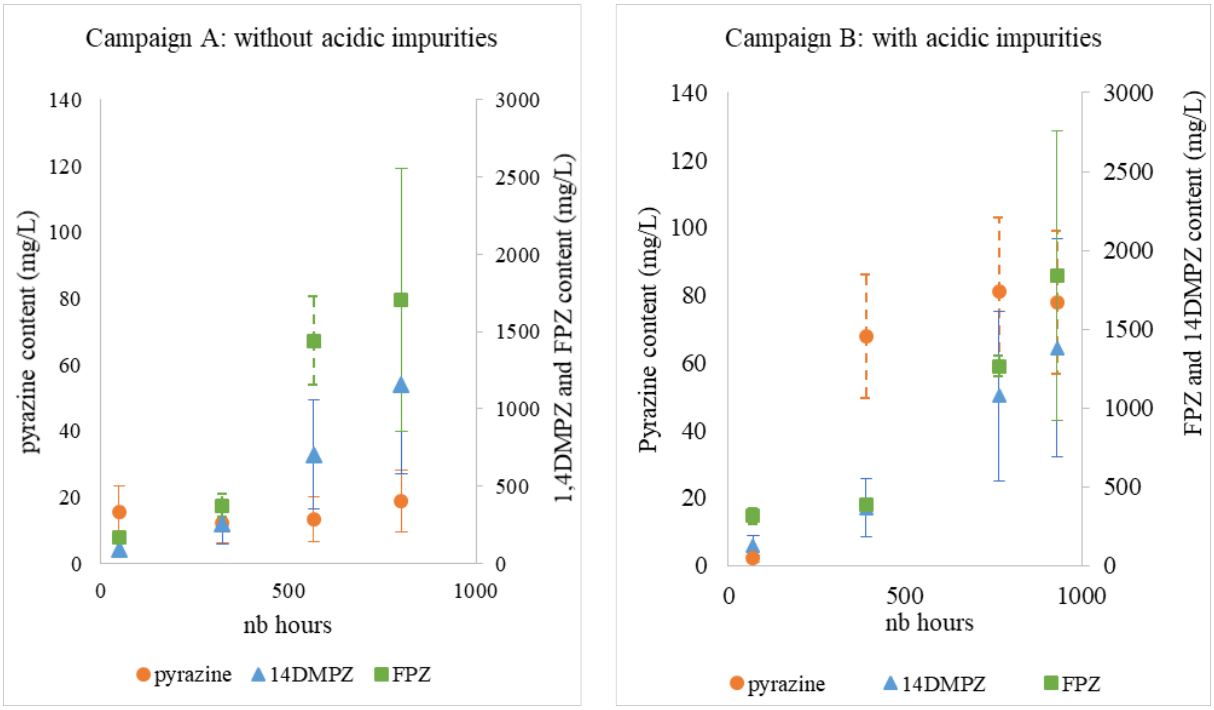

Figure 29: Evolution of the concentration of pyrazine, 1,4-DMPZ and FPZ in the campaigns A and B. The error bars indicated in dotted lines correspond to uncertainty of the method corresponding to the repeatability of the results. The error bars in unbroken lines correspond to the acceptance limit of 50% of the quantification method (according to the accuracy profile concept).

3.3 Monitoring of the gaseous emissions

Among the degradation products formed in the liquid phase of the solvent, some can be emitted with the treated flus gas. The aim of this part of the study was to identify degradation products in the gaseous effluents. The method involved is described in section 2.9. This is to our knowledge the first study about the characterization of the emissions from the blend 1MPZ/PZ on a CO_2 capture pilot plant. 14 organic compounds were identified as degradation products in the flue gas emitted. These compounds are presented in **Table 27** and an example of obtained chromatogram is given in **Figure 30**. Confirmation of the identification was realized by analyzing commercial standards. 10 pyrazine derivatives were identified. Among them, 7 were identified in the liquid phase of the solvent (compounds in italic in **Table 27**). White et al. (2015) [180] investigated the atmospheric degradation of PZ using FTIR, sampling on Tenax® TA tubes and on DNPH (2,4-dinitrophenylhydrazine) cartridges and also identified (without confirming) pyrazine as degradation product. 5 piperazine derivatives were identified, among them 1MPZ the constituent amine of the solvent, which seems to be the most emitted compound regarding to the intensity of the pic in the chromatogram (**Figure 30**), and 1-piperazineethanamine. 1-piperazineethanamine has already been identified as thermal degradation product of PZ by Freeman et al. (2012) [91]. Emissions of 1MPZ could be caused by a vaporization

phenomenon, but no studies are available about the vapor-liquid equilibrium of the blend 1MPZ/PZ/Water to confirm this hypothesis.

Table 27: Compounds identified in the gaseous emissions

	Peak nb	compound	CAS
Pyrazine derivatives	*1*	*Pyrazine*	*290-37-9*
	2	*2,6-Dimethylpyrazine*	*105-50-9*
	3	*2-Methylpyrazine*	*109-08-0*
	4	*2-Ethyl-3-methylpyrazine*	*15707-23-0*
	5	*2,3,5-Trimethylpyrazine*	*14667-55-1*
	6	*2,3-Dimethylpyrazine*	*5910-89-4*
	7	2-Acetylpyrazine	22047-25-2
	8	*2,2'-Bipyrazine*	*10199-00-5*
Piperazine derivatives	*9*	*1,4-Dimethylpiperazine*	*106-58-1*
	10	1-Methylpiperazine	109-01-3
	11	*1,2,4-Trimethylpiperazine*	*120-85-4*
	12	1-Piperazineethanamine	140-31-8
	13	*1,4-Diformylpiperazine*	*4164-39-0*
Amine derivative	14	1-Methyl-1H-pyrrole	96-54-8
Alcohol derivative	15	2-Ethylhexanol	104-76-7

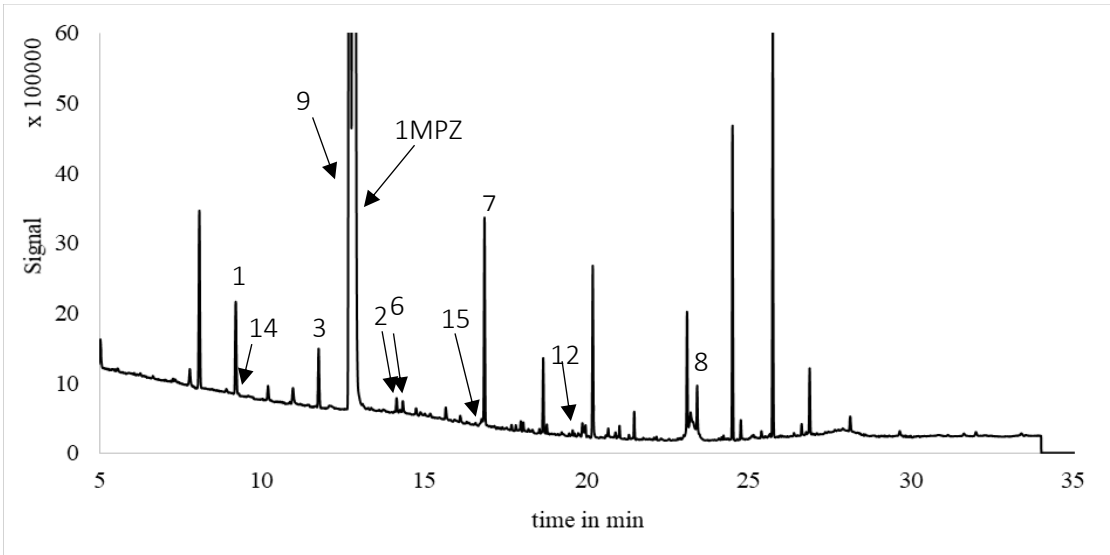

Figure 30: Chromatogram obtained after the analysis by TDU-GC-MS of a Tenax TA tube sampled with 12L of treated flue gas at 800 hours of degradation. Unidentified peaks may correspond to artefacts of the sampling sorbent or to contaminations.

Among the identified compounds, five were selected for the development of a quantitative method, namely pyrazine, 2-methylpyrazine, acetylpyrazine, 1-methylpiperazine and 1,4-dimethylpiperazine in order to estimate the emitted content. The results show that the emissions were in the range of the ng/L for pyrazine, 2-methylpyrazine and 2-acetylpyrazine (**Figure 31**) for the two campaigns. 1.4DMPZ emitted concentrations were between 60 and 1700 ng/L. The highest emissions were observed for 1MPZ with concentrations ranging from 1 to 7 µg/L (**Figure 32**). However, these loss of 1MPZ are very low as they correspond to less than 1% of the initial concentration of the amine in the solvent. The implementation of a washing unit could potentially lower these emissions. The addition of acidic impurities in the campaign B did not have any effect on the quantity of emitted compounds.

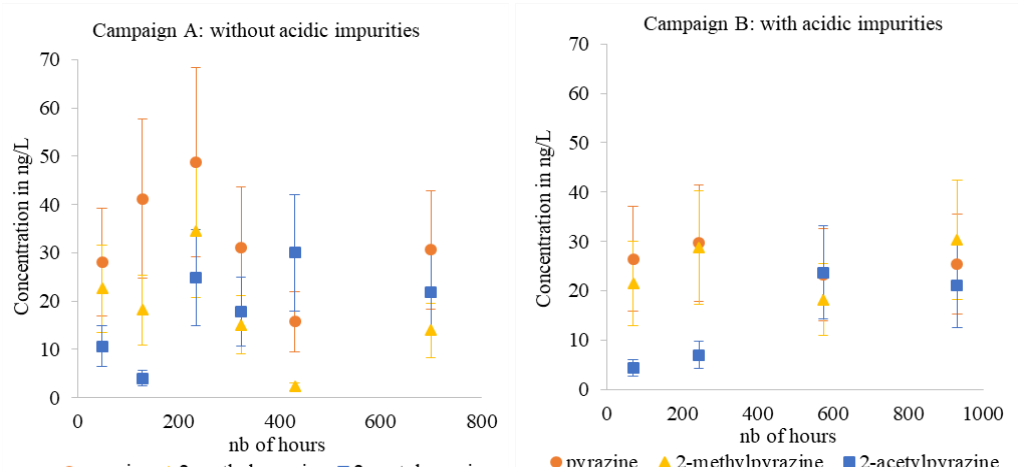

Figure 31: Monitoring of the emissions of pyrazine, 2-methylpyrazine and 2-acetylpyrazine in the campaigns A and B. The error bars correspond to the acceptance limit of 30% of the quantification method (Cuccia et al., 2017).

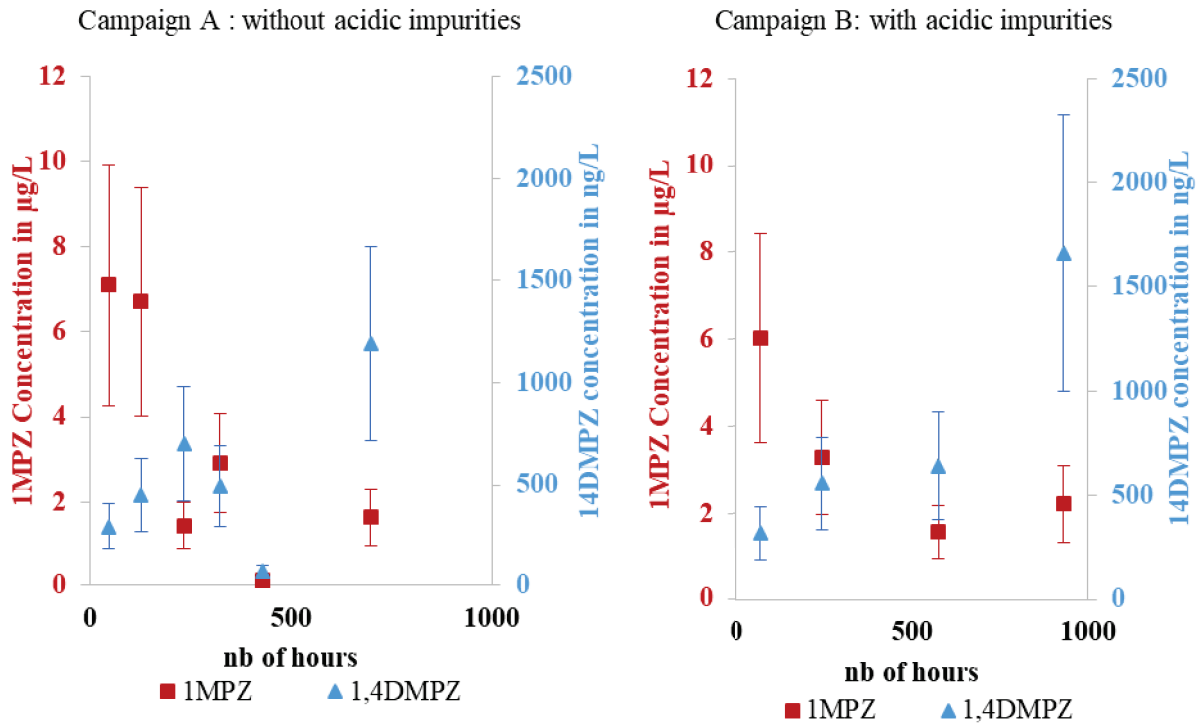

Figure 32: Monitoring of the emissions of 1MPZ and 14DMPZ in the campaigns A and B. The error bars correspond to the acceptance limit of 30% of the quantification method (Cuccia et al., 2017).

4 Conclusion

The blend 1MPZ-PZ-Water seems to be a promising solvent for post-combustion CO_2 capture in terms of capture performances. The loadings of 0.7 and 0.3 for the rich and lean solvent respectively are higher than those of MEA which are 0.5 and 0.3 [32]. After 900 hours of cycling in the LEMEDES-CO2 pilot plant, 23 degradation products were identified in the liquid phase of the solvent against 32 in the case of MEA degradation [32]. Among them were found piperazine derivatives, alkylpyrazines, aliphatic amines and organic acids. Quantification was realized on 5 compounds: oxalic and formic acids, pyrazine, 14DMPZ and FPZ. The highest concentrations were found for formic acid (3000 mg/L +/-20%) and FPZ (2000 mg/L +/-50%). The presence of acidic impurities (in the campaign B) limited the formation of the quantified organic acids. Regarding the gaseous emissions, 15 compounds were identified in the treated fumes against 35 in the case of MEA degradation. Among them, 5 were quantified: pyrazine, 2-methylpyrazine, 2-acetylpyrazine, 1MPZ and 1.4DMPZ. The highest concentrations were found for the constituent amine of the solvent, 1MPZ, in the range of the µg/L. A partial vaporization of 1MPZ could explain these emissions. This is more believable than a formation of 1MPZ from PZ during time. These emissions could be limited by the implementation of a water wash section. Further work is ongoing about the proposal of reactional mechanisms to explain the formation of these compounds.

Acknowledgments

We would like to thank Aïcha El Khamlichi (ADEME engineer) for the monitoring of this doctoral project and ADEME (French Agency of Environment and Energy Management) for the financial support.

Monitoring of the blend 1-methylpiperazine/piperazine/water for post-combustion CO_2 capture. Part 2: reactional mechanisms proposal.

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Abstract

Aqueous blend of 1-methylpiperazine (1MPZ) and piperazine (PZ) appears to be a promising solvent for post-combustion CO_2 capture in terms of energy needed for the process. An experimental study of the degradation of the blend 1MPZ/PZ was carried out on the lab-scale CO_2 capture pilot plant LEMEDES-CO2 during 800 and 955 hours. Complementary analytical strategies involving liquid and gas chromatography were developed, in order to identify and quantify degradation products formed in the liquid phase of the solvent, but also degradation products emitted with the treated flue gas. 27 degradation products were identified among them piperazine derivatives, organic acids and amines derivatives. The present study aims at proposing reactional mechanisms in order to explain and understand the formation of these compounds. Some of the proposed pathways were already described in the field of oxidative and thermal PZ degradation. For the other compounds not previously identified in the field of PZ degradation, reactional mechanisms were proposed involving additions, and oxidative radical reactions.

1 Introduction

Amine-based post-combustion CO_2 capture is nowadays the most promising technology to reduce the CO_2 emissions on already existing power plants [16]. The process is based on the reversible absorption of CO_2 at low temperature (40-70°C) and atmospheric pressure by the amine. The amine is then regenerated at high temperature (100-150°C) and pressure (between 1 and 5 bars) to emit pure CO_2 intended for storage [16,25]. The benchmark solvent of the process is monoethanolamine (MEA), which has been used since decades for gas purification [18]. MEA has many advantages i.e. high solubility in water, low viscosity, high CO_2 cyclic capacity, but also low cost. The two main drawbacks of MEA for the capture process are the high energy penalty (around 20%) [5] and the irreversible degradation involving the formation of degradation products potentially toxic for human and the environment [14,15]. This degradation also leads to loss of solvent, involving addition of fresh solvent, thus leading to additional costs. Current studies focus on innovative amines or amine blends that would limit those two main drawbacks.

Alkanolamines blends and piperazine blends seem to be promising in term of energy needed for the process [48,50] thus reducing the energy penalty generated. PZ can be used at up to 150°C and is resistant to oxidative degradation. However, in absence of appropriate CO_2 loading, concentrated PZ can precipitate [40,222]. An alternative is the use of PZ as an activator in amine blends, like methyldiethanolamine/PZ [67], 2-methylpiperazine/PZ [70], 2-amino-2-methylpropan-1-ol/PZ [34] or *N*-(2-aminoethyl)piperazine/PZ [69], without any precipitation concerns. Li et al. [49] studied the solubility and the energy for CO_2 absorption in piperazine derivatives and their mixture. The results showed that one of the most promising blend is composed of 1-methylpiperazine (1MPZ) and PZ, leading to a reduction of the energy consumption of 20% when compared with MEA [50]. Degradation of the blend 1MPZ/PZ (30/10 %wt.) was carried out in our previous study [225] on a lab scale pilot plant with conditions representative of post-combustion CO_2 capture during 900 hours. Our study permitted, after the development of complementary analytical strategies, the identification of 23 degradation products in the liquid phase of the solvent and 14 emitted with the treated flue gas. Among them were compounds already identified in the field of PZ degradation [72,93,226]. The aim of the present work is to propose reactional mechanisms in order to explain the formation of these compounds and to confirm they are true degradation products and not sampling nor analytical artefacts.

2 Materials and methods

2.1 Solvent preparation

Preparation of the blend 1MPZ/PZ was realized gravimetrically by mixing and heating until dissolution commercial PZ (≥99% assay, Merck, Fontenay-sous-Bois, France) and 1MPZ (99% assay, Sigma-Aldrich, Saint-Quentin-Fallavier, France) with distilled water (18.2 MΩ).

2.2 Chemicals

Ethylenediamine (99%) was purchased from Alfa Aesar (Schiltigheim, France). Ammonia 32% extra pure was purchased from Merck (Lyon, France). Pyrazine (≥99%), 1-methyl-1H-pyrrole (99%), 2-methylpyrazine (≥99%), 1,4-dimethylpiperazine (98%), 1-methylpiperazine (99%), piperazine (reagent plus, 99%), 2,6-dimethylpyrazine (≥98%), 2,3-dimethylpyrazine (≥95%), 2-ethylpyrazine (≥98%), 1,2,4-trimethylpiperazine, 2-ethyl-3-methylpyrazine (≥98%), 2,3,5-trimethylpyrazine (≥99%), 2-ethylhexanol, 2-acetylpyrazine (≥99%), 1-piperazineethanamine (99%), 1,4-diformylpiperazine (98%), 1-piperazinecarboxaldehyde (≥90%), 2,2'-bipyrazine (97%), 2-piperazinone 97%, acetaldehyde (anhydrous, ≥99.5%), methylamine (40 % wt. in H_2O), 1,2-diaminopropane (99%), *N*-methylethylenediamine (95%), sodium lactate (98%), propanoic acid (99.5%) were purchased from Sigma Aldrich (Saint-Quentin-Fallavier, France). Oxalic acid (99.8%) was purchased from VWR (Fontenay-sous-Bois, France). Formic acid (99%) was purchased from Carlo Erba (Val-de-Reuil, France).

2.3 Pilot plant description

The blend 1MPZ/PZ/Water (30/10/60 w/w/w) was degraded on the LEMEDES-CO2 lab-scale equipment [90,158] from EDF R&D (**Figure 33**). A fully detailed description of the device was made in our previous work [225]. The MEA experimental protocol, more particularly the absorption and stripping temperatures was used as a basis to this amine blend, in order to compare its stability with MEA's one.

Two degradation campaigns were carried out during 800 and 955 hours. The parameters of each campaign are given in **Table 28**. The aim of the second campaign was to study the impact of acidic impurities i.e. sulphurous acid (H_2SO_3) and nitric acid (HNO_3). A synthetic flue gas was injected at the bottom of reactor. It contained 15% CO_2 (≥99.7%, Air Liquide, Mitry Mory, France), 82% N_2 (≥99.995%, Air Liquide, Mitry Mory, France) and 3% air (composed of 20.9% of oxygen). Total absolute pressure during absorption was 1.0 bar. The gas flow rate was 1800 NL/h at 42°C and the solvent flow rate was 3L/min. The total volume of solvent was 1.5 L. For the regeneration step a pressure of 4 bar in the reactor was first applied with N_2 as entering flue gas during 1 min. Then the solvent was heated up to 123°C and maintained during 6 seconds which enabled the regeneration of the amine and the release of CO_2. Released CO_2 was exhausted.

The control system followed many parameters such as temperature, pressure and gas composition and operated continuously and automatically (24h/24 and 7d/7). Samples were taken from the liquid and gas phase and analysed at regular intervals. Solvent sampling was done once a week at the bottom of the reactor for the CO_2 rich amine and the CO_2 lean amine. All samples were stored in brown flaks at 4◦C

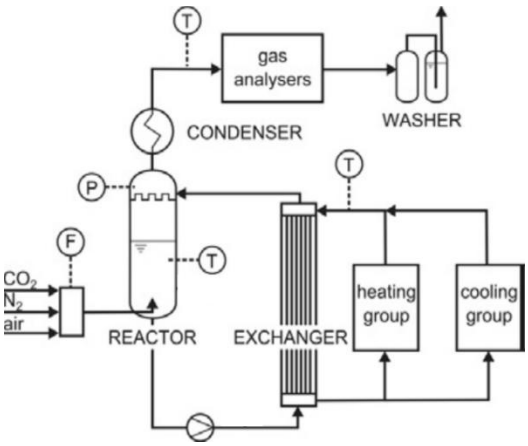


Figure 33: LEMEDES-CO2 lab-scale equipment F: flowmeter; T: temperature probe; P: pressure sensor).

Table 28 : Characteristics of the two degradation campaigns

Campaign	A	B
Composition (1MPZ/PZ % wt.)	30/10	30/10
Duration	800 h	955 h
Number of cycles	400	478
Absorption duration	80 min	80 min
Impurity additives	-	H_2SO_3 (4.8 g / week) HNO_3 (3.9 g / week)

2.4 Ionic chromatography (IC)

2.4.1 Cation ionic chromatography

Degradation products formed during the campaigns were identified using ionic chromatography (IC). An ICS 1000 equipped with an autosampler from Thermo Fisher (Villebon-sur-Yvette, France) was used. Samples were diluted 1000 times with water, and then 25 µL were injected for the separation. A guard column (IonPac^{TM} CG19RFIC^{TM} 4 x 50 mm) was placed before the analytical column (IonPac^{TM} CS19RFIC^{TM} 4 x 250 mm) to prevent the analytical column from contaminations. An eluent generator permitted the delivery of adjustable concentrations of methanesulfonic acid (MSA). The system was equipped with a 4-mm anionic Suppressor. Detection was performed with a conductimetric cell. Both

columns and conductimetric detectors were thermostated at 35°C. The initial MSA concentration was 2mM, raised at 35 mM from 35 to 135 min.

2.4.2 Anion ionic chromatography

Anionic species were identified using ionic chromatography (IC). The same device as previously described was used. A guard column (IonPac AG11 4 x 50 mm) was placed before the analytical column (IonPac AS11 4 x 250 mm) to prevent the analytical column from contaminations. The system was equipped with a 4-mm cationic suppressor. Detection was performed with a conductimetric cell. Both columns and conductimetric detectors were thermostated at 35°C. The separation was realized with an elution gradient of KOH starting from 0.5 mM from 0 to 30 min then raised to 40 mM in 30 min then decreased at 0.5 mM from 80 to 120 min. The flow rate was 1.5 mL/min and the applied current of 149 mA. The column and the detector were thermostated at 35°C.

2.5 Gas chromatography-Mass Spectrometry (GC-MS)

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer from Agilent Technologies (Massy, France). The device was equipped with a MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated liquid injections, HS-SPME and thermodesorption (TDU) analyses. Two columns (Chromoptic, Villejust, France) were used to separate the compounds; a non-polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm, 1 µm) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm, 0.5 µm). 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. Detection was performed with a mass spectrometer using electronic ionization (EI) source (70 eV) heated to 250°C. The scan range was 25 to 250 amu. NIST spectra data base was used for the pics identification. Each identification proposal was confirmed by the injection of commercial standards when available.

2.5.1 Direct liquid injections

For liquid injection procedure, real samples were diluted 10 times in methanol before injecting 1µL in split mode (1:5) at 280°C.

2.5.2 Headspace Solid Phase MicroExtraction – GC-MS (HS-SPME-GC-MS)

For Head Space – Solid Phase MicroExtraction (HS-SPME) procedure, the volume of sample introduced in the 20 mL HS vial was 5 mL. A 75µm Carboxen/PDMS SPME fibre obtained from Supelco (Sigma Aldrich, Saint Quentin Fallavier, France) was used. The fully automated HS-SPME procedure was the same as described by Rey et al., 2013 [199]. This method was initially developed for the identification and the quantification of alkylpyrazines. It was applied here to the identification of other degradation products present in the liquid phase.

2.6 LC-MS

Analysis were performed on a LC Agilent 1100 coupled with a MS Waters micromass ZQ 4000 with ESI source. It was used in positive mode with a source temperature of 120°C. The chromatographic separation was realized with a Thermo Hypercarb column (150 mm x 3 mm, 5 µm-particles). The mobile phase was composed of (A) water + ammonia to reach a pH of 10.8 and (B) Methanol + 0.1% formic acid at a flow rate of 350 µL/min. 5 µL of sample previously diluted by 100 in mobile phase A were injected. The solvent gradient started at 100% of A for 10 min before reaching a ratio of 80:20 (A:B v:v) in 8 min. This ratio was maintained for 12 min

2.7 Gas phase sampling

Gas sampling was performed in order to identify degradation products emitted in the gas phase during the process. The same method as described in our previous study [192] was applied here. A Tenax TA® tube (Gerstel, Saint-Priest, France) was placed after the condenser to avoid any humidity problems, and a flow of 200 mL/min during 60 min was pumped through the solid phase. Flow rate was controlled with a rotameter, and air was pumped with an ambient air sampler from Supelco (Sigma Aldrich, Saint Quentin Fallavier, France).

2.8 Analysis of the gas phase by TDU-CIS-GC-MS

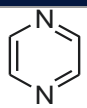
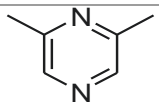
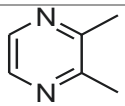
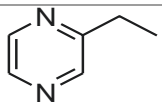
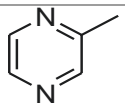
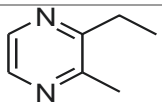
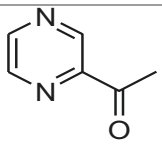
For thermodesorption of tubes, gas flow rate of helium was 40 mL/min in splitless mode. Initial temperature of desorption was 35°C held for 2 min then raised to 300°C at 120°C/min and held for 6 min. Desorbed molecules were cryofocused in the injector at -40°C with liquid CO_2. Then temperature increased from - 40°C to 300°C at 12°C/s and the molecules were injected in the column in splitless mode. The same GC/MS method as for liquid samples was used with a CP-SIL8 CB-MS column.

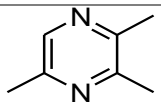
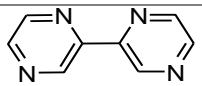
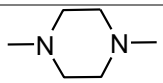
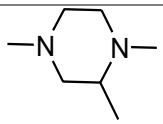
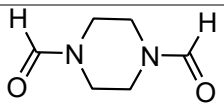
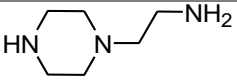
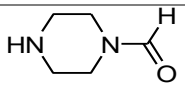
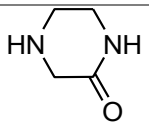
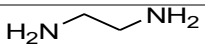
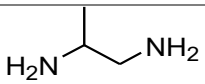
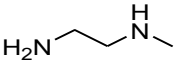
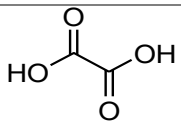
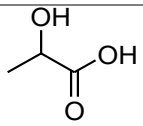
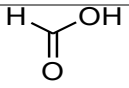
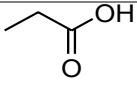
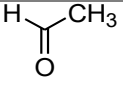
3 Results

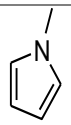
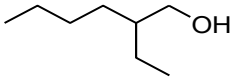
3.1 Degradation products identified from the blend 1MPZ/PZ

27 degradation products were identified from the blend 1MPZ/PZ (30/10 % wt.). Among them, 23 were detected in the liquid phase of the solvent, and 14 with the treated flue gas. The main classes of compounds were piperazine derivatives, alkylpyrazines, aliphatic amines, organic acids and other amine derivatives (Table 29). Aliphatic amines and organic acids were detected by IC, whereas alkylpyrazines and piperazines derivatives were detected by GC-MS. In the liquid phase of the solvent, alkylpyrazines were detected thank to HS-SPME-GC-MS, thus encouraging the use of complementary analytical methods. The addition of acidic impurities did not have any impact on the nature of the formed compounds. In order to explain the formation of these compounds, and potentially limit their formation, reactional mechanisms have to be proposed.

Table 29 : Degradation products identified in the liquid and gaseous phases

	Compounds	CAS	Structure	Presence	
				Liquid phase	Treated Flue gas
Alkylpyrazines	Pyrazine	290-37-9		X	X
	2,6-Dimethylpyrazine	105-50-9		X	X
	2,3-Dimethylpyrazine	5910-89-4		X	X
	2-Ethylpyrazine	13925-00-3		X	
	2-Methylpyrazine	109-08-0		X	X
	2-Ethyl-3-methylpyrazine	15707-23-0		X	X
	2-Acetylpyrazine	22047-25-2			X

	2,3,5-Trimethylpyrazine	14667-55-1		X	X
	2,2'-Bipyrazine	10199005		X	X
Piperazine derivatives	1,4-Dimethylpiperazine	106-58-1		X	X
	1,2,4-Trimethylpiperazine	120-85-4		X	X
	1,4-Diformylpiperazine	4164-39-0		X	X
	1-Piperazineethanamine	140-31-8			X
	1-Formylpiperazine	7755922		X	
	2-Piperazinone	5625-67-2		X	
Aliphatic amines	Ethylenediamine	107-15-3		X	
	Ammonia	1336-21-6	NH_3	X	
	Methylamine	74-89-5	$MeNH_2$	X	
	1,2-Diaminopropane	78-90-0		X	
	N-methyl-ethylenediamine	109-81-9		X	
Organic acids	Oxalic acid	144-62-7		X	
	Lactic acid	79-33-4		X	
	Formic acid	64-18-6		X	
	Propionic acid	79-09-4		X	
	Acetaldehyde	75-07-0		X	

Amine derivative	1-Methyl-1H-pyrrole	96-54-8		X
Alcohol derivative	2-Ethylhexanol	104-76-7		X

3.2 Reactional mechanisms proposal

Each mechanism described in this study is based on previous published works about PZ degradation or on propositions. Each of the proposed pathways has to be taken carefully, as none of the reactional schemes were assessed by organic synthesis.

3.2.1 Formation of piperazine derivatives

Six piperazine derivatives were formed during the degradation of the blend 1MPZ/PZ, namely 1-formylpiperazine, 1,4-diformylpiperazine, 1,4-dimethylpiperazine, 1-piperazineethanamine, 2-piperazinone and 1,2,4-trimethylpiperazine.

Two studies proposed reactional mechanisms to explain the formation of 1-formylpiperazine and 1,4-diformylpiperazine [91,93]. Both studies suggested the reaction of PZ with formic acid (**Figure 34**). The addition of formic acid on the amino function of PZ would lead to the intermediate **1**, which after water elimination would lead to the formation of 1-formylpiperazine. The same sequence applied on the second amino group of PZ would bring to the formation of 1,4-diformylpiperazine.

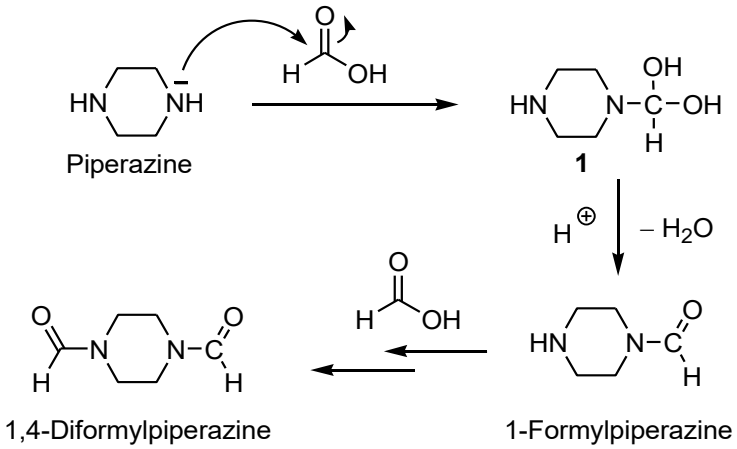


Figure 34: Formation of 1-formylpiperazine and 1,4-diformylpiperazine

To our knowledge, no study suggested a reactional mechanism for the formation of 1,4-dimethylpiperazine. Its formation would be explained by the Eschweiler-Clarke reductive alkylation of amines reaction involving two successive additions of formaldehyde on PZ, or one addition of formaldehyde on 1MPZ [227,228]. The proposed reaction pathway is given in **Figure 35**. Formaldehyde

has not been identified in the degraded solvent, presumably because of its rapid oxidation to formic acid which has been detected.

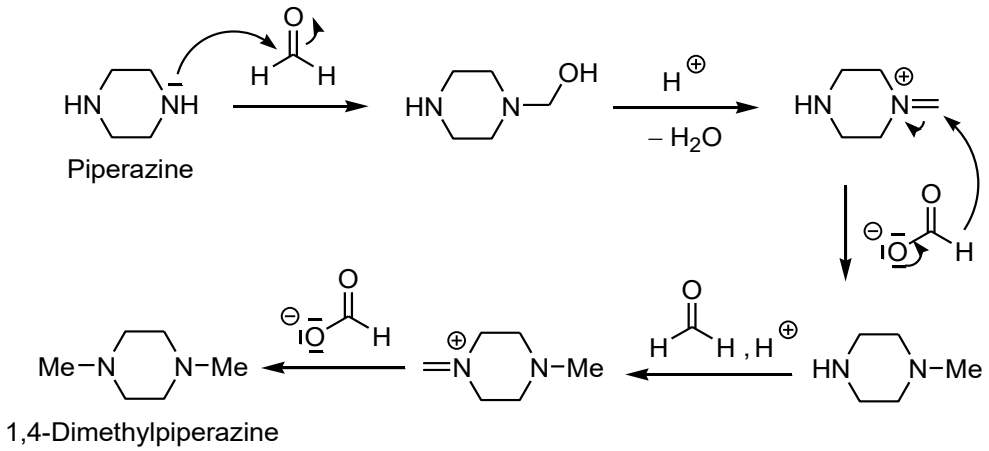


Figure 35: Formation of 1,4-dimethylpiperazine

1-Piperazineethanamine's mechanism formation has already been proposed by Freeman et al. [72]. The suggested mechanism involved the reaction of two PZ resulting in the formation of the intermediate 1-[2-(2-aminoethyl)aminoethyl]piperazine (AEAEPZ). The reaction between AEAEPZ and PZ would lead to the formation of two molecules of 1-piperazineethanamine (Figure 36).

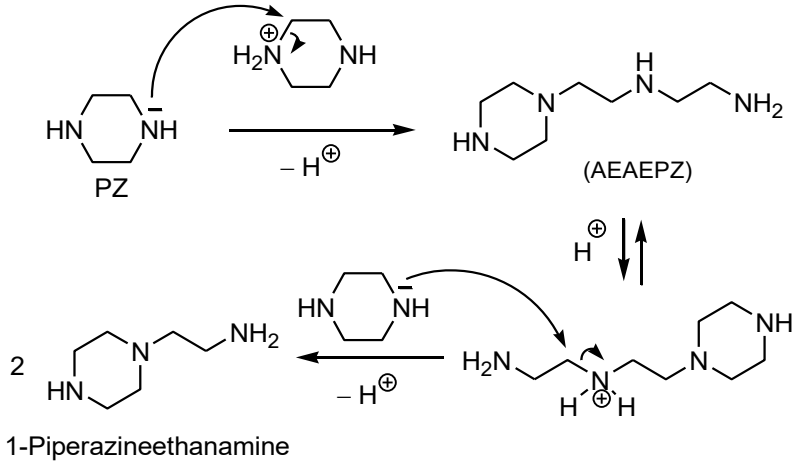


Figure 36: Formation of 1-piperazineethanamine

Formation of 2-piperazinone (or 2-oxopiperazine) has been proposed by Wang et al. (2014) [93]. The proposed mechanism is given in Figure 37 where PZ oxidation would be assumed to be initiated through a radical forming step, involving the formation of the free radical **2**. After reaction of **2** with oxygen, the intermediate peroxyl radical **3** would be expected. The radical **3** would then be converted to the hydroperoxide **4** by intermolecular hydrogen-abstraction. The reduction of **4** would allow the formation of the hemiaminal **5**. The carboxylic acid **7** could come from the oxidation of the aldehyde **6** corresponding to the open form of the hemiaminal **5**. The ring closure of **7** would finally bring to 2-oxopiperazine.

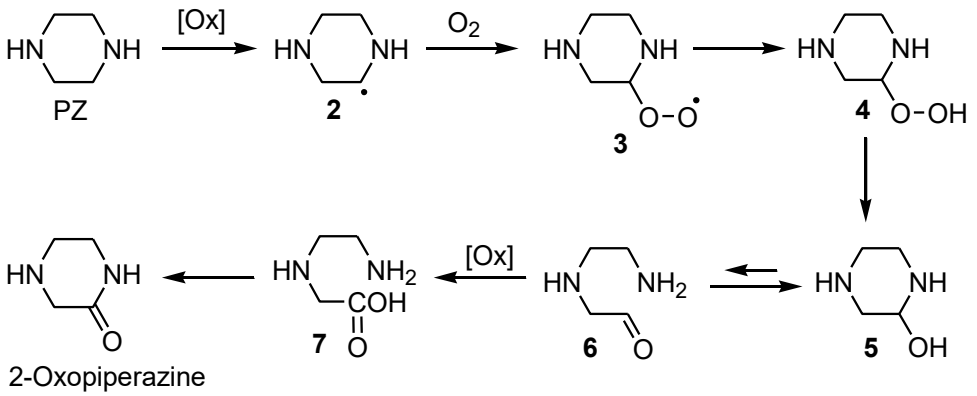


Figure 37: Formation of 2-oxopiperazine

To our knowledge, no study suggested a pathway formation for 1,2,4-trimethylpiperazine. We proposed a mechanism, given in Figure 38, where oxidation of 1,4-dimethylpiperazine would lead to the hemiaminal intermediate 8. After water elimination, 8 would bring to the intermediate 9. The enediamine 9 would then react with formaldehyde to form the hydroxyl intermediate which after water elimination would bring to the intermediate 10. 10 would then react with formic acid to form 1,2,4-trimethylpiperazine.

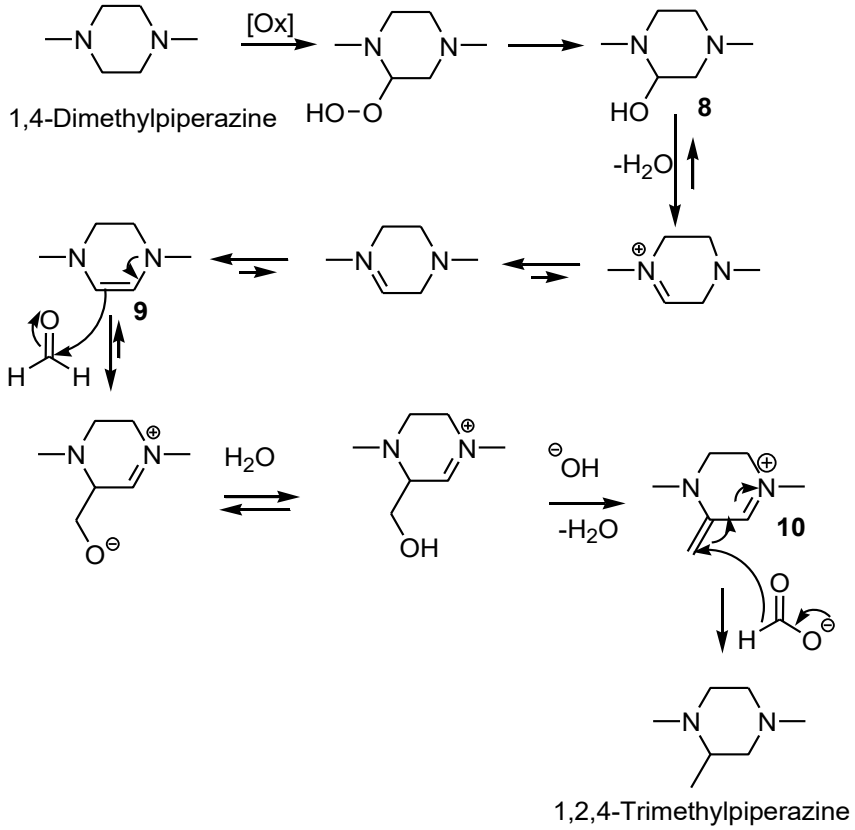


Figure 38: Formation of 1,2,4-trimethylpiperazine

3.2.2 Formation of alkylpyrazines

Alkylpyrazines have been identified for the first time in the field of MEA degradation by Rey et al., [199]. A pathway proposal was made, where two molecules of aminoacetaldehyde react to form the pyrazine ring after water elimination. The same type of reaction [229] is proposed in our study in order to explain the presence of the various forms of alkylpyrazines (**Figure 39**). Ethylenediamine is proposed to be the precursor of seven of the pyrazines formed: 2-methylpyrazine **15**, 2-ethylpyrazine **16**, 2,6-dimethylpyrazine **17**, 2,3,5-trimethylpyrazine **18**, 2,3-dimethylpyrazine **19**, pyrazine **14** and 2-acetylpyrazine **20**. Ethylenediamine would possibly react with glyoxal **11**, methylglyoxal **12** or 2,3-butanedione **13** to form the corresponding pyrazine derivatives. The benzylic oxidation of 2-ethylpyrazine **16** would afford the detected 2-acetylpyrazine **20**. The formation of 2-ethyl-3-methylpyrazine could be explained by the condensation of 1,2-diaminopropane with glyoxal **11** (**Figure 40**). We have to mention that glyoxal, methylglyoxal nor 2,3-butanedione have been detected in the degraded solvent. This may be caused by concentrations under the limits of detection of the chromatographic method and/or because of the high reactivity of the two aldehydes.

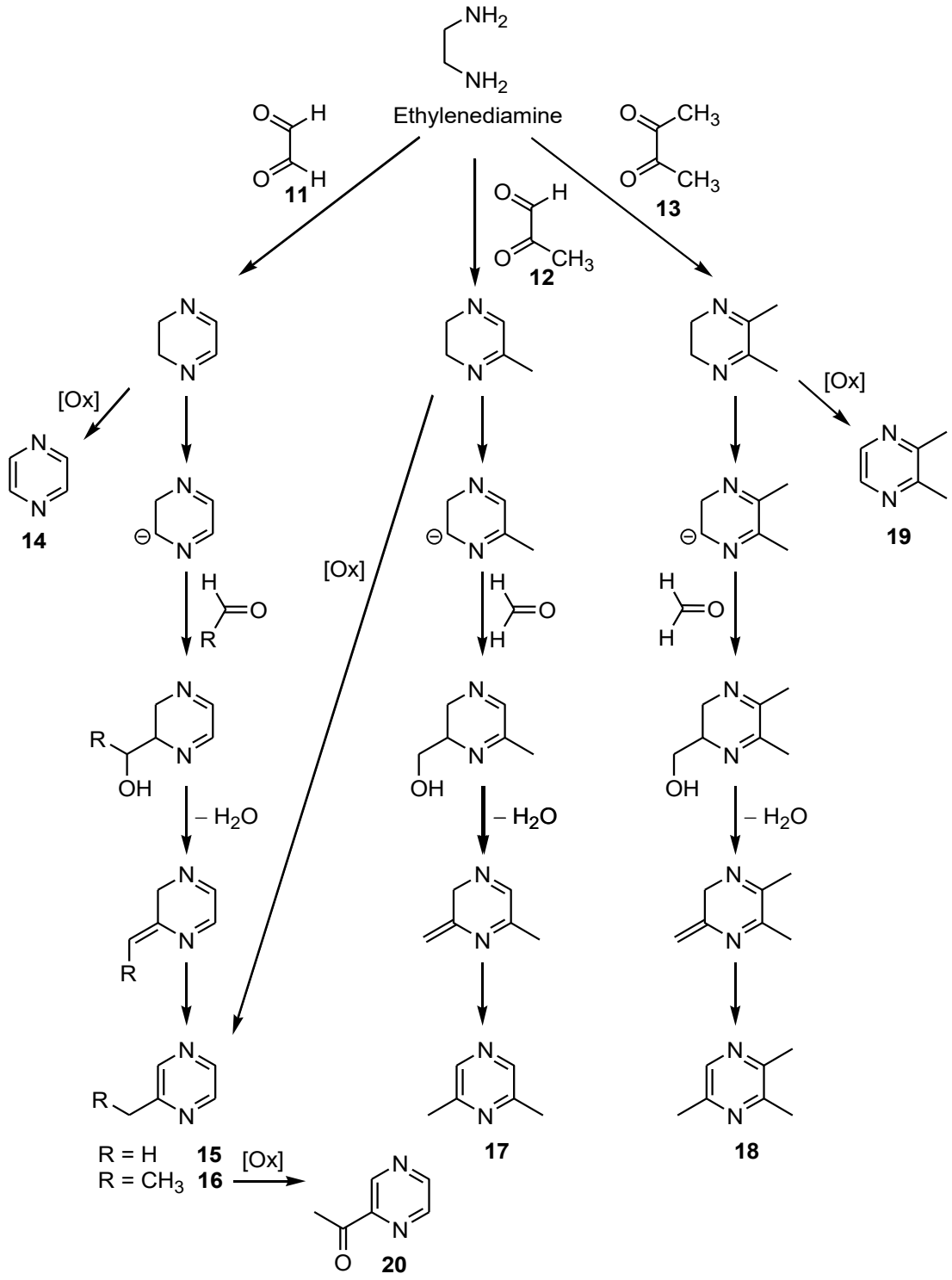


Figure 39: Formation of five alkylpyrazines

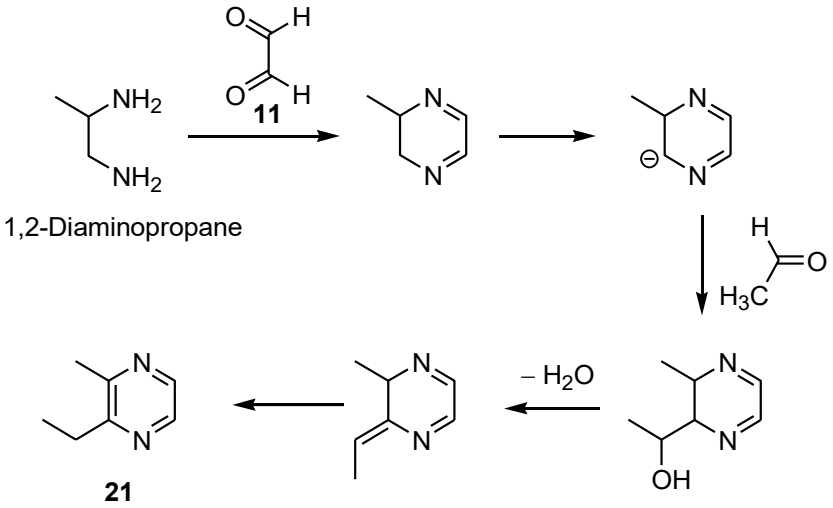


Figure 40: Formation of 2-ethyl-3-methylpyrazine

To our knowledge, no published work suggested a reactional mechanism involving PZ or 1MPZ to explain the formation of 2,2'-bipyrazine. A formation pathway is proposed in Figure 41. The oxidation of PZ would lead to the intermediate 22. The mechanistic hypothesis proposed here would involve the imine-enamine tautomerization of 2,5-dihydropyrazine 22 into the intermediate 1,4-dihydropyrazine 23. The latter would then react with another molecule of protonated 22 leading to 24, precursor of 2,2'-bipyrazine.

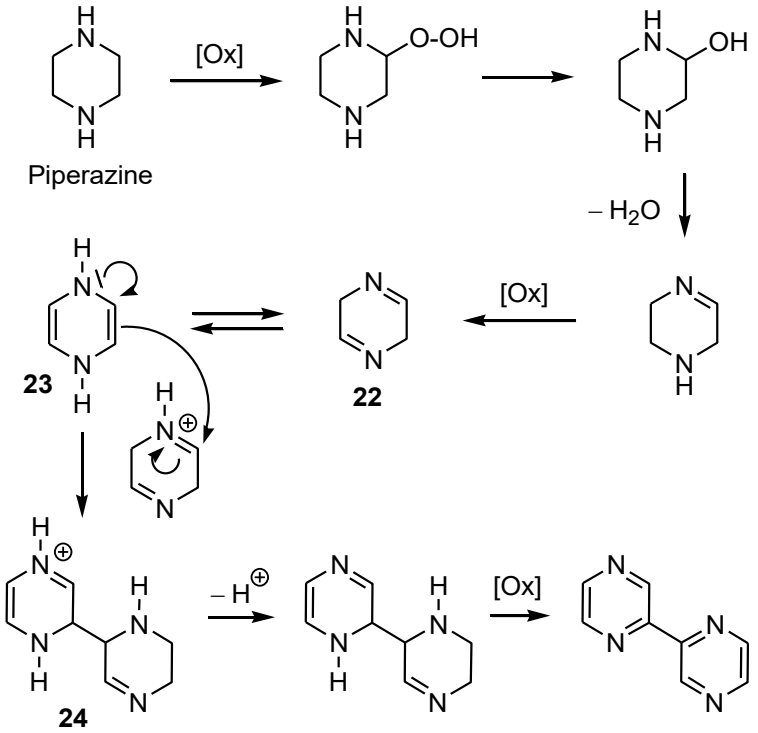


Figure 41: Formation of 2,2'-bipyrazine

3.2.3 Formation of amines derivatives

Six amines derivatives were formed during the degradation of the blend 1MPZ/PZ, namely ethylenediamine, methylamine, 1,2-diaminopropane, *N*-methylethylenediamine, ammonia and 1-methyl-1H-pyrrole.

Wang et al. (2014) suggested a mechanism to explain the formation of ethylenediamine and oxalic acid [93]. The same type of reaction is suggested in the present work and is presented in **Figure 42**. After oxidation of PZ, the intermediate **5** would be formed in equilibrium with his opened form **6** (equilibrium in favor of **5**). The oxidation of **6** followed by the hydrolysis of the resulting imine would afford ethylenediamine and glyoxal. Successive oxidations of glyoxal would lead to the formation of glyoxylic and oxalic acids. Gouedard et al. [230] described the formation of formic acid through decarboxylation of oxalic acid, or by decarboxylation followed by oxidation of glyoxylic acid, leading to the formation of formaldehyde as intermediate. Oxidation of ethylenediamine would lead to the formation of the imine **25**, which after hydrolysis would bring to the formation of ammonia and the corresponding aldehyde **26**. The same type of mechanism can be applied to explain the formation of *N*-methylethylenediamine, when the reaction begins with 1MPZ instead of PZ (**Figure 43**). The hydrolysis of the imine form of *N*-methylethylenediamine **27** would finally lead to methylamine.

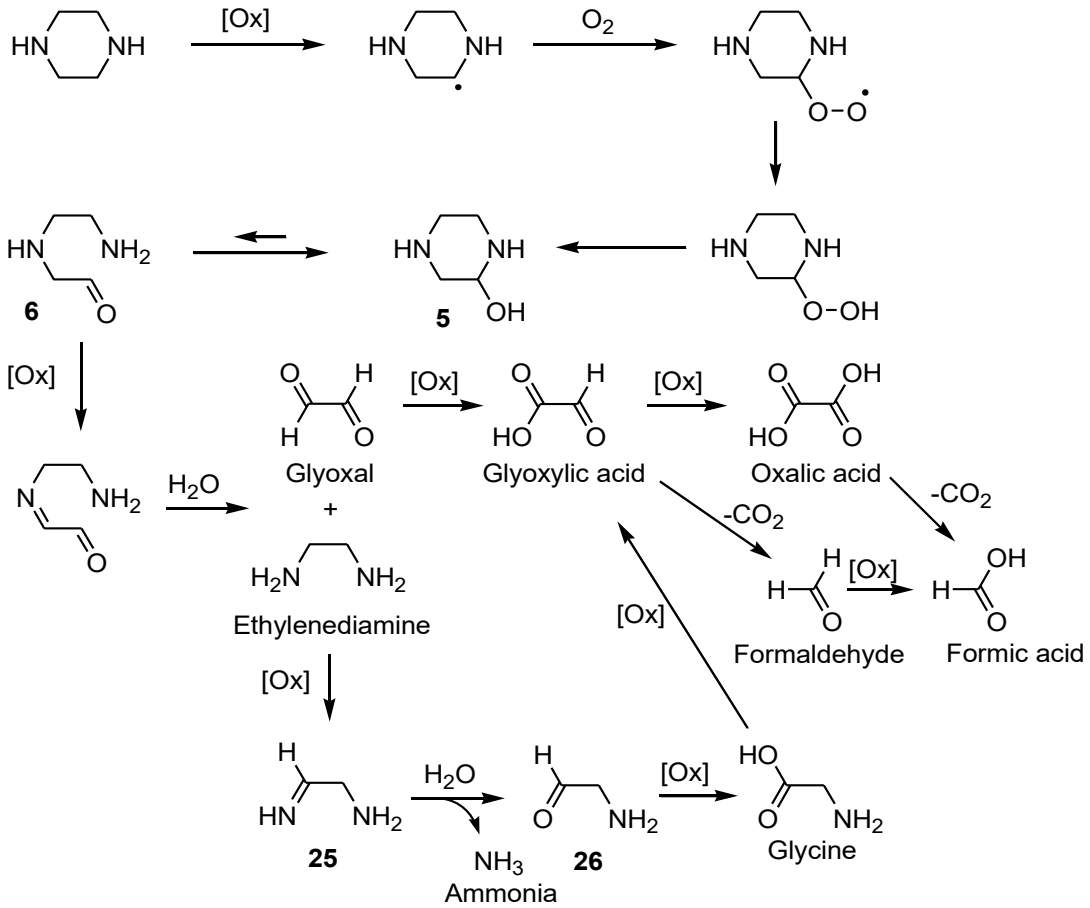


Figure 42: Formation of ethylenediamine and oxalic and formic acids

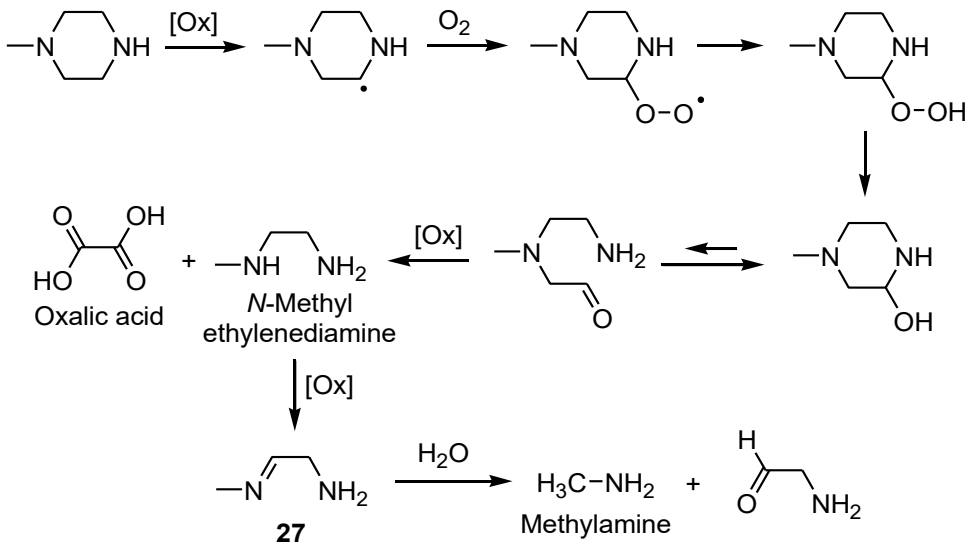


Figure 43: Formation of N-methylethylenediamine and methylamine

Methylamine and ammonia would as well be formed according to another pathway presented in Figure 44. In this case, a nucleophilic addition on the alpha carbon of PZ or 1MPZ followed by ring opening would lead to the intermediate 28. After a second nucleophilic addition on the protonated form of 28, ammonia or methylamine would be generated by elimination when PZ and 1MPZ respectively would initially react.

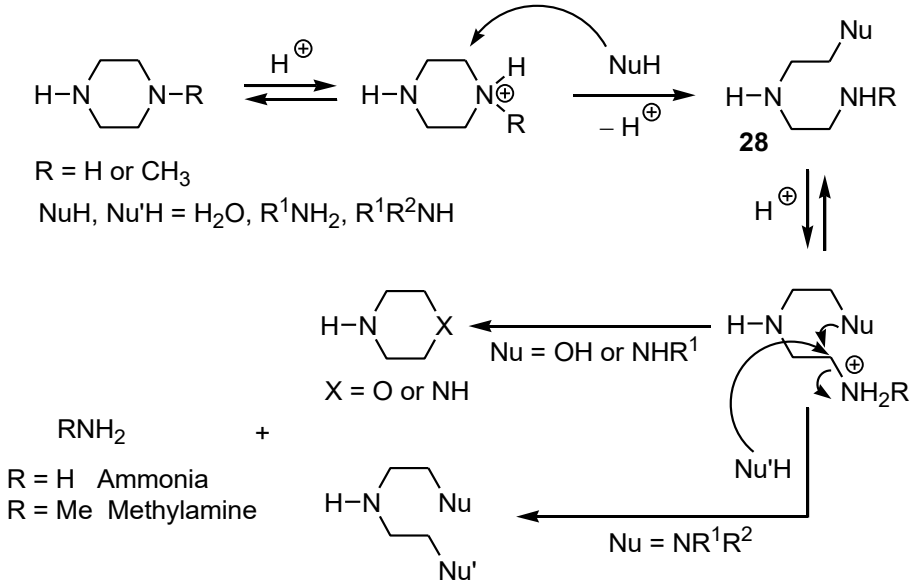


Figure 44: Formation of ammonia and methylamine

Figure 45 presents a mechanism to explain the formation of *N*-methylpyrrole. *N*-methylpyrrole would result from the reaction between *N*-methylethylenediamine and acetaldehyde. In a first step, *N*-methylethylenediamine would be oxidized and hydrolyzed to form the aldehyde 29. This intermediate would react with the enolic form of acetaldehyde 30 through an aldolisation process, to form the

intermediate **31**. After nucleophilic intramolecular addition of the amine part of **31** to its aldehyde function, and water elimination, *N*-methylpyrrole would be formed.

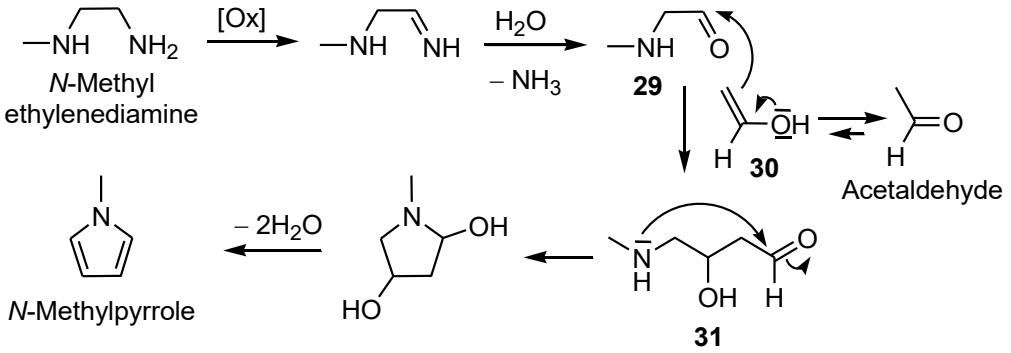


Figure 45: Formation of *N*-methylpyrrole

3.2.4 Formation of organic acids and acetaldehyde

Four organic acids and one aldehyde were listed after the degradation of the blend 1MPZ/PZ. Oxalic and formic acids formations were already explained in **Figure 42**.

Acetaldehyde's formation would be explained by the presence of ethylenediamine (**Figure 46**). Ammonia loss on ethylenediamine would lead to the enamine **32**, which after tautomerization into an imine and hydrolysis would form acetaldehyde.

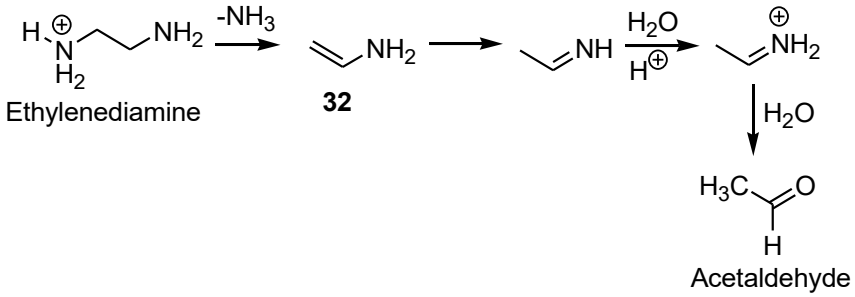


Figure 46: Formation of acetaldehyde

The formation of lactic acid would be explained by the the dispropotionation of methylglyoxal. Regarding propanoic acid, its formation has already been described by Gouedard et al. [230] and would be explained by the reaction of acetaldehyde and formaldehyde through an aldolisation reaction (**Figure 47**).

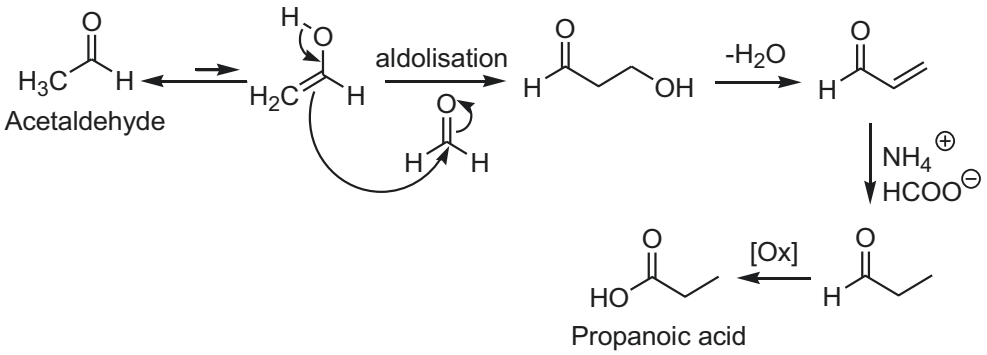


Figure 47: Formation of propanoic acid [230]

4 Conclusion

Reactional pathways were proposed for 25 of the 27 listed degradation compounds, in order to explain their formation after cycling during 900 hours of the blend 1MPZ/PZ. Most of the suggested pathways involved oxidations through radical formation and nucleophilic additions, thus suggesting the impact of the absorption step involving oxidative degradation. For two compounds, namely 1,2-diaminopropane and 2-ethylhexanol, no formation proposal was made but consideration is still ongoing. Further work should be done in order to study the impact of oxidation inhibitors additives on the formation of degradation products.

Acknowledgments

We would like to thank Aïcha El Khamlichi (ADEME engineer) for the monitoring of this doctoral project and ADEME (French Agency of Environment and Energy Management) for the financial support.

Chapitre 4 : Etude du solvant MDEA/MEA/Eau

Ce chapitre, sous la forme d'un article, présente les études réalisées sur le deuxième solvant innovant du projet : le mélange méthyldiéthanolamine, monoéthanolamine et eau.

Une campagne de dégradation d'une durée de 900 heures a été réalisée au sein du laboratoire LEMEDES-CO2 d'EDF R&D Chatou. Cette campagne a été réalisée sans ajout d'impuretés acides en raison de l'absence de différence notoire dans la nature des produits de dégradation formés lorsque le solvant 1MPZ/PZ a été étudié. Le même mode opératoire que celui mis en œuvre dans le cadre de la dégradation du mélange 1MPZ/PZ a été mis en œuvre. Ce mode opératoire correspond aux conditions classiques du procédé impliquant la MEA 30 %, et permettra de comparer les performances de ce solvant à celles du mélange MDEA/MEA. Seules ont été optimisées les durées des étapes d'absorption et de régénération, dans l'objectif d'atteindre les taux de charges riche et pauvre optimaux présentés dans le Tableau 3.

Des stratégies analytiques impliquant les chromatographies en phase liquide et gazeuse ont été développées dans l'objectif d'évaluer la stabilité des amines majoritaires, e.g. la MDEA et la MEA, et d'identifier d'éventuels produits de dégradation formés en phase liquide et émis en phase gazeuse. Au total, 22 produits de dégradation ont été identifiés : 12 d'entre eux ont été détectés au sein de la phase liquide du solvant et 11 au sein de la phase gazeuse correspondant aux fumées traitées émises en sortie du procédé. Parmi les composés identifiés, 9 ont déjà été identifiés dans la littérature en tant que produits de dégradation de la MEA ou de la MDEA, et des schémas réactionnels ont été proposés.

Monitoring of the blend Monoethanolamine/Methyldiethanolamine/Water for post-combustion CO_2 capture.

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Sumbitted the 1st March 2018 in International Journal of Greenhouse Gas Control

Abstract

The blend MEA/MDEA (5/25 %wt.) was studied on the LEMEDES-CO2 lab-scale pilot plant, with representative conditions of post-combustion CO_2 capture for power generation during 900 hours. CO_2 loadings were determined and showed average values of 0.12 and 0.40 respectively for the lean and rich solvents. Stability of the two amines, namely MEA and MDEA was monitored using ionic chromatography (IC); results did not show any significant degradation of MDEA during the campaign, in contrary to MEA which showed a significant degradation in the range of 0.03 points per day. Analytical methods involving GC-MS and IC were developed in order to identify potential degradation products in the liquid phase of the solvent. Study of the composition of the gaseous emissions was also realized using sampling on different solid sorbents followed by a thermal desorption and GC-MS analysis. A total of 22 compounds were listed including amines, organic acids, and pyrazines derivatives. 12 degradation products were found in the solvent itself and 11 in the treated flue gas among which MDEA the constituent amine of the blend. Most of the identified compounds were already identified in the case of MEA and MDEA were individually considered. A quantitative monitoring was carried out for formic and oxalic acids. Results showed concentrations reaching 500 mg/L for oxalic acid and 1400 mg/L for formic acid.

1 Introduction

Post-combustion CO_2 capture using amine solvents is nowadays the most promising technology to limit the CO_2 emissions from already existing fossil fuel-fired power plants [16]. The process is based on CO_2 absorption by chemical reaction using amines solutions. Primary, secondary or tertiary amines of whom alkanolamines can be used i.e. monoethanolamine (MEA) [30–32,102,114,135,231] which is the benchmark solvent of the process, diethanolamine (DEA) [106,107], 2-amino-2-methyl-1-propanol (AMP) [38,106,107,232] or methyldiethanolamine (MDEA) [106,107,109]. Some of them have been used for many years industrially for gas purification e.g. MEA, DEA, MDEA or diisopropanolamine [18]. The two main drawbacks of the post-combustion CO_2 capture process are the high energy penalty (essentially caused by the regeneration step) [5] and the degradation of solvents involving the formation of degradation products potentially toxics for human and environment [15]. Current studies focus on innovative amines or amine blends that would limit those two main drawbacks.

Mixed amines are known to provide the advantages of individual amines regarding absorption and regeneration without the disadvantages of each one [46]. Primary and secondary amines e.g. MEA and DEA, are very reactive with fast absorption rate, but are limited in terms of CO_2 loading capacity compared to tertiary amines like MDEA because of the stoichiometry of the reaction [28]. Actually, two moles of primary or unhindered secondary amines react with one mole of CO_2 to form one mole of carbamate. On the contrary, tertiary or hindered amines have a higher theoretical capacity of one mole of CO_2 per mole of amine [28]. Alkanolamines blends [48] and piperazine (PZ) blends [49] seem to be promising in terms of energy needed for the process. Among the PZ blends studied, the blend 1-methylpiperazine (1MPZ) / PZ showed an energy consumption smaller than MEA by 20% [50]. We recently studied this blend in terms of stability and degradation, in conditions representative of post-combustion CO_2 capture [225]. In the case of alkanolamines blends, the mix MEA/MDEA showed encouraging properties as a huge heat-duty reduction could be obtained when compared with MEA alone [48]. Stability of this blend has only been studied by two teams [47,48]. Dawou et al., (1996) degraded the blend MEA/MDEA (≈ 5%/40%) in presence of CO_2 at temperatures from 120 to 180°C in batch mode and identified 14 degradation products after analysis by GC-MS of the degraded solvent. However, the degradation method involved by Dawodu et al., (1996) is not representative of industrial conditions and does not permit to conclude about the stability of the blend. On the contrary, Idem et al., (2006) compared the blend MEA/MDEA to 5M MEA on two CO_2 capture pilot plants representative of industrial conditions providing different sources and composition of flue gas (combustion of natural gas vs coal). The results showed that stability of the blend during time was lowered (degradation rates of 2.3 mol%/day for MEA and 1.5 mol%/day for MDEA) in comparison to MEA (degradation rate of 0.5

mol%/day) when using the coal-fired CO_2 capture pilot plant with the addition of a corrosion inhibitor. This degradation was insignificant when using the pilot plant fed with flue gas from combustion of natural gas without the addition of any inhibitor of corrosion. A supposition was made about the possible catalyst action of this inhibitor to the degradation, or because of the more complex composition of the flue gas from coal combustion. These results are encouraging as gas-fired power plants seem to be less polluting and surpassing coal-fired power plants [73,233]. Regarding the degradation products formed, six were identified, without any information about the concentration nor the composition of the gaseous effluents. The aim of the present work is to study the stability of the blend MEA/MDEA (5/25 %wt.) during 900 hours of degradation on a lab-scale pilot plant with conditions representative of post-combustion CO_2 capture [90,158]. Simulations will be performed on Aspen Plus software in order to have informations regarding optimal CO_2 loadings to reduce the energy consumption of the process. To complete the study realized by Idem et al. [48], potential degradation products will be identified in both the liquid phase of the solvent and the treated flue gas thanks to the development of complementary analytical strategies involving gas and liquid chromatography. Reactional mechanisms will finally be proposed for the formed degradation products in order to explain their formation and to assess that they are true degradation products and not artefacts.

2 Modelling MEA/MDEA blend-based process for CO_2 capture

Simulations of a typical amines-based process for CO_2 capture (see **Figure 48**) were performed using Aspen Plus© software. 5%/25% weight of MEA/MDEA blend was simulated and results are compared to simulation results of MEA-based process.

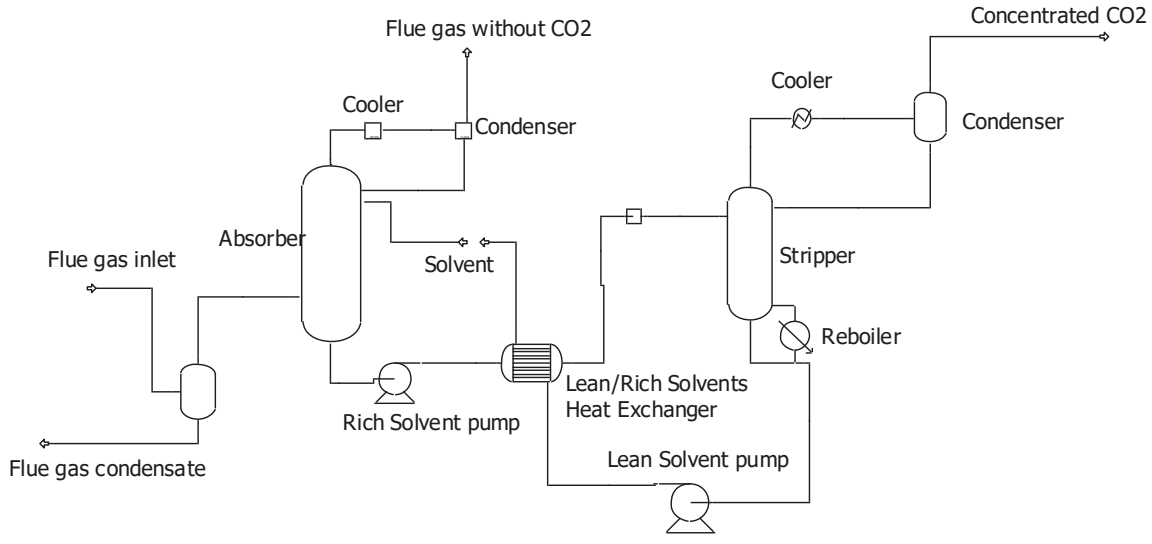


Figure 48: amines-based CO2 capture process flow diagram as simulated using Aspen Plus.

2.1 Objective of simulation

The objective of these simulations was to have deeper insight into the impact of operating parameters of the process on energy consumption of a given process's fixed performance of 90% CO_2 capture. Simulation could also be a useful tool as guideline for experimental operations.

2.2 Simulation parameters

The main energy impacted by operating parameter is the reboiler heat duty for solvent regeneration. This latter energy is a sum of three types of energy: sensible heat necessary to bring the solvent to the boiling state, stripping heat equivalent to latent heat of evaporation and desorption kinetic reaction heat which is equivalent to heat of absorption. This latter depends on the solvent type, on CO_2 partial pressure and on solvent CO_2 loading. The operating parameters of most influence are the solvent concentration in the aqueous solution, the relative ratio of the different solvents in the blend and the ratio of liquid over gas flow rates. This latter ratio is directly impacted by CO_2 loading in the lean solvent. Lower is the lean solvent's CO_2 loading, higher is solvent regeneration heat duty in the stripper reboiler. However, increasing the lean loading in order to decrease the reboiler duty will decrease the cyclic capacity of the solvent as the maximum loading is limited by the solvent characteristics for given pressure and temperature. Indeed, decreasing cyclic capacity will increase solvent flow rate in order to capture constantly 90% of CO_2. Increasing solvent flow rate will increase sensible heat which is necessary before evaporation stripping. Depending on the solvent type, this increasing of sensible heat could overcome the energy gained in stripping by increasing CO_2 loading in lean solvent. Optimum should be retrieved with a CO_2 loading minimizing stripping energy but not increasing too much sensible heat.

The thermodynamic model used for the aqueous phase is ELECNRTL (Electrolyte Non-Random Two Liquid) in the standard form proposed by Aspen Plus software within a chemical kinetic pack generated by the software itself. For gas phase, RKS (Riedlich-Kwong-Soave) model is used. The flue gas characteristics at the inlet of CO_2 capture unit are given in the Table 30 below. They are simplified by avoiding any pollutant such as SOx and NOx but are representative of mains species composition and concentration of coal power plant flue gas.

Table 30: Simulated flue gas characteristics

Temperature	°C	110
Pressure	bar	1.2
Mass flow rate	kg/h	500,0
Mole flow rate	mole/h	18
Composition		
CO_2	%vol.	16
H_2O	%vol.	8
N_2	%vol.	76
O_2	%vol.	6

The solvents simulated are the following:

1. 30% weight of pure MEA + 70% weight H_2O;
2. 5% weight MEA + 25% weight MDEA + 70% weight H_2O;
3. 6% weight MEA + 36% weight MDEA + 58% weight H_2O
4. 10% weight MEA + 30% weight MDEA + 60% weight H_2O

2.3 Simulation results

The results are presented in Figure 49. As expected, there is an optimal loading and a liquid/gas ratio for which the reboiler duty is minimized.

Figure 49 shows also clear different levels between reboiler heat duty of MEA in one hand and MEA/MDEA blends in the other hand. All MEA/MDEA blends show lower minimum energy demand in solvent regeneration relatively to 30% weight aqueous MEA energy demand. With similar global amines concentration in the aqueous solution to 30% weight MEA solvent, the blend 5%/25% weight MEA/MDEA shows a lower minimum of reboiler duty around 3,33 GJ/ton CO_2 while for 30% MEA, the minimum reboiler duty is over 3,73 GJ/ton CO_2. Even with similar liquid/gas ratio to 30% MEA one, the 5%/25% MEA/MDEA blend shows lower reboiler duty than for 30% MEA. The two other amines blends 6%/36% and 10%/30% show even lower liquid/gas ratio than 30% MEA and 5%/25% MEA/MDEA blend (see Figure 49 left) simultaneously with much more lower reboiler heat duty, around 3 GJ/ton CO_2. Figure 49 right shows for all MEA/MDEA blends a lower optimum CO_2 lean loading, less than 0.07 mole CO_2/mole amines for the MDEA blends versus 0.24 for the MEA.

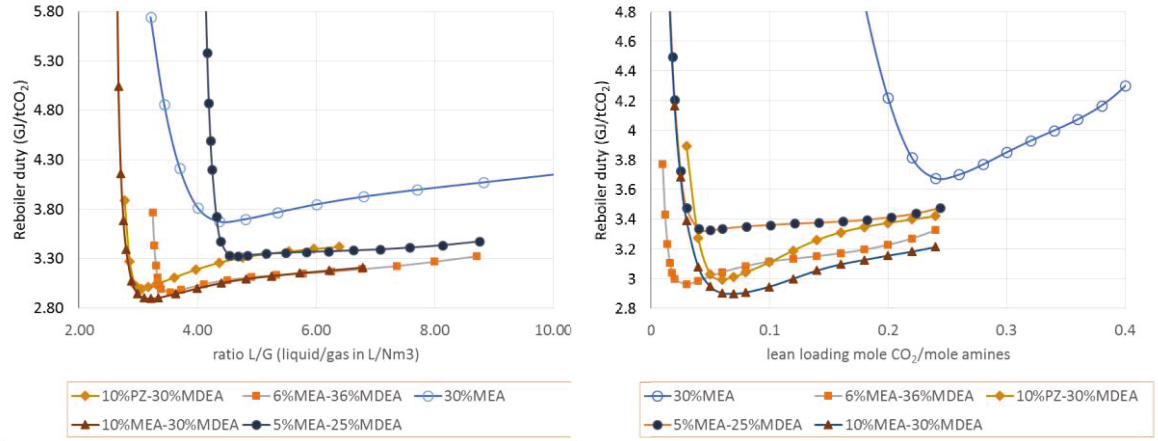


Figure 49: Reboiler heat duty versus liquid/gas ratio (left) and versus CO_2 lean loading (right)

2.4 Simulation conclusion

The simulations of 30% weight MEA-based process and three MDEA-based blends, 5%/25%, 6%/36% and 10%/30% weight MEA/MDEA were performed using Aspen Plus software. MDEA-based solvents show lower reboiler heat duty than pure MEA-based solvent at the same 30% weight concentration in the aqueous solution. Higher MDEA concentration solvents show even lower reboiler duty and lower liquid/gas ratio. Usual MDEA weight concentration in the petrochemical industry is 40% to which activator is added to enhance reaction kinetic of absorption involved with MDEA. Usual activators are MEA and Piperazine. Here, MEA is experimented in blend with MDEA as described below with the ratio 5%/25%. This ratio has been selected in order to limit corrosion phenomena, and to be in the same proportion than the blend MEA 30%, to compare their performances.

3 Materials and methods

3.1 Solvent preparation

Preparation of the blend MEA/MDEA (5/25 %wt.) was realized gravimetrically by mixing commercial MEA (99%) and MDEA (98%) purchased from Alfa Aesar (Schiltigheim, France) with distilled water (18.2 mΩ).

3.2 Chemicals

Ammonia 32% extra pure was purchased from Merck (Lyon, France). Pyrazine (≥99%), 2-methylpyrazine (≥99%), sodium lactate (98%), 2-(methylamino)ethanol (98%), diethanolamine (≥99%), oxazolidin-2-one (98%), 1,2-ethanediol (99,8%), 3-methyl-2-oxazolidinone (99,5%) 1-methylimidazole (99%), *N,N*-dimethylformamide (99,8%), *N*-(2-hydroxyethyl)imidazole (97%) and 2-ethylhexanol (≥99,6%) were purchased from Sigma Aldrich (Saint Quentin Fallavier, France). Oxalic acid (99,8%) was purchased from VWR (Fontenay Sous Bois, France). Formic acid (99%) was purchased from Carlo Erba (Val-de-Rueil, France). *N,N*-dimethylethanolamine (99%) and *N*-(2-hydroxyethyl)formamide (97%) were purchased from Alfa Aesar (Schiltigheim, France). *N*-(2-hydroxyethylpyrrole) was purchased from Tygersci (Hopkinsville, USA).

3.3 Pilot plant description

The blend MEA/MDEA/Water (5/25/70 w/w/w) was degraded on the LEMEDES-CO2 lab-scale equipment [90,158] from EDF R&D (**Figure 50**). A fully detailed description of the device was made in our previous work [225]. The MEA experimental protocol, more particularly the absorption and stripping temperatures was used as a basis to this amine blend, in order to compare its stability with MEA's.

The degradation campaign lasted around 900 h (600 cycles). A synthetic flue gas was injected at the bottom of reactor. It contained 15% CO_2 (≥99.7%, Air Liquide, Mitry Mory, France), 82% N_2 (≥99.995%, Air Liquide, Mitry Mory, France) and 3% air (composed of 20.9% of oxygen). Total absolute pressure during absorption was 1.0 bar. The gas flow rate was 1800 NL/h at 42°C and the solvent flow rate was 3L/min. The total volume of solvent was 1.5 L. For the regeneration step a pressure of 4 bar in the reactor was first applied with N_2 as entering flue gas during 1 min. Then the solvent was heated up to 123°C and maintained during 6 seconds which enabled the regeneration of the amine and the release of CO_2. Released CO_2 was exhausted. The characteristics of the campaign are presented in **Table 31**.

The control system followed many parameters such as temperature, pressure and gas composition and operated continuously and automatically (24h/24 and 7d/7). Samples were taken from the liquid and gas phase and analysed at regular intervals. Solvent sampling was done one time a week

at the bottom of the reactor for the CO_2 rich amine and the CO_2 lean amine. All samples were stored in brown flaks at 4°C

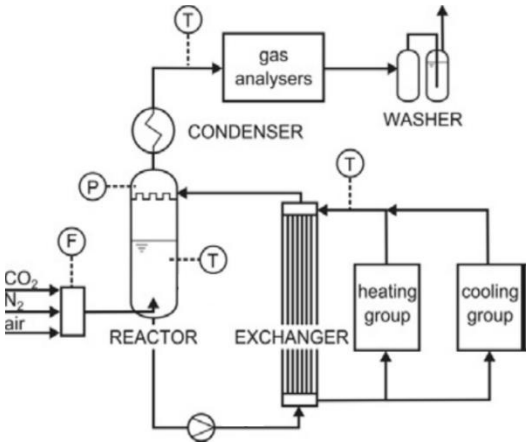


Figure 50: LEMEDES-CO2 lab-scale equipment F: flowmeter; T: temperature probe; P: pressure sensor).

Table 31: Characteristics of the degradation campaign

Composition (MEA/MDEA % wt.)		5/25
Absorption	Temperature	42°C
	Gas composition	15% CO_2 / 82% N_2 / 3% Air
	Pressure	1 bar
	Duration	60 min
Regeneration	Temperature	123°C
	Gas composition	15% CO_2 / 82% N_2 / 3% Air
	Pressure	4 bar
	Duration	30 min (including heating and cooling times)
Duration		900 hours
Number of cycles		600

3.4 Water content measurement

The water content of the amine blend was measured using a V20 Karl Fisher from Mettler (Viroflay, France). The reagent used for the titration were Hydranal-Composite 5K and Methanol dry from Sigma Aldrich (Saint Quentin Fallavier, France). Uncertainty of measurements corresponding to the repeatability of the results was ± 5%.

3.5 Amine titration

The total amine concentration was measured by acidic titration using a T50 Karl Fisher from Mettler (Viroflay, France) titrator with automatic equivalence point detection. 0.4 to 0.6 g of sample were added to 50 mL of deionized water, and placed on the device. The solution was then titrated with

0.2 M of HCl to reach a pH of 2. The amount of acid needed to reach the second equivalence point was used to calculate the total amine concentration. Uncertainty of measurements corresponding to the repeatability of the results was ± 5%.

3.6 Total Inorganic Carbon measurement (TIC)

A TOC-L CSH from Shimadzu (Marne la Vallée, France) was used to determine the total inorganic carbon content of the solvent. The 50X diluted sample was acidified in 30 wt% phosphoric acid to gaseous CO_2. The CO_2 emitted was then measured with an infrared analyzer. Previous calibration of the dispositive (using a 1000 ppm standard) permitted to calculate the amount of inorganic carbon contained in the solution. CO_2 loading was then calculated using the amount of inorganic carbon in mol/kg divided by the total amine concentration in mol/kg. Uncertainty of measurements corresponding to the repeatability of the results was ± 5%.

3.7 Ionic chromatography (IC)

3.7.1 Cation ionic chromatography

MEA and MDEA were individually quantified using ionic chromatography (IC). An ICS 1000 equipped with an autosampler from Thermo Fisher (Villebon-sur-Yvette, France) was used. Samples were diluted 20000 times with water, and then 25 µL were injected for the separation. A guard column (IonPac^{TM} CG19RFIC^{TM} 4 x 50 mm) was placed before the analytical column (IonPac^{TM} CS19RFIC^{TM} 4 x 250 mm) to prevent the analytical column from contaminations. An eluent generator permitted the delivery of adjustable concentrations of methanesulfonic acid (MSA). The system was equipped with a 4-mm anionic Suppressor. Detection was performed with a conductimetric cell. Both columns and conductimetric detectors were thermostated at 35°C. The separation was realized in isocratic mode with 3 mM of MSA and permitted the separation of the two amines in 12 min. A quantification method has been developed and validated with the total error concept and the accuracy profile [136,192] with an acceptance limit of 20% and 30% respectively for MDEA and MEA in the range of interest. The same device was also used to track degradation products formed in the liquid phase of the solvent. In this case, the solvent was diluted 1000 times in water before injection. The initial MSA concentration was 2mM, raised at 35 mM from 35 to 135 min. The other parameters were the same as previously described.

3.7.2 Anion ionic chromatography

Anionic species were identified and quantified using ionic chromatography (IC). The same device as previously described was used. A guard column (IonPac AG11 4 x 50 mm) was placed before the

analytical column (IonPac AS11 4 x 250 mm) to prevent the analytical column from contaminations. The system was equipped with a 4-mm cationic suppressor. Detection was performed with a conductimetric cell. Both columns and conductimetric detectors were thermostated at 35°C. The separation was realized with an elution gradient of KOH starting from 0.5 mM from 0 to 30 min then raised to 40 mM in 30 min then decreased at 0.5 mM from 80 to 120 min. The flow rate was 1.5 mL/min and the applied current of 149 mA. The columns and the detector were thermostated at 35°C. A quantification method was developed for formic and oxalic acids. This method has been previously validated [225] using the accuracy profile concept with acceptance limits of 20% on a matrix composed of 1MPZ/PZ (30/10 %wt.). In the present work, the matrix is also composed of amines thus no modification of the behavior of the method are expected.

3.8 Gas chromatography-Mass Spectrometry (GC-MS)

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer from Agilent Technologies (Massy, France). The device was equipped with a MPS (MultiPurpose Sampler) auto sampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated liquid injections, HS-SPME and thermodesorption (TDU) analyses. Two columns (Chromoptic, Villejust, France) were used to separate the compounds; a non-polar fused silica capillary column CP-SIL8 CB-MS (30 m x 0.25 mm, 1 µm) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm, 0.5 µm). 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. Detection was performed with a mass spectrometer using electronic ionization (EI) source (70 eV) heated to 250°C. The scan range was 25 to 250 amu. NIST spectra data base was used for the peaks identification. Identification proposals were confirmed by the injection of commercial standards when available.

3.8.1 Direct liquid injections

For liquid injection procedures, real samples were diluted 10 times in methanol before injecting 1 µL in split mode (1:5) at 280°C.

3.8.2 Headspace Solid Phase MicroExtraction – GC-MS (HS-SPME-GC-MS)

For Head Space – Solid Phase MicroExtraction (HS-SPME) procedures, the volume of sample introduced in the 20 mL HS vial was 5 mL. A 75 µm Carboxen/PDMS SPME fibre obtained from Supelco (Sigma Aldrich, Saint Quentin Fallavier, France) was used. The fully automated HS-SPME procedure was

the same as described by Rey et al., 2013 [199]. This method was initially developed for the identification and the quantification of alkylpyrazines. It was applied here to the identification of other degradation products present in the liquid phase.

3.9 Gas phase sampling

Gas sampling was performed in order to identify degradation products emitted in the gas phase during the process. The same method as described in our previous study [192] was applied here. Three different sorbents were used and compared: Tenax® TA, Tenax® GR and Carbopack™ B/Carbopack™ X (Chromoptic, Villejust, France). The sampling tube was placed after the condenser to avoid any humidity problems [192], and a flow of 200 mL/min during 60 min was pumped through the solid phase. Flow rate was controlled with a rotameter, and air was pumped with an ambient air sampler from Supelco (Sigma Aldrich, Saint Quentin Fallavier, France).

3.10 Analysis of the gas phase by TDU-CIS-GC-MS

For thermodesorption of tubes, gas flow rate of helium 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 cryofocused in the injector at -40°C with liquid CO_2. Then temperature increased from - 40°C to 300°C at 12°C/s and the molecules were injected in the column in splitless mode. The same GC/MS method as for liquid samples was used with a CP-SIL8 CB-MS column.

4 Results

4.1 Monitoring of the degradation campaign

The monitoring of the campaign consisted in the analysis of the water content, the total amine concentration, and the Total Inorganic Carbon for the determination of the CO_2 loading. The CO_2 loading results showed an average value of 0.12 for the lean solvent and 0.40 for the rich one. These values are in full agreement with the results of Aspen plus simulation of the process (0.05 and 0.44) and are quite stable during time (**Figure 51**). Results obtained about the stability of the water and amine concentration during the campaign are presented in **Figure 52**. Total amine concentration (including potential amine degradation products) was stable during time. Water content was as well stable during time even if a slow decrease correlated with a small increase of the amine concentration can be seen. In order to have more information regarding the stability of the two amines in solution, samples were analyzed by IC for their content in MDEA and MEA. Results are shown in the **Figure 53**. Results did not show any significant degradation of MDEA during the campaign, in contrary to MEA which showed a significant degradation in the range of 0.03 points per day. The next step of this study is the identification of potential degradation products formed during the process.

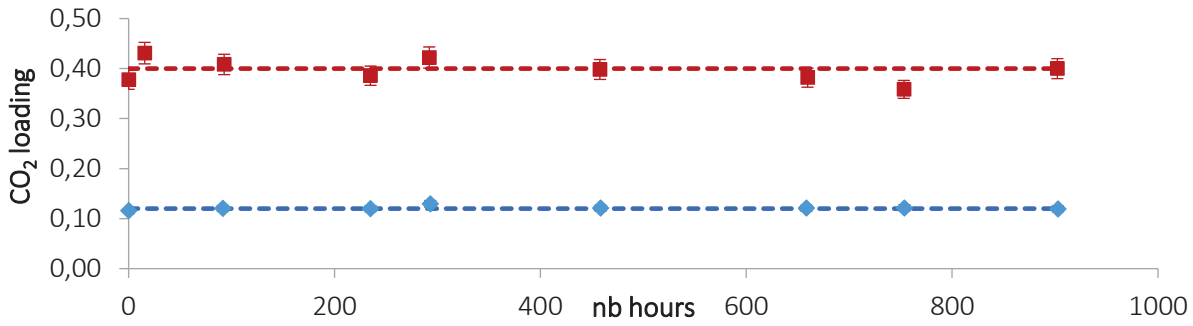


Figure 51: Monitoring of the CO_2 loading during time. Error bars correspond to uncertainty of the method.

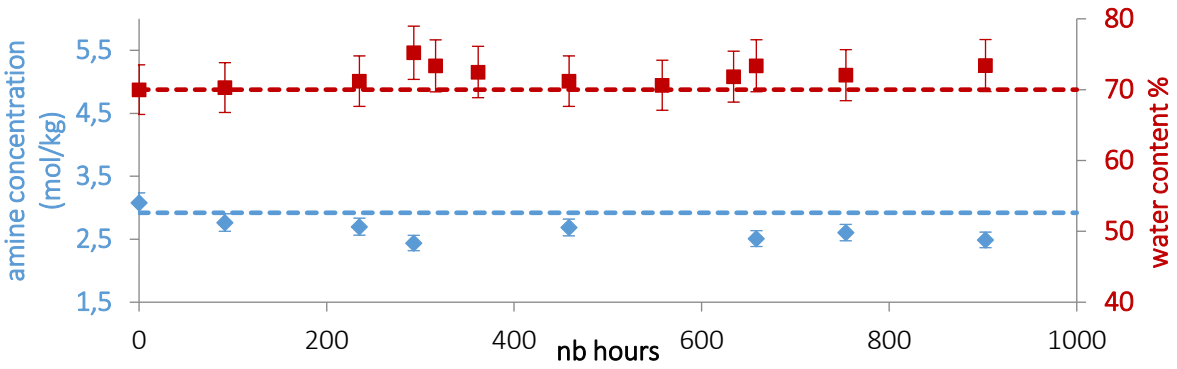


Figure 52: Monitoring of the water and amine concentrations during the degradation campaigns. Error bars correspond to the uncertainty of the method.

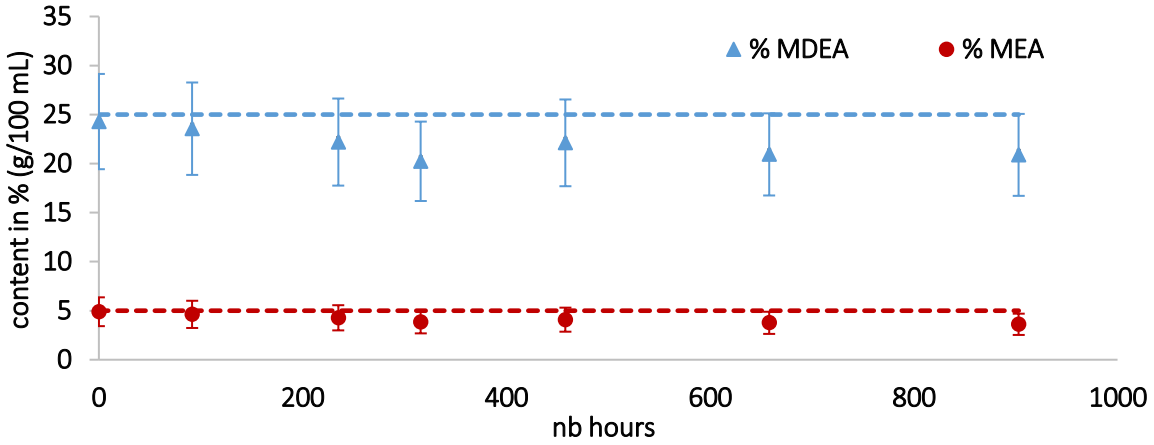
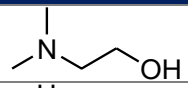
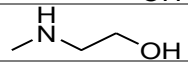
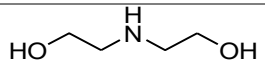
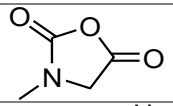
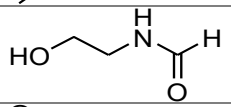
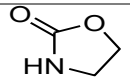
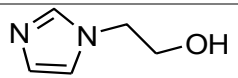
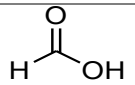
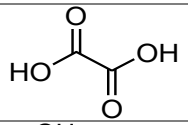
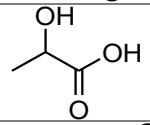
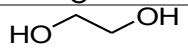


Figure 53: Monitoring of the concentration of MDEA and MEA during de degradation campaign. Error bars correspond to acceptance limits of 20% and 30% respectively for MDEA and MEA.

4.2 Degradation products in the liquid phase of the solvent

Twelve degradation products were identified in the liquid phase of the solvent using complementary analytical strategies i.e. GC-MS, HS-SPME-GC-MS and IC (**Table 32**). An example of chromatogram obtained after the analysis by GC-MS is given in **Figure 54**. Eight nitrogen containing compounds, three organic acids and one alcohol were identified. Among them were four compounds already identified as degradation products of the blend MEA/MDEA by Dawodu et al. (1996) [47]: *N,N*-dimethylaminoethanol, 2-(methylamino)-ethanol, diethanolamine, and 1-(2-hydroxyethyl)imidazole. Only one compound could not be confirmed by the injection of commercial standard because unavailable: 3-methyl-2,5-oxazolidine-dione. Among the compounds identified by Idem et al. [48] a single one was detected in this study: 1,2-ethanediol. The other compounds were not detected. This may be caused by the low levels of formation of these compounds or by the synthetic and clean character of the flue gas to treat. Actually, two of the compounds detected by Idem et al. were suspected to be formed because of the presence of SO_2 in the flue gas stream [48].

Table 32: Degradation compounds identified in the liquid phase of the solvent (STD: identification confirmation with commercial standard)

	Compounds	Structure	CAS	GC-MS	HS-SPME-GC-MS	IC	STD
Nitrogen containing derivatives	*N*,*N*-Dimethylethanolamine		108-01-0	X			X
	2-(Methylamino)ethanol		109-83-1	X	X		X
	Ammonia	NH_3	7664-41-7			X	X
	Diethanolamine		111-42-2	X			X
	3-Methyl-2,5-oxazolidinedione		5840-76-6	X			-
	N-(2-hydroxyethyl)formamide		693-06-1	X			X
	Oxazolidin-2-one		497-25-6	X			X
	1-(2-Hydroxyethyl)imidazole		1615-14-1	X			X
Organic acids	Formic acid		64-18-6			X	X
	Oxalic acid		144-62-7			X	X
	Lactic acid		79-33-4			X	X
Alcohol	1,2-Ethanediol		107-21-1	X			X

Most of the identified compounds are well known degradation products of MEA alone [15,42,82,89,107,147,160] and MDEA alone [36,42]. Reactional mechanisms have already been studied and proposed for 9 of the listed compounds namely *N,N*-dimethylethanolamine, 2-(methylamino)ethanol, diethanolamine, *N*-(2-hydroxyethyl)formamide, oxazolidin-2-one, 1-(2-hydroxyethyl)imidazole, formic and oxalic acids, and 1,2-ethanediol [15,37,42,47,107,234]. *N,N*-dimethylethanolamine was explained by methylation of one molecule of MDEA and demethylation of another molecule of MDEA [15,37]. This reaction also led to the formation of diethanolamine. Formation of 2-(methylamino)-ethanol have been described starting from MDEA [47]. The formation of oxazolidin-2-one was explained by Lepaumier et al. (2009) [107]: the reaction of MEA with CO_2 led to a carbamate, which can be transformed in oxazolidin-2-one. *N*-(2-hydroxyethyl)imidazole could be obtained after reaction between MEA, ammonium bicarbonate, formaldehyde and glyoxal [235]. Carboxylic acids formation have been described in two studies following two different pathways [42,234]. The pathway proposed by Lepaumier et al. [42] also explained the formation of 1,2-ethanediol. *N*-(2-hydroxyethyl)formamide formation has been studied by Lepaumier et al. (2011) [30] and was explained by the reaction of MEA with formic acid. These mechanisms are presented in Figure 55 and Figure 56.

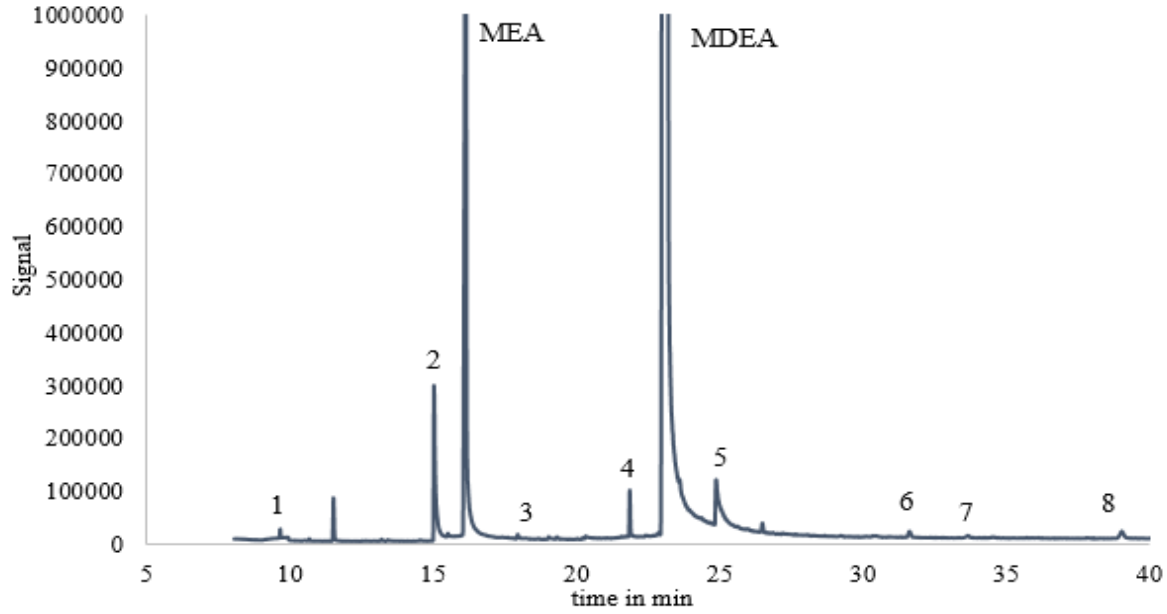


Figure 54: Chromatogram obtained after the analysis by GC-MS of the solvent at 900h of degradation. 1: *N*,*N*-dimethylethanolamine; 2: 2-(methylamino)-ethanol; 3: 1,2-ethanediol; 4: 3-methyl-2,5-oxazolidine-dione; 5: diethanolamine; 6: N-(2-hydroxyethyl)formamide; 7: Oxazolidin-2-one; 8: 1-(2-Hydroxyethyl)imidazole.

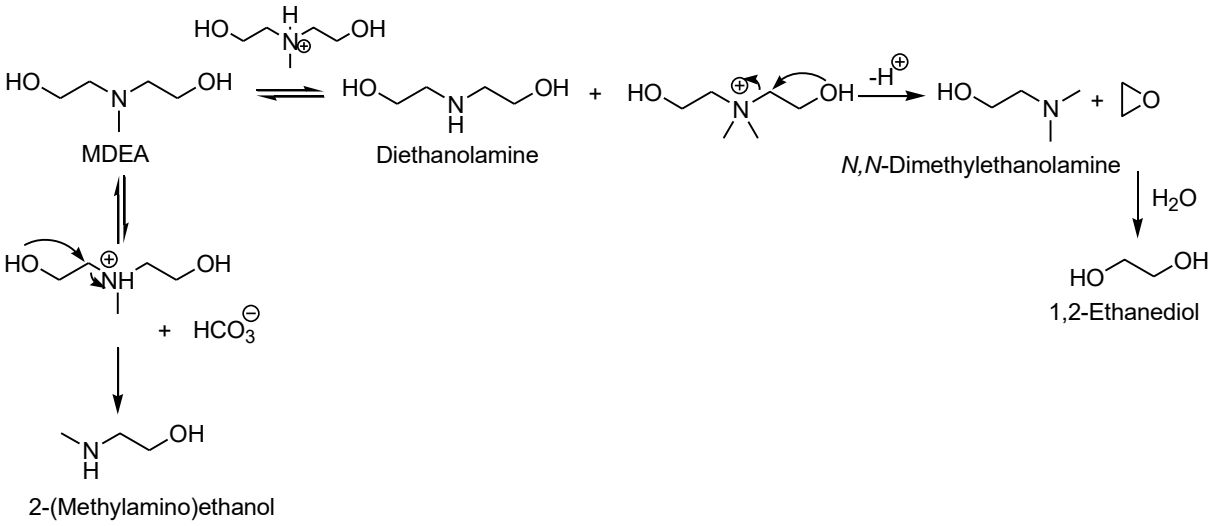


Figure 55: Pathway degradation of MDEA, taken from [14,41,162]

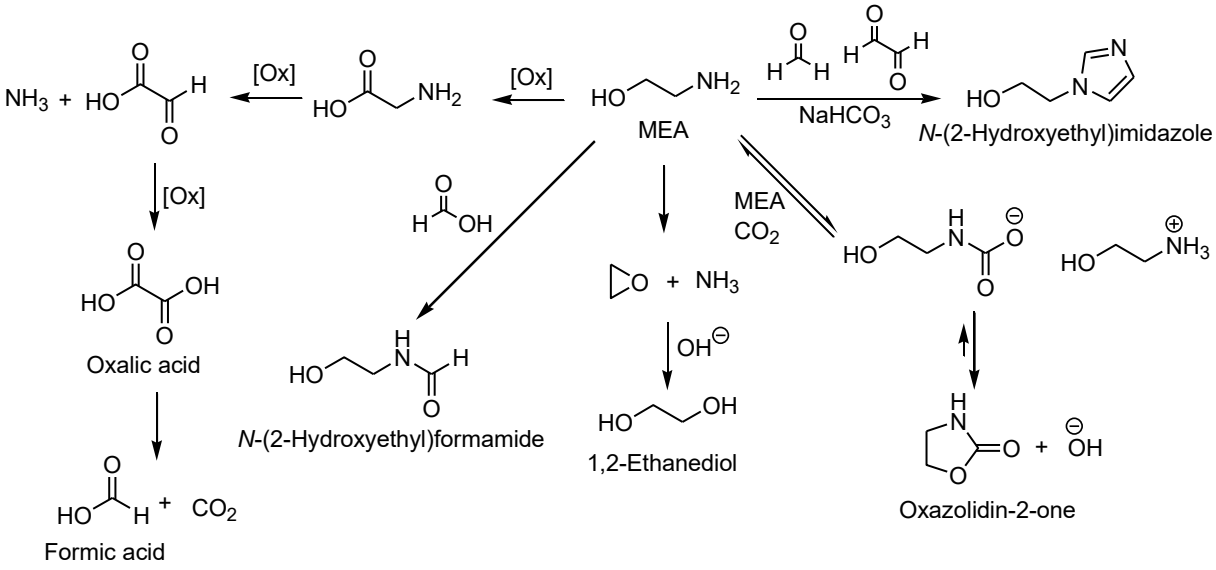


Figure 56: Pathway degradation of MEA, taken from [14,37,162,166,167]

To our knowledge, no pathway has been suggested to explain the formation of 3-Methyl-2,5-oxazolidine-dione. We suggested a pathway involving the carboxylation of 2-(methylamino)ethanol followed by its oxidation and water elimination allowing cyclization (Figure 57).

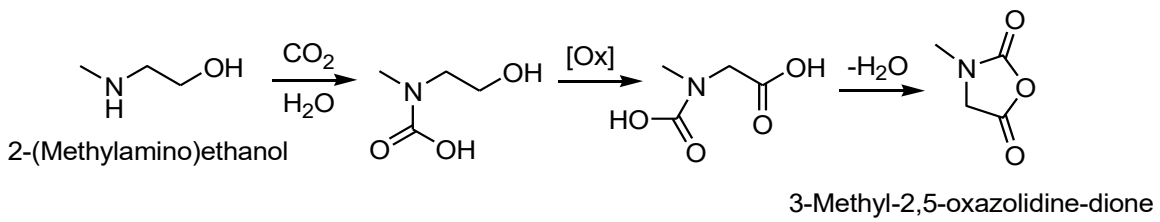


Figure 57: Formation of 3-methyl-2,5-oxazolidine-dione

Quantification has been realized on two organic acids: oxalic and formic acid (Figure 58). The quantification method has been validated for the two compounds using the accuracy profile concept with an acceptance limit of 20%. Results showed concentrations reaching 1400 mg/L +/-20% for formic acid and 500 mg/L +/-20% for oxalic acid. These values correspond to less than 1% of the initial amine concentration. Although no significant loss of MDEA have been seen over time, some degradation products may be formed in significant concentrations, thus confirming the relevance of performant analytical strategies. The next part of this work is to study the composition of the treated flue gas.

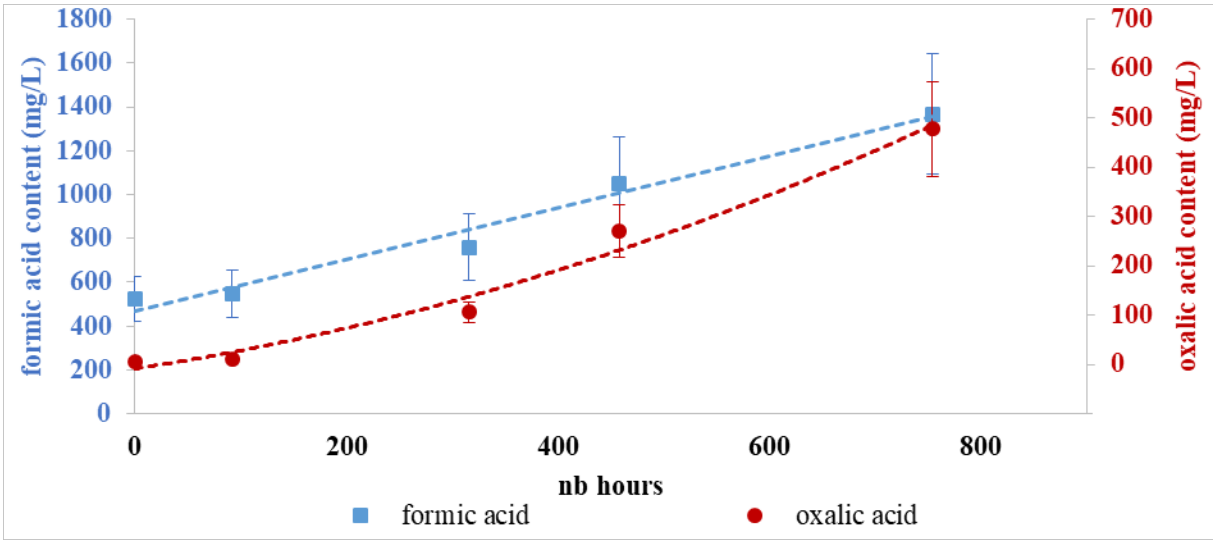


Figure 58: Quantification of oxalic and formic acids during time. The uncertainty corresponds to the limits of acceptability of 20% of the method.

4.3 Monitoring of the gaseous emissions

In order to identify compounds emitted within the treated flue gas, samplings were realized every week according to the method described in section 2.7 on three different sorbents: Tenax® TA, Tenax® GR and Carbopack™ B/Carbopack™ X. 11 compounds were listed (**Table 33**) among them amines, alcohols and pyrazines. When available, identification was confirmed with the injection of commercial standards. Two compounds could not be confirmed because not commercially available: 3-methyloxazolidine and 3-oxazolidine ethanol. Only one compound was listed in both liquid and gaseous phases of the solvent: *N,N*-dimethylaminoethanol. MDEA, the main amine constituent of the solvent was also detected in the treated flue gas, suggesting a potential vaporization of the compound. **Figure 59** compares the area of the peaks corresponding to each compound after the extraction on the three sorbents. All the listed compounds were detected on Tenax® TA sorbent, but for some compounds e.g. 1-methylimidazole or *N,N*-dimethylaminoethanol, the extraction recoveries were better for Tenax®GR and Carbopack™ B/Carbopack™ X, suggesting the interest of using the three sorbents. One of the drawback of using these sorbents is the potential generation of artefacts [236]. In order to avoid biased identification, analysis of clean tubes and ambient air sampled tube was frequently achieved in order to eliminate compounds not involved in the degradation of the studied solvent. **Figure 60** shows a chromatogram obtained after the analysis by GC-MS of a Tenax® TA tube sampled after 900 hours of degradation. To our knowledge no studies have been realized about the composition of the gaseous emissions from the blend MEA/MDEA.

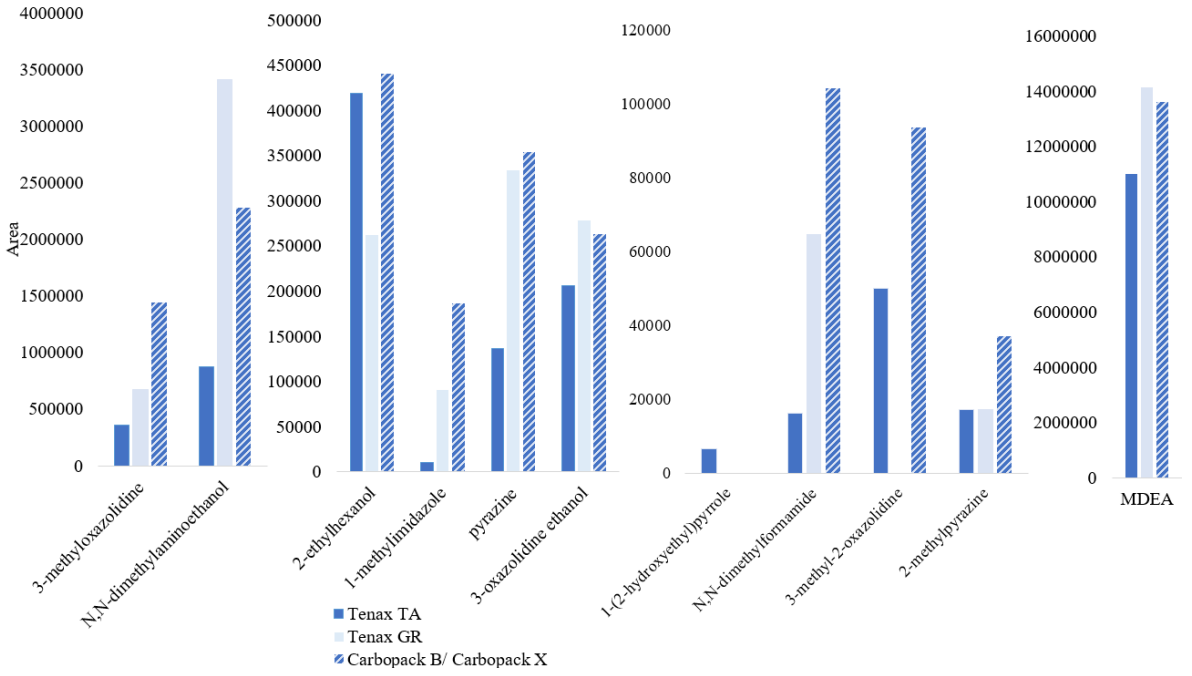


Figure 59: Comparison of the areas of the peaks of the compounds after sampling and thermal desorption on the three sorbents

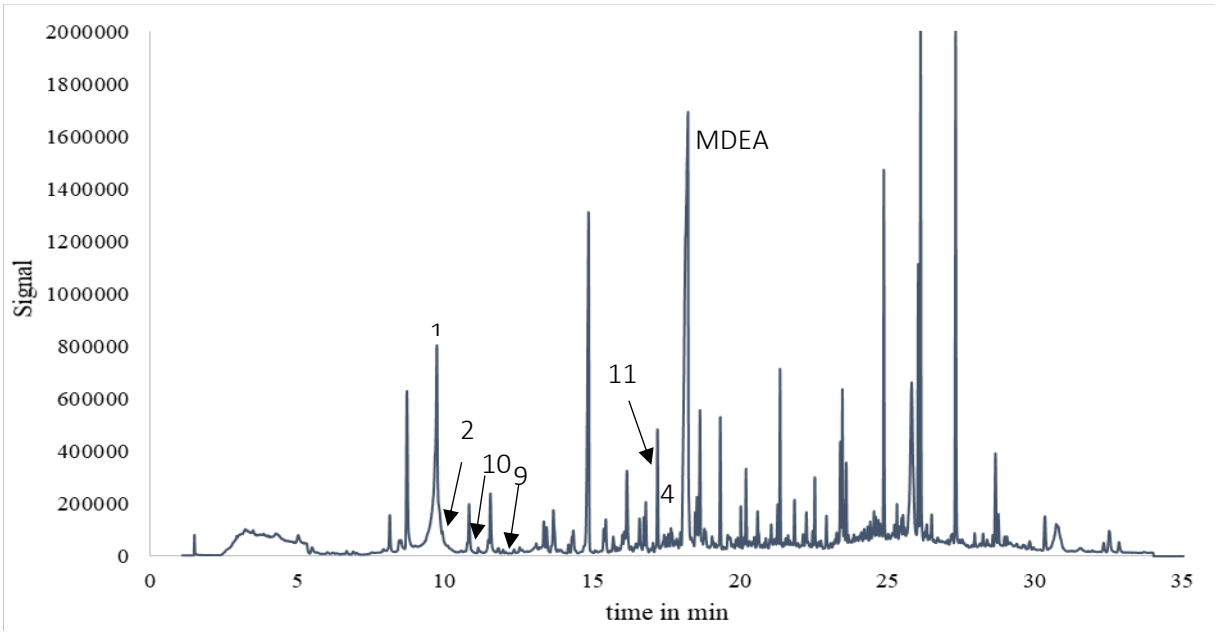
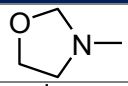
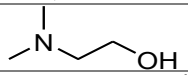
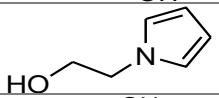
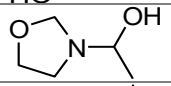
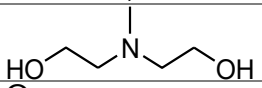
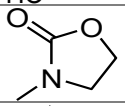
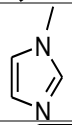
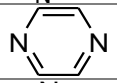
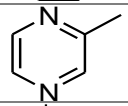
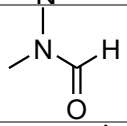
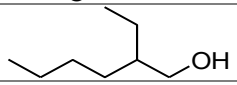


Figure 60: Chromatogram obtained after the analysis by TDU-CIS-GC-MS of a Tenax TA tube sampled at 900 hours of degradation. Unidentified peaks may correspond to artefacts of the sampling sorbent or to contaminations.

Table 33: Compounds identified in the gaseous emissions

		Compounds	Structure	CAS	Sorbent			STD
					Tenax® TA	Tenax® GR	Carbopack™ B/ Carbopack™ X	
Nitrogen containing derivatives	1	3-Methyloxazolidine		27970-32-7	X	X	X	-
	2	*N*,*N*-Dimethylaminoethanol		108-01-0	X	X	X	X
	3	1-(2-Hydroxyethyl)pyrrole		6719-02-4	X			X
	4	3-Oxazolidine ethanol			X	X	X	-
	5	MDEA		105-59-9	X	X	X	X
	6	3-Methyl-2-oxazolidinone		19836-78-3	X		X	X
	7	1-Methylimidazole		616-47-7	X	X	X	X
Alkylpyrazines	8	Pyrazine		290-37-9	X	X	X	X
	9	2-Methylpyrazine		109-08-0	X	X	X	X
Amides	10	*N*,*N*-Dimethylformamide		68-12-2	X	X	X	X
Alcohols	11	2-Ethylhexanol		104-76-7	X	X	X	X

Four of the identified compounds have already been listed in the field of emissions from MEA degradation [32]: *N*-(2-hydroxyethyl)pyrrole, pyrazine, 2-methylpyrazine and *N,N*-dimethylformamide. A reactional mechanism has been proposed by Gouedard [230] for the formation of *N*-(2-hydroxyethyl)pyrrole involving the reaction of MEA with glycolaldehyde. The formation of alkylpyrazines among which pyrazine and 2-methylpyrazine have been described in the field of MEA degradation [199].

We suggested different pathways to explain the formation of four of the listed compounds. 3-Methyloxazolidine would be formed after the reaction of 2-(methylamino)ethanol with formaldehyde leading to the intermediate **33**. After water elimination and intramolecular reaction, 3-methyloxazolidine would be formed (**Figure 61**).

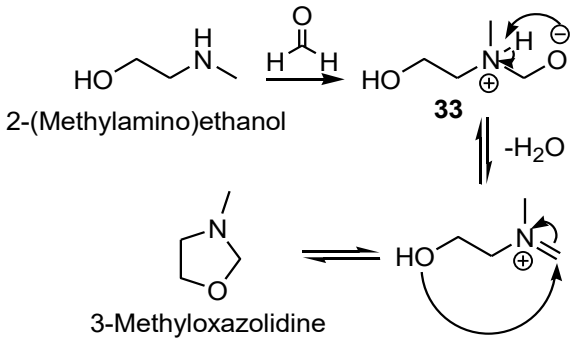


Figure 61: Formation of 3-methyloxazolidine

A second pathway would explain the formation of this compound starting from MEA. After reaction with formaldehyde followed by a water elimination, formation of oxazolidine would be expected. Oxazolidine would then react with formaldehyde to form the intermediate **34**, which after its deshydratation into and iminium would react with formate to form 3-methyloxazolidine. The formed oxazolidine would also react with acetaldehyde to generate 3-oxazolidine ethanol (**Figure 62**).

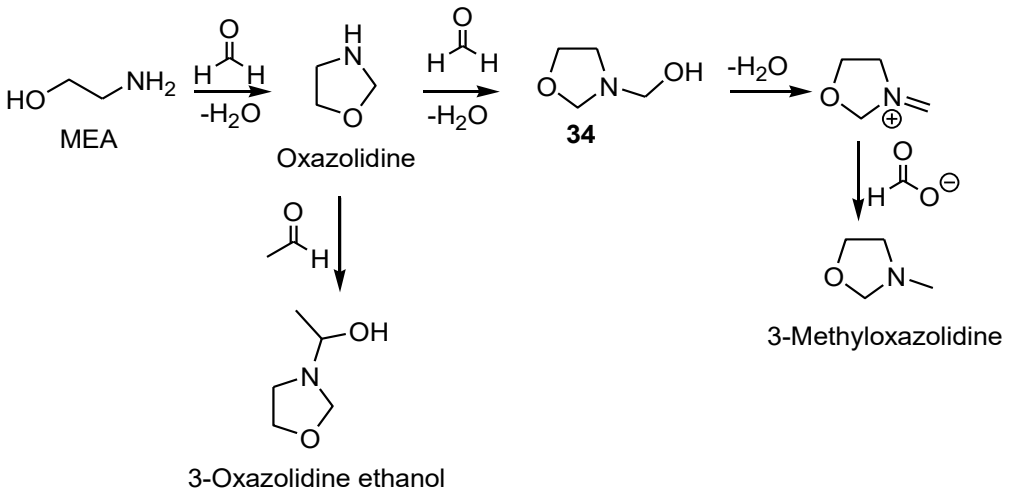


Figure 62: Formation of 3-oxazolidine ethanol and 3-methyloxazolidine

A proposal was made to explain the formation of 3-methyl-2-oxazolidinone; this compound would be formed after the reaction of 2-(methylamino)ethanol with CO_2 followed by a water elimination (Figure 63).

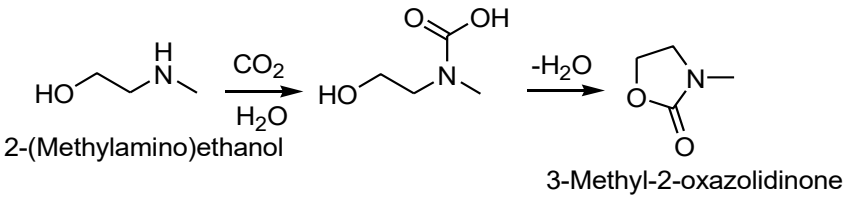


Figure 63: Formation of 3-methyl-2-oxazolidinone

Finally, 1-methylimidazole would be formed after the reaction of glyoxal with methylamine and ammonia leading to the intermediate **35**. This latter would then react with formaldehyde or glyoxylic acid to form 1-methylimidazole (Figure 64).

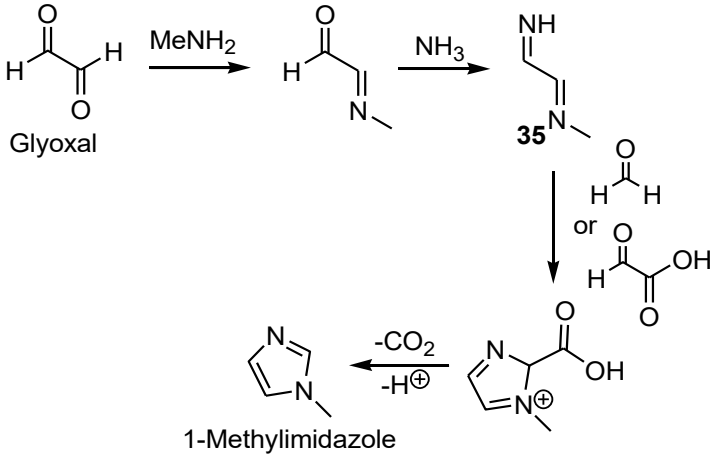


Figure 64: Formation of 1-methylimidazole

5 Conclusion

Stability and CO_2 capture performances of the blend MEA/MDEA (5/25 %wt.) were studied during 900 hours on a CO_2 capture pilot plant representative of industrial conditions. CO_2 loadings of 0.12 and 0.40 were in the same range than for MEA and in accordance with literature and simulations [48]. Analysis performed during the entire campaign did not show any significant degradation of MDEA over time in contrary to MEA which showed a significative degradation in the range 0.03 points per day. Complementary analytical strategies were developed in order to identify potential degradation products in the solvent himself and in the gaseous effluents. 22 degradation products were listed: 12 in the liquid phase of the solvent, 10 in the treated flue gas, and one detected in both phases. Among them were found MEA and MDEA degradation products already identified in the literature [15,37,42,47,89]. Reactional pathways were proposed in order to explain the formation of these compounds, except for *N*,*N*-dimethylformamide and 2-ethylhexanol suggesting their presence as artefact. The results obtained in the present work are promising for an utilization of this blend in the field of post-combustion CO_2 capture. Further work should be done by studying the stability of the blend with gas-fired flue gas and on longer time.

Acknowledgments

We would like to thank Aïcha El Khamlichi (ADEME engineer) for the monitoring of this doctoral project and ADEME (French Agency of Environment and Energy Management) for the financial support.

Chapitre 5 : Comparaison des solvants étudiés

Les deux principales limitations du procédé industriel de captage du CO_2 en post-combustion utilisant la MEA 30 %, solvant modèle au procédé, sont d'une part la pénalité énergétique engendrée [13] et d'autre part la dégradation des amines conduisant à un besoin de renouvellement du solvant, et par conséquent à des coûts supplémentaires [15]. Comme nous l'avons indiqué dans le chapitre 1, plusieurs points sont à prendre en compte pour la sélection d'un solvant. Les principaux critères concernent les performances thermodynamiques vis-à-vis du captage du CO_2, les besoins énergétiques requis pour le procédé, la dégradation du solvant, son coût, sa toxicité et son comportement vis-à-vis des phénomènes de corrosion et de précipitation [27]. Trois solvants dits innovants en termes de besoin énergétiques par rapport au solvant modèle MEA 30 % ont été sélectionnés dans le cadre de cette étude i.e. les mélanges 1MPZ/PZ, MDEA/MEA et DMEA/PZ. Aucun de ces mélanges n'a en revanche été étudié en termes de stabilité chimique dans des conditions représentatives des conditions industrielles du procédé de captage du CO_2 en post-combustion. Or, ces informations font partie des critères de sélection des solvants et sont indispensables afin d'apporter des éléments de réponse quant à l'utilisation potentielle de ces mélanges à l'échelle industrielle.

Dans les chapitres précédents, les solvants innovants 1MPZ/PZ et MDEA/MEA ont été étudiés et caractérisés en termes de stabilité chimique au sein du laboratoire LEMEDES-CO2. Des méthodes analytiques complémentaires impliquant la chromatographie en phase liquide et la chromatographie en phase gazeuse ont permis d'identifier près de 40 produits de dégradation. Ces études ont porté à la fois sur la phase liquide du solvant dégradé, mais également sur la phase gazeuse émise en sortie du banc d'essai.

Ce dernier chapitre, sous la forme d'un article, présente l'étude réalisée sur le troisième et dernier solvant innovant du projet, le mélange DMEA/PZ, en le comparant aux deux autres solvants étudiés dans les mêmes conditions opératoires, caractéristiques du procédé MEA 30 %. Cette comparaison a porté sur deux des points limitants du procédé : l'énergie requise pour le procédé et la stabilité chimique des amines. La première partie de cet article a pour objectif de comparer les propriétés thermodynamiques des trois solvants du projet par rapport à la MEA 30 %. La seconde partie comparera le comportement de ces solvants vis-à-vis de la dégradation après 900 heures de captage.

Comparison in similar operating conditions of the stability of three innovative blends for post-combustion CO_2 capture: 1MPZ/PZ, DMEA/PZ and MDEA/MEA

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Abstract

Post-combustion CO_2 capture using aqueous amine solvents is currently the most promising technology to limit the CO_2 emissions. The present work aimed at comparing the thermodynamic properties for CO_2 capture and the chemical stability of three innovative amine blends namely 1-methylpiperazine/piperazine (1MPZ/PZ 30wt%/10wt%), dimethylaminoethanol/piperazine (DMEA/PZ 35wt%/5wt%) and methyldiethanolamine/monoethanolamine (MDEA/MEA 25wt%/5wt%) with monoethanolamine's (MEA), the benchmark solvent of the process. Degradation of the three blends was realized during around 900 hours for each one on the LEMEDES-CO2 lab-scale CO_2 capture pilot plant from EDF R&D in similar operating conditions typical of MEA process. The temperatures, pressures and gas flow rates during the absorption and regeneration steps were the same as those used in the presence of MEA as CO_2 capture solvent. The only different setting was the absorption duration, optimized for each blend in order to reach optimum CO_2 loadings. Most promising results were obtained for the blend MDEA/MEA, for which a reduction of 10% on the reboiler heat duty can be reached when compared to MEA 30%, and a slow degradation of MEA in the range of 0.03 points per day was observed combined with no significant degradation for MDEA.

1 Introduction

Post-combustion CO_2 capture using amine solvents is currently the most promising technology to reduce the CO_2 emissions from already existing fossil fuel-fired power plants [16]. The process, based on CO_2 absorption by chemical reaction using amines solutions, is efficient as it permits to emit CO_2 pure at 99% with a recovery of 90%. The main drawbacks of the process are its high energy penalty [12] and the irreversible degradation of the used amine which involves the formation of degradation products potentially toxics for human and the environment [14,15]. This degradation is also responsible of additional costs, as fresh solvent has to be added in order to support the amine loss. Monoethanolamine (MEA) is the benchmark solvent of the process and its degradation has been largely studied [30–32,101–105]. Many studies focus today on innovative amines or amine blends that would limit the two main disadvantages of the process.

Recently, Li et al. [45,49] screened for their energetic performances seven piperazine derivative and five blends with piperazine (PZ) through Vapor-Liquid Experiments (VLE) for CO_2 solubility. Results showed that the most promising solvents were the blends 1-methylpiperazine (1MPZ) with PZ and *N,N*-dimethylaminoethanol (DMEA) with PZ. The blend 1MPZ/PZ was studied thermodynamically by Chen et al. (2017) [50] which concluded that a reduction of 20% of the energy consumption could be reached with this solvent when compared with MEA. Other blends composed of primary or secondary alkanolamines with tertiary alkanolamines are promising e.g. the blend *N*-methyldiethanolamine (MDEA)/MEA which showed a reduction of the heat duty for regeneration when compared to MEA [48]. Degradations of the blends 1MPZ/PZ and MDEA/MEA were achieved on our previous studies [225,237] on a lab-scale CO_2 capture pilot plant and permitted the identification of respectively 27 and 22 degradation products for the blends 1MPZ/PZ and MEA/MDEA.

The aim of the present study is to compare the thermodynamic performances for CO_2 capture (cyclic capacity, heat of absorption and reboiler heat duty) through Aspen Plus simulations and the chemical stability after 900 hours of cycling on the CO_2 capture pilot plant LEMEDES-CO2 [90] of the three amine blends namely 1MPZ/PZ, MEA/MDEA and DMEA/PZ. Degradation experiments were performed in similar operating conditions commonly used during MEA process in order to mimic the three blends' behavior on units built for MEA. During each campaign, samplings were done every week and analysis were performed by Ionic Chromatography in order to quantify the main amines and to conclude about their stability during time.

2 Solvent properties

When unavailable in the literature, simulations of a typical amines-based process for CO_2 capture were performed using Aspen Plus © software for the blends of interest, in order to determine the best amines ratio [237]. Results are compared to simulation results of MEA based process

2.1 Modelling amine blend-based process for CO_2 capture

Heat of absorption was calculated using approximation of Gibbs-Helmholtz equation:

$$\Delta H_{\text{abs}} \approx R \, \frac{\ln P_{\text{CO2.2}} - \ln P_{\text{CO2.1}}}{\frac{1}{T_2} - \frac{1}{T_1}}$$

These results have to be taken carefully as Gibbs-Helmholtz equation is known to be imprecise. This equation gives only rough approximation of heat of absorption. CO_2 partial pressure was calculated using Aspen Plus mixing and flashing blocs for temperature in the range of 40-120°C and for optimal CO_2 lean loading. All other parameters are simulation results of absorption/desorption process optimized for reboiler heat duty minimization.

2.2 Simulation results

The simulation results i.e. CO_2 loadings, cyclic capacities, heats of absorption and reboiler heat duties of the three blends are presented in **Table 34** (some of the presented data were unavailable). The three blends namely 1MPZ 30wt% + PZ 10wt%, DMEA 35wt% + PZ 5wt% and MDEA 25wt% + MEA 5wt% were selected in order to reduce the energy consumption of the process when compared to MEA 30wt%.

Cyclic capacity of the blend MDEA 25wt% + MEA 5wt% has been determined and correspond to the difference of moles of CO_2 absorbed in the solution per unit of volume of solution during the absorption step and the one in the regeneration step [238]. Higher is the cyclic capacity, higher is the amount of CO_2 carried and lower is the flow rate of solvent to be applied thus leading to a decrease of the sensible heat. In the present study, cyclic capacity of the blend MDEA 25wt% + MEA 5wt% is lower than 30wt% MEA's. Regarding the Heat of absorption, values obtained for the blend MDEA 25wt% + MEA 5wt% at 120°C are more favorable than those obtained for MEA 30%, which would decrease the energy needed for the desorption step.

The main energy impacted by operating parameters is the reboiler heat duty for solvent regeneration which can be minimized for an optimal CO_2 loading. For the three blends of interest, this energy was lower than for MEA 30wt%. The blend MDEA 25wt% + MEA 5wt% showed a reboiler heat duty of 3.33 GJ/t_{CO2}, while for MEA 30wt% this value was higher and around 3.77 GJ/t_{CO2}. Best results were obtained for the ratio 1MPZ 30wt% + PZ 10wt% for which a reduction of the reboiler heat duty

close to 20% was observed when compared with MEA 30wt% [50]. Even if a not inconsiderable decrease of the energy needed for the process would be reached for the three blends, it is necessary to study their chemical stability, also involved in the energy penalty of the process.

Table 34: Thermodynamic comparison of the three blends

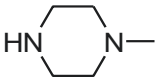
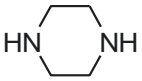
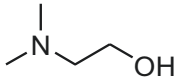
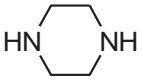
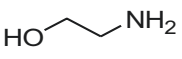
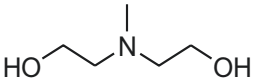
	Lean CO_2 loading (mol/mol)	Rich CO_2 loading (mol/mol)	Cyclic capacity (g/kg)	H_{abs} (kJ/mol)	Reboiler heat duty (GJ/t_{CO2})
30% MEA	0.240	0.507	54.9	-56/-99 (40°C/120°C)	3.77
30% 1MPZ/10%PZ [50]	0.100	0.640	NA	NA	2.988
35%DMEA/5%PZ [45]	0.200	0.400	NA	NA	2.9-3.5
25%MDEA/5%MEA [237]	0.050	0.436	49.2	-63/-82 (50°C/120°C)	3.33

3 Material and methods

3.1 Solvent preparation

Preparations of the three amine blends were realized gravimetrically by mixing commercial amines (Table 35) with distilled water (18.2 MΩ).

Table 35: Composition of the studied solvents

	Compounds	Abb.	Structure	% wt.	Purity	Source
A	1-Methylpiperazine	1MPZ		30	99%	Sigma Aldrich
	Piperazine	PZ		10	≥99%	Merck
B	*N,N*-Dimethylaminoethanol	DMEA		35	≥99%	Alfa Aesar
	Piperazine	PZ		5	≥99%	Merck
C	Ethanolamine	MEA		5	99%	Alfa Aesar
	N-Methyldiethanolamine	MDEA		25	98%	Alfa Aesar

3.2 Pilot plant description

The three blends were degraded on the LEMEDES-CO2 lab-scale equipment [90,158] from EDF R&D (**Figure 65**). A fully detailed description of the device was made in our previous work [225]. The MEA experimental protocol, more particularly the absorption and stripping temperatures, was used as a basis to these amine blends, in order to compare their chemical stability and CO_2 capture performances.

The three degradations campaigns lasted around 900 h. A synthetic flue gas was injected at the bottom of the reactor. It contained 15% CO_2 (≥99.7%, Air Liquide, Mitry Mory, France), 82% N_2 (≥99.995%, Air Liquide, Mitry Mory, France) and 3% air (composed of 20.9% of oxygen). Total absolute pressure during absorption was 1.0 bar. The gas flow rate was 1800 NL/h at 42°C and the solvent flow rate was 3 L/min. The total volume of solvent was 1.5 L. For the regeneration step a pressure of 4 bar in the reactor was first applied with N_2 as entering flue gas during 1 min. Then the solvent was heated up to 123°C which enabled the regeneration of the amine and the release of CO_2. Released CO_2 was exhausted. Absorption and regeneration durations were optimized for each blend in order to reach optimum CO_2 loadings. The parameters of each campaign are given in **Table 36**.

The control system followed many parameters such as temperature, pressure and gas composition and operated continuously and automatically (24h/24 and 7d/7). Samples were taken from the liquid and gas phase and analysed at regular intervals. Solvent sampling was done one time a week at the bottom of the reactor for the CO_2 rich amine and the CO_2 lean amine. All samples were stored in brown flaks at 4◦C.

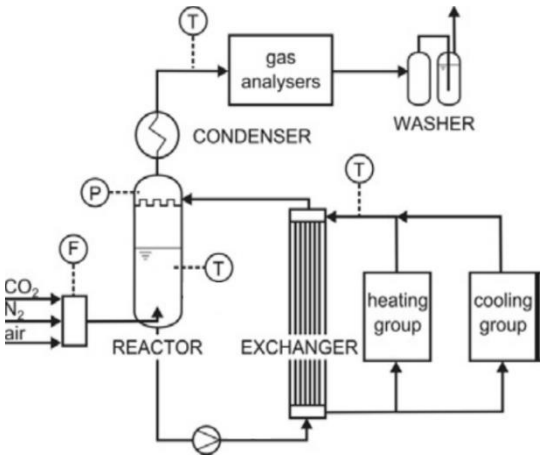


Figure 65: LEMEDES-CO2 lab-scale equipment (F: flowmeter; T: temperature probe; P: pressure sensor)

Table 36: Characteristics of the degradation campaigns

Solvent		1MPZ/PZ	DMEA/PZ	MDEA/MEA
Absorption	Temperature	42°C		
	Gas composition	15% CO_2 / 82% N_2 / 3% Air		
	Pressure	1 bar		
	Duration	**80 min**	**60 min**	**60 min**
Regeneration	Temperature	123°C		
	Gas composition	15% CO_2 / 82% N_2 / 3% Air		
	Pressure	4 bar		
	Duration	30 min (including heating and cooling times)		
Duration		800 hours	840 hours	900 hours
Number of cycles		400	600	600

3.3 Water content measurement

The water content of the three blends was measured using a V20 Karl Fisher from Mettler (Viroflay, France). The reagents used for the titration were Hydranal-Composite 5K and Methanol dry from Sigma Aldrich (Saint-Quentin-Fallavier, France). Uncertainty of the method was estimated by repeatability measurements and was ± 5 %.

3.4 Amine titration

The total amine concentration (alkalinity) was measured by acidic titration using a T50 Karl Fisher titrator from Mettler (Viroflay, France) with automatic equivalence point detection. 0.4 to 0.6 g of sample were added to 50 mL of deionized water, and placed on the device. The solution was then titrated with 0.2 M of HCl to reach a pH of 2. The amount of acid needed to reach the first equivalence point was used to calculate the total amine concentration. Uncertainty of the method was estimated by repeatability measurements and was ± 5 %.

3.5 Total Inorganic Carbon Measurement (TIC)

A TOC-L CSH from Shimadzu (Marne la Vallée, France) was used to determine the total inorganic carbon content of the solvent. The 50X diluted sample was acidified in 30 wt% phosphoric acid to gaseous CO_2. The CO_2 emitted was then measured with an infrared analyzer. Previous calibration of the dispositive (using a 1000 ppm standard) permitted to calculate the amount of inorganic carbon contained in the solution. CO_2 loading was then calculated using the amount of inorganic carbon in mol/kg divided by the total amine concentration in mol/kg. Uncertainty of the method was estimated by repeatability measurements and was ± 5 %.

3.6 Ionic chromatography

PZ, MEA, MDEA and 1MPZ were individually quantified using ionic chromatography. An ICS 1000 equipped with an autosampler from Thermo Fisher (Villebon-sur-Yvette, France) was used. Samples were diluted 20000 times with water, and then 25 µL were injected for the separation. A guard column (IonPac^{TM} CG19RFIC^{TM} 4 x 50 mm) was placed before the analytical column (IonPac^{TM} CS19RFIC^{TM} 4 x 250 mm) to prevent the analytical column from contaminations. An eluent generator permitted the delivery of adjustable concentrations of methanesulfonic acid (MSA). The system was equipped with a 4-mm anionic Suppressor. Detection was performed with a conductimetric cell. Both columns and conductimetric detectors were thermostated at 35°C. **Table 37** gives the eluting strength of each separation. Quantification methods have been developed in the range of interest and validated with the total error concept and the accuracy profile for the blends 1MPZ/PZ and MDEA/MEA [136,192]. Uncertainties of the quantifications results of the blend DMEA/PZ correspond to repeatability measurements.

Table 37: MSA concentrations for the three separations

	1MPZ/PZ	DMEA/PZ	MDEA/MEA
MSA concentration	Isocratic: 25 mM	Gradient: 7 mM (0 to 10 min) then 25 mM in 5 min (15 min to 30 min)	Isocratic: 3 mM
Analysis duration	10 min	20 min	12 min
Uncertainty	10%	<5%	MEA: 30% MDEA: 20 %

4 Experimental results

4.1 CO_2 loadings

CO_2 loadings were determined during the three degradation campaigns and are presented in **Table 38.** Obtained results showed a stability of the CO_2 loadings during time for each study, and are in the same range in accordance with optimum loadings presented in **Table 34** (except for the blend DMEA/PZ).

Table 38: Comparison of the CO_2 loadings

	Lean CO_2 loading (mol/mol)	Rich CO_2 loading (mol/mol)
30% 1MPZ/10%PZ	0.28	0.63
35%DMEA/5%PZ	0.15	0.65
25%MDEA/5%MEA	0.12	0.40

4.2 Monitoring of the stability of the blends

Stability of the three blends was evaluated during 900 hours by monitoring the total amine concentration and by quantifying each remaining constituent amine of the blends. The obtained results are presented in **Figure 66** and **Figure 67**. Dotted lines in **Figure 66** correspond to initial amines concentrations for the blends 1MPZ/PZ and MEA/MDEA and to the decrease tendency for the blend DMEA/PZ.

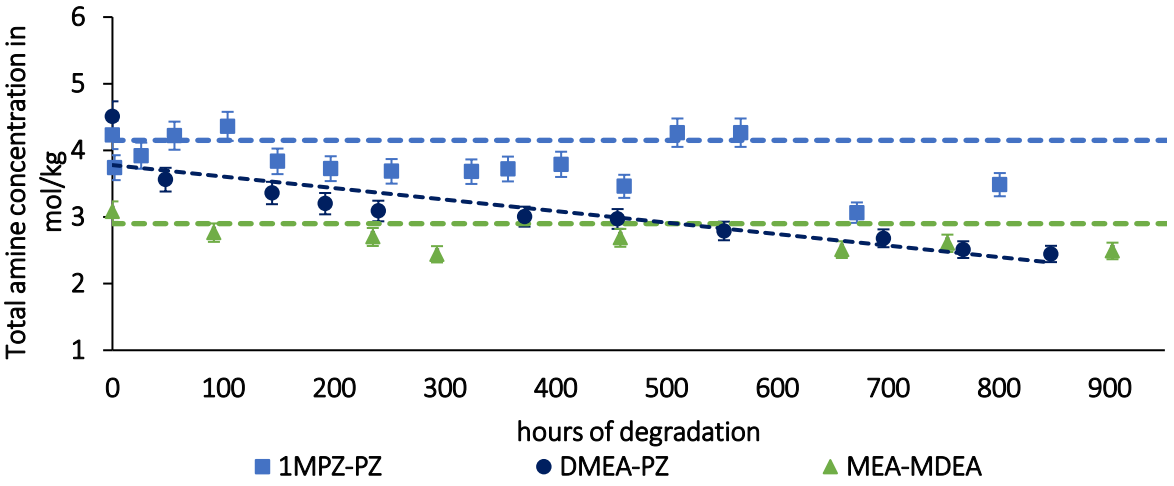


Figure 66: Monitoring of the total amine concentration of the three blends. Error bars correspond to uncertainties of the quantification method.

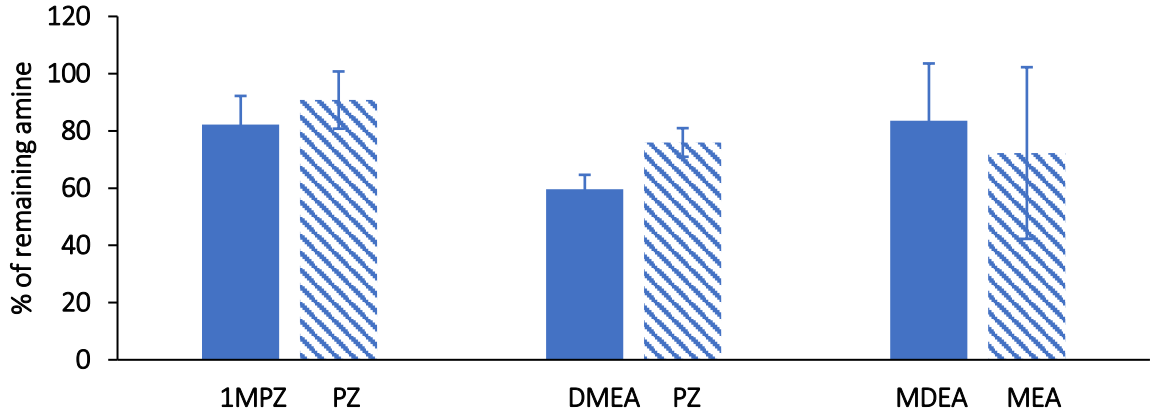


Figure 67: Percentage of remaining constituent amine of each blend. Error bars correspond to uncertainties of the quantification method.

4.2.1 DMEA/PZ blend

Monitoring of the blend DMEA/PZ showed a significant decrease of the total amine concentration during time (**Figure 66**). DMEA and PZ concentrations decreased respectively from 0.4 points and 0.04 points per day (**Figure 67**). Three types of phenomena would explain this decrease of amines. The first hypothesis would be a thermal or chemical degradation of amine during time, involving the formation of degradation products. The second one would be a vaporization of DMEA due to its high volatility and the third one would be rather a mechanical entrainment of small solvent droplets and aerosols due to high flow rate of injected gas. A part of these two latter types of solvent losses, escaping from the condenser, would be emitted with the treated fumes. Emission of solvent in the treated fumes was confirmed by the analysis of the treated flue gas, showing a huge peak of DMEA on the corresponding chromatogram. To our knowledge, no study has been realized about the volatility of the blend DMEA/PZ. The only available data concerned DMEA [239,240] and indicated that a temperature of 143°C at 4 bar or 100°C at 1 bar should be reached to evaporate the compound. Simulations realized on Aspen Plus© software showed, *a posteriori*, that the entering gas flow rate was too high (currently of 1800 NL/h) and not adapted to this blend. Relatively to MDEA and even to more volatile MEA, DMEA lost in gas phase of Aspen Plus© equilibrium flash tank model (Aspen ELECNRTL, electrolyte non-random tow liquid thermodynamic model) is much higher and increases with increasing amount of gas injected in the flash tank. Higher volatility of DMEA relatively to MDEA and MEA is also shown by Aspen ELECNRTL model which calculates higher vapor pressure of DMEA relatively to MEA and to MDEA. These results are in accordance with studies of Lepaumier at al. [86,107] where the entering flue gas pressure (0 or 20 bar at 140°C) had a negative impact on the remaining DMEA concentration as it leads to a "degradation" rate of 30%.

Even if a reduction of the reboiler heat duty could be reached when compared to MEA 30wt%, the blend DMEA/PZ is not adapted to a CO_2 capture process designed for MEA. A thorough adaptation of the operating conditions should be done in order to improve the chemical stability of the solvent and to limit the amine loss.

4.2.2 1MPZ/PZ and MDEA/MEA blends

The total amine concentration of the blend MDEA/MEA did not show any significant variation (**Figure 66**). In order to corroborate these results, quantification of remaining MEA and MDEA have been achieved (**Figure 67**). The results did not show any significant degradation for MDEA, instead of MEA which showed a significant degradation in the range of 0.03 points per day.

Fluctuations of the total amine concentration could be seen for 1MPZ/PZ (**Figure 66**), but these fluctuations were not significative. However, quantification of the two main amines did show a significant degradation for both amines in the range of 0.2 points and 0.06 points per day respectively for 1MPZ and PZ.

Both blends were characterized for their degradation products formed in the liquid phase of the solvents and for their composition of the treated flue gas [225,237]. Although a slow or no significant loss of amine have been seen during time, some degradations products were identified. Results showed the formation of 27 compounds after the degradation of the blend 1MPZ/PZ, among which 14 emitted with the treated flue gas. 22 degradation products were listed the case of MEA/MDEA, with 11 compounds detected in the gaseous effluents.

When compared with MEA, the blend MDEA/MEA seem to be more chemically stable. Indeed, close to 50 degradation products were identified in the field of MEA degradation. 38 of them were also reported to be emitted with the treated flue gas [32,241]. After 1960 hours of operation on the Technology Centre Mongstad with an initial MEA mass of 30088 Kg, 7622 Kg of pure MEA loss was reported, thus corresponding to 25% loss. This loss was also reported to be of 1.6 ± 0.1 kg/ton CO_2 captured [241]. In the present study, no significant loss of MDEA was reported after 900 hours of degradation for the blend MDEA/MEA vs 0.03 points per day for MEA, corresponding to around 4% total amine loss after 900 hours. In the case of the blend 1MPZ/PZ, this degradation was slightly higher with a loss of 1MPZ of 0.2 points per day vs 0.06 points for PZ corresponding to a total amine loss of approximatively 22% after 900 hours of degradation. Energy consumption was also lower for the two blends when compared with MEA, especially for the blend 1MPZ/PZ for whom this reduction reached 20%.

When compared with MEA 30wt%, the best compromise in terms on energy needed for the process and chemical stability is obtained for the blend MDEA 25wt% + MEA 5wt%. In order to compare the obtained results with MEA's, studies of the degradation of this blend should be performed on longer times e.g. 2000 hours. Indeed, even if the reboiler heat duty is lower for the blend MDEA/MEA (3.33 GJ/t_{CO2} vs 3.7 GJ/t_{CO2} for MEA 30wt%), degradation of this blend have to be estimated on longer times, in order to predict and take into account costs associated with a potential degradation, and to confirm the results obtained in the present study.

5 Conclusion

The blends 1MPZ 30wt% + PZ 10wt%, DMEA 35wt% + PZ 5wt% and MDEA 25wt% + MEA 5wt% were compared for their thermodynamic properties for CO_2 capture and chemical stability in conditions representative of post-combustion CO_2 capture for MEA process during 900 hours. All the three blends showed a reduction on the energy needed for the process when compared to MEA. Cycling of the blend DMEA 35wt% + PZ 5wt% showed 0.4 points loss per day of DMEA, mainly by its partial vaporization. Further work on this blend should be realized after adapting the operating conditions of the process, especially the entering gas flow rate. Best results were obtained for the mix MDEA 25wt% + MEA 5wt%, where a stability of MDEA was seen during time, and a slow loss of MEA in the range of 0.03 points per day. This blend showed a reduction of the reboiler heat duty of approximately 10% in comparison to MEA 30wt%. Regarding the blend 1MPZ 30wt% + PZ 10wt% this reduction was estimated to be 20% [50]. A decrease of the 1MPZ concentration of 0.2 points per day was observed after 900 hours of cycling, thus suggesting the need of fresh amine addition on longer degradation times. The results obtained in the present study suggest that the most promising solvent is the blend MDEA 25wt% + MEA 5wt%. Further work on longer time (e.g. 2000 hours) should be done on this blend in order to study corrosion phenomena, the impact of NOx and SOx in the entering flue gas, and to confirm the results presented in this study.

Acknowledgments

We would like to thank Aïcha El Khamlichi (ADEME engineer) for the monitoring of this doctoral project and ADEME (French Agency of Environment and Energy Management) for the financial support.

Conclusions générales et perspectives

Le captage du CO_2 en post-combustion par absorption chimique via l'utilisation de solvants aminés est aujourd'hui la technologie la plus mature en vue d'une réduction des émissions de CO_2 issues de la combustion de ressources fossiles [16]. Les deux limitations de la technologie sont la pénalité énergétique de l'ordre de 11 %-pts sur le rendement de la centrale [13] et la dégradation des solvants aminés [15]. L'objectif de ce travail était d'étudier la dégradation de trois solvants dits innovants présélectionnés pour leurs bonnes performances en termes de besoins énergétiques requis pour le procédé. Des mélanges à base de pipérazine et d'alcanolamines ont été retenus et sont constitués de 1-méthylpipérazine (30 %), de pipérazine (10 %) et d'eau (60 %) (1MPZ/PZ) pour le premier solvant, de méthyldiéthanolamine (25 %), de monoéthanolamine (5 %) et d'eau (70 %) (MDEA/MEA) pour le second solvant, et de diméthylaminoéthanol (35 %), de pipérazine (5 %) et d'eau (60 %) (DMEA/PZ) pour le troisième solvant. Chacun de ces mélanges a montré une réduction de l'énergie requise au rebouilleur, réduction pouvant aller jusqu'à 20 % par rapport à la MEA 30 % dans le cas du mélange 1MPZ/PZ [50].

Ces trois solvants ont été dégradés pendant près de 900 heures dans des conditions représentatives des conditions industrielles sur un dispositif expérimental construit par EDF R&D (Chatou). Pour chaque campagne de dégradation réalisée, un mode opératoire caractéristique (en termes de température et de pression) d'un procédé impliquant un solvant constitué de MEA 30 % a été appliqué. Parallèlement à ces essais de dégradation, des méthodes analytiques complémentaires impliquant les chromatographies en phase gazeuse et liquide ont été développées et certaines d'entre elles validées, pour le suivi quantitatif des amines constituantes des solvants, ainsi que pour l'identification et la quantification des potentiels produits de dégradation formés en phase liquide. Dans l'objectif de caractériser la composition de la phase gazeuse émise en sortie du dispositif (correspondant aux fumées traitées émises), une méthode innovante dans le domaine du captage du CO_2 a été développée. Cette méthode implique la pré-concentration des composés émis, via leur piégeage sur un tube commercial contenant une phase solide (tube Tenax® TA) suivi de la thermodésorption de ce tube et son analyse en GC-MS. Cette méthode offre l'avantage d'être simple à mettre en œuvre et d'être utilisable directement sur site. Une méthode de quantification des composés émis en phase gazeuse a ensuite été développée et validée pour cinq composés cibles issus de la dégradation de la MEA 30 % [192]. Cette méthode a été appliquée pour l'identification des produits de dégradation émis avec les fumées traitées des trois solvants du projet, et pour la quantification de cinq produits issus de la dégradation du solvant 1MPZ/PZ.

Parallèlement à ces études expérimentales, un modèle de dégradation (reposant entre autre sur les données de caractérisation présentées en Annexe 2) à l'échelle du procédé permettant de prédire la quantité de solvant consommée par le procédé a été développé par une équipe d'ingénieurs d'EDF R&D et par une stagiaire de fin d'étude. Ce modèle a dans un premier temps été appliqué au solvant modèle MEA 30 %, puis aux solvants 1MPZ/PZ et MDEA/MEA du projet.

Trois campagnes de dégradation ont été réalisées pour l'étude du solvant 1MPZ/PZ, dont deux dans des conditions identiques en présence de fumées synthétiques (constituées de CO_2, N_2 et O_2) et une en présence d'impuretés acides. Les résultats obtenus ont montré la formation de 27 produits de dégradation dont 23 présents dans la phase liquide du solvant, et 14 émis avec les fumées traitées. Aucune différence dans la nature des composés identifiés n'a été observée lorsque la campagne était réalisée en présence d'impuretés acides. Un suivi quantitatif des teneurs en 1MPZ et PZ au sein du solvant a été réalisé et a montré une baisse significative des deux amines de l'ordre de 0,2 points et 0,06 points par jour respectivement pour la 1MPZ et la PZ. Des schémas réactionnels ont été proposés dans l'objectif d'expliquer la formation des composés formés. La formation de ces composés s'explique principalement par des mécanismes d'oxydation, suggérant l'intérêt d'une étude en présence d'inhibiteurs de type antioxydants.

Une campagne de dégradation a été réalisée pour l'étude des solvants DMEA/PZ et MDEA/MEA. Vingt-deux produits de dégradation ont été identifiés comme issus de la dégradation du solvant MDEA/MEA, dont 12 détectés dans la phase liquide du solvant, et 11 émis en phase gazeuse. Parmi ces composés, 9 ont déjà été identifiés dans la littérature en tant que produits de dégradation de la MEA ou de la MDEA, et des schémas réactionnels ont été proposés impliquant principalement des mécanismes d'oxydation. Un suivi quantitatif en chromatographie ionique a été réalisé dans l'objectif de suivre la stabilité des teneurs en MDEA et MEA au cours du temps. Aucune baisse significative de la teneur en MDEA n'a été observée, contrairement à la MEA où une baisse significative de l'ordre de 0,03 points par jour a été observée. A l'inverse, l'étude du solvant DMEA/PZ a montré une perte non négligeable de l'ordre de 0,4 points par jour de la teneur en DMEA au cours du temps, essentiellement par vaporisation. Des études complémentaires ont montré que le mode opératoire du procédé caractéristique de la MEA 30 % n'était pas adapté à ce solvant (débit des fumées entrantes trop important). Une utilisation de ce solvant implique par conséquent une mise au point des conditions opératoires.

Au vu des résultats obtenus au cours de ce projet, le solvant MDEA/MEA semble offrir le meilleur compromis en termes de stabilité chimique et de besoins énergétiques requis pour le procédé. Certes, l'énergie au rebouilleur requise est supérieure à celle du mélange 1MPZ/PZ de l'ordre de 10 %

(mais inférieure à la MEA 30 % de 10 %), mais le mode opératoire appliqué dans le cadre de cette étude n'a montré aucune perte significative de l'amine majoritaires MDEA au cours du temps, contrairement au mélange 1MPZ/PZ. Le mélange MDEA/MEA semble donc prometteur et pourrait être utilisé sur des unités industrielles de captage déjà existantes et construites pour un procédé à base de MEA 30 %.

Dans la continuité de cette étude, il serait intéressant d'étudier la stabilité chimique de ce solvant sur des durées beaucoup plus longues (e.g. six mois, soit 4000 heures) en présence de fumées alimentées en NOx et en SOx, afin de se rapprocher encore plus des conditions industrielles. Des études sur la résistance de ce solvant vis-à-vis des phénomènes de corrosion seraient également intéressantes, puisque c'est un facteur non négligeable dans le choix d'un solvant de captage du CO_2. Il serait également pertinent de quantifier les émissions des composés émis avec les fumées traitées, et d'étudier la toxicité des produits de dégradation formés.

Le captage et le stockage du CO_2 apparaît à ce jour comme une option inévitable pour respecter les objectifs carbone ambitieux que se fixent les pays développés. Le choix d'un « bon solvant » sera un atout déterminant aussi bien dans l'optique de la construction d'unités de captage à grande échelle, que pour celles à plus petite échelle destinées à fonctionner au niveau de micro-systèmes économiques régionaux.

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Annexe 1: analytical methods used for the analysis of amine and degradation products in CO_2 capture solvents

Compounds	Solvent composition	Sample treatment	Dilution matrix	Dilution factor	Method	References
1H-pyrrole	MEA	HS-SPME	-	-	GC-MS	[32]
1-(2-hydroxyethyl)piperazin-2-one	MEA	dilution	methanol	10	GC-MS	[32]
1,3-diaminopropane (1,3-DAP)	1,3-DAP	dilution	-	-	IC	[127]
1,4-dimethylpiperazine	MEA	dilution	methanol	10	GC-MS	[32]
	MEA	-	-	-	GC-MS	[107]
	PZ	dilution	-	-	IC	[125]
1-methylpiperazine	PZ	dilution	-	-	IC	[39,125]
2-oxopiperazine	PZ & AMP/PZ	-	-	-	GC-MS	[93]
2,5-piperazinedione	PZ & AMP/PZ	-	-	-	GC-MS	[93]
2,4-dimethylpyridine	AMP	-	-	-	GC-MS	[85]
	AMP	-	-	-	UV (200-400 nm)	[85]
2-amino-2-hydroxymethyl-1,3-propanediol (AHPD)	AHPD	dilution	water	25	LC-RID	[123]
2-(dimethylamino)ethanol	MEA	dilution	water	100	LC-MS/MS	[139]
2-amino-2-methylpropan-1-ol (AMP)	AMP	-	-	-	GC-MS	[107]
	PZ blend	dilution	water	2000 to 10000	IC	[130]
2-methylpiperazine	MEA	dilution	methanol	10	GC-MS	[32]
	PZ	dilution	-	-	IC	[39]
2-oxazolidinone	MEA	HS-SPME	-	-	GC-MS	[32]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	10000	LC-MS/MS	[129,139,140]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	water	10 to 100	GC-MS	[30]

	MEA	dilution	methanol	10	GC-MS	[90]
4-(2-hydoxyethyl)piperazin-2-one	MEA	dilution	water	10000	LC-MS/MS	[129,140]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	methanol	10	GC-MS	[32,90]
ammonium	MEA	-	-	-	IC	[83,126]
	MEA	dilution	water	100	LC-MS/MS	[140]
bicine	MEA	dilution	water	1000	LC-MS/MS	[32]
	MEA	-	-	-	NMR	[124]
Dimethylethanolamine (DMEA)	DMEA	-	-	-	GC-MS	[107]
	DMEA	dilution	water	-	IC	[127]
Bis(2-hydroxypropyl)amine (DIPA)	DIPA	dilution	water	-	IC	[127]
N,N'-diethylethanolamine	DEEA	dilution	water	5	GC-MS	[242]
	DEEA	dilution	water	-	IC	[127]
Diethylenetriamine (DETA)	DETA	dilution	water	-	IC	[127]
Diethanolamine (DEA)	MEA	dilution	water	1000	LC-MS/MS	[32]
	MEA	-	-	-	LC-MS	[87]
	MEA	dilution	water	100	LC-MS/MS	[129]
	MEA	-	-	-	NMR	[124]
	DEA	-	-	-	GC-MS	[107]
ethylenediamine	PZ	dilution	-	-	IC	[72]
	PZ	dilution	water	1000	IC	[122]
	PZ; AMP/PZ	-	-	-	GC-MS	[93]
	PZ; AMP/PZ	dilution	ethanol	100 to 150	GC-MS	[142]
glycine	MEA	dilution	water	1000	LC-MS/MS	[32]
hexamethyleneimine	PZ	dilution	-	-	IC	[72]
homopiperazine	PZ	dilution	-	-	IC	[72]
Methyldiethanolamine (MDEA)	PZ blend	dilution	water	2000 to 10000	IC	[130]
monoethanolamine	MEA	-	-	-	GC-FID	[32]

	MEA	-	-	-	GC-MS	[107]
	MEA/PZ	-	-	-	GC-MS	[143]
	MEA	dilution	water	10000	LC-MS /MS	[30]
	MEA	dilution	-	1000000	LC-MS/MS	[144]
	MEA	dilution	water	10000	LC-MS/MS	[139,140]
	MEA	dilution in 0.1% ammonium hydroxide			GC-FID	[31,124]
	MEA	dilution	water	-	IC	[127]
	MEA	-	-	-	IC	[83]
	MEA	-	-	-	IC	[126]
	MEA	dilution	water	50	LC-RID	[123]
	MEA	dilution	acetonitrile/water 50:50	10	LC-RID	[141]
	MEA	dilution	water	40	LC-RID	[84]
	MEA	dilution	water	60	LC-RID	[145]
morpholine	PZ	dilution	-	-	IC	[72]
N-methyl-1,3-diaminopropane (MAPA)	MAPA	dilution	water	-	IC	[127]
N-(2-((2-aminoethyl)amino)ethyl)-piperazine	PZ	dilution	water	1000	IC	[122]
N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidinone	MEA	dilution	water	10 to 100	GC-MS	[30]
N-(2-aminoethyl)piperazine	PZ	dilution	water	1000	IC	[122]
N-(2-hydroxyethyl)pyrrole	MEA	HS-SPME	-	-	GC-MS	[32]
N-(2-hydoxyethyl)ethylenediamine	MEA	dilution	methanol	10	GC-MS	[32]
	MEA	dilution	(water + 0,01% formic acid) / methanol : 9:1	500	LC-HR-MS	[135]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	10 to 100	GC-MS	[30,107]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	water	-	IC	[127]

	MEA	dilution	water	1000	LC-MS/MS	[32]
N-(2-hydoxyethyl)glycine	MEA	dilution	methanol	10	GC-MS	[32,90]
	MEA	dilution	water	10000	LC-MS/MS	[129]
	MEA	dilution	water	1000	LC-MS/MS	[32]
N-(2-hydroxyethyl)imidazole	MEA	dilution	methanol	10	GC-MS	[32,90]
	MEA	dilution	water	10 to 100	GC-MS	[30]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	(water + 0,01% formic acid) / methanol : 9:1	500	LC-HR-MS	[135]
	MEA	dilution	water	10000	LC-MS/MS	[129,140]
	MEA	-	-	-	NMR	[124]
	MEA	-	-	-	LC-ELSD	[82,83]
N-(2-hydroxyethyl)imidazolidin-2-one	MEA	dilution	water	10000	LC-MS/MS	[32]
	MEA	dilution	(water + 0,01% formic acid) / methanol : 9:1	500	LC-HR-MS	[135]
	MEA	dilution	water	100	LC-HR-MS	[103]
	MEA	dilution	water	2	GC-FID	[141]
	MEA	dilution	water	10 to 100	GC-MS	[30]
	MEA	-	-	-	NMR	[124]
N-(2-hydroxyethyl)piperazine	PZ	dilution	water	1000	IC	[122]
N,N,N'-trimethylethylenediamine (N,N,N’-triMEDA)	(N,N,N’-triMEDA)	-	-	-	GC-MS	[107]
N,N,N',N'-tetramethylethylenediamine (TMEDA)	TMEDA	-	-	-	GC-MS	[107]
N,N'-Bis-(2-hydroxyethyl)urea	MEA	dilution	water	1000	LC-MS/MS	[32]
N,N'-bis(2-hydroxyethyl)ethylenediamine	MEA	dilution	water	1000	LC-MS/MS	[32]
N,N-dimethylethylenediamine (N,N-diMEDA)	(N,N-diMEDA)	-	-	-	GC-MS	[107]
N-ethylpiperazine	PZ	dilution	water	1000	IC	[122]

N-formylpiperazine	PZ	dilution	water	1000	IC	[122]
	PZ & AMP/PZ	-	-	-	GC-MS	[93]
oxazolidine	MEA	HS-SPME	-	-	GC-MS	[32]
	MEA	dilution	water	1000	LC-MS/MS	[32]
oxazoline	MEA	HS-SPME	-	-	GC-MS	[32]
piperazine	MEA/PZ	-	-	-	GC-MS	[143]
	PZ	dilution	water	25	HPLC-RID	[123]
	PZ	dilution	water	2000	IC	[93]
	PZ	dilution	-	-	IC	[72]
	PZ	dilution	-	10000	IC	[122]
	PZ	dilution			IC	[127]
piperidine	PZ	dilution	-	-	IC	[72]
N-(2-aminoethyl)piperazine	PZ	dilution	ethanol	10 to 150	GC-MS	[142]
pyrrolidine	PZ	dilution	-	-	IC	[72]
pyrazine	MEA	dilution	methanol	10	GC-MS	[32]
trimethylpyridines	AMP	-	-	-	GC-MS	[85]

Annexe 2 : Premiers éléments de caractérisation du réacteur en vue de sa modélisation

Une des finalités de ce projet de thèse est fournir des données afin de pouvoir effectuer une modélisation du banc d'essai LEMEDES-CO2 et ainsi caractériser son comportement vis-à-vis de différents solvants aminés. Le modèle obtenu permettra, à terme, d'évaluer au cours du temps et des conditions opératoires les pertes de solvant, ainsi que les performances de captage vis-à-vis du CO_2. Ce modèle permettra également de prendre en compte les impacts liés aux changements de propriétés physiques du solvant liés à sa dégradation, tels que la viscosité ou la tension de surface.

La modélisation nécessite dans un premier temps la caractérisation du réacteur à l'aide de deux mesures: la détermination du coefficient de transfert en phase liquide (k_La) d'une part, et d'autre part la distribution des temps de séjour (DTS).

Dans cette annexe sont présentés les essais expérimentaux réalisés dans l'objectif de caractériser le réacteur du dispositif expérimental utilisé tout au long de ce projet. La conception du modèle a été réalisée par une équipe d'ingénieurs d'EDF R&D et a fait l'objet d'un stage de fin d'étude. La modélisation du banc d'essai a été réalisée par leurs soins sans que je n'y prenne part et ne sera donc pas présentée dans ce manuscrit.

1 Détermination du coefficient de transfert en phase liquide k_La

La détermination du coefficient de transfert en phase liquide (k_La) a été réalisée dans l'objectif de caractériser le transfert de matière au sein du banc d'essai. Ce paramètre permettra d'évaluer l'efficacité de l'échange liquide-gaz du réacteur. Le coefficient de transfert en phase gazeuse (k_Ga) n'a en revanche pas été déterminé, les réactions étudiées ayant essentiellement lieu au sein de la phase liquide.

1.1 Méthode expérimentale de détermination du k_La

Dans le cadre de cette étude, la détermination expérimentale du k_La a été réalisée par la méthode dite dynamique, basée sur la mesure de la concentration en oxygène dissous dans de l'eau au cours de sa désorption [243]. Cette méthode consiste à saturer en oxygène de l'eau, puis à chasser l'oxygène dissous en faisant buller de l'azote. La concentration en oxygène dissous est alors mesurée au cours du temps, et les données obtenues permettent de déterminer le k_La via la relation **(1)** avec C_0 concentration à saturation d'oxygène dans l'eau et C_t concentration en oxygène à l'instant t de désorption. Après

intégration de cette relation, on obtient l'équation **(2)**. Le tracé de la courbe ln (C_O/C_t) = f(t) permettra d'avoir accès au k_La par détermination de la valeur de la pente de la courbe.

$$\frac{dC}{dt} = k_L a(C_0 - C_t) \quad (1)$$

$$k_L a.\, t = Ln(\frac{C_0}{C_t}) \quad (2)$$

1.2 Protocole expérimental

Le réacteur a dans un premier temps été rempli avec 1500 g d'eau distillée. L'eau a ensuite été saturée en oxygène en faisant passer un débit de 8 L/min d'air (issu du réseau EDF R&D de Chatou, constituée de 20,9 % de dioxygène). Un débit de 30 L/min de N_2 (≥99,995%, Air Liquide, Mitry Mory, France) caractéristique de la phase d'absorption ou un débit de 4,5 L/min caractéristique de la phase de régénération a ensuite été appliqué afin de chasser l'oxygène dissous en solution. Des mesures de la concentration en oxygène dissous ont été réalisées à l'aide d'une sonde CellOX® 325 (WTW) à différents temps de barbotage de N_2, entre 0 (correspondant à la valeur de C_0) et 300 secondes, avec 13 points de mesure au total. Chaque cycle (saturation et mesures) a été répété trois fois. Pendant ces essais, la pompe de circulation du dispositif était en fonctionnement à un débit de 3 L/min.

1.3 Résultats

Les résultats obtenus ont été représentés graphiquement et sont présentés dans les **Figures A1** et **A2**. La **Figure A1** présente l'évolution de la concentration en oxygène dissous en solution au cours du temps dans les deux conditions de l'essai : 4,5 L/min (régénération) ou 30 L/min (absorption) de N_2.

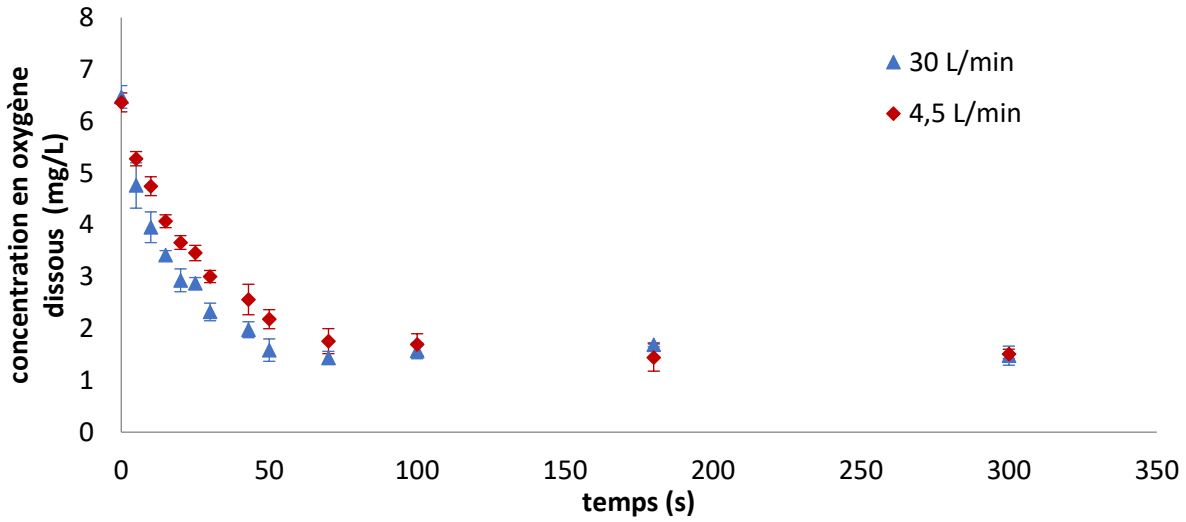

Figure A1 : Evolution de la concentration en oxygène dissout au cours du temps (n=3)

Dans les deux cas, la concentration en oxygène dissous n'atteint pas la valeur zéro, et ce, malgré un temps de barbotage de N_2 long (jusqu'à une heure). Cette observation peut s'interpréter par un

défaut d'étanchéité lié à l'installation. D'après la **Figure A1**, il est observé que la baisse de teneur en oxygène dissous est plus rapide lorsque le débit de N_2 est plus élevé.

Les données expérimentales obtenues ont ensuite été retraitées de manière à représenter $\ln(C_0/C_t)$ en fonction du temps (**Figure A2**), et ainsi accéder à la valeur du k_La par régression linéaire. Les valeurs obtenues sont respectivement de 0,024 (± 0,0018) s^{-1} et 0,019 (± 0,0024) s^{-1} pour un débit de 30 L/min et de 4,5 L/min. Les incertitudes correspondent aux écarts types déterminés sur la répétition des essais (n=3). Ces valeurs sont comprises dans l'ordre de grandeur attendu pour une colonne à bulle (entre 0,005 et 0,12), et sont donc cohérentes [228].

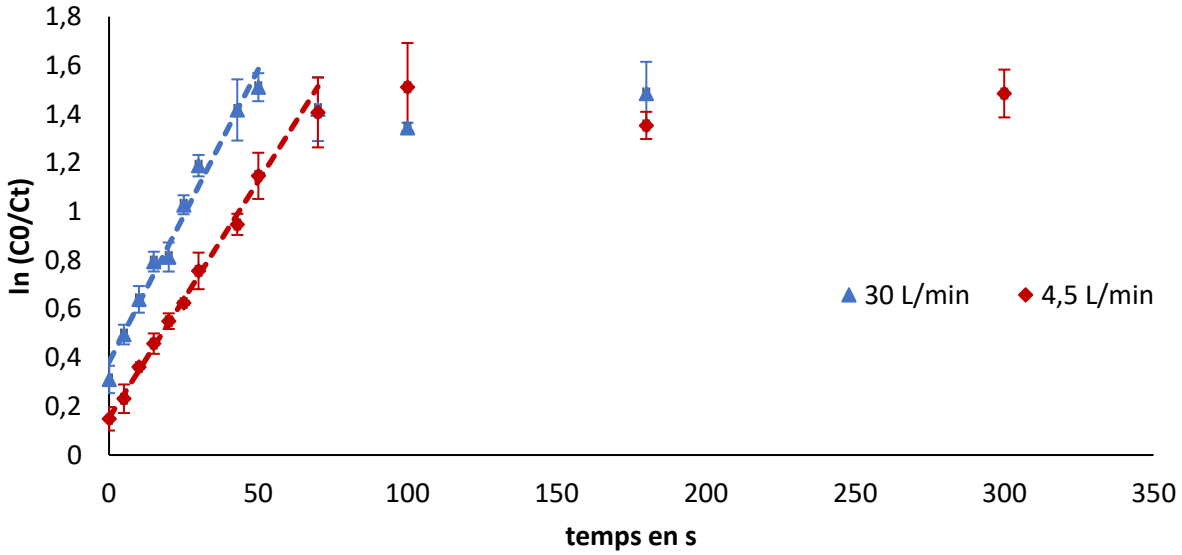

Figure A2 : ln (C0/Ct) = $k_La.t$ (n=3)

2 Distribution de Temps de Séjour (DTS)

La Distribution de Temps de Séjour (DTS) permet de décrire l'écoulement d'un fluide au sein d'un réacteur. Sa détermination a deux intérêts principaux ; elle permet d'une part de diagnostiquer la présence de zones stagnantes au niveau du dispositif expérimental, et d'autre part d'établir un modèle systémique de l'écoulement utilisable pour la modélisation globale du banc d'essai en fonctionnement. Cette détermination a été effectuée du côté liquide, milieu dans lequel les réactions du procédé ont lieu. Les écoulements idéaux les plus décrits sont l'écoulement piston, caractérisé par un temps de séjour unique pour toutes les molécules, et l'écoulement en mélange parfaitement agité, caractérisé par des temps de séjour quelconques où la composition du fluide est uniforme en tout point.

2.1 Protocole expérimental

La détermination expérimentale de la DTS s'effectue à l'aide de traceurs injectés au sein du réacteur et pouvant être suivis via des mesures physiques telles que la conductivité. L'objectif étant de suivre le cheminement du fluide dans le système.

Le traceur utilisé pour cette étude est la saumure (solution saturée en chlorure de sodium). 1,5 mL de cette solution ont été injectés par le haut du réacteur contenant 1,5 L d'eau déminéralisée. L'injection s'est effectuée directement dans la phase liquide du réacteur, au niveau de la zone de turbulence. La conductivité a ensuite été mesurée à l'aide d'une sonde située en bas du réacteur, et enregistrée au cours du temps avec une fréquence d'acquisition de 0,1 s.

Ces essais ont été réalisés dans différentes conditions opératoires, proches de celles mises en œuvre au cours du procédé de captage (**Tableau A1**). Les conditions A permettent une étude à une température de l'eau de 45°C, température caractéristique de la phase d'absorption, mais en absence de gaz. Les conditions B sont proches des conditions d'absorption avec une température du liquide à 45°C et une composition et un débit de gaz injectés identiques à celles de la phase d'absorption (débit total de 30 L/min). Les conditions C sont proches des conditions de la phase de régénération du procédé, même si une température de 123°C n'a pas pu être atteinte en raison de la composition du liquide utilisé (100 % d'eau). Dans chacun des cas, la pompe de circulation est en route de manière continue à un débit de 3 L/min. Chacun des trois types d'essais a été répété trois fois.

Tableau A1 : Conditions opératoires pour la détermination de la DTS

Conditions	A	B	C
Température de l'eau	45°C	45°C	80°C
Composition des gaz entrants	0	21,7 L/min de N_2 + 4 L/min d'air + 4,25 L/min de CO_2	4,5 L/min de N_2

2.2 Résultats obtenus

La conductivité a été mesurée en fonction du temps pour chacun des essais décrits dans le Tableau A1 et les résultats sont donnés dans la Figure A3. Le temps t = 0 correspond à l'injection du traceur dans le réacteur.

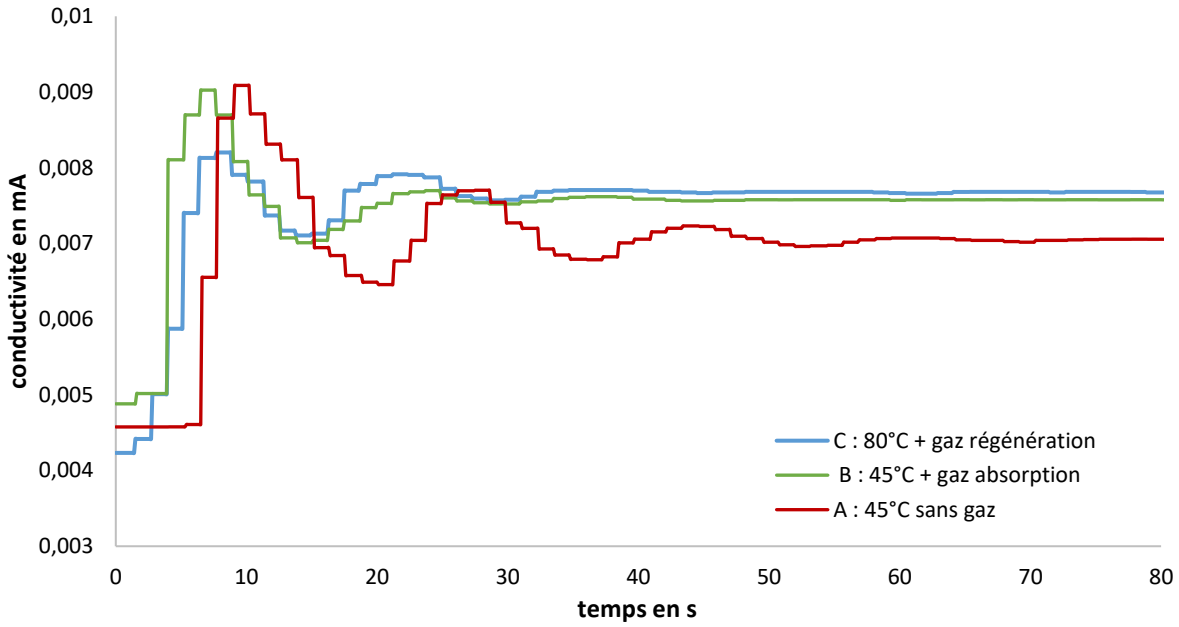

Figure A3 : Courbes expérimentales de la mesure de conductivité en fonction du temps

L'allure globale des trois courbes est similaire même si quelques différences peuvent être observées.

Une différence est tout d'abord observée entre le temps d'injection et l'observation d'une augmentation du signal. Dans le cas des conditions B, représentatives de conditions d'absorption, une augmentation du signal conductimétrique est observée après 4 s. Dans le cas C, une augmentation du signal est observée de manière progressive à partir de 4 s pour atteindre son maximum à 6 s. Dans le cas des conditions A, l'augmentation du signal est observée à 6 s, soit un retard de 2 s par rapport aux conditions B où 30 L/min de gaz ont été injectés au sein du réacteur. Ces premières observations montrent donc l'impact du débit de gaz entrant sur le chemin parcouru par le traceur.

Chacun des signaux est par ailleurs caractérisé par la présence de pics, 2 pour les conditions B et C, et 3 pour la condition A, jusqu'à atteindre un plateau. Ce phénomène s'explique par le fait que le banc d'essai soit un système fermé, la solution de saumure circulant de manière continue entre le réacteur et l'échangeur de chaleur, ce qui conduit à une homogénéisation progressive de la concentration du traceur dans la solution. Cette homogénéisation est plus lente en l'absence de gaz entrant au sein du réacteur.

Ces résultats ont permis, en première approximation, de considérer le banc d'essai comme un réseau de trois cellules parfaitement agitées (Figure A4).

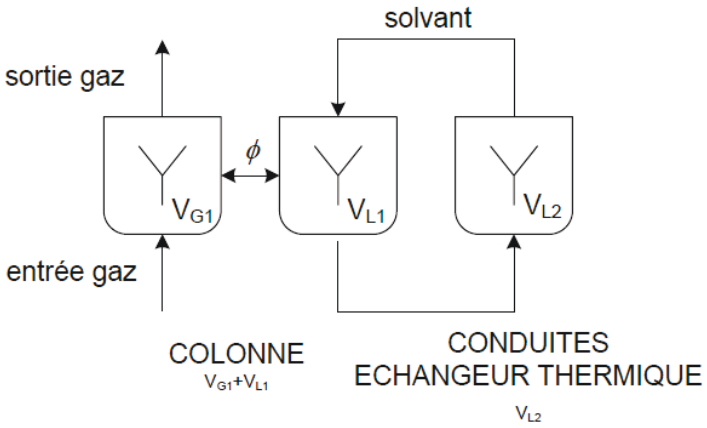

Figure A4 : Système gaz-liquide associant trois cellules parfaitement agitées

3 Conclusions

Des essais de caractérisation du réacteur ont été réalisés et ont permis de valider les hypothèses de modélisation sur le coefficient de transfert en phase liquide ainsi que sur la distribution des temps de séjour. Le modèle a dans un premier temps été construit en se basant sur la MEA en vue de son application aux solvants MDEA/MEA et 1MPZ/PZ.

Annexe 3: data used to obtain the presented accuracy profile in figures 18 and 19

Pyrazine

Reference concentration (mg/L)			180	360	720	900
			Determined concentrations with validation samples (mg/L)			
Affine model	day 1	n=1	160	290	651	768
		n=2	157	332	688	746
		n=3	172	347	676	716
	day 2	n=1	168	345	667	725
		n=2	175	348	652	689
		n=3	190	326	646	768
	day 3	n=1	168	361	627	804
		n=2	190	379	673	814
		n=3	178	339	682	833
	day 4	n=1	161	360	598	810
		n=2	173	351	632	648
		n=3	172	307	665	761
Quadratic model	day 1	n=1	171	277	612	741
		n=2	169	312	651	716
		n=3	181	325	638	682
	day 2	n=1	162	355	680	735
		n=2	171	358	666	701
		n=3	187	335	660	777
	day 3	n=1	168	361	627	804
		n=2	190	379	673	814
		n=3	178	339	681	833
	day 4	n=1	156	369	610	815
		n=2	169	359	644	660
		n=3	168	313	676	769
Linear model	day 1	n=1	220	335	655	759
		n=2	217	373	689	740
		n=3	230	386	678	714
	day 2	n=1	172	348	667	725
		n=2	179	350	653	689
		n=3	194	329	647	769
	day 3	n=1	189	378	637	810
		n=2	210	395	682	819
		n=3	199	356	690	838
	day 4	n=1	192	384	613	818
		n=2	203	375	646	662
		n=3	203	333	678	771

2-methylpyrazine

Reference concentration (mg/L)			34	68	136	170
			Determined concentrations with validation samples (mg/L)			
Affine model	day 1	n=1	33	54	128	151
		n=2	33	66	139	148
		n=3	35	69	132	139
	day 2	n=1	33	71	143	160
		n=2	37	71	135	163
		n=3	40	60	136	165
	day 3	n=1	29	65	114	145
		n=2	35	67	122	152
		n=3	33	61	122	157
	day 4	n=1	34	57	106	129
		n=2	34	66	114	147
		n=3	35	68	116	158
Quadratic model	day 1	n=1	35	52	120	144
		n=2	35	62	132	141
		n=3	36	65	124	132
	day 2	n=1	30	74	146	162
		n=2	36	75	140	165
		n=3	40	62	140	166
	day 3	n=1	29	65	115	146
		n=2	34	67	123	153
		n=3	32	61	123	157
	day 4	n=1	32	60	113	135
		n=2	32	71	121	151
		n=3	32	72	123	161
Linear model	day 1	n=1	41	60	128	148
		n=2	40	70	137	145
		n=3	42	73	131	137
	day 2	n=1	31	72	148	166
		n=2	36	72	141	170
		n=3	39	60	141	172
	day 3	n=1	29	64	112	142
		n=2	35	66	120	149
		n=3	33	60	120	154
	day 4	n=1	37	60	110	134
		n=2	37	69	119	153
		n=3	37	71	121	165

DMF

Reference concentration (mg/L)			18	36	72	90
			Determined concentrations with validation samples (mg/L)			
Affine model	day 1	n=1	20	30	77	90
		n=2	19	36	85	90
		n=3	18	37	78	89
	day 2	n=1	16	31	73	84
		n=2	21	32	67	83
		n=3	22	28	68	85
	day 3	n=1	17	42	74	96
		n=2	20	40	84	106
		n=3	21	38	82	113
	day 4	n=1	20	32	56	78
		n=2	21	38	57	86
		n=3	21	39	66	89
Quadratic model	day 1	n=1	20	28	73	91
		n=2	20	32	83	91
		n=3	19	34	74	89
	day 2	n=1	16	31	73	83
		n=2	21	32	66	83
		n=3	22	27	68	85
	day 3	n=1	16	45	76	95
		n=2	20	43	84	103
		n=3	21	41	83	108
	day 4	n=1	19	38	63	81
		n=2	20	45	64	87
		n=3	21	46	72	89
Linear model	day 1	n=1	24	33	74	85
		n=2	24	38	81	85
		n=3	23	39	75	84
	day 2	n=1	13	28	69	80
		n=2	18	29	63	79
		n=3	19	24	65	81
	day 3	n=1	21	44	74	95
		n=2	24	43	83	104
		n=3	25	41	82	110
	day 4	n=1	23	36	61	85
		n=2	23	42	62	93
		n=3	24	43	71	96

NDMA

Reference concentration (mg/L)			180	360	720	900
			Determined concentrations with validation samples (mg/L)			
Affine model	day 1	n=1	174	300	666	811
		n=2	171	337	714	782
		n=3	177	353	687	742
	day 2	n=1	177	353	723	813
		n=2	187	356	694	759
		n=3	202	333	695	846
	day 3	n=1	140	333	622	820
		n=2	166	351	678	852
		n=3	154	326	690	886
	day 4	n=1	171	346	581	811
		n=2	178	337	610	625
		n=3	175	294	641	749
Quadratic model	day 1	n=1	179	290	644	800
		n=2	177	324	695	768
		n=3	182	338	665	724
	day 2	n=1	169	372	740	822
		n=2	181	375	714	773
		n=3	199	350	714	851
	day 3	n=1	143	330	617	817
		n=2	168	347	673	851
		n=3	156	323	685	886
	day 4	n=1	161	368	611	822
		n=2	168	358	639	653
		n=3	164	308	668	767
Linear model	day 1	n=1	197	317	667	805
		n=2	194	353	713	778
		n=3	200	367	686	739
	day 2	n=1	156	345	741	838
		n=2	166	348	711	780
		n=3	182	323	711	874
	day 3	n=1	156	348	635	831
		n=2	182	366	690	863
		n=3	170	341	702	896
	day 4	n=1	159	342	590	833
		n=2	165	333	621	637
		n=3	162	287	653	767

Pyrrole

Reference concentration (mg/L)			18	36	72	90
			Determined concentrations with validation samples (mg/L)			
Affine model	day 1	n=1	20	30	69	80
		n=2	19	37	74	79
		n=3	20	38	71	75
	day 2	n=1	16	32	68	82
		n=2	17	33	69	79
		n=3	17	34	66	88
	day 3	n=1	16	30	57	86
		n=2	19	33	59	82
		n=3	17	28	64	84
	day 4	n=1	17	31	61	69
		n=2	17	35	61	81
		n=3	17	35	69	90
Quadratic model	day 1	n=1	20	29	67	79
		n=2	20	35	73	78
		n=3	20	37	70	73
	day 2	n=1	16	33	69	82
		n=2	17	33	69	79
		n=3	17	34	66	88
	day 3	n=1	16	30	58	86
		n=2	19	34	60	83
		n=3	17	29	64	84
	day 4	n=1	17	31	61	69
		n=2	17	34	61	81
		n=3	18	34	69	90
Linear model	day 1	n=1	23	33	69	80
		n=2	22	39	75	79
		n=3	23	40	72	75
	day 2	n=1	17	32	67	80
		n=2	18	32	67	77
		n=3	18	34	65	85
	day 3	n=1	17	30	57	85
		n=2	20	34	58	82
		n=3	18	29	63	83
	day 4	n=1	20	33	62	71
		n=2	20	37	63	82
		n=3	20	37	70	91

Annexe 4 : Etude de l'effet de matrice sur la quantification par GC-MS de 3 produits de dégradation du solvant 1MPZ/PZ/Eau

Dans le cadre de l'étude de la dégradation du solvant innovant 1MPZ/PZ/Eau, trois produits de dégradation ont été choisis pour le développement d'une méthode d'analyse quantitative : la 1,4-diméthylpipérazine, la pyrazine et la 1-formylpipérazine. Comme nous l'avons précisé dans le chapitre 1 du manuscrit, la quantification des produits de dégradation issus de solvants utilisés au cours du procédé de captage du CO_2 en post-combustion se fait classiquement sans prétraitement particulier, l'échantillon à analyser étant simplement dilué avant analyse. Dans le cadre de notre étude, nous nous sommes interrogés sur un potentiel effet de la matrice aminée (30 % 1MPZ + 10 % PZ) sur la quantification de nos composés. Nous avons pour cela étudié la réponse en GC-MS de nos composés dans différentes matrices 1MPZ/PZ commerciales.

1. Comparaison des étalonnages en milieu pur et milieu réel

Dans un premier temps, un étalonnage a été réalisé en préparant cinq solutions contenant les trois composés à des teneurs différentes dans le méthanol (milieu pur). Cet étalonnage a ensuite été comparé à un étalonnage réalisé sur des solutions préparées en milieu réel (30 % 1MPZ + 10 % PZ + 60 % Eau) et diluées par 10 dans le méthanol. Aucune différence de signal n'a été observée dans le cas de la 1,4-diméthylpipérazine et de la N-formylpipérazine. En revanche, une différence de signal a été observée dans le cas de la pyrazine. Le même essai a été réalisé en faisant varier le type de fournisseur des amines constituantes de la matrice, les résultats sont donnés en **Figure A5**. Les différentes provenances des matrices étudiées sont données dans le **Tableau A2**.

Tableau A2 : Matrices comparées

	Matrice 1	Matrice 2
1MPZ	Alfa Aesar	Sigma Aldrich
PZ	Sigma Aldrich	VWR

Comme le montrent les résultats donnés en **Figure A5**, une différence de signal peut être observée selon la matrice pour la pyrazine et la 1-formylpipérazine. Deux types de comportements sont observés : une erreur de type constante pour la pyrazine, et de type proportionnelle pour la 1-formylpipérazine. La méthode de quantification choisie pour ces composés sera donc la méthode des ajouts dosés.

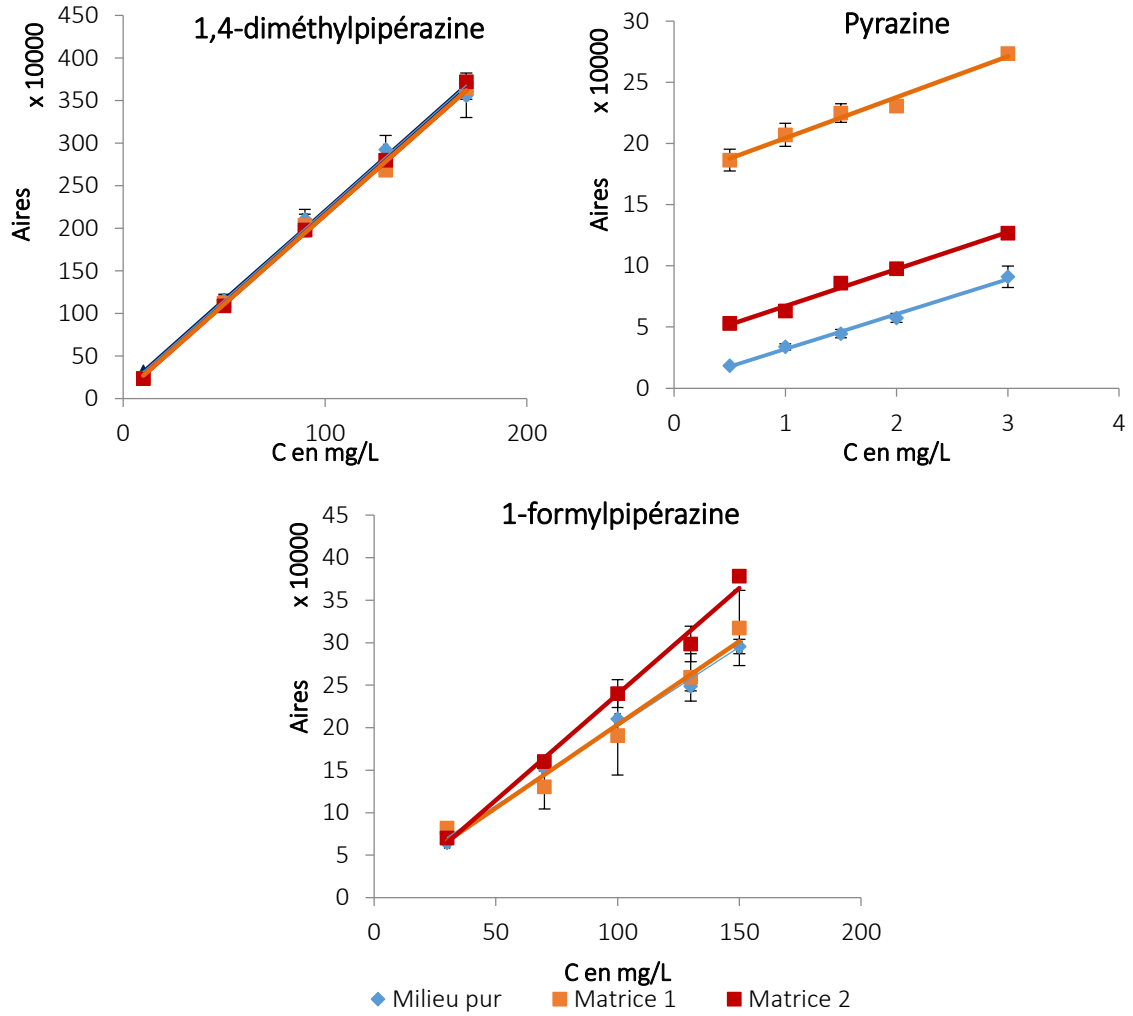

Figure A5 : Etalonnages en fonction des matrices 1MPZ/PZ (les barres d'erreur correspondent à la répétabilité des mesures : n=3)

2. Méthode des ajouts dosés

La méthode des ajouts dosés permet de quantifier un composé en solution en prenant en compte la matrice dans laquelle il se trouve. Expérimentalement, cette méthode est mise en œuvre en dopant l'échantillon à doser avec des masses connues d'analyte cible, le signal chromatographique augmentant alors après chaque ajout. Après régression linéaire portant sur l'aire du pic d'intérêt en fonction de la masse ajoutée, la quantité initiale d'analyte cible est alors déterminée et correspond à l'intersection de la droite avec l'axe des abscisses. Un exemple de détermination de la masse de 1-formylpipérazine est donné dans la **Figure A5**. Dans la présente étude, les échantillons à analyser ont été dopés trois fois avec trois masses d'analyte différentes.

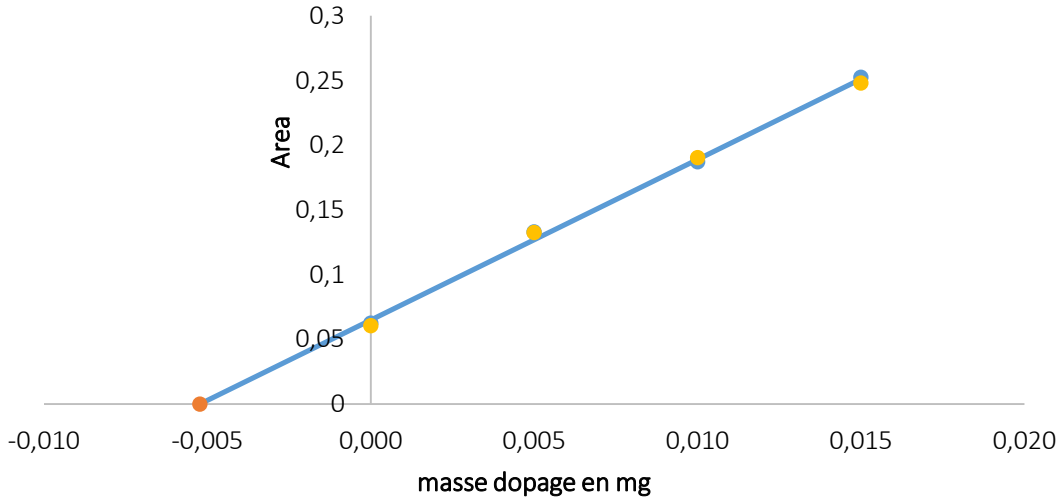

Figure A5 : Détermination de la masse de 1-formylpipérazine par la méthode des ajouts dosés

Une quantification des deux composés (pyrazine et 1-formylpipérazine) non réalisée par la méthode des ajouts dosés induit par conséquent une erreur non négligeable.

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Abstract

Post-combustion CO_2 capture using amine solvents is nowadays the most promising technology to limit the CO_2 emissions from already existing power plants. The two main limitations of the process are the high energy penalty and the irreversible degradation of amines involving the formation of degradation products potentially toxic for human and the environment. This degradation implies the need of fresh solvent addition, bringing to additional costs. Within the scope of this project, three innovative solvents were selected for their good thermodynamic properties for CO_2 capture: the blends 1-methylpiperazine / piperazine (1MPZ/PZ 30/10 %wt.), dimethylaminoethanol / piperazine (DMEA/PZ 35/5 %wt.) and methyldiethanolamine/monoethanolamine (MDEA/MEA 25/5 %wt.). The three blends were degraded in conditions representative of industrial conditions for post-combustion CO_2 capture on a lab scale pilot plant constructed by EDF R&D. Similar experimental protocols as used for MEA 30% were set for the three blends. Complementary analytical methods involving gas and liquid chromatography were developed in order to monitor the stability of the constituent amines, and to identify and quantify potential degradation products formed. These methods permitted the characterization of both the liquid phase of the solvent and the gaseous phase corresponding to the treated flue gas. Identification of degradation products formed was in a first step realized using NIST data base, followed by the injection of commercial standards, and finally by the proposal of reactional pathways, explaining the formation of the considered compounds.

The obtained results regarding the blend 1MPZ/PZ showed the formation of 27 degradation products among which 23 present in the liquid phase of the solvent and 14 emitted with the treated fumes. A quantitative monitoring of the two main amines (1MPZ and PZ) was performed and showed a significant decrease in the range of 0.2 points and 0.06 points per day respectively for 1MPZ and PZ. CO_2 loadings, allowing to evaluate the performance of the solvent, were determined and were of 0.63 for the rich solvent and 0.28 for the lean solvent. Study of the blend MDEA/MEA permitted the identification of 22 degradation products, 12 in the liquid phase of the solvent and 11 in the treated flue gas. No significant decrease of MDEA concentration was seen during time, in contrary to MEA which showed a significant decrease in the range of 0.03 points per day. Rich and lean CO_2 loadings were determined and were respectively of 0.40 and 0.12. Reactional mechanisms were proposed for the two blends, in order to explain the formation of the identified compounds. Cycling of the blend DMEA/PZ showed an amine loss of around 0.4 points per day, essentially caused by vaporization. This lost was caused by the experimental protocol (entering gas flow rate too high) adapted for MEA 30%. The use of this solvent thus imply an adapted process development.

Results obtained during this project showed that the blend MDEA/MEA would offer the best compromise in terms of chemical stability and energy needed for the process. This solvent presents degradation rates lower than the blends 1MPZ/PZ and DMEA/PZ and would enable a reduction of the reboiler heat duty in the range of 10% when compared to MEA 30% the benchmark solvent of the process.

Résumé

Le procédé de captage du CO_2 en post-combustion par absorption chimique est aujourd'hui la technologie la plus mature en vue d'une réduction des émissions de CO_2 issues de procédés industriels. Les deux principales limitations de la technologie sont la pénalité énergétique engendrée par le procédé, et la formation de produits de dégradation potentiellement toxiques pour l'Homme et l'environnement. Cette dégradation du solvant implique un appoint de solvant frais à mesure que le solvant se dégrade, ce qui induit des coûts supplémentaires. Dans le cadre de ce projet de thèse, trois solvants innovants ont été présélectionnés pour leurs bonnes propriétés thermodynamiques de captage : les mélanges 1-méthylpipérazine / pipérazine (1MPZ 30 %/PZ 10 %), diméthylaminoéthanol / pipérazine (DMEA 35 %/PZ 5 %) et méthyldiéthanolamine/monoéthanolamine (MDEA 25 %/MEA 5 %). Ces trois solvants ont été étudiés en termes de stabilité chimique dans des conditions représentatives des conditions industrielles du captage de CO_2 en post-combustion sur un dispositif expérimental construit par EDF R&D Chatou. Des modes opératoires similaires, développés à l'origine pour un procédé à base de MEA 30 %, solvant modèle au procédé, ont été mis en œuvre pour les trois solvants. Des méthodes analytiques complémentaires impliquant les chromatographies liquide et gazeuse ont été développées dans l'objectif de suivre les teneurs en amines constituantes du solvant au cours du temps, et d'identifier et quantifier les potentiels produits de dégradation formés aussi bien dans la phase liquide du solvant que dans les fumées traitées émises. Cette identification des produits de dégradation a été réalisée dans un premier temps à l'aide de la base de données de spectres NIST, puis par l'injection d'étalons commerciaux, et enfin par la proposition de mécanismes réactionnels justifiant la possible formation des produits considérés.

Les résultats obtenus concernant l'étude du solvant 1MPZ/PZ ont montré la formation de 27 produits de dégradation dont 23 présents dans la phase liquide du solvant, et 14 émis avec les fumées traitées. Un suivi quantitatif des teneurs en 1MPZ et PZ au sein du solvant a par ailleurs été réalisé et a montré une baisse significative des deux amines de l'ordre de 0,2 points et 0,06 points par jour respectivement pour la 1MPZ et la PZ. Les valeurs de taux de charge, permettant d'évaluer l'efficacité de captage du solvant, ont été déterminées et sont de 0,63 pour le solvant riche en CO_2 et de 0,28 pour le solvant pauvre en CO_2. Concernant l'étude du solvant MDEA/MEA, 22 produits de dégradation ont été identifiés, dont 12 détectés dans la phase liquide du solvant, et 11 émis en phase gazeuse. Aucune baisse significative de la teneur en MDEA n'a été observée, contrairement à la MEA pour laquelle une baisse significative de l'ordre de 0,03 points par jour a été observée. Les taux de charges riche et pauvres ont également été déterminés et sont respectivement de 0,40 et de 0,12. Des mécanismes de formation ont par ailleurs été proposés dans l'objectif d'expliquer la formation des produits formés. L'étude du mélange DMEA/PZ a en revanche montré une perte de 0,4 points par jour par volatilisation. Cette perte importante s'est avérée être due au mode opératoire du procédé (débit des fumées entrantes trop important), caractéristique du procédé utilisant la MEA 30 %. Une utilisation de ce solvant implique donc un nouveau développement adapté du procédé.

Au vu des résultats obtenus au cours de ce projet, le solvant MDEA/MEA semble offrir le meilleur compromis en termes de stabilité chimique et de besoins énergétiques requis pour le procédé. Ce solvant présente des taux de dégradation inférieurs aux mélanges 1MPZ/PZ et DMEA/PZ, et permettrait une réduction de l'énergie au rebouilleur de l'ordre de 10 % par rapport à la MEA 30 %, solvant modèle au procédé.