Study of the MEA degradation in a CO2 capture process based on partial oxy-combustion approach

Study of the MEA degradation in a CO_2 capture process based on partial oxy-combustion approach

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Abstract

Partial oxy-combustion is a novel approach for CO_2 capture that can be applied to mitigate the CO_2 emissions from stationary sources, particularly in fossil-fuels power plants. Some benefits have been identified related to the highly CO_2 concentrated flue derived from the application of this technology. The hybrid process combining oxy-combustion with post-combustion approach can theoretically lead to around 25% decrease of the overall energy consumption compared with oxy-combustion process. Improvements of the overall CO_2 capture process are mainly focused on CO_2 chemical absorption stage. Therefore, the evaluation of the solvent behaviour under these new operating is required to verify the strengths of partial oxy-combustion as a promising CCS technology.

In this work, the degradation of a conventional solvent - MEA 30wt% - was studied under rich CO_2 environments at typical operating conditions of CO_2 absorption. The degradation tests were performed in a semi-batch rig. Variations on key absorption parameters such as temperature and O_2 concentration in the flue gas were also studied. MEA losses were determined during the experiments and the most relevant degradation compounds were identified. In this respect, ammonia emissions from the exit gas were measured using a 0.1N sulphuric acid to recovery the ammonia leaving the semi-batch rig.

Results from this work concluded that the use of a higher CO_2 concentrated flue gas reduced the MEA degradation at absorber conditions. In particular, a 60%v/v CO_2 the flue gas reduced up to 50% of MEA losses compared with post-combustion conditions (15%v/v CO_2). However, the MEA losses reduction is limited at elevated temperatures. NH_3 emissions were also reduced of about 75% when high CO_2 concentration were used. This work concluded that partial oxy-combustion technology can substantially reduce the MEA degradation at absorption conditions and thereby this novel CCS approach may become competitive respect to post-combustion.

Keywords: degradation, absorption, solvent, amine, CO_2 capture

1. Introduction

Emissions of greenhouse gases (GHG) have drastically increased in the last decades, primarily due to the use of fossil fuels such as oil, coal and natural gas, which are responsible of about 70% of the total GHG emissions worldwide.(IEA 2015b) Particularly, carbon dioxide (CO_2) is of concern as it has reached atmospheric concentrations up to 400 ppm.(IEA 2015a) Post-combustion capture using an amine-based chemical absorption can be potentially applied to mitigate CO_2 emissions from stationary sources but some disadvantages must be addressed before its large deployment into the industrial and energy sectors. In this respect, solvent degradation represents one of the key issues hindering a large deployment of this technology.

Rao and Rubin estimated that solvent degradation contributes to 10% of the CO_2 capture costs.(Rubin and Rao 2002)

Amines degrade in presence of O_2 present in the flue gas, referred as oxidative degradation, and also at temperatures over 120°C during solvent regeneration, namely thermal degradation.(Rochelle 2012; Gouedard et al. 2012; F. Vega et al. 2014) Even though oxidative degradation takes place in the absorber, it also appears inside the cross-exchanger, which heats up the amine prior to be introduced into the stripper. This occurs due to the fact that the rich solvent leaving the absorber still contains dissolved O_2 that promotes further reactions with the solvent.(Rochelle 2012; Closmann and Rochelle 2011) Solvent degradation results in operational issues such as fouling, foaming and waste management. The presence of solvent degradation compounds can also contribute to enhance pipework corrosion.(Martin et al. 2012) In addition to the above-mentioned operational issues, amines can be emitted with the cleaned gas due to their volatility and may react under atmospheric conditions via photo-oxidation to form a variety of compounds, namely nitrosamines, nitramines, nitramides and amides. These compounds have been recently identified as carcinogenic and potentially harmful to human health and the environment.(Nielsen et al. 2010; Nielsen et al. 2011)

There is a large number of degradation studies reported, primarily referred to MEA and other amine-based solvents such as PZ(Freeman, Davis, and Rochelle 2010), AMP(Wang and Jens 2012), MMEA (Lepaumier et al. 2011), DEA (Lepaumier, Picq, and Carrette 2009; Eide-Haugmo et al. 2011), DEEA (Gao et al. 2014; Gao et al. 2015) and MDEA.(Lawal, Bello, and Idem 2005; Closmann and Rochelle 2011). Most of them focused mainly on one of the degradation mechanisms occurred at either the absorber or the stripper conditions. Several lab-scale apparatus were reported from the literature. Both batch(Wang and Jens 2012; Lawal, Bello, and Idem 2005; Lepaumier et al. 2011) and semi-batch(Sexton and Rochelle 2011; Sanna et al. 2014; Closmann and Rochelle 2011) reactors have been employed in most of degradation studies. Respect to batch reactors, Lepaumier(Lepaumier et al. 2011) utilized 316L stainless steel cylinders in which MEA was placed and heated at 135°C (stripper conditions) to evaluate thermal degradation without presence of air and CO_2, whereas Fostas et. al.(Fostås et al. 2011) used a lab-scale autoclave reactor to simulate the oxidative degradation at absorber conditions. Da Silva used a close-batch reactor to study the oxidative degradation of MEA. This apparatus used 1 L of partially loaded MEA (0.4 mole CO_2 per mole amine) and the flue gas – air - was pumped counter-currently in closed loop.

In the other hand, Sexton and Rochelle studied the oxidative degradation of MEA using a jacketed semi-batch reactor to maintain the desired temperature at 55°C.(Sexton and Rochelle 2011). Other authors such as Vevelstad and Da Silva employed a similar semi-batch apparatus to carry out oxidative degradation experiments at temperatures up to 75°C, using 0.35 L/min air plus 7.5 mL CO_2 as a main flue gas composition in the recycle loop. Some recent studies have integrated the overall degradation process to evaluate both the oxidative and thermal degradation mechanisms in a cyclic absorption-desorption lab-scale rig. In this latter study, the effect on degradation rates due to the presence of both dissolved and entrained oxygen into the cross-exchanger and stripper were also taken into account.(Closmann and Rochelle 2011)

In terms of operating conditions, a variety of flue gas compositions have been utilized. Supap et. al.(Supap et al. 2009) studied the effects of SO_2 on the MEA degradation using a flue gas derived from coal or natural gas fired power plant containing different O_2-CO_2 environments and Fostas et. al.(Fostås et al. 2011) studied the influence of a flue gas containing NO_x on the nitrosamine formation. However, there are no studies focused on the impact on the degradation process related to the use of highly CO_2 concentrated flue gas.

Sophisticated analytical methods for solvent quantification and degradation products identification have been typically used, including gas chromatography coupled with mass

spectrometry (GC-MS), liquid chromatography coupled with mass spectrometry (LC-MS), high performance liquid chromatography coupled with mass spectrometry (HPLC- MS).(Gouedard et al. 2012; F. Vega et al. 2014; Supap et al. 2006)

Generally, degradation experiments require long tests, between 21 and 56 days, to detect any evidence of solvent degradation. In some cases, the experiments were extended for 30 weeks.(F. Vega et al. 2014) Some authors reported low rates associated to the degradation process. A 3.8 mM/h rate was measured when MEA 5-7M degraded at 55°C using a 0.1 L/min of flue gas (98% v/v O_2 and 2% v/v CO_2) and the experiments were extended up to 500 hours.(Sexton and Rochelle 2011) Other studies carried out by Lawal et. al. produced degradation rates of MEA 5M ranging between 0.11-0.54 mM/h in batch reactors at the same temperature.(Lawal, Bello, and Idem 2005) These experiments were prolonged over 300 hours to provide any degradation rate measurements. The presence of cations derived from Fe and Cu promotes the solvent degradation and speed up the degradation rates, mainly in oxidative degradation studies.

Recently, a new hybrid approach between post-combustion and oxy-combustion has been developed as a promising alternative for carbon capture.(Favre, Bounaceur, and Roizard 2009; Doukelis et al. 2009; Fernando Vega, Navarrete, Alonso-Fariñas, et al. 2014; Fernando Vega, Navarrete, Cano, et al. 2014) It consists of the use of an oxygen-enriched air as oxidizer during the combustion stage to produce a higher CO_2 concentrated flue gas followed by a CO_2 separation process based on a chemical absorption approach. This hybrid process can lead to a further energy reduction of penalties related to both oxygen production and solvent regeneration. According to Favre et. al., the hybrid process combining oxy-combustion with post-combustion approach can theoretically lead to about 22-35% decrease of the overall energy consumption compared with oxy-combustion process using natural gas as a fuel.(Favre, Bounaceur, and Roizard 2009) Regarding solvent degradation, most of studies have been focused on post-combustion applications in which CO_2 concentration is below 15% v/v. The use of high O_2 concentrations and metal cations such as Fe^{+2} and Cu^{+} have been also used to enhance the degradation rates and, thereby, to reduce the run time. In respect to this new hybrid approach, CO_2 concentration in the flue gas increases due to the use of a highly O_2 concentrated oxidizer and the impact that these novel operating conditions have on the global degradation process should be studied.

Therefore, this work aims at studying the impact of higher CO_2 concentrated flue gas on the solvent degradation that occurs in the absorber. In particular, this work is focused on the behaviour of MEA degradation in presence of different flue gases with a CO_2 composition ranging between 15 - 80% v/v which correspond to conventional flue gas composition from post-combustion and oxy-combustion processes, respectively.(Favre, Bounaceur, and Roizard 2009; Huang et al. 2012) Oxy-combustion technology compromises a quench and a compression and purification unit (CPU) for CO_2 separation, avoiding the implementation of a CO_2 chemical absorption unit. According to Favre et al., partial oxy-combustion might reach a minimal separation energy in the range of 40%-50%v/v CO_2 in the flue gas that implies a 50%-60%v/v O_2 concentration in the oxidizer used in a conventional pulverized coal boiler [REF].The influence of most relevant parameters such as temperature and O_2 content in the flue gas has been also evaluated. The evolution of MEA concentration along the time allows to understand more about the effects on the degradation rates and mechanism. The key degradation compounds reported from the literature have been identify in the liquid and the concentration of volatile compounds such as ammonia in the exit gas have been also determined.

2. Experimental

MEA was selected as solvent in this work and was supplied by Acros Organics (purity of 99 vol.%). Cylinders containing the synthetic flue gas were provided by Linde. The certificate analysis (DIN EN ISO 6141) assess a level of uncertainty of the synthetic flue gas composition within +/- 1%. The 0.1 N sulphuric acid solution was obtained from Panreac with a level of uncertainty within +/- 1%.

Three parameters were studied on the degradation lab-rig, namely CO_2 and O_2 concentration and temperature (Table 1). In respect to the synthetic flue gas composition, the effects of both O_2 and CO_2 concentrations on MEA degradation were evaluated. In particular, the O_2 concentration varies from 3% v/v to 6% v/v, based on the traditional exhaust gas composition from pulverized coal boilers [3-5% v/v].(DOE-NETL 2010) In addition, the CO_2 concentration represents the most relevant operational parameter from a partial oxy-combustion capture process, ranging between 15% v/v (air-firing mode) to 60% v/v CO_2 in the flue gas, which corresponds with partial oxy-combustion capture using a 80% v/v enriched-air as oxidizer.(Favre, Bounaceur, and Roizard 2009; Fernando Vega, Navarrete, Cano, et al. 2014) Partial oxy-combustion becomes economically unfeasible in comparison with oxy-combustion technology as CO_2 concentrations is set over 60%v/v which is considered the high limited value of this parameter. Temperature effects were also studied in this work. CO_2 absorption is an exothermic reaction, where energy is released when CO_2 reacts with the amine and thereby it produces a temperature profile along the absorber that can reach 70°C into the absorber under conventional absorber configurations.(Mangalapally et al. 2012; Von Harbou, Mangalapally, and Hasse 2013) Therefore, two representative temperatures, 50°C and 70°C, were chosen to be tested in the degradation lab-rig.

Table 1. Test matrix of the experimental planning carried out in this work

Parameter	Operating range															
CO_2 (% v/v)	15				20				40				60			
O_2 (% v/v)	3		6		3		6		3		6		3		6	
Temperature (°C)	50	70	50	70	50	70	50	70	50	70	50	70	50	70	50	70

The evolution of MEA degradation was studied for 30 days in a semi-batch degradation apparatus, as illustrated in Fig. 1. Sixteen tests were carried out with different settings, using synthetic flue gas with a defined composition of O_2 and CO_2, balanced with N_2. The oxidative and thermal degradation took place in four semi-batch reactors where the MEA 5M solutions were previously placed. Therefore, four different experiments can be run in the degradation apparatus at the same time. Each reactor consists of a 250 ml 3-neck round bottom flask stirred at 340 rpm. Each pair of reactors was placed into two thermal baths heated with an electric resistance. PID controllers were used to maintain the desirable temperature during the tests.

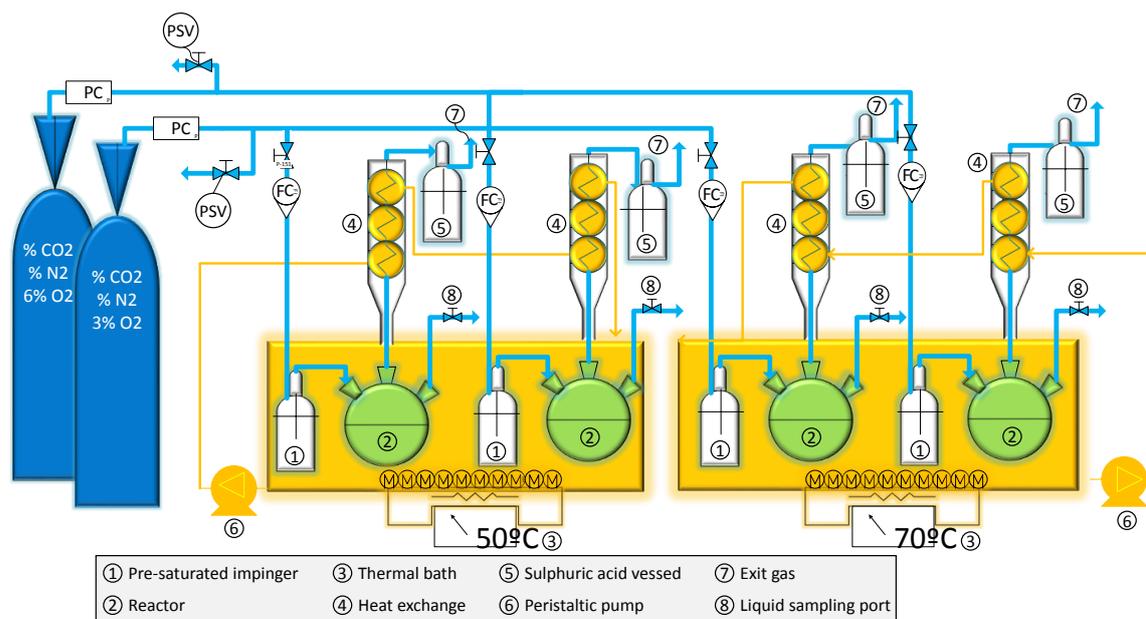| ① Pre-saturated impinger | ③ Thermal bath | ⑤ Sulphuric acid vessed | ⑦ Exit gas |
| ② Reactor | ④ Heat exchange | ⑥ Peristaltic pump | ⑧ Liquid sampling port |

Figure 1. Schematic diagram of the semi-batch amine degradation apparatus

The solvent was exposed to a 0.1 L/min of flue gas which was bubbled into the solution. The synthetic flue gases leaving the cylinders were measured using four mass–flow controllers to provide the desirable gas-flow. After that, they were pre-saturated with water before being introduced into the stirred 3-neck round bottom flasks. Once the synthetic flue gas bubbled through the solution, it passed through the heat exchangers to avoid excessive water condensation and to assess the water balance during the experiments. The thermal-oil from the thermal bath was pumped to control the operating temperature of the heat exchangers. Finally, the exit gas from each experiment was bubbled into various impingers were the sulphuric acid solution was placed in accordance with American standard (Conditional test method - 027) for volatile ammonia determinations.(EPA 2008) 3-ml liquid samples were withdrawn from the reactors using a glass syringe at different intervals along the experiments for MEA concentration and degradation compounds determinations. The sulphuric acid solution was recovered four times, after 6, 15, 24 and 30 days, for each experiment for ammonia determinations. Enough amount of ammonia is required to be retained into the sulphuric acid solution in order to measure ammonia concentrations over the detection limit set by the analytical methods described below.

MEA concentration was measured using a HPLC-MS method, as previously reported.(Sanna et al. 2014) The HPLC-MS/MS equipment was a QTRAP MS coupled with Perkin Elmer HPLC. The separation column used was a X Bridge BEH Amide (10 cm x 2.1 mm), 2.5 microns, using 0.1% formic acid in water and 0.1% methanol in water as eluent. Calibration curves were obtained using MEA standard solutions containing 50, 100, 200, 300, 500, 700 and 1000 ppb. Samples were diluted $1/10^6$ and the injection volume was 10^{-2} ml for the MEA concentration determinations.

The identification of the most relevant degradation compounds (Table 2) in the liquid were carried out using an Ultra High Performance Liquid Cromatography (U-HPLC) method. A UHPLC-HR/MS equipment ORBITRAP ELITE MS coupled with Dionex UHPLC was used. The same separation column and the eluents used for MEA concentration measurements were utilized in these analysis. The method for the identification of each degradation compound was based on a comparison of the theoretical mass of each pseudomolecule ion with the experimental measurement. Samples were diluted 1/1000 to be detected with an accuracy

below 10 ppm using this method due to the low concentrations in which they were found in the samples.

Table 2. Main degradation compounds of MEA(F. Vega et al. 2014)

Oxidative degradation compound	Abbreviation	MW
Ammonia	-	17
Formic Acid	-	46
Acetic Acid	-	60
2-oxazolidone	OZD	87
N-(2-hydroxyethyl)formamide	HEF	89
N-(2-hydroxyethyl)imidazole	HEI	112
N-(2-hidroxyethyl)-glycine	HEGly	119
N-(2-hydroxyethyl)piperazin-3-one	HEPO	144
N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	HEHEAA	162
N,N'-Bis (2-hydroxyethyl)oxamide	BHEOX	176
Thermal degradation compound	**Abbreviation**	**MW**
1-amino-2-propanol	-	75
2-oxazolidone	OZD	87
N-(2-hidroxyethyl)-ethylenediamine	HEEDA	104
1-(2-hydroxyethyl)-2-imidazolidone	HEIA	130
N,N`-bis(2-hidroxyethyl)urea	UREA	148
N-(2-aminoethyl)-N'-(2-hydroxyethyl)imidazolidinone	AEHEIA	173
N,N´-bis(2-hydroxyethyl)imidazolidin-2-one	BHEI	174
N,N,N -tris(2-hydroxyethyl)ethylenediamine	THEED	192

The quantification of volatile ammonia carried by the exit gas was determined using an ion-ammonium selective electrode from Crison Technologies™, which is designed to measure the presence of ammonium cation in aqueous solutions. Ammonia was captured in the sulphuric acid solution and then measured in the solution as ammonium cations. The ammonia concentration in the captured solution – 0.1 N sulphuric acid - is measured from a logarithmic calibration curve where the concentration of ammonium cations is plotted as function on the voltage peaks (mv). The calibration curve was constructed using 0, 5, 10, 25 and 50 mg/L standard solutions of ammonia in aqueous solution.

3. Results and discussion

The degradation of MEA 5M was studied at conventional CO_2 absorption conditions under different partial oxy-combustion levels, using CO_2 compositions in the flue gas from 20% v/v to 60% v/v. The influence of the above-mentioned operating parameters have on the solvent degradation process was evaluated by determining MEA concentration in aqueous solution along 30 days. Solvent concentration variations allowed not only calculating MEA losses during the experiments, but also determining the impact of different operating conditions on the degradation rates. In addition, NH_3 represents one of the most relevant volatile degradation compounds derived from the oxidative degradation of MEA and NH_3 emissions at the reactors outlets were also determined at several intervals during the experiments.

3.1 MEA degradation analysis

The results from the MEA degradation experiments are discussed in this section. A comparison with post-combustion experiments using a 15% v/v CO_2 flue gas is also further discussed below, particularly in terms of MEA degradation.

3.1.1 Effect of CO₂ concentration

The impact of the CO_2 flue gas composition, and thereby the CO_2 partial pressure, on the MEA degradation process is shown in Figure 2.
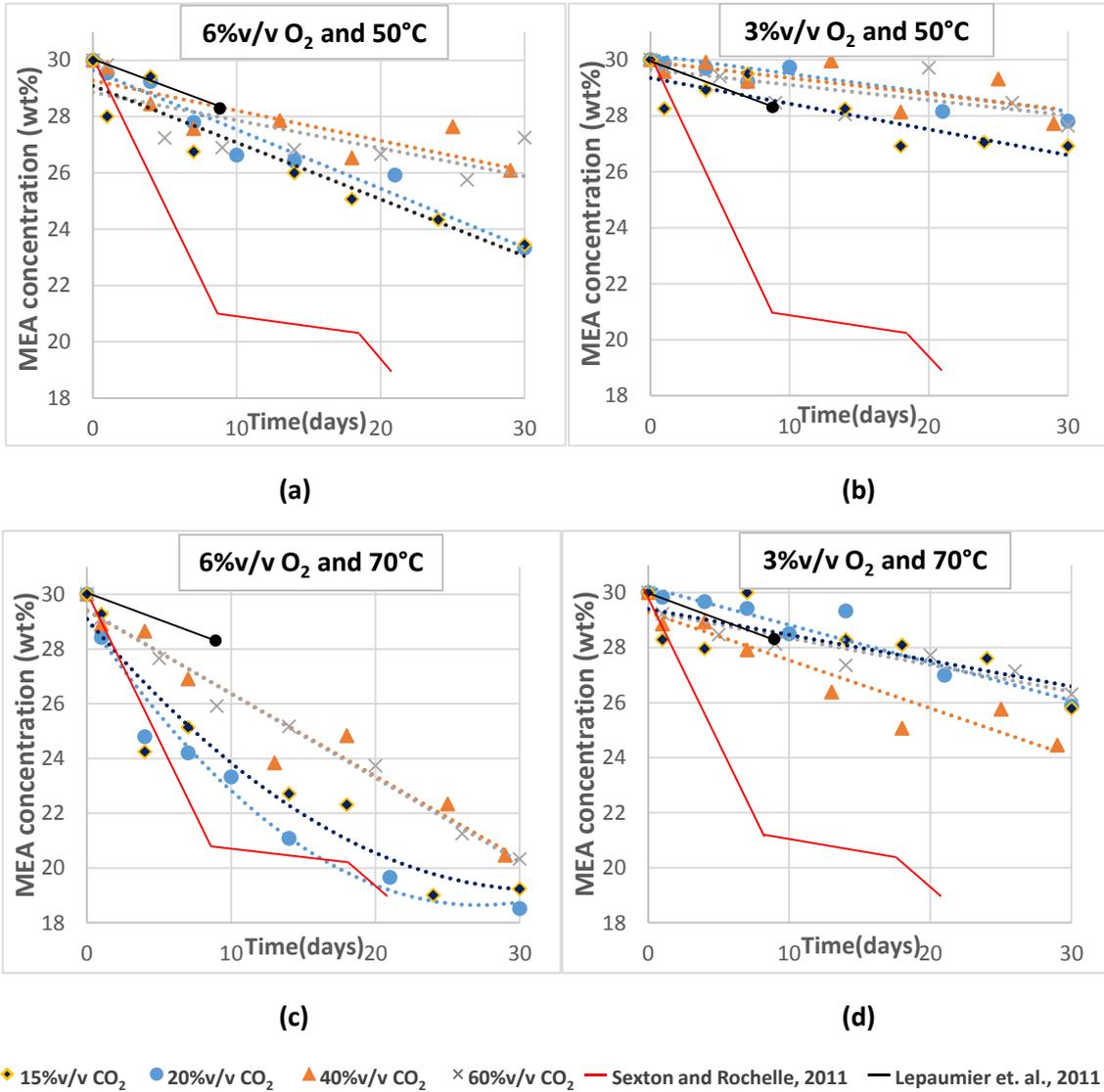

Figure 2. MEA concentration in aqueous solution plotted versus time at several experimental conditions: (a) 6%v/v O_2 and 50°C, (b) 3%v/v O_2 and 50°C, (c) 6%v/v O_2 and 70°C, (d) 3%v/v O_2 and 70°C. Oxidative degradation experiments at 55°C from Sexton and Rochelle(Sexton and Rochelle 2011) and Lepaumier et al.(Lepaumier et al. 2011) were plotted.

In general, the use of a more CO_2 concentrated flue gas reduced the MEA degradation process at absorber conditions, presented in Fig. 2. The evolution of the MEA content in the aqueous solution showed a nearly linear trend in most experiments. This trend suggested a constant degradation rate of the solvent. Only the experiments run at 6% v/v O_2 and 70°C exhibited high degradation rates under low CO_2 concentrations such as 15-20% v/v CO_2. As it can be seen in Fig. 2c, the same behaviour was observed from Sexton and Rochelle´s experiments – 98% v/v O_2 and 2% v/v of CO_2 flue gas at 55 °C - as it was compared with the evolution of MEA concentration using a 6% v/v O_2 and 15-20% v/v CO_2 flue gas at 70 °C. In addition, these experiments changed towards linear trends, and also lower degradation rates, as the CO_2

concentration in the flue gas was increased to values over 20% v/v CO_2 (Figs. 2). The presence of CO_2 had impacted on the oxidative degradation mechanism, reducing the MEA degradation rates observed in the experiments. Studies of the kinetics of SO_2 and O_2 induced degradation of MEA conducted by Supap et. al. stated a similar effect in terms of MEA degradation rate when CO2 concentration was increased.(Supap et al. 2009)

It should be noted that the experiments carried out using 6%v/v O_2 in the flue gas provided the highest MEA degradation levels. In addition, the inhibiting effect on the MEA degradation process due to the presence of an elevated CO_2 concentration in the flue gas was clearly observed in Figures 2a and 2c. Under the above-mentioned O_2 content, experiments using a flue gas composed with 15-20%v/v CO_2 degraded MEA from the initial 30 wt% up to 24 wt% and 19 wt% at 50°C and 70°C, respectively. The experiment that provided the maximum degradation of MEA was run using a 6% v/v O_2 and 15% v/v CO_2 flue gas at 70 °C in which the reduction of the initial MEA concentration in the aqueous solution reached up to 38%. Flue gas containing 40 (Δ) and 60 (X) %v/v CO_2 decelerated the degradation rates observed at lower CO_2 concentrations and also enhanced the MEA resistance under degradation conditions. In fact, MEA concentration was reduced about 14% compared with the initial 30wt% since the operating temperature was set at 50°C, which corresponded with a 50% below the MEA degradation levels provided at lower CO_2 flue gas compositions. When 70°C was set as operating temperature, those operational advantages related to the use of more CO_2 concentrated flue gas were partially limited, resulting in a MEA concentration reduction of 32%, which was 15% lower compared to post-combustion capture (15% v/v CO_2) conditions.

In relation to the experiments involving 3%v/v O_2 in the flue gas (Figure 2 b,d), the MEA degradation variations related to the presence of higher CO_2 concentration were less relevant than those produced at 6% v/v. Therefore, the inhibiting effect was almost neglected. In fact, the runs operating at 70°C showed a small MEA concentration variation (from 25.70 %wt to 26.80 %wt). Similarly, the MEA concentration varied from 26.92 %wt to 27.25%wt at 50°C. Other works from Lepaumier et. al.(Lepaumier et al. 2011) and Davis and Rochelle(Davis and Rochelle 2009) reported MEA losses below 6% operating in semi-batch conditions at 55°C. These experiments provided MEA concentrations around 28wt% after 9 and 7 days, respectively, which were in accordance with the values obtained from 3% v/v O_2 experiments in this work (Figs. 2).

Therefore, the inhibiting effect related to the presence of 40-60 v/v % CO_2 in the flue gas was more effective under low temperatures (50°C), where the solvent degradation process was governed by oxidative mechanisms. In this case, higher CO_2 content in the flue gas shifted the CO_2-MEA solubility equilibrium towards higher CO_2 loaded aqueous solutions. Thus, the presence of more dissolved CO_2 in the bulk MEA aqueous solution may make difficult the O_2-MEA interactions by limiting the O_2 mass transfer. However, the above-described phenomena resulted in an undesired enhancement of the MEA degradation via carbamate polymerization in experiments run at 70°C, where this thermal mechanism became relevant during the degradation process. MEA losses almost double as temperature varied from 70°C to 50°C (Figs. 2). Higher CO_2 partial pressure in the flue gas provided a higher presence of carbamate ion in the aqueous solution and thereby a major likelihood associated to solvent polymerization reactions.

3.1.2 Effect of temperature

The temperature effect on the MEA degradation process is shown in Fig. 3. The operating temperature at the absorber had an effect on the MEA degradation rates observed during the experiments. Experiments carried out at 70°C significantly enhanced the MEA degradation process. The reduction of the MEA concentration in aqueous solution was almost doubled at 70°C, particularly in those runs involving 6%v/v O_2 in the flue gas.

The combination of 6%v/v O_2 and 15-20%v/v CO_2 in flue gas at 70°C accelerated the MEA degradation rate after 15 days. In particular, the MEA reduction increased from 12-13% at 50°C, to 30% at 70°C, which implies a 60% increase of the degradation rate. The MEA degradation rates observed from day 15 to day 30 was somehow slowed down due to the lower concentration of MEA (already partially degraded. Therefore, the final MEA concentration reduction was 38% after 30 days resulting only 8% higher compared to that after 15 days.
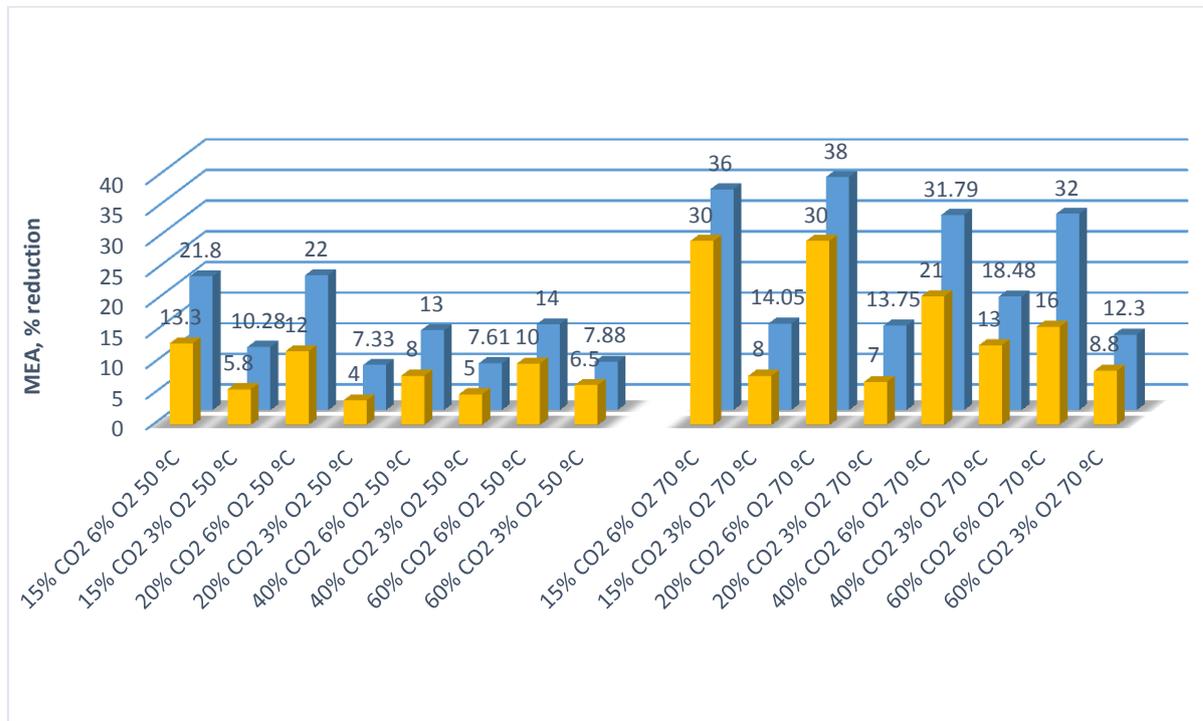

Figure 3. MEA reduction percentage obtained from experiments run at 50°C (left) and at 70°C (right). The MEA degradation was evaluated at two stages: 15 days (yellow bars – first row) and 30 days (blue bars – second row).

The inhibiting effect of elevated CO_2 concentration in the flue gas on MEA degradation process was also reduced at 70°C. The MEA degradation at 70°C showed a lower degradation inhibition under elevated CO_2 concentrations when 6%v/v O_2 was used. Moreover, the inhibiting effect occurred at elevated CO_2 concentrations in the flue gas could be neglected in experiments run at 3%v/v O_2 in the flue gas. MEA losses associated to these experiments ranged between 14.05% and 13.75%, in post-combustion (15% v/v) and 20% v/v experiments, to 18.48% and 12.3%, in 40% v/v and 60% v/v CO_2 experiments, respectively. Therefore, the inhibiting effect associated to elevated CO_2 concentration was further diminished at 3%v/v O_2 in the flue gas.

Therefore, higher temperature in the absorber increased the MEA degradation processes, especially those related to oxidative mechanisms. It also should be pointed out that degradation effects derived from thermal mechanisms may be enhanced under temperatures

over 70°C. In fact, degradation compounds such as urea, HEIA and BHEI were only identified in experiments conducted at 70°C. Those degradation compounds, typically formed from thermal degradation compounds, were not detected at low temperature experiments. The presence of high CO_2 concentration in the flue gas might enhance their formation rates, even at temperatures far from those that thermal degradation effects become significant.

3.1.3 Effects of O_2 concentration

The amount of O_2 in the flue gas was the key for the solvent degradation occurred at CO_2 absorption conditions.(Rochelle 2012; Gouedard et al. 2012; F. Vega et al. 2014) The presence of higher O_2 content (6% v/v) in the flue gas drastically enhanced the MEA degradation in most of the experiments, as shown in Table 3. Using 6% v/v O_2 in the degradation experiments resulted in significant reductions (30%) of the MEA concentration. The final MEA concentration in the aqueous solution was -of 20%wt when 6%v/v O_2 was used, whereas, MEA concentrations over 25%wt resulted from experiments using 3% v/v O_2 after 30 days.

Most of the MEA degradation is based on oxidative mechanisms under the operating conditions at the absorber, and thereby, the increase in the O_2 concentration in the flue gas produced a further increase of the solvent losses during the experiments. The inhibitor effects due to the CO_2 in the flue gas were also observed in those experiments. As it can be seen from results reported in Table 3, experiments run under partial oxy-combustion conditions enhanced the MEA resistance to oxidative degradation in comparison with conventional post-combustion conditions (15%v/v CO_2).

Table 3. MEA concentration in aqueous solution for post-combustion case (15%v/v CO_2) and partial oxycombustion case (60%v/v CO_2) after 30 days

| Test Conditions			Final MEA concentration (%wt)
O_2 (%v/v)	CO_2 (%v/v)	Temperature (°C)	
3	15	50	26.92 ± 0.10
		70	25.70 ± 0.40
	60	50	27.63 ± 0.50
		70	26.80 ± 0.20
6	15	50	23.45 ± 0.10
		70	19.20 ± 0.40
	60	50	27.25 ± 0.50
		70	20.30 ± 0.20

3.2 NH$_3$ emissions

The NH_3 emissions from the exhaust gas leaving the degradation vessels were measured at several time intervals along 30 days for each experiment. The mean values of NH_3 emissions were calculated from the analysis of the NH_4^+ cations in water solution (see Section 2) and the total volume of flue gas bubbled through the MEA aqueous solution for each interval. Figures 4 presents the mean average NH_3 emissions calculated at four intervals as indicated below.
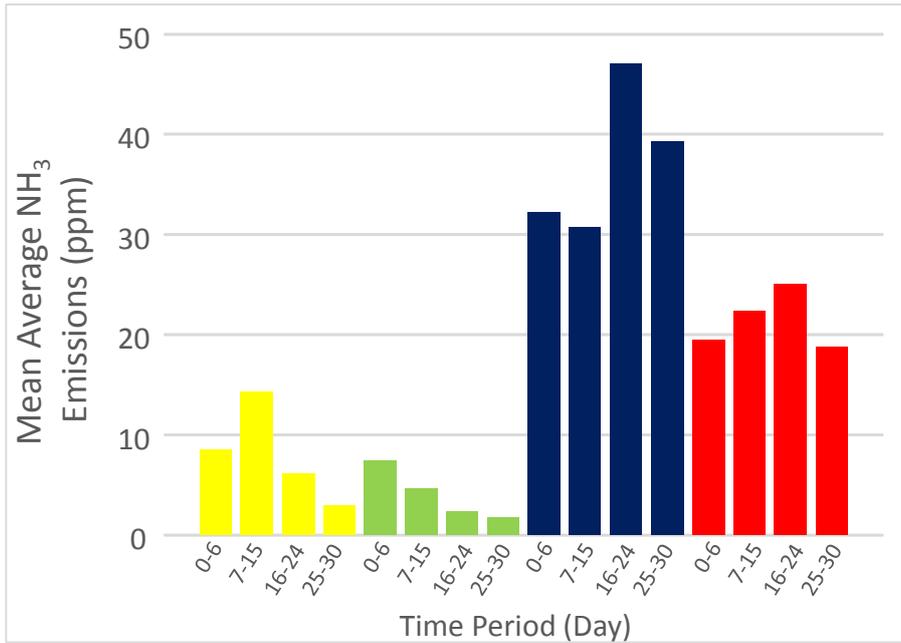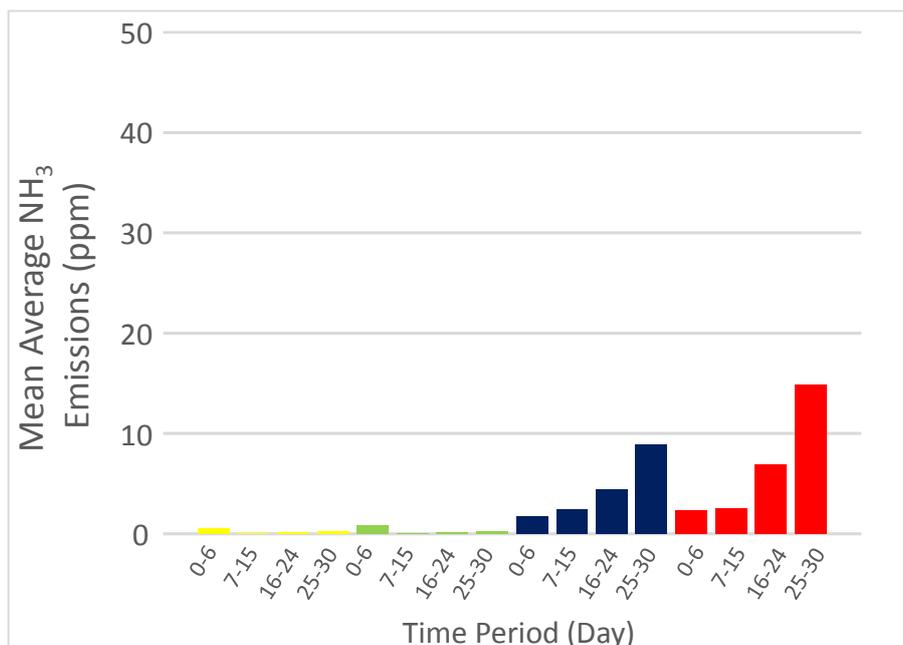
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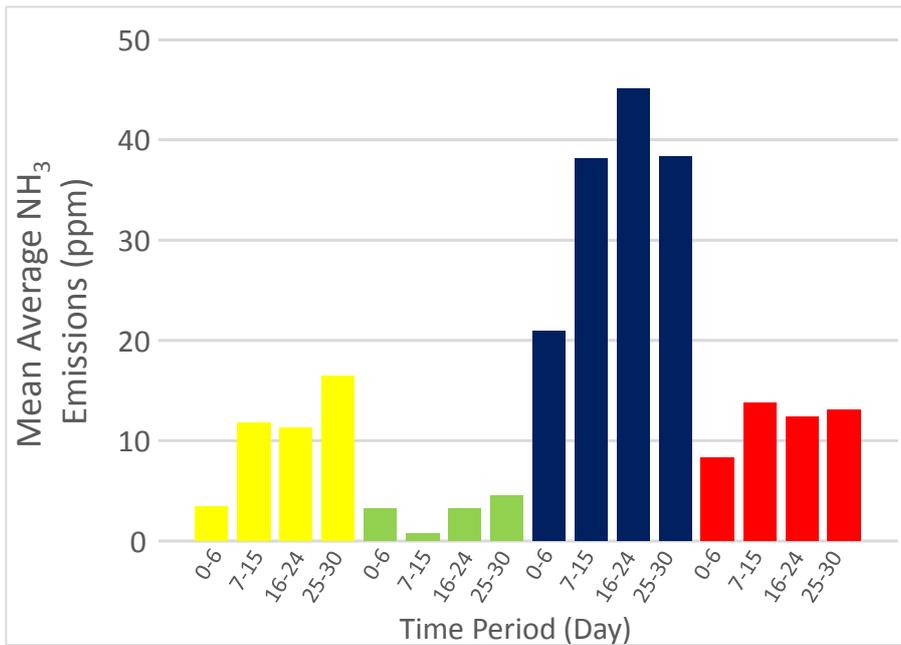
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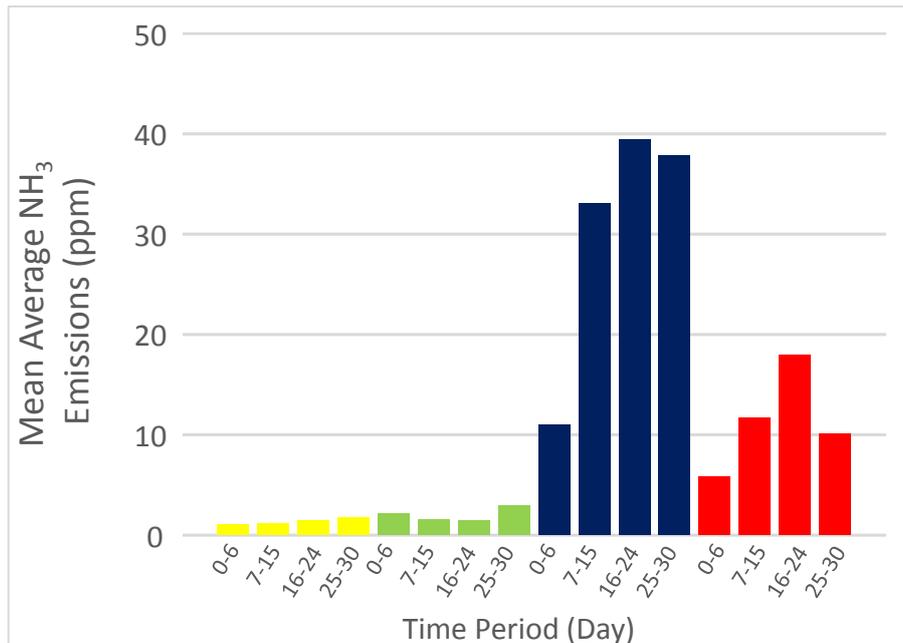
(c)

(d)

Figure 4. Evolution of NH_3 emissions measured in the lab-rig exhaust gas: (a) 15%v/v CO_2, (b) 20%v/v CO_2, (c) 40%v/v CO_2 and (d) 60%v/v CO_2. The experiments plotted in those figures were set at 6%v/v O_2 and 50°C (yellow bars), 3%v/v O_2 and 50°C (green bars), 6%v/v O_2 and 70°C (blue bars) and 3%v/v O_2 and 70°C (red bars)

According to the results summarized in Fig. 4, the NH_3 emissions were further reduced in all the experiments as the CO_2 concentration in the flue gas increased. Experiments operating at lower temperatures (50°C – yellow and green bars in Figs. 4) produced mean average NH_3 emissions below 3 ppm as CO_2 concentration was set over 40%v/v. In cases operating at elevated temperatures (70°C – blue and red bars in Figs. 4), further reductions in NH_3

emissions were observed which were estimated around a 75% reduction compared with post-combustion capture case.

NH_3 is one of the most relevant degradation compounds derived from oxidative degradation of amine solvent, particularly from MEA. Therefore, the above observations confirm that a more CO_2 concentrated flue gas partially inhibits the oxidative degradation of MEA and further reductions in terms of MEA degradation can be achieved, leading to a more long-term efficient use of MEA as solvent.
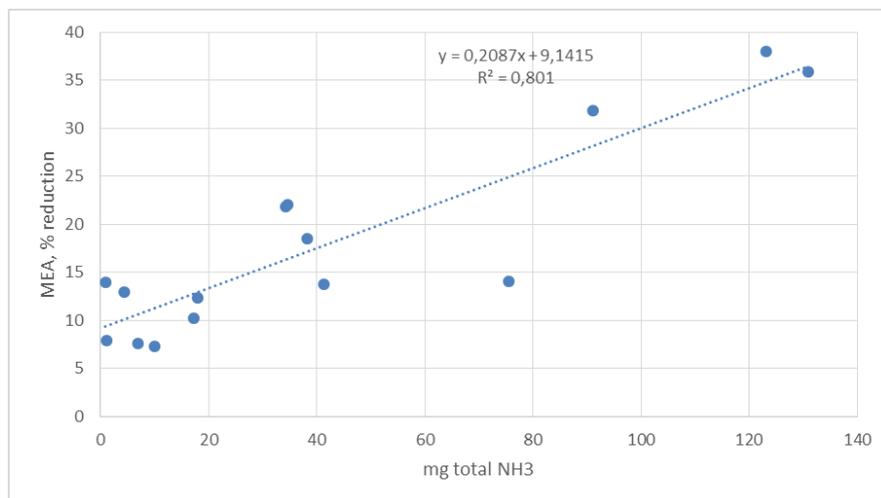

Figure 5. Reduction of MEA concentration plotted versus total NH_3 emissions

In addition, NH_3 emissions are further related to the MEA degradation level. Figure 5 clearly showed that a direct relationship existed between the reduction of the MEA concentration in aqueous solution and the total mass of NH_3 emitted in the exit gas along each experiment, expressed as total milligrams emitted in the exhaust gas. As it can be concluded from Fig. 5, both parameters are closely related and thereby the NH_3 emission may be used to monitor the MEA degradation level in CO_2 capture processes involving amine-based solvents.

4. Conclusions

A new hybrid approach between post-combustion and oxy-combustion is considered a promising alternative for carbon capture. It can lead to a further energy reduction of the penalties related to both oxygen production and solvent regeneration. Solvent degradation in CO_2 capture processes based on MEA-based chemical absorption was studied under partial oxy-combustion conditions for the first time and compared to post-combustion conditions. The influence of key operating parameters such as oxygen content and absorption temperature was also evaluated in a semi-batch rig. In general, the use of a higher CO_2 concentrated flue gas, mainly derived from partial oxy-combustion operations, reduced the oxidative MEA degradation at absorber conditions. Results extracted from the semi-batch experiments have demonstrated that a 60%v/v CO_2 in the flue gas can reduce up to 50% the oxidative degradation of MEA compared to post-combustion conditions (15%v/v CO_2). The CO_2-MEA solubility equilibrium displacement allows increasing the amount of CO_2 dissolved into the solvent aqueous solution to hinder the O_2-MEA interactions and thus limit the O_2 mass transfer in the bulk liquid. However, the positive inhibitor effect related to elevated CO_2 concentrations is limited to absorption temperatures below 70°C, due to carbamate polymerization enhancement at higher temperatures. Degradation compounds derived from thermal mechanisms such as urea, HEIA and BHEI were only identified at 70 ˚C. In addition, the

oxygen content is the most relevant parameter observed in this work, in terms of MEA degradation at absorber conditions. Experiments using 6%v/v O_2 in the flue gas produced MEA losses above 30% from the initial MEA concentration, even in presence of CO_2 concentrations over 40%v/v in the flue gas.

NH_3 emissions were reduced of about 75% in all the experiments at higher CO_2 concentrations, compared with post-combustion conditions. Since NH_3 emissions are directly related to the MEA degradation, their detection can be used as an indirect way of quantifying the MEA losses due to oxidative degradation mechanisms.

Therefore, partial oxy-combustion could potentially reduce the oxidative degradation of MEA and thereby might reduce the operational costs regarding waste management and solvent make-up. The use of a more CO_2 concentrated flue gas partially inhibited the oxidative degradation of MEA in semi-batch conditions. CO_2 capture operations under partial oxy-combustion conditions could provide further reductions in terms of MEA degradation, leading to a more long-term efficient use of MEA as solvent.

5. Acknowledgements

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