GHGT-12

Accelerated MEA degradation study in hybrid CO_2 capture systems

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Abstract

CO_2 capture systems are typically divided into pre- post- and oxyfuel- combustion systems. However, the interest on hybrid systems, which integrate elements of more than one of the above systems, is attracting major attention in recent times due to the potential higher energy efficiency. In this work, degradation studies have been conducted to identify operational issues related to amines degradation. Oxidative MEA degradation in presence of flue gas resembling oxygen enriched combustion has been investigated. MEA loss was 27% when flue gas with 15% CO_2 was used at 70°C, while only 20% loss was found in the presence of 50% CO_2, indicating that hybrid CO_2 capture systems may be used to decrease amine degradation of traditional post-combustion technologies. N-(2-hydroxyethyl)piperazin-3-one, N-(2-hydroxyethyl)-2-(2-hydroxyethylamino) acetamide, 2-oxadolidone, N-(2-hydroxyethyl)imidazole and N-N'-bis(2-hydroxyethyl)oxamine have been identified as MEA degradation products.

Keywords: CCS, CO_2 capture, amine degradation, hybrid systems.

1. Introduction

Post-combustion capture using chemical absorption by aqueous amine-solutions is the most mature and industrially developed CO_2 capture technology.

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The amine-based chemical absorption process has been used in CO_2 and H_2S removal from gas-treating plants for decades [1]. Monoethanolamine (MEA) is considered as a benchmark solvent, as it is widely used due to its high cyclic capacity, significant absorption-stripping kinetic rates at low CO_2 concentration and high water solubility [1]. However, the high energy penalty related to amines regeneration and solvent degradation represent key issues hindering a large deployment of this technology. Moreover, the operating costs related to amine degradation have been estimated to be around 10% of the total CO_2 capture cost [2].

Degradation studies have been conducted to identify potential environmental and operational issues related to amine degradation compounds [1,3]. The authors have recently conducted a review of amine degradation processes [4]. Two main types of amine degradation have been identified: 1) thermal degradation and, 2) oxidative degradation in which O_2 participates [4, 5]. Oxidative degradation occurs in the presence of O_2, which will react with MEA to produce ammonia and other products more corrosive than the starting amine. Dissolved oxygen that does not react in the absorber will react in the cross exchanger or the stripper, where the temperature is 100-120°C [5].This type of degradation has become a key issue in chemical absorption process for the CO_2 separation from the flue gas in fossil fuels power plants, where the O_2 concentration varies typically between 3-5%. Oxidative degradation can be decoupled from thermal degradation by operating at 40-70ºC [6,7]. Oxidative degradation is a very slow process, where a typical test lasts for about 4 weeks [8], so that semi-batch experiments have been used to simulate the conditions of oxidative degradation in the absorber, where flue gas containing excess oxygen from combustion continuously contacts the charged amine [3]. Liquid Chromatography combined with Mass Spectrometry (LC-MS) is typically used to quantify amine concentration remained in the solution [8] and can also be used to quantify degradation products with molecular weight higher than 50 a.m.u. For compounds with lower that 50 a.m.u., GC-MS is used [9].

Recently, hybrid systems that link different elements among the main CO_2 capture systems have been proposed. It has been suggested that these systems such as post-combustion capture with oxygen enriched combustion, may be cheaper and more energy efficient than traditional CO_2 capture systems [10]. Therefore, this work focus on the investigation of oxidative MEA degradation in presence of flue gas with higher CO_2 concentration than traditional air-fired boilers, resulting from oxygen enriched combustion [11].

2. Method

The degradation studies were carried out for 30 days at 70°C, 1bara, using synthetic flue gases with 15 or 50 vol.% CO_2 and 3 or 6vol.% O_2, balanced with N_2. The oxidative degradation set-up consisted of a 500 mL 3-neck stirred flask, where the 5M MEA solutions were exposed to the specific gases above-mentioned and stirred at 900 rpm.
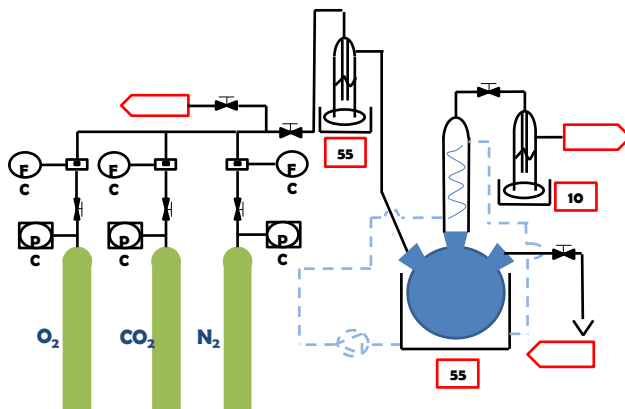

Figure 1 MEA degradation apparatus.

The gases leaving the gas cylinders (1L/min) were saturated with water before being introduced into the 3-neck stirred flask. The experiment was carried out in a fume cupboard. 5-ml samples were withdrawn every 3 days using a glass syringe to be analyzed.

The measurements of the MEA concentration change and the identification of the degradation products were carried out using a Liquid Chromatograph (LC). A LC-MS/MS equipment 6460 Triple Quadrupole MS coupled with 1290 Infinity LC Chromatography and Infinity auto sampler 1200 series G4226A from Agilent Technologies was used. The molecules were ionized by an electrospray ionization source (ESI). The column used was an Ascentis Express RP-Amide HPLC Column with dimensions: 15 cm x 4.6 mm; 2.7 microns; CAT#53931-U, using 25 mM formic acid in water as eluent (0.6 mL/min). 25 mM acid formic in water was required as eluent.

Calibration curves were obtained using standard solutions containing 10, 15, 20, 25, 30, 35, 40, 45, 50 ppm MEA with internal standard solution of 20 and 40 ppm MEA. LC samples were prepared diluting 100 µl in 10 ml for two times and the injection volume was 10 µl.

3. Results

3.1. Amine degradation

The degradation studies show that the O_2 partial pressure affects significantly the amine degradation. Intermediate solution concentrations, as that used in this work (5M), exhibit the effects of both kinetics and O_2 mass transfer control on MEA degradation rate [12]. To eliminate any mass transfer resistance, the solutions were vigorously stirred at 900rpm during the laboratory experiments. Temperature was set at higher temperature compared to that found in absorption columns typically employed for these applications [13-15]. The temperature increase from the typical 50ºC was used to speed up the degradation process and reduce the experimental time up to 30 days. Figure 1 shows the MEA degradation over 30 days. In presence of high CO_2 concentration (50vol.%), the solubility and diffusion coefficient of O_2 decrease, and consequently, the amine degradation rates decrease as well, as previously suggested [16]. MEA losses were 27% and 17% in presence of 15% and 50% CO_2 in 3%-O_2 concentrated flue gas, respectively. The degradation increased by 7% and 23%, when the O_2 content was 6% instead of 3%. The presence of higher O_2 concentration in the flue gas strengthened kinetic and O_2 diffusion into the solution, limiting the benefits that the presence of higher CO_2 concentration in the flue gas produced on oxidative degradation process.
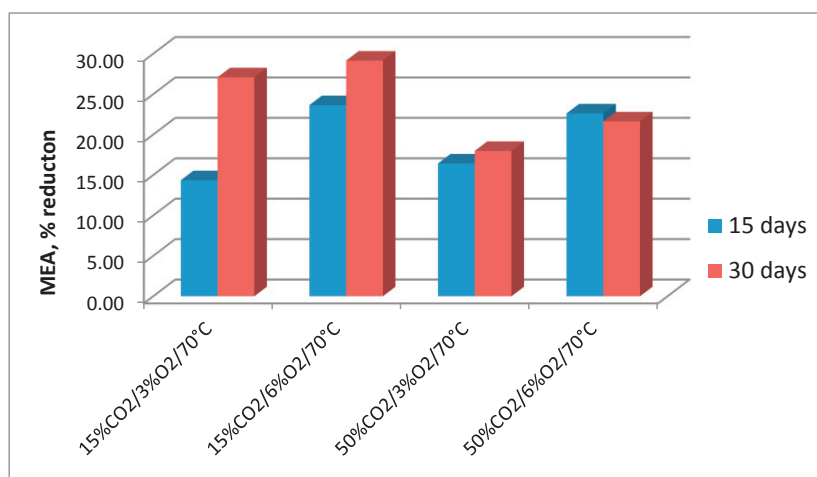

Figure 2 MEA degradation over 30 days.

Although it seems that higher CO_2 concentration in the flue gas avoids partially oxidative degradation, it should be noticed that more than 90% of the total degraded amine was achieved in presence of 50% CO_2 after 15 days, whereas experiments in presence of 15% CO_2 required more time to achieve same level of degradation.

3.2. Degradation products

The method used was not able to identify low molecular weight MEA degradation products such as ammonia, formic acid, acetic acid. However, some high molecular weight compounds were identified. The main degradation products identified by LC-MS were HEPO (N-(2-hydroxyethyl)piperazin-3-one) and HEHEAA (N-(2-hydroxyethyl)-2-(2-hydroxyethylamino) acetamide). The HEHEAA signal intensity increase from day 3 to day 18, and then it decreases indicating its conversion in HEPO [17,18]. This phenomena agrees with the mechanisms proposed by Supap and Arduengo that indicates HEPO formation by dehydration of HEHEAA [16,17]. Other compounds such as OZD (2-oxadolidone), HEI (N-(2-hydroxyethyl)imidazole) and BHEOX (N-N'-Bis(2-hydroxyethyl)oxamine) were also identified.

Table 1. Identified degradation products.

Main Degradation Product	Abbreviation	MW
2-oxazolidone	OZD	87
N-(2-hydroxyethyl)imidazole	HEI	112
N-(2-hydroxyethyl)piperazin-3-one	HEPO	144
N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	HEHEAA	162
N,N'-Bis (2-hydroxyethyl)oxamide	BHEOX	176

4. Conclusions

The degradation of MEA during CO_2 capture in hybrid post-combustion capture with oxygen enriched combustion has been studied. Presence of oxygen and temperatures over 50ºC shortened the amine degradation experiments that typically require several weeks or the presence of degradation promoters to be studied. MEA loss was 27% when flue gas contained 15% CO_2. HEPO and HEHEAA, OZD, HEI and BEHOX were identified as MEA degradation products under the studied conditions. The degradation increased by a maximum of 23%, when the O_2 content was 6% instead of 3%. This work indicates that hybrid CO_2 capture systems may be used to decrease the amine degradation of traditional post-combustion technologies and related costs.

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