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Oxidative degradation of a novel AMP/AEP blend designed for CO_2 capture based on partial oxy-combustion technology

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HIGHLIGHTS

- A novel solvent showed high resistance resulting in lower degradation rates than MEA.
- The AEP and AMP loss was half than MEA under the same operating conditions.
- Higher CO_2 concentrations partially inhibited the degradation of the AMP/AEP blend.
- NH_3 emissions were decreased up to 70% under partial oxy-combustion conditions.
- NH_3 emission measurements can be used for monitoring solvent degradation.

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ABSTRACT

Solvent degradation and volatile compound emissions are two of the major concerns about the deployment of carbon capture technologies based on chemical absorption. In this context, partial oxy-combustion might reduce the solvent degradation due to the use of a higher CO_2 concentrated flue gas. This work evaluates the oxidative degradation of a novel AMP/AEP blend, namely POS #1, under partial oxy-combustion conditions. The effects of temperature and flue gas composition were evaluated in terms of solvent loss, degradation rates, NH_3 emissions and degradation products. The experiments were set at temperatures up to 70 °C and two levels of O_2 concentration – 3%v/v and 6%v/v. The CO_2 concentration of the flue gas ranged between 15%v/v and 60%v/v CO_2.

The novel solvent POS#1 showed high resistance to degrade and resulted in lower degradation rates than MEA in all the operating conditions evaluated in this work. The maximum degradation of AEP and AMP was 24% and 19%, respectively. MEA degraded almost double under the same conditions. Temperature and O_2 concentration enhanced the oxidative degradation of POS #1. However, the use of higher CO_2 concentration in the flue gas led to lower degradation rates of AEP and AMP and hence oxidative degradation was partially inhibited under partial oxy-combustion conditions. The presence of higher CO_2 content in the flue gas decreased the NH_3 production and a 70% reduction of its emissions was achieved as the CO_2 concentration shifted from 15%v/v to 60%v/v. Other major degradation compounds such as formate and 2,4-lutidine were also decreased. New degradation products were not identified so that the suggested degradation pathways proposed in the literature were not influenced by the presence of higher CO_2 concentrations.

1. Introduction

The transition towards a low-carbon energy system relies on improving process efficiency and the deployment of renewable energy production [1]. The energy sector contributes with two-third of the greenhouse gas (GHG) emissions worldwide and the primary energy demand is expected to increase 30% by 2040 [2]. In this framework, carbon capture and storage (CCS) technologies are considered a frontline option to meet the European Commission (EC) 2030 strategy aims (40% reduction of GHG emissions in 2030 compared to the 1990 emission levels) and the reduction targets proposed by the Paris Agreement in last Conference of Parties (COP-21) [3].

Among CO_2 capture technologies, partial oxy-combustion is emerging as a promising approach that might reduce the energy penalties related to the overall CO_2 capture process [4]. It is based on the use of oxygen-enriched air as an oxidizer to produce a higher CO_2

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concentrated flue gas that should enhance the CO_2 separation process, typically based on chemical absorption [5]. Partial oxy-combustion can potentially reduce the costs associated to both the high purity O_2 production required from oxy-combustion technology and the CO_2 separation process related to post-combustion technology [6]. According to Favre et al., partial oxy-combustion might achieve a 25% energy reduction of the CO_2 capture process [7].

In addition, solvent degradation, which contributes up to 10% of the total CO_2 capture costs, constrains the development of chemical absorption and its application in CCS technologies [8,9]. Further concerns about emissions of volatile solvents and their reaction to form carcinogens compounds, such as nitramines and nitrosamines in the atmosphere, are currently limiting their use as a CO_2 mitigation approach [10]. Recent studies on monoethanolamine (MEA) degradation showed that the operating conditions derived from partial oxy-combustion can lead to a substantial reduction of both the solvent degradation rates and the emissions of volatile degradation compounds and solvents under absorption conditions [11]. The presence of elevated CO_2 concentration in the flue gas likely limits the O_2 mass-transfer into the bulk liquid and hence inhibits the encounters between the solvent and O_2 [12].

These main findings described above encourage research to develop new solvent formulations and blends that can improve the overall performance of the CO_2 capture process in terms of faster absorption kinetics, higher CO_2 absorption capacity, lower energy requirements for solvent regeneration and higher resistance to thermal and oxidative degradation [12–15]. Primary amines such as monoethanolamine (MEA) have been proposed to be blended with tertiary amines, showing lower energy requirements during the solvent regeneration stage [16]. Potassium carbonate promoted with piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP)/PZ blends has also showed further improvements on the absorption kinetics [17,18]. In this respect, a new solvent blend, namely partial oxy-combustion solvent (POS #1), resulted in a high performance for CO_2 capture under partial oxy-combustion conditions. POS #1 combines AMP with aminoethyl piperazine (AEP) showing an excellent behaviour in terms of absorption kinetics and cyclic CO_2 capacity, particularly at 40%v/v CO_2 concentration in the flue gas [19].

AMP has shown a high resistance to be degraded both thermally and in presence of O_2 [20,21]. Its resistance is not altered as it is blended with other amino-based solvents [22]. The low degradation rates showed at high temperature make AMP an attractive solvent [23]. Its use should allow to operate the stripping stage at elevated temperatures. Elevated stripping pressure lead to higher stripping temperature, which might reduce further the energy consumption during the regeneration stage [24]. AMP resulted highly resistant to degrade in comparison with other primary amines. It is unlikely possible to abstract one hydrogen atom from the tertiary carbon of the α-position nitrogen atom due the molecular structure of AMP and hence the formation of radicals via hydrogen abstraction is inhibited [20,21]. Table 1 summarizes the most relevant degradation compounds reported from the literature. With respect to oxidative degradation compounds, Lepaumier explained that methylation reactions should be a primary degradation step for AMP degradation [20]. A new degradation pathway has been proposed by Wang and Jens in which AMP may degrade via peroxyl radical formation [22].

AEP belongs to piperazines that also showed low degradation rates at temperatures below 150 °C [13]. Although AEP provided an elevated resistance to oxidative degradation, the degradation rates were higher than both aqueous solution of PZ and AEP/PZ blends [25]. The main degradation compounds identified from AEP degradation studies are summarized in Table 2. Most of them were identified from thermal degradation experiments in combination with other solvents. Although here is no specific studies on AEP degradation mechanism, Freeman suggested that AEP is as nucleophile as PZ and hence AEP might attack different protonated AEP to form thermal degradation compounds. Most likely, AEP reacts with protonated either the α-nitrogen or nitrogen from the primary amino group [26,27].

For oxidative degradation pathways, hydrogen abstraction of one of the methylane carbon in the ring is suggested to be the initial step to produce oxidative degradation of AEP. Peroxyl radical might react in alkaline medium to produce peroxide via intermolecular hydrogen abstraction [27].

This work aims at evaluating the degradation of POS #1 under partial oxy-combustion conditions in order to confirm both the resistance of the AMP/AEP blend under these new operating conditions and the capacities of this technology to decrease solvent degradation. The effects of key operating parameters such as temperature and oxygen concentration are also studied. The degradation of AMP and AEP are further discussed in terms of solvent loss, main degradation compounds, volatile compound emissions and degradation mechanisms.

Although degradation pathways and the most relevant degradation compounds from oxidative degradation of AMP and AEP have been studied at different O_2 partial pressure and temperatures, the effect of CO_2 concentration in the flue gas is still unknown. In this work, the influence of higher CO_2 content in the bulk gas on the degradation product formation will be evaluated and new insights about major degradation products and their possible degradation pathways will be further discussed.

2. Experimental procedure

AEP and AMP solvents were supplied by Acros Organics with purity over 99 vol.%. The solution were prepared using deionized water. The synthetic flue gas with different CO_2/O_2 compositions were provided in 50 L-cylinders by Linde. The certificate analysis of the cylinders (DIN EN ISO 6141) guarantees a level of uncertainty of the within +/−1%. The sulphuric acid required for ammonia emission determination was provided in a 0.1 N aqueous solution format by Panreac with a level of uncertainty within +/−1%.

In this work, operating parameters such as the absorption temperature, the CO_2 and the O_2 concentration of the synthetic flue gas were studied in order to evaluate their effects on the oxidative degradation behaviour of POS#1 solvent – AEP/AMP blend –. A summary of the ranges evaluated in this work is reported in Table 3. Variations of the CO_2 composition of the synthetic flue gas simulate the different level of oxygen-enriched air used in partial oxy-combustion capture. Conventional post-combustion capture represents a 15%v/v CO_2 – typically CO_2 composition from air-firing coal combustion [30] – whereas higher CO_2 concentrations imply a higher oxygen content in the oxidizer for partial oxy-combustion operations. The maximum CO_2 concentration studied in this work was 60%v/v CO_2, corresponding to an 80%v/v oxygen-enriched oxidizer during the combustion process [11]. According to Favre at al., higher values of the oxygen-enriched air should not produce further reductions on the overall energy requirements of the CO_2 capture process under partial oxy-combustion conditions respect to post-combustion and oxy-combustion [7]. In addition, the O_2 concentration varied from 3% v/v to 6% v/v and the operation temperature was evaluated at the operating temperature and the temperature bulge in a conventional CO_2 chemical absorption process −50 °C and 70 °C, respectively. Two experiments were conducted at 100 °C to evaluate the oxidative and thermal degradation at elevated temperature. A detailed description of the experimental parameters is reported in previous work [11].

Fig. 1 shows a scheme of the lab-rig used in this work. A detailed description of the lab-rig and the operating procedure can be extracted from previous work [11]. Briefly, the lab-rig consists of a 250-mL semi-batch stirred reactor where the AMP/AEP blend was placed. The initial solvent concentration was 15%p/p AMP and 20%p/p AEP, which is under patent application [31]. As it can be seen in Fig. 1, four experiments could be performed in parallel. Synthetic flue gas was supplied from cylinders and the desired flue gas flow – 0.1 mL/min – was