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Kinetic characterization of solvents for CO_2 capture under partial oxy-combustion conditions

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Abstract

Partial oxy-combustion is proposed as a new carbon capture concept based on the use of oxygen-enriched air as an oxidizer instead of air during the combustion stage followed by a CO_2 chemical absorption. This novel approach has showed potential advantages compared with other CCS technologies that may lead to a further reductions of the energy penalties related to the CO_2 separation process. In this work, a lab-scale apparatus operating under semi-batch conditions was used for the kinetic evaluation of potassium carbonate (K_2CO_3), aminoethylpiperazine (AEP) and methyldiethanolamine (MDEA) and monoethanolamine (MEA). Four experiments were set for each solvent where the flue gas composition varied from 15%v/v (post-combustion) to 60%v/v. In general, the use of a more CO_2 concentrated flue gas enhanced the CO_2 absorption process and the kinetic was significantly improved under partial oxy-combustion conditions. The CO_2 loading also increased in the presence of a more CO_2 concentrated flue gas for each solvent tested. Those results strengthened partial oxy-combustion as a potential CCS approach in comparison with more mature technologies such as post-combustion and oxy-combustion.

Keywords: CCS; CO_2 capture; solvent; kinetic; absorption

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1. Introduction

In recent years, much effort are focused in the field of CCS technologies in order to achieve further improvements on energy efficiency and novel solvent formulation in comparison with conventional (non-CCS) power plants. In this sense, new capture concepts are currently under research that can improve performance of the CO_2 separation process in terms of lower efficiency penalty, capture costs and, therefore, electricity costs related to those from actual state-of art of CCS and low-carbon technologies in comparison with conventional CCS technologies. It is estimated that CO_2 capture accounts for 70–90% of the total operating costs of an entire CCS unit operates in an energy-intensive process [1,2].

In respect to the most feasible options on CCS technologies, concerns about the energy consumption required for solvent regeneration and high purity oxygen production are the major drawbacks for the commercial deployment of post-combustion and oxy-combustion technologies, respectively. Partial oxy-combustion is proposed as a new carbon capture concept consisting of a hybrid CO_2 capture process between post-combustion and oxy-combustion. It is based on the use of oxygen-enriched air as an oxidizer instead of air for fossil-fuel combustion stage followed by a CO_2 separation process based on chemical absorption [3, 4, 5]. This novel approach has showed potential advantages compared with other CCS technologies that may lead to a further reductions in terms of both CO_2 capture and electricity costs [6]. Improvements on the CO_2 separation process should be identified to balance the energy requirements associated to oxygen-enriched air production for fossil fuel combustion stage and, therefore, make partial oxy-combustion competitive in comparison with post-combustion and oxy-combustion capture. The aim of this work is to evaluate the kinetic behavior of conventional solvents proposed for post-combustion under partial oxy-combustion conditions. Partial oxy-combustion development requires support from the above-mentioned advantages to be considered as a real CCS capture option. In this respect, improvements on the absorption kinetics areconsidered the first step towards significant reductions of the energy consumption associated with the overall CO_2 capture process.

2. Methodology

A lab-scale apparatus operating under semi-batch conditions was used for the kinetic evaluation of a number of selected solvents. A detailed description of the lab-scale apparatus can be found in a previous work [3]. Three different solvents were studied - potassium carbonate (K_2CO_3), aminoethylpiperazine (AEP) and methyldiethanolamine (MDEA), all of them with analysis grade 99% of purity. Aqueous solutions of these solvents were compared with the benchmark solvent – MEA 30%p/p – which was tested under the same conditions.

A preliminary evaluation of the solvent behavior in aqueous solution was performed before choosing the optimal composition of aqueous solution that ensure the stability of the blend. Solid formation during the preparation of the different blends must be avoided, among others considerations such as low volatility and viscosity, high CO_2 capacity and solvent degradation.

Several experiments for each solvent were performed in which the CO_2 concentration of the flue gas varies between 15%v/v - 60%v/v. The kinetics of the CO_2 absorption process were evaluated from both the gas phase and the liquid phase. To evaluate the kinetic behavior from the gas phase, the CO_2 absorption rate was determined using a FTIR analyzer installed in the exhaust gas leaving the reactor. The FTIR analyzed allowed to determine the evolution of the CO_2 absorption rates expressed as the CO_2 flow-rate (mL/min) transferred from the bulk gas phase to the liquid phase by means of the Eq. 1, obtained from Li et al. [7]:

$$R_{abs} \left(\frac{mL\,CO_2}{\min} \right) = Q_{fg} \, * \, \frac{\left[Y_{CO_2}^{IN} - Y_{CO_2}^{OUT} \right]}{\left[1 - Y_{CO_2}^{OUT} \right]} \tag{1}$$

Where,

R_{abs}, represents the CO_2 absorption rate expressed in mL CO_2/min.

Q_{fg}, denotes the synthetic flue gas flow-rate expressed in mL/min.

$Y_{CO_2}^{IN}$ and $Y_{CO_2}^{OUT}$, denote the molar CO_2 flue gas composition at the inlet and the outlet of the rig.

In respect to the evaluation of the liquid phase, aliquots of loaded solvents were withdraw at different intervals during the experiments to determine the CO_2 loading evolution, referred as mole CO_2 per mole solvent. Therefore, the evolution of the CO_2 loading of the solvents is evaluated for each experiment. According to Lin et at. [8], the system response to a step input change in terms of CO_2 composition of the flue gas could be treated as a general first order dynamics system. The system response can be defined using a characteristic time (τ) and an equilibrium CO_2 loading (α^*) as Eq. 2 shows:

$$\alpha(t) \; = \; \alpha^* \, * \, (1 - e^{-\frac{t}{\tau}}) \tag{2}$$

In which,

$\alpha(t)$, denotes the CO_2 loading in the liquid phase as a function of time.

α^*, denotes the CO_2 saturated loading at equilibrium.

t, denotes experimental time expressed in min.

τ, denotes the characteristic time of the absorption process expressed in min.

The experiments were extended until the equilibrium was reached. In this case, the CO_2 concentration of the exhaust gas leaving the reactor is compared with the CO_2 concentration at the inlet to ensure a completely saturation of the solvent in aqueous solution.

3. Results

The preliminary test regarding the solvent stability in aqueous solution determined the appropriate compositions of the solvents were K_2CO_3 30%p/p, AEP 30%p/p and MDEA 50%p/p that were further studied in the lab-scale semi-batch apparatus. In general, the CO_2 composition of the flue gas had a relevant impact on the absorption kinetics, as it described in the following sections.

3.1. Gas phase evaluation

From the gas phase evaluation, the Fig.1 summarizes the evolution of the CO_2 absorption rates for the experiments using AEP 30%p/p and 20%v/v, 40%v/v and 60%v/v CO_2 concentration. This solvent exhibited a significant increase of the CO_2 absorption rate from CO_2 concentrations above 20%v/v, which meant that equilibrium was reached faster than in the 15%v/v (post-combustion test). Similar behavior was obtained in MEA experiments [3]. The presence of CO_2 concentrations higher than 20%v/v speeded up the CO_2 absorption process and a substantial change of the solvent kinetic behavior was also observed.
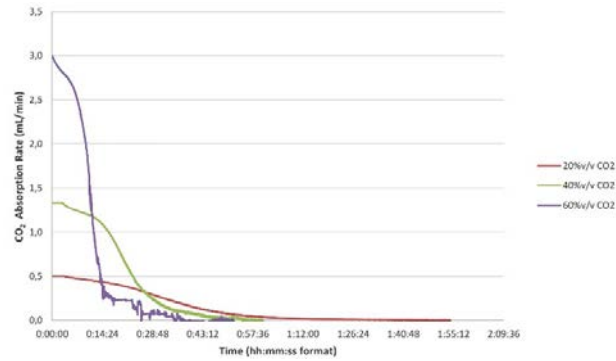
Fig. 1. CO_2 absorption rates obtained from the experiments using AEP run in the semi-batch lab-scale rig.

In K_2CO_3 30%p/p and MDEA 50%p/p experiments, the presence of more CO_2 content in the flue gas had no influence on the kinetics and the absorption process occurred following the same pattern in all the cases. However, the CO_2 absorption rate obtained in MDEA 50%p/p experiments was globally increased at higher CO_2 concentrations as occurred in MEA and AEP experiments, as Fig. 2 shows.
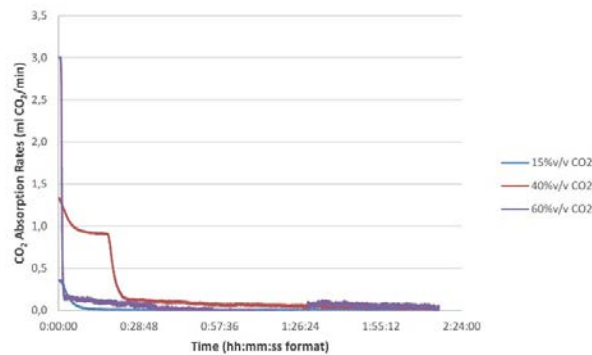

Fig. 2. CO_2 absorption rates obtained from the experiments using MDEA run in the semi-batch lab-scale rig.

3.2. Liquid phase evaluation

The evolution of the CO_2 loading also exhibited higher values in the experiments using higher CO_2 concentrated flue gas for all the solvent tested. In MEA 30%p/p cases, a flue gas composed of 60%v/v CO_2 reached a CO_2 loading up to 0.60 mole CO_2/mole solvent at equilibrium, whereas the experiment performed using 15%v/v CO_2 provided 0.48 mole CO_2/mole. Therefore, an increase of 25% in the CO_2 loading at equilibrium was accomplished with MEA 30%p/p using a four times higher CO_2-concentrated flue gas than the conventional flue gas composition derived from air-fired coal combustion. The rest of solvent studied in this work follow the same trend as it is shown in Fig. 3.
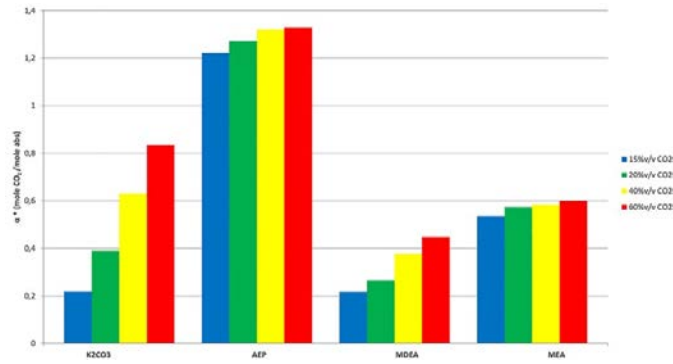
Fig. 3. CO_2 loading at several CO_2 concentrations of the flue gas for each solvent studied in this work.

The higher increase of the CO_2 loading was achieved for K_2CO_3 30%p/p and MDEA 50% p/p which the CO_2 loading at 60%v/v CO_2 were four times and two times higher respect to 15%v/v CO_2 experiments, respectively (Table 1).

Table 1. α^* and α enhancement (%) at several CO_2 concentrations of the flue gas for each solvent studied in this work.

	MEA		MDEA		K_2CO_3		AEP	
	α^*	$\Delta\alpha$ (%)	α^*	$\Delta\alpha$ (%)	α^*	$\Delta\alpha$ (%)	α^*	$\Delta\alpha$ (%)
15% CO_2	0.535	---	0.216	---	0.217	---	1.221	---
20% CO_2	0.573	7.1	0.265	22.5	0.390	79.4	1.272	4.2
40% CO_2	0.584	9.2	0.376	73.6	0.630	189.8	1.320	8.1
60% CO_2	0.599	12.0	0.448	107.0	0.835	283.8	1.329	8.8

Fig. 4 represents the characteristic time for all the experiments carried out in this work. A favored kinetic by means of a reduction of the characteristic time was found for each solvent as CO_2 concentration was increased. AEP 30%p/p and MEA 30%p/p showed the fastest absorption kinetics, providing characteristic time below 2000 s in most of the experiments. K_2CO_3 30%p/p significantly reduced the characteristic time in this conditions but both solvents – including MDEA – showed slow kinetics even though at elevated CO_2 concentrations.
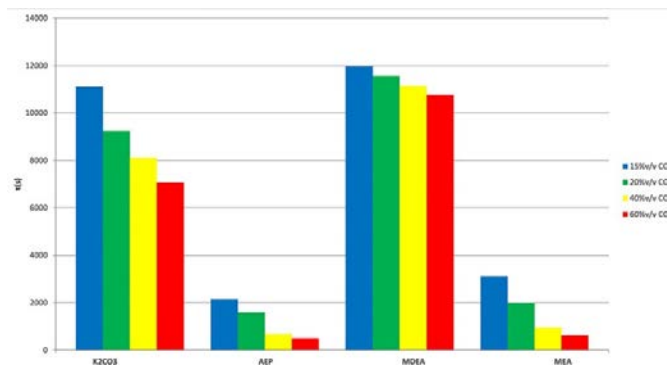

Fig. 4. Characteristic time at several CO_2 concentrations of the flue gas for each solvent studied in this work.

4. Conclusions

A lab-scale apparatus operating under semi-batch conditions was used for studying the absorption kinetic of K_2CO_3 30%p/p, AEP 30%p/p and MDEA 50%p/p under partial oxy-combustion conditions. MEA 30%p/p was also tested as benchmark. Several experiments for each solvent were performed in which the CO_2 concentration of the flue gas varies between 15%v/v - 60%v/v. In particular, an increase of the CO_2 content in the flue gas significantly enhanced the CO_2 absorption process in both terms, CO_2 absorption rate and CO_2 loading. The use of a more CO_2 concentrated flue gas enhanced the CO_2 absorption process for any solvent tested in this work. The kinetic significantly improved under those conditions, showing a further reduction of the characteristic time of the system response. The CO_2 loading achieved higher values – up to four times for K_2CO_3 30%p/p– as CO_2 concentration was shifted from 15%v/v to 60%v/v. Those results strengthened partial oxy-combustion as a potential CCS approach. The favored kinetics could lead to large reductions of the absorption equipment size. The feasibility of this novel technology could also have impact on the global performance of the separation process, particularly on the energy requirements associated to the solvent regeneration.

Acknowledgements

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