Bench-Scale Study for CO_2 Capture Using AMP/PZ/Water Mixtures

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In the present study, the efficacy of CO_2 capture by aqueous AMP/PZ mixtures was studied in a closed-loop absorber-desorber system. The two columns were operated at 313 and 383 K. Inside the absorber, the liquid was circulated at a flow rate of 4 L/h, while gas (CO_2-N_2 mixture, CO_2 12 mol%) was fed at varying flow rates (0.88-1.25 m^3/h). Material and energy balances were performed. The rich and lean loading of the liquid was 0.61 and 0.21 mol CO_2/mol amine, and the extent of CO_2 removal from the gas phase was 85%. The energy required to regenerate the liquid (3.78 MJ/kg CO_2) was reduced by 3.4% when the heat exchange between the rich and lean amine solutions in a counter-current contact was realised.

1. Introduction

The uncontrolled release of carbon dioxide (CO_2) from flue gas in thermal power stations has significantly contributed to climate change. To mitigate CO_2 emissions, post-combustion capture technology is most commonly employed (Kenig et al., 2003). Aqueous solutions of alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA) or N-methyldiethanolamine (MDEA), are extensively used as solvents in closed-loop absorber-desorber arrangements (Kohl and Nielsen, 1997; Lang et al., 2017). However, MEA and DEA can be regenerated only at high temperature and MDEA is less reactive (Singh et al., 2013). 2-Amino-2-methyl-1-propanol (AMP) is a promising alternative amine with high CO_2 loading capacity. AMP is the sterically hindered form of the primary amine MEA. Since AMP is easily regenerable, even at low temperature, common problems encountered during high-temperature desorber operation such as corrosion of equipment and amine loss due to degradation are avoided. The reactivity of AMP can be augmented by the addition of piperazine (PZ), a very reactive secondary, cyclic diamine (Lu et al., 2017). AMP/PZ mixtures merge the useful properties of both amines, and thus, are encouraging. Although several features, such as reaction kinetics, mass transfer modelling and equilibrium, are widely reported (e.g., Puxty and Rowland, 2011; Usman, 2012; Tong et al., 2013), the analysis of the regenerative features of this blend is scarce (Lin and Wang, 2013; Krotki et al., 2016). In this work, the performance of AMP/PZ mixtures was studied in a bench-scale absorption-regeneration setup. From a mass balance, CO_2 capturing efficiency was determined. Using an energy balance, the regeneration energy requirement was calculated. The influence of liquid/gas flow rates on cyclic loading capacity and regeneration energy was studied. Finally, in an attempt to reduce the energy requirement, the effect of heat integration between the rich and lean amine solutions on the functioning of the system was studied, too.

2. Theory

2.1 Reaction pathways

During the absorption process, conventional primary and secondary amines (denoted here by Am_1H) such as MEA and DEA react with CO_2 to form a stable carbamate according to a two-step zwitterion mechanism (Caplow, 1968; Danckwerts, 1979; Vaidya and Kenig, 2007):

$$CO_2 + Am_1H \leftrightarrow Am_1H^+COO^- \tag{1}$$

$$Am_1H^+COO^- + Am_1H \rightarrow Am_1COO^- + Am_1H_2^+ \tag{2}$$

The overall reaction, which is the sum of the reactions represented by eqs. 1 and 2, is given by:

$$CO_2 + 2\,Am_1H \leftrightarrow Am_1COO^- + Am_1H_2^+ \tag{3}$$

PZ forms both mono- and bis-carbamate upon reaction with CO_2. In contrast, due to steric hindrance, AMP (denoted by Am_2H) is less susceptible to the formation of carbamate through the following reaction:

$$CO_2 + 2\,Am_2H \leftrightarrow Am_2COO^- + Am_2H_2^+ \tag{4}$$

Besides, the carbamate of AMP is unstable. Upon hydrolysis, it reverts to AMP and bicarbonate; this is represented as follows:

$$Am_2COO^- + H_2O \leftrightarrow Am_2H + HCO_3^- \tag{5}$$

Thus, the overall reaction with AMP in aqueous solutions is given by the sum of reactions represented by eqs. 4 and 5:

$$CO_2 + Am_2H + H_2O \leftrightarrow Am_2H_2^+ + HCO_3^- \tag{6}$$
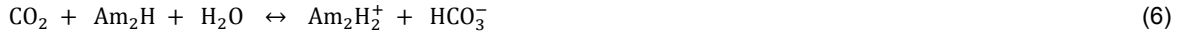
In aqueous AMP/PZ mixtures, the carbamates of PZ transfer CO_2 to AMP and PZ is regenerated. In addition, CO_2 reacts with other bases present in the system, viz. H_2O and OH^-, as follows:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{7}$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \tag{8}$$

2.2 Performance of absorber-desorber arrangement

One useful feature of the absorbent is its CO_2 loading capacity (α), i.e. moles of CO_2/moles of amine. The difference between the loading capacity of the rich (α_{rich}) and lean (α_{lean}) solutions is called the cyclic capacity. The second useful characteristic of the absorbent is its regeneration energy requirement (expressed as MJ/kg of CO_2). Procedures for its estimation are well-documented (see e.g., Oexmann and Kather, 2010; Dinca and Badea, 2013; Kim et al., 2015). It comprises the heat of desorption, sensible heat and heat of vaporization (Nwaoha et al., 2017). According to Xie et al. (2013), the heat of desorption (Q_{des}) depends upon physical dissolution and chemical reactions between CO_2 and amine and is expressed by:

$$Q_{des} = \frac{\Delta h_{abs}}{M_{CO_2}} \tag{9}$$

Here, M_{CO_2} and Δh_{abs} denote the molecular weight of CO_2 (g/mol) and the heat of absorption (kJ/mol). The latter is estimated from the Gibbs-Helmholtz equation (Oexmann and Kather, 2010):

$$\frac{d(\ln P_{CO_2}^*)}{d(1/T)} = \frac{\Delta h_{abs}}{R} \tag{10}$$

Here, $P_{CO_2}^*$, R and T denote the equilibrium partial pressure of CO_2, gas constant and temperature. Sensible heat (Q_{sens}) is found from the relation between the specific heat capacity (C_p, kJ/(mol K)) and the temperature approach (ΔT, K), *viz.* from the difference between the temperature of the lean solution leaving the bottom of the desorber and rich solution entering the top of the desorber (Oexmann and Kather, 2010):

$$Q_{sens} = \frac{C_p \Delta T}{(\alpha_{rich} - \alpha_{lean}) x_{amine} M_{CO_2}} \tag{11}$$

where x_{amine} denotes the mole fraction of amine in the liquid. Finally, the heat of vaporisation (Q_{vap}) depends upon the concentration of water in the amine mixture (Chakma et al., 1997) and is represented by:

$$Q_{vap} = \frac{p_{H_2O}}{p_{CO_2}} \frac{\Delta h_{vap}}{M_{CO_2}} \tag{12}$$

Here, Δh_{vap} is the latent heat of vaporisation of water (kJ/mol). The partial pressures (kPa) of water and CO_2 are denoted by p_{H_2O} and p_{CO_2}. Their values can be calculated by Antoine equation and Dalton's law (Hopkinson et al., 2014). From eqs. 9, 11 and 12, the regeneration energy (Q_{reg}) is determined by using the relation:

$$Q_{reg} = Q_{des} + Q_{sens} + Q_{vap} \tag{13}$$

3. Experimental section

3.1 Materials

2-Amino-2-methyl-1-propanol (AMP, purity 98%) was purchased from Spectrochem Pvt. Ltd., Mumbai. Piperazine (PZ, purity 98%) was purchased from S. D. Fine Chemicals. Pvt. Ltd., Mumbai. Gas cylinders containing CO_2 and nitrogen (N_2) gas (purity 99.95%) were purchased from Inox Air Products Ltd., Mumbai. CO_2 buffer solution was procured from Thermo-Scientific, Mumbai.

3.2 Methodology

The performance of AMP/PZ mixtures (2/0.5 M) was investigated in a bench-scale apparatus. This setup consisted of two tray columns, absorber and desorber (both 2-inch diameter tray columns, 1.23 and 1.54 m high, and made of SS316), operating in a closed-circulation loop. Each column was equipped with a storage tank (20 L). Two dosing pumps were used to feed the solutions from the storage tanks to the columns. An oil bath was used to maintain the desired temperature. Two mass flow controllers (MFCs) were provided for feeding CO_2 and N_2 from the gas cylinders. Using a digital control panel, the column temperature was adjusted to the desired value. The desorber was equipped with seven temperature sensors, each one after three trays, while the absorber was provided with five temperature sensors and five sample collection ports, each one after three trays. A schematic diagram of this apparatus is represented in Figure 1a. The operating conditions used in this work are shown in Table 1. The following experimental procedure was used: the reservoir tanks were filled with the aqueous AMP/PZ mixture, and the liquid circulation rate (L, L/h) was adjusted to the desired value using the dosing pumps. Both absorber and desorber columns were heated to the desired temperature (*viz.* 313 and 383 K) using the oil bath. Gaseous mixture of CO_2 and N_2 was introduced at the absorber bottom using MFCs. The total gas flow rate is denoted by G (m^3/h). After reaching the steady state, column temperatures were recorded. Then liquid samples were collected from the sampling ports, while the gaseous sample was collected from the top of the absorber. The liquid sample was analysed using CO_2 anion-selective electrode to determine the CO_2 loading of the absorbent (α), whereas the gaseous sample was analysed for CO_2 content using GC technique (HayeSep-DB column 80/100 mesh, carrier H_2). To reduce the regeneration energy requirement, the setup was slightly modified: instead of using water as the heat transfer medium (cf. conventional setup in Figure 1a), the rich and lean solvents were brought in contact counter-currently for improved heat transfer. The diagram for the modified setup is shown in Figure 1b.
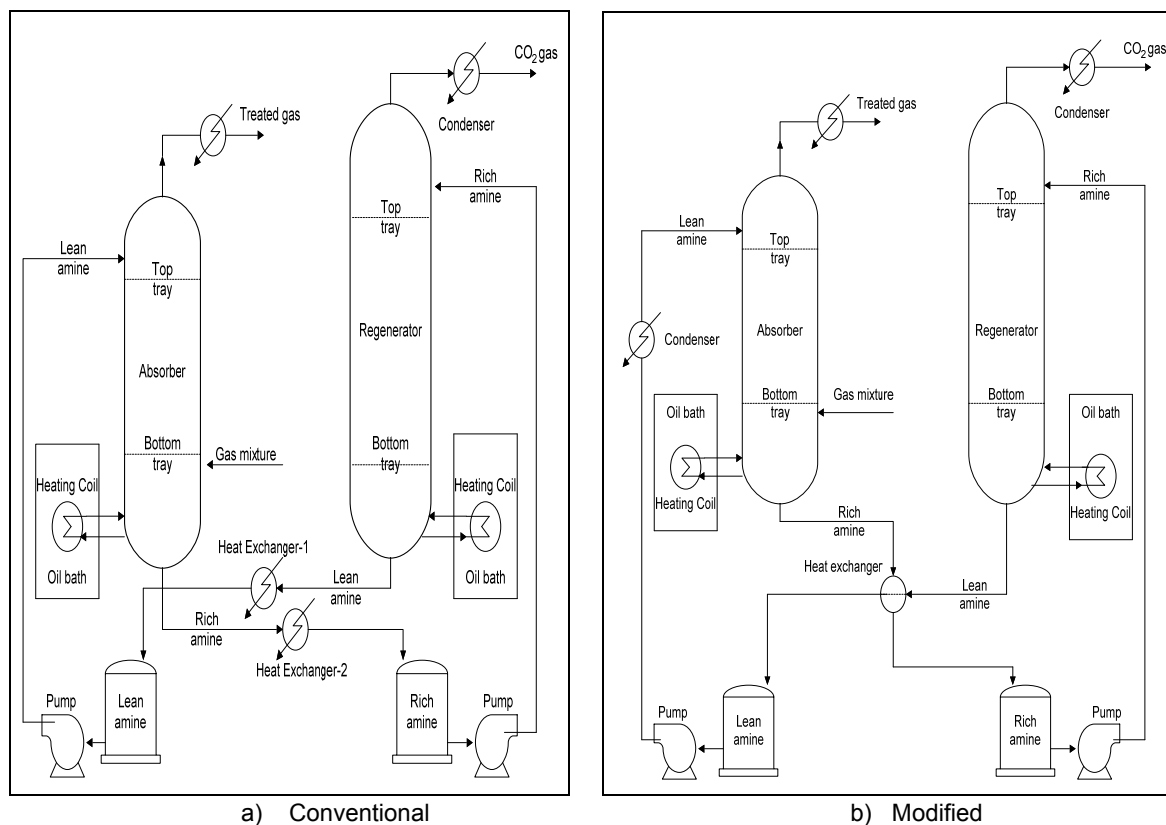

| a)   Conventional | b)   Modified |

Figure 1: Schematic of conventional (a) and modified (b) closed-loop absorption-desorption setup

Table 1: Operating conditions of closed-loop system

Parameters	Values	Units
Gas flow rate (G)	0.88-1.25	m^3/h
CO_2 composition at absorber inlet	12	mol%
Liquid circulation flow rate (L)	4	L/h
Absorber temperature	313	K
Absorber-desorber pressure	101.3	kPa
Desorber temperature	383	K

4. Results and Discussion

4.1 Influence of L/G ratio on loading capacity and CO_2 recovery

The effect of changing L/G ratios on system performance was studied by varying G for a fixed value of L. The results are represented in Table 2. When the liquid circulation rate was fixed (L=4 L/h) and gas flow rate G was reduced from 1.25 to 0.88 m^3/h, the loading capacity of the rich solution grew two-fold from 0.3 to 0.61 mol/mol. The corresponding rise in capacity of the lean solution was significant (from 0.06 to 0.21 mol/mol). On the whole, the cyclic loading capacity increased from 0.24 to 0.4 mol/mol with the rise in L/G ratio from 3.2 to 4.54 L/m^3. Besides, from material balance, it was found that the extent of CO_2 recovery improved from 35.8 to 84.8%. Thus, the performance of the chosen blend at high L/G ratios was promising.

Table 2: Result summary of closed-loop apparatus

Solvent flow rate (L) (L/h)	Gas flow rate(G) (m^3/h)	L/G (L/m^3)	α_{rich} (mol/mol)	α_{lean} (mol/mol)	Cyclic loading (mol/mol)	CO_2 recovery (%)
	1.25	3.20	0.30	0.06	0.24	35.8
	1.20	3.31	0.35	0.09	0.26	40.1
4	1.12	3.57	0.42	0.13	0.29	48.4
	1.00	3.99	0.51	0.17	0.34	63.3
	0.88	4.54	0.61	0.21	0.40	84.8

4.2 Effect of L/G ratio on regeneration energy

From the energy balance, the regeneration energy (Q_{reg}) requirement of aqueous AMP/PZ mixtures (2/0.5 M) was determined for both configurations shown in Figures 1a and 1b. The variation in energy constraint with the loading of rich and lean solutions is shown in Figures 2a and 2b. For the conventional configuration shown in Figure 1a, the energy need ($Q_{reg,a}$) was lowered from 3.96 (for α_{rich}= 0.30 and α_{lean}= 0.06 mol/mol) to 3.78 MJ/kg of CO_2 (for α_{rich}= 0.61 and α_{lean}= 0.21 mol/mol). Similarly, for the modified setup shown in Figure 1b, the energy requirement ($Q_{reg,b}$) decreased from 3.89 (for α_{rich}= 0.30 and α_{lean}= 0.06 mol/mol) to 3.65 MJ/kg of CO_2 (for α_{rich}= 0.61 and α_{lean}= 0.21 mol/mol). The stripping energy need was lowered, due to the reduction in sensible heat and a smaller temperature approach. The dependence of $Q_{reg,b}$ on L/G ratios for the modified setup is shown in Figure 3. Stripping energy requirement changed from 3.89 to 3.65 MJ/kg of CO_2 when the L/G ratio rose from 3.2 to 4.54 L/m^3. Two conclusions can be drawn: first, the rise in L/G ratios (and hence, the loading capacity) is beneficial for reduced energy requirement, and second, the modified setup (with heat integration between rich and lean solutions) performs better than the conventional one.

4.3 Comparison with past works

In Figure 4, comparison with values of the energy constraint reported in past works on AMP/PZ mixtures is shown. The best value reported in this work (3.65 MJ/kg of CO_2) is lower than the values reported by Singh et al. (2013) and Tatarczuk et al. (2015). The lower energy need in our work can be attributed to the improved performance in the modified configuration.
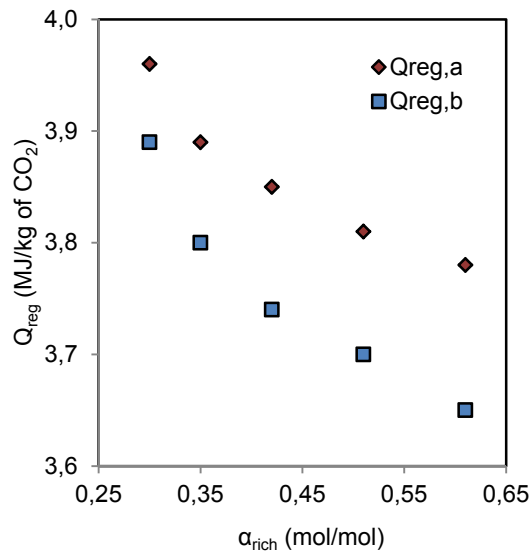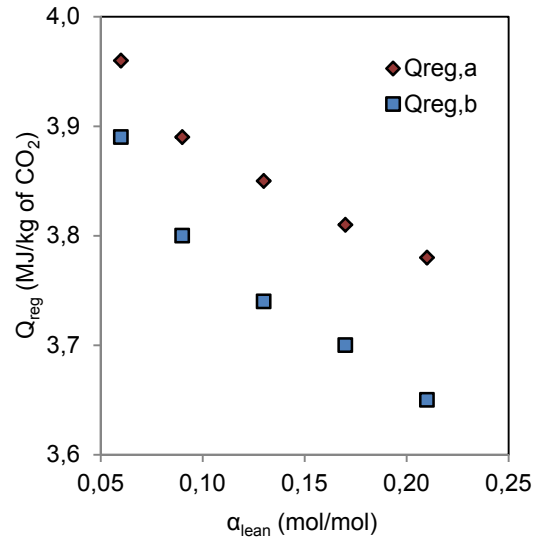
Figure 2a: Energy need vs. rich solvent loading

Figure 2b: Energy need vs. lean solvent loading
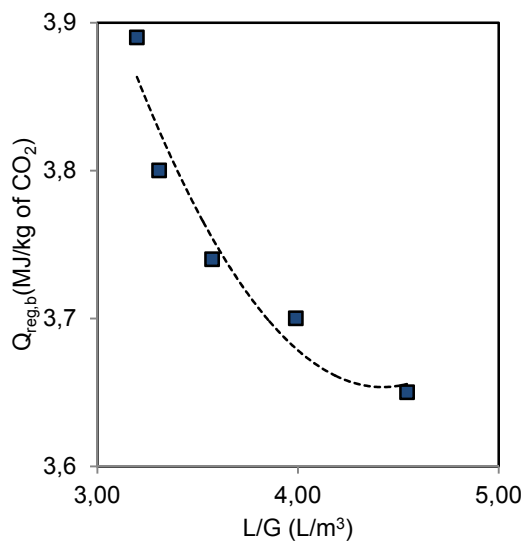

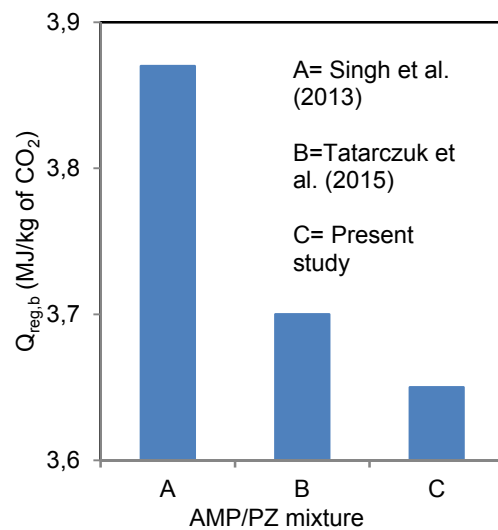*Figure 3: Influence of L/G on regeneration energy*

Figure 4: Comparison with past works

5. Conclusions

In the present study, the performance of aqueous 2/0.5 M AMP/PZ mixture was investigated in an absorber-desorber arrangement. The absorber and desorber were maintained at 313 and 383 K, respectively. For a fixed liquid circulation flow rate (4 L/h), a gas containing 12% CO_2 was fed to the absorber at different flow rates (0.88-1.25 m^3/h). At high L/G ratios, amine loading improved and regeneration energy was lowered. The best results were: cyclic loading capacity=0.4 mol/mol, CO_2 removal=84.8% and energy constraint=3.78 MJ/kg CO_2. Finally, when the rich and lean amine solutions were in a counter-current contact for the heat exchange, the energy need was further lowered to 3.65 MJ/kg CO_2. This work will assist in the development of absorber-desorber loops for improved CO_2 capture at low regeneration cost.

Acknowledgments

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