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Screening and Characterization of Advanced Amine Based Solvent Systems for CO2 Post-Combustion Capture

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Abstract

Carbon dioxide chemical absorption with amine based solvents is currently the state-of-the-art technology for post-combustion carbon capture. However, many technical challenges still remain that need to be addressed to make it cost-effective. Through bench-scale tests, this research work is focused on developing and characterizing advanced amine-based solvents. Screening of amine solvents is performed to identify suitability on the basis of solvent maximum concentration, rich CO_2 loading, lean CO_2 loading, cyclic CO_2 loading and energy requirement. The five alkanolamine solvents which are experimented upon in this work are: monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), Piperazine (PZ) and 2-Amino-2-methyl-1-propanol (AMP). These solvents are taken as reference solvents to allow comparison with literature data and to establish confidence in the experimental methods used for solvent evaluation. CO_2 outlet concentration curves from the absorption experiments show that piperazine reaches equilibrium faster than any other solvent and the CO_2 loading capacity from phosphoric acid titration method is highest in piperazine with a value of 0.92.

1. Introduction

The traditional CO_2 capture process utilizing conventional amine solvents is highly energy intensive and also poses several other challenges such as solvent degradation, corrosion, foaming and evaporation. For the base case, the regeneration energy requirement of monoethanolamine (MEA) solvent is around 3.7 GJ/t CO_2 [1] which results in large operating costs. According to recent DOE/NETL studies, MEA-based CCS will increase the cost of electricity of a new pulverized coal plant by 80-85% and reduce the net plant efficiency by about 30% [2]. To address these challenges, it is complementary to develop advanced energy efficient and stable solvents for CCS. Mixed amines have been reported to maximize the desirable qualities of the individual amines. Substantial reductions in energy requirements and modest

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reduction in solvent circulation rates have been reported for amine blends relative to the corresponding single amine system of similar total amine concentration [3]. The addition of small amounts of MEA to AMP results in a significant enhancement of CO_2 absorption rates [4]. In comparison with single amine based systems, an amine mixture can offer a solution to these problems by compensating each other's drawbacks. A solution consisting of tertiary and primary amines or tertiary plus secondary amines, retains much of the reactivity of primary or secondary amines at similar or reduced solvent circulation rates and offers low regeneration costs similar to those of tertiary amines, due to enhanced bicarbonate formation and a higher CO_2 cyclic capacity [5]. Consequently, by blending a primary or secondary alkanolamine with a tertiary alkanolamine, bulk CO_2 removal is easily accomplished while regeneration energy costs are minimized. The amine concentration can also be altered to achieve precisely the desired separation for a given process configuration.

2. Background

At the Department of Chemical Engineering in Masdar Institute, state of the art experimental facilities have been developed for synthesis, screening, and evaluation of new amine solvents and their mixture for CO_2 absorption. Potential solvents/blends have been evaluated on the basis of their CO_2 absorption capacity and initial absorption rate in a solvent screening apparatus that consists of six identical bubble column reactors each 250 ml. The criteria for selection of a certain amine are primarily based on the absorption capacity, reaction kinetics, and the potential for regeneration. Currently a series of aqueous amine based solvents and mixtures are being investigated to study their absorption behavior on the basis of the absorption and regeneration experimental results. In the absorption experiments the solvents are treated with saturated 10-15 Vol % CO_2 balanced with N_2 at temperature of 20-50 °C until equilibrium is reached. For regeneration experiments, N_2 gas flow-rate is used as a stripping gas at a temperature of 90-150 °C. CO_2 concentration from six reactor outlets is detected by individual Infrared gas analyzer, and relative rates of absorption, equilibrium absorption capacity and regeneration capacity of solvent/mixtures are measured. Optimal design and operation of absorption and regeneration columns requires more detailed knowledge of several parameters e.g. vapor-liquid equilibrium, enthalpy, and kinetics of CO_2 in the solvents.

3. Experimental Setup and Activities

The three experimental setups used in this work are: solvent screening, vapour-liquid equilibrium, and phosphoric acid titration.

3.1. Solvent Screening (SS) Setup

The solvent screening set-up as shown in Figure 1 consists of six batch reactors with stainless steel cap that has connection for temperature controller and gas stream in-feed pressure controller with each working independently. The reactors are coupled with oil baths to ensure constant absorption reaction temperature and a magnetic stirrer for uniform mixing of solvent during experimental run. 100 -150 ml samples of solvents are used in each reactor which has a maximum capacity of 250ml. The total pressure in each reactor is maintained at 1 bar, with 12kPa CO_2 partial pressure and 40°C. Mass flow controllers are used to obtain desired partial pressure of CO_2 by manipulating the volumetric rate of nitrogen and CO_2. This mixed stream, which passes through water saturator, is stored in the make-up vessel until stable pressure is built up to ensure equal flow into the reactors. The operation of the solvent screening set-up is fully automated. Gas stream from each reactor passes through a condenser to remove water vapour before it is analyzed using infrared CO_2 analyzer on real time basis. The recorded data of CO_2 partial pressure against time are presented in Figure 3-6.
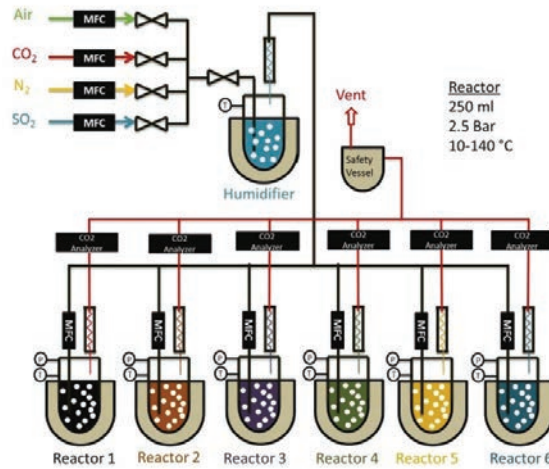
Figure 1: Solvent Screening Set-up

3.2 Vapour Liquid Equilibrium (VLE) Set-up

The set-up in Figure 2 is essentially similar to the screening apparatus but with a larger capacity and higher operational range in terms of temperature and pressure. Samples from screening and VLE set-ups are further analyzed using 85% phosphoric acid titration method. CO_2 stripping takes place at an average value of 150°C. CO_2 is released and passed through a condenser to remove water vapour and the amount of CO_2 is recorded using the laboratory software. The loading capacity of each of the solvent investigated is calculated and presented in Table 1.
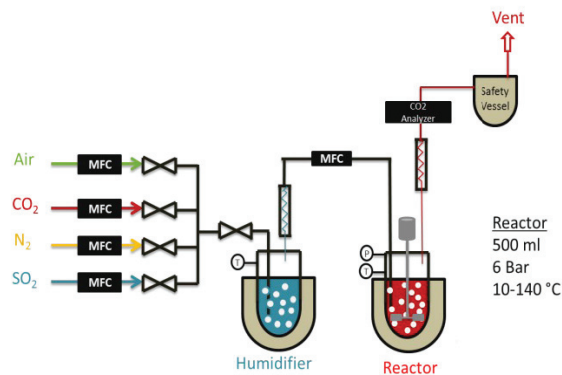

Figure 2: Vapour-Liquid Equilibrium Set-up

4. Results

4.1. CO₂ Outlet Concentration from SS setup

In each of Figure 3- 6, it is observed that the partial pressure is lower for the higher concentration. This is due to the availability of more solvent molecules to absorb CO_2. The reactivity and the rate of reaction are depicted by the length of time it takes each solvent to reach equilibrium. For MDEA, it takes about an average of 36 hours for both concentrations. For AMP, 50wt% concentration showed lower partial pressure, with both concentrations reaching equilibrium at 25 hours. Though piperazine is at significantly lower concentration, it shows faster absorption rate with equilibrium state attained at 13 hours for 10wt% and 17 hours for 20wt% concentration. It takes 22 hours for both concentrations of DEA to reach equilibrium. Table 1 presents the loading capacity. Piperazine is found to be of higher loading capacity among the solvents investigated.
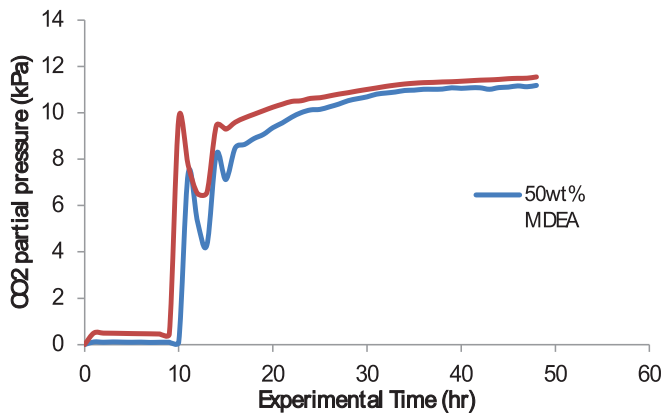

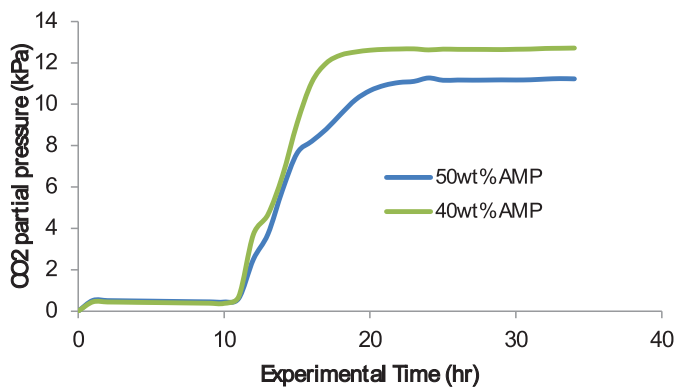Figure 3: CO_2 partial pressure vs. time in MDEA
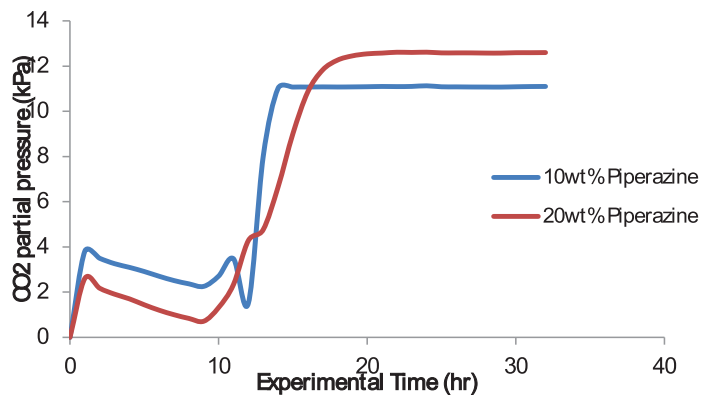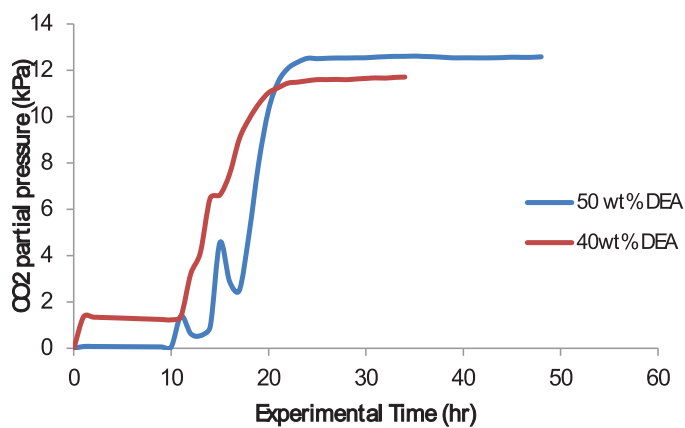

Figure 4: CO_2 partial pressure vs. time in AMP

Figure 5: CO$_2$ partial pressure vs. time in Piperazine

Figure 6:CO$_2$ partial pressure vs. time in DEA

Table 1: Loading capacity of solvents under batch process

Solvent	Loading Capacity (mol/mol)
40wt% MDEA	0.52
40wt% DEA	0.62
40wt% AMP	0.82
10wt% Piperazine	0.92

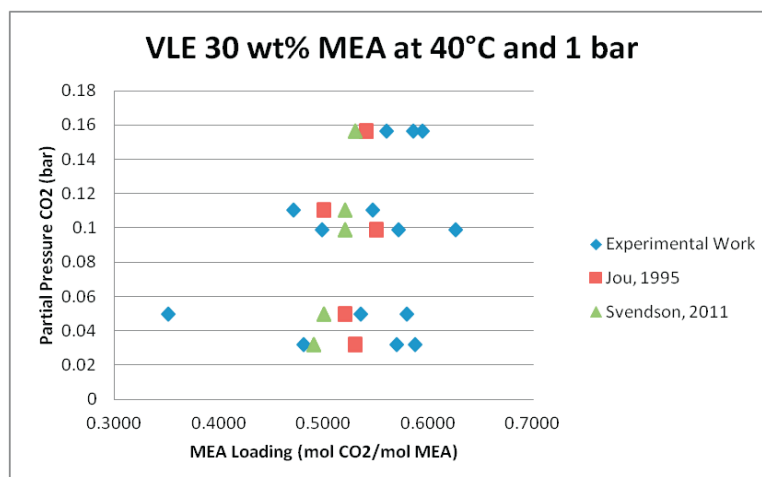*4.2. CO$_2$ Loading Capacity from VLE setup*

Figure 7: MEA VLE data comparison with literature

5. Conclusions

The solvent screening experiment shows that piperazine has a higher absorption capacity and faster rate under batch process than any of the other solvents investigated. Further work is ongoing at blending various amines with a view to characterizing the absorption rate, loading capacity, cyclic loading and vapour-liquid equilibrium etc.

References

1.   Mangalapally, H.P., et al., *Pilot plant experimental studies of post combustion CO_2 capture by reactive absorption with MEA and new solvents.* Energy Procedia, 2009. 1(1): p. 963-970.

2.   Fout, T., J.T. Murphy, and A.P. Jones, *DOE/NETL's Carbon Capture R&D Program for Existing Coal-Fired Power Plants*. 2009, National Energy Technology Laboratory.

3.   Aboudheir, A., P. Tontiwachwuthikul, and R. Idem, *Rigorous model for predicting the behaviour of CO_2 absorption into AMP in packed-bed absorption columns.* Industrial Engineering Chemical Research, 2006. 45: p. 2553-2557.

4.   Sakwattanapong, R., A. Aroonwilas, and A. Veawab, *Reaction rate of CO_2 in aqueous MEA-AMP solution: experiment and modelling.* Energy Procedia, 2009. 1: p. 217-224.

5.   Yang, H., et al., *Progress in carbon dioxide separation and capture: a review.* Journal Of Environmental Sciences China, 2008. 20: p. 14-27.