Applied Energy 205 (2017) 1002–1011

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Analysis of the reduction of energy cost by using MEA-MDEA-PZ solvent for post-combustion carbon dioxide capture (PCC)

Rui Zhang[a], Xiaowen Zhang[a], Qi Yang[b], Hai Yu[c], Zhiwu Liang[a,*], Xiao Luo[a,*]

[a] Joint International Center for CO_2 Capture and Storage (iCCS), Provincial Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing Carbon-dioxide Emissions, College of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan 410082, PR China
[b] CSIRO Manufacturing, Clayton, Victoria 3168, Australia
[c] CSIRO Energy, Newcastle, NSW 2300, Australia

HIGHLIGHTS

- MEA-MDEA-PZ can reduce 15.22–49.92% energy cost for CO_2 capture.
- The energy cost was analysised based on the carbamate and bicarbonate.
- The heat of CO_2 absorption in MEA-MDEA-PZ with different mix ratio were studied.
- More MDEA and less PZ in MEA-MDEAPZ benefits bicarbonate formation.

ARTICLE INFO

Keywords:
Caron dioxide
Amine
MEA
MDEA
PZ
Energy

ABSTRACT

The blends of monoethanolamine (MEA), *N*-methyl-diethanolamine (MDEA) and piperazine (PZ) as a solvent for CO_2 capture were investigated in terms of CO_2 absorption-desorption performance. The total concentration of the blends was 6M mixed with different amine molar ratios, 3M MEA-2.5M MDEA-0.5M PZ (Blend-1), 3M MEA-2M MDEA-1M PZ (Blend-2) and 3M MEA-1.5M MDEA-1.5M PZ (Blend-3). The CO_2 equilibrium solubility, absorption capacity, initial absorption rate, speciation, relative energy consumption and heat of absorption for each blend were investigated in this work. The results showed that Blend-3 had the best CO_2 absorption performance in terms of the CO_2 equilibrium solubility, initial CO_2 absorption rate and CO_2 absorption capacity compared to Blend-1 and Blend-2 and 5M MEA. ^{13}C NMR spectroscopy was used to quantify species formed in the CO_2-loaded MEA-MDEA-PZ solution and the results shows that Blend-1 system produced more bicarbonate and less carbamate compared to Blend-2 and Blend-3 systems. The heat of CO_2 absorption was calculated using Gibbs-Helmholtz equation and the results showed that MEA-MDEA-PZ systems had lower absorption heat than that of MEA, DEA, AMP, PZ and trio-amine blends of MEA-AMP-PZ. For the CO_2 desorption performance, three blends studied in this work had lower relative energy consumption for the solvent regeneration compared to 5M MEA and Blend-1 showed the best desorption performance. Among these blends, an increase in molar ratio of MDEA/PZ in the blends led to a decrease in energy consumption and an increase in cyclic capacity and the CO_2 desorption rate. In addition, the blend of MEA-MDEA-PZ reduced the energy consumption by 15.22–49.92% compared to 5M MEA.

1. Introduction

Organic amines based carbon dioxide (CO_2) capture has been regarded as the most mature method to reduce CO_2 emission from the nature gas processing, refinery gas processing and power plants [1–3]. Primary or secondary amine has a faster reaction kinetics with CO_2 but with a higher energy consumption for the solvent regeneration [4,5]. Tertiary amines require less energy for the solvent regeneration but they absorb CO_2 slowly [6–8]. To avoid shortcomings of different types of amines, the blend of primary/secondary amine and tertiary amine has attracted more attention in the development of more efficient amine absorbents [9,10]. The published studies show that the blends of the primary/secondary amine and the tertiary amine can react with CO_2 faster than single tertiary amine and consume less energy than the single primary/secondary amines [11]. This indicates that the blended amines can combine the advantages of single amine.

---

* Corresponding authors.
E-mail addresses: zwliang@hnu.edu.cn (Z. Liang), x_luo@hnu.edu.cn (X. Luo).

http://dx.doi.org/10.1016/j.apenergy.2017.08.130
Received 5 June 2017; Received in revised form 4 August 2017; Accepted 12 August 2017
0306-2619/

The most commonly studied primary amine is monoethanolamine (MEA) [10,12–14] and tertiary amine is methyl diethanolamine (MDEA) [15–18]. Piperazine (PZ) has also caught much attention and been investigated intensively either as a sole absorbent or as a promoter in mixed amine absorbents for CO_2 absorption in aqueous medium [19–22]. It has been reported that PZ can significantly increase the CO_2 absorption rate when it is used as an addictive in mixed amine solutions [23]. The reaction kinetics between the CO_2 and PZ has been reported by Derks et al. [24].

Furthermore, the trio-amine systems have also attracted attention as alternative absorbent blends for the CO_2 capture. Liu et al. has investigated the CO_2 regeneration performances of MEA/MDEA dual-amine blends and MEA/MDEA/AMP trio-amine blends [25]. Their study shows that the trio-amine blends need shorter desorption time compared to the dual-amine blends under the same conditions. Less CO_2 desorption time helps reduce the size of the desorber, and therefore save the investment cost and reduce the heat consumption. Nwaoha et al. investigated the MEA-AMP-PZ system and found that the blended solvent of three amines had a lower energy consumption for the solvent regeneration compared to MEA [26,27]. Their results also showed that the MEA-AMP-PZ had a higher absorption capacity than the PZ-AMP [28]. Their results further pointed that the trio-amine solvent which contained a relatively low concentration of PZ avoided the formation of precipitate which occured in the dual-amine solvent due to high PZ concentration [28].

It is known that bicarbonate and carbamate formed in the CO_2 absorption process play positive and negative effect on energy saving in solvent regeneration process respectively. In many studies, ^{13}C NMR spectroscopy has been used to determine the species formed in CO_2 loaded amine solution [29,30]. Zhang et al. investigated the effect of MDEA as an additive in MEA to promote bicarbonate formation at the lower CO_2 loading stage [31]. No details about the formation of bicarbonate and carbamate in the trio-amine blends have been reported.

In this work, the MEA, MDEA and PZ were selected to prepare trio-amine blends for CO_2 absorption and desorption study. The maximum concentration of PZ in the blend was limited at 1.5M [32]. The objective of this work, is to investigate the performance of MEA-MDEA-PZ for CO_2 capture in terms of CO_2 solubility, heat of CO_2 absorption, speciation and relative solvent regeneration energy consumption. The MEA-MDEA-PZ (6M, 3:2.5:0.5), MEA-MDEA-PZ (6M, 3:2:1) and MEA-MDEA-PZ (6M, 3:1.5:1.5) were investigated under different experimental conditions. 5M MEA as a commonly used solvent in industrial was also studied in this work as a benchmark. The quantitative ^{13}C NMR spectroscopy was used to determine the concentration of each species in the CO_2 loaded amine solution at 25 °C. Meanwhile, the CO_2 desorption performance was also evaluated in terms of the relative energy consumption, the CO_2 desorption rate and cyclic capacity.

2. Experimental and calculation

2.1. Chemicals

MEA, MDEA and PZ were purchased from Sigma Aldrich and used without further purification. The details of these amines including their structure and dissociation constant (pKa) [33] are shown in Table 1. CO_2 (> 99.9%) and N_2 gases (> 99.999%) were purchased from BOC. Bronkhorst mass flow-controllers were used to control gas flow rates in experiments. The pH value of each sample solution was measured using Oakton pH110 meter at 25.0 °C.

2.2. CO_2 absorption experiments

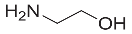
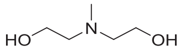
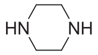
The CO_2 absorption experiment was performed using the experimental set-up shown in Fig. 1(a). The N_2 and CO_2 were used to simulate the flue gas of different CO_2 partial pressure by adjusting the ratios of their flow rates. In CO_2 absorption experiments, 100 mL of fresh aqueous amine solution with planned concentration was injected into a round bottom reactor and immersed into the water bath with a magnetic stirrer. The water bath temperature was maintained at 40 °C by using a temperature controller. The flow rates of N_2 and CO_2 gases were controlled by mass flow controllers and the CO_2 partial pressure was set as 15.1 kPa. The CO_2 loading at different absorption time (1, 2, 5, 10, 15, 20, 25, 30, 40, 50, 70, 80 and 480 min) was determined by titration using 1 M HCl [6,34].

The measurement of CO_2 equilibrium loading was processed using the reported method by Liang et al. [35]. The schematic diagram for the measurement of CO_2 equilibrium solubility is shown in Fig. 1(c). The mixed N_2 and CO_2 with the planned CO_2 partial pressure was first introduced into the saturation unit to compensate the loss of water from the vent of reactor. Both of the saturation unit and the reactor unit were immersed into a thermostatic water-circulation bath set at chosen temperatures. The wetted mixed gas was then flowed into the reactor unit to react with amine solution. A condenser system was also equipped at the top of the reactor unit to recover the evaporated water and amine. The total gas flow rate was set at 50 mL/min. 20 mL amine solution was introduced into the reactor. The CO_2 equilibrium solubility was measured at 30–45 °C at the CO_2 partial pressure of 9.67–101 kPa. Each run of the equilibrium solubility measurement was kept for18 h, and the CO_2 solubility was determined by titration using 1 M HCl solution [6,34]. A series CO_2 saturated amines at 18 h absorption time were remained for further CO_2 absorption. Sample were taken at 1 h interval to obtain the CO_2 loading until CO_2 loading increase stopped. The CO_2 loading figures obtained from the latest two samples were the same then it can be inferred that the CO_2-amine-H_2O system reached the vapor-liquid-equilibrium status. This final CO_2 loading was considered as the CO_2 equilibrium solubility at the corresponding temperature and CO_2 partial pressure.

2.3. CO_2 desorption experiments

The CO_2 desorption experiment was performed using a lab-scale set-up shown in Fig. 1 (b) following the published method [36]. 1000 mL of CO_2 rich amine solution, which was obtained at 40 °C under CO_2 partial pressure of 15.1 kPa, was placed in a 2000 mL three-necked flask. A condenser was equipped on the top of the flask and circulated with cooling water to minimize the loss of amine and water. A mechanical agitator was placed on the top of the flask and set at 350 rpm. The reaction was heated with an oil bath and the range of the regeneration temperature was from 65 to 98 °C. The CO_2 desorption time was not recorded until the amine solution temperature reached 65 °C. To avoid

Table 1
The details of amines used in this work.

Amine	Abbreviation	Mol Wt	Purity (%)	Molecular structure	pKa
Monoethanolamine	MEA	61.08	99.0		9.50
N-methyl-diethanolamine	MDEA	119.16	99.0		8.56
Piperazine	PZ	86.14	99.0		9.71, 5.41