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DMCA-MCA HYBRID WITH HIGH ABSORPTION RATE AND LOW ENERGY PENALTY FOR CO_2 CAPTURE

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ABSTRACT

The hybrid of amines is regarded as a promising alternative to MEA owing to its good performance on kinetics and thermodynamics for CO_2 absorption. The primary/secondary amine can serve as absorption accelerator and the tertiary amine act as CO_2 sinker and regeneration promoter. In this study, a novel hybrid comprising of N-methylcyclohexyamine (MCA) and N, N-dimethylcyclohexylamine (DMCA) was put forward. The absorption kinetics using DMCA-MCA for CO_2 absorption was investigated in a wetted wall column. The results showed that the total mass transfer coefficient of DMCA-MCA approach 2.02×10^{-10} mol/cm^2·s·Pa, which was 1.2-folder higher than 5M monoethanolamine (MEA) as the benchmark. Moreover, the CO_2 absorption capacity of DMCA-MCA hybrid reached 3.94 mol/L, significantly higher than 2.70 mol/L of 5M MEA. The thermodynamics was evaluated in a high pressure reactor, implying that the total regeneration heat was 2.20 GJ/t CO_2, which was much less than MEA (3.99 GJ/t CO_2). The results can benefit for developing novel absorption technology with DMCA-MCA solvent with a rapider absorption rate, higher absorption capacity and lower heat duty for CO_2 capture.

Keywords: CO_2 capture; hybrid amine; absorption rate; regeneration heat

1. INTRODUCTION

Emission of CO_2 from the coal-fired boilers has incurred serious greenhouse effect, resulting in a severe climate change throughout the world[1, 2]. However, this promise might be difficult to realize due to the unfeasible consumption on CO_2 capture, using monoethanolamine (MEA) absorption method as state-of-the-art technology during the industrial process[3]. The energy requirement related to regeneration of MEA solvent (approximately 4.0 GJ/t CO_2) accounts for 60%–80% of the total energy consumption, which will increase the electricity cost by approximately 81% for a supercritical power plant[4, 5]. Hence, developing the alternative to MEA with a high absorption rate and low heat duty is still the great challenge to depress the global climate warming.

To address this issue, many researchers have focused on the amine hybrid solvents for an optimal trade-off between kinetics and thermodynamics[6]. This hybrid is usually consisted of two amines, i.e. primary-tertiary amines or secondary-tertiary amines. It is attributed to the fact that the primary or secondary amines feature a rapid CO_2 absorption rate, while their absorption capacities are relatively confined[7]. In contrast, the tertiary amines have a higher absorption capacity but lower absorption rate[8]. Consequently, the hybrid is promising to combine the high capacity and low enthalpy of tertiary amine with the high absorption rate of primary or secondary amine[9].

As a promising lipophilic amine for CO_2 absorbing, N, N-dimethylcyclohexylamine (DMCA) has a higher cyclic capacity and regeneration rate than the other conventional tertiary amines[10]. Zhang[11] conducted extensive research on CO_2 loading capacity, kinetics, regeneration rate and residual loading of DMCA-DPA (dipropylamine) system, indicating that DMCA plays the role of the main absorbent with a high loading for CO_2 absorption and low residual loading after the

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regeneration. On the other hand, MCA (N-methylcyclohexanone) is considered as an effective activator that can substaintially facilitate the absorption of CO_2 with a higher absorption rate and capacity than MEA[12]. Compared with the 30 lipophilic amines [13], MCA achieved a faster absorption rate, higher recycling capacity and lower reaction enthalpy in CO_2 removal, which had better potential than the traditional secondary amines. Interestingly, although the viscosity of the pure solvents follows the sequence as MEA>MCA>H_2O, as reported by Zhang[12], their aqueous solution turned into MCA+ H_2O>MEA+ H_2O> H_2O. It can be ascribed to the molecular interaction, especially the modification of the hydrogen bond between MCA and water to extend the molecular chain. Thus the hybrid of DMCA-MCA can serve as a candidate with a fast absorption rate, high absorption capacity and low desorption energy consumption. However, little information is available about this hybrid on its kinetics and thermodynamics, resulting in less evaluating the technical feasibility in CO_2 capture.

In this paper, we screened the DMCA-MCA absorption system with different proportions. The kinetics of CO_2 absorption with DMCA-MCA was investigated in a wetted wall column (WWC). The thermodynamics was evaluated by a high pressure reactor. The results can benefit to developing a novel alternative to the traditional MEA technology for CO_2 capture from the coal-fired boilers.

2. MATERIALS AND METHODS

2.1 Materials

DMCA (purity ≥ 98 wt%) and MCA (purity ≥ 99 wt%) were obtained from Aladdin Industrial Corporation, China. MEA (purity ≥ 99 wt%) was purched from Kermel Chemical Reagents Co., China. CO_2 (purity ≥ 99.99 vol%) and N2 (purity ≥ 99.99 vol%) were supplied by Xicheng Gas Co., China.

2.2 Experimental procedure

CO_2 loading and CO_2 absorption capacity were explored using CO_2 bubbling reactor. In the screening test, pure CO_2 (120 ml/min, 100 min, at 303 K and atmospheric pressure) was supplied to test the CO_2 loading in DMCA-MCA (3M-1M), DMCA-MCA (2M-2M), DMCA-MCA (1M-3M) and MEA (5M) absorbent. The CO_2 loading was determined by the titration apparatus. The WWC was used to measure the kinetics of CO_2 absorption. The detailed parameters of the WWC are presented in figure 1. The CO_2 absorption flux and total mass transfer coefficient K_G can be calculated according to research [14, 15].

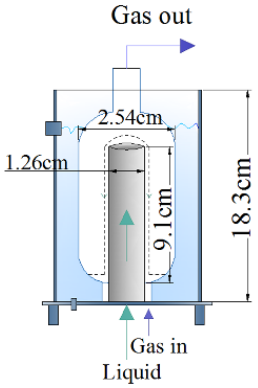

Fig 1 The detailed parameters of the wetted wall column

2.3 Theory and calculation of regeneration heat

The total regeneration heat (Q_{reg}), which includes three components, reaction heat (Q_{rxn}), sensible heat (Q_{sens}) and latent heat (Q_{latent}).

$$Q_{reg} = Q_{rxn} + Q_{sens} + Q_{latent} \quad (1)$$

These components can be calculated according to literature [16, 17]. The temperature difference between the bottom and top of the stripper is set as 10 °C[18].

3. RESULTS AND DISCCUSION

3.1 Phase separation analysis

The lower critical solution temperature (LCST) and phase change separation phenomenon have been investigated[12]. LCST is the critical temperature below which the components of a mixture are miscible. The critical CO_2 loading is the CO_2 loading above which the components of a mixture are miscible. The effects of temperature and CO_2 loading on DMCA-MCA hybrid amine absorbent were illustrated in figure 2.

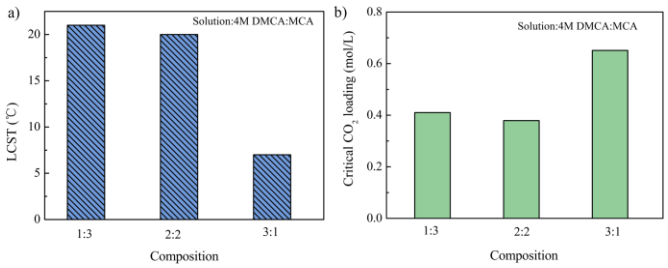

Fig 2 (a) LCST of DMCA-MCA solution (b) the critical CO_2 loading of DMCA-MCA solution (at 25 °C)

The LCST increases with the increasing of MCA content in the absorbent. However, a separation between the liquid phases involving DMCA-MCA hybrid was still observed at 21 °C. Interestingly, the absorption of CO_2 can convert the biphasic solution into a single liquid phase. Employing DMCA-MCA (1M-3M) as an

example, when the CO_2 loading achieved 0.41 mol/L, the mixture changed from biphasic solution to a single liquid phase. The critical CO_2 loading is much lower than that of CO_2 lean loading, indicating that the solution in the whole absorption and desorption process is always homogeneous.

3.2 CO_2 absorption

CO_2 absorption experiments were conducted to explore the hybrid amine solvent with fast absorption rate and high absorption capacity. The CO_2 loading in different DMCA-MCA hybrid amine solvents versus absorption time were presented in figure 3a. When the total amine concentration was maintained at 4.0 mol/L, the absorption rate was increased significantly with the increase of MCA concentration. Surprisingly, DMCA-MCA (1M-3M) shows the highest absorption rate in the whole range among DMCA-MCA hybrid amine solvents and 5M MEA. The initial overall mass transfer coefficients of CO_2 in DMCA-MCA were compared with several hybrid amine solvent and 5M MEA. The results are shown in figure 3b. The overall mass transfer coefficient of CO_2 in DMCA-MCA is higher than that of 5M MEA. This phenomenon agreed well with the results in figure 3a. MCA is a secondary amine with smaller steric hindrance than tertiary amine DMCA. Moreover, MCA is miscible with water that differs from DMCA. Thus, the biphasic behavior caused by the incorporation of DMCA would decrease the mass transfer between the liquid and gas phase. Consequently, the increase of MCA content in the DMCA-MCA absorbent will enhance the reaction rate.

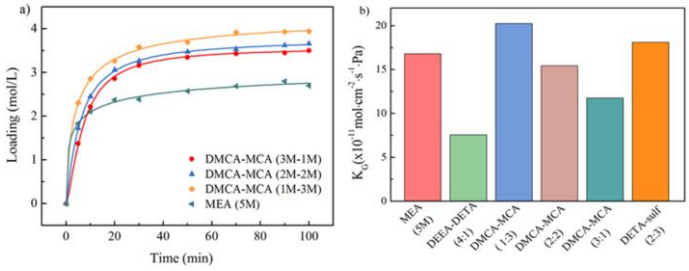

Fig 3 (a) The CO_2 loading in different DMCA-MCA hybrid versus absorption time. (303K, gas flow rate (Vg)=20 ml/s) (b) The initial absorption rate of DMCA/MCA hybrid with different blending ratios, 5M MEA and several hybrid amine absorbents. (303 K, Vg=33.33 ml/s, CO_2 loading=0 mol/L)

As observed in ^{13}C NMR spectra, only bicarbonate is detected in the absorption product. Thus, the shuttle mechanism could be inferred for MCA which enable MCA capture equivalent moles of CO_2. It was confirmed in Zhang's research[12]. Due to the smaller steric hindrance of MCA than that of DMCA, an increased absorption capacity is obtained with increasing ratio of MCA in DMCA-MCA hybrid. As seen in figure 3a, CO_2 absorption capacity of 3.50-3.94 mol/L was obtained for DMCA-MCA, which is significantly higher than that of 5M MEA (2.70 mol/L). It implied that DMCA-MCA hybrid requires a less energy penalty.

3.3 Regeneration heat analysis

Exploring energy-efficient amine solvent with low regeneration heat requirement was important. The regeneration heat of DMCA-MCA system was investigated. As mentioned in section 2.3, the regeneration heat was composed of three parts: reaction heat (Q_{rxn}), sensible heat (Q_{sens}) and latent heat (Q_{latent}). DMCA-MCA have a low reaction heat of 1.61-1.68 GJ/t CO_2 [19], which is substantially lower than that the conventional 5M MEA (1.93 GJ/t CO_2)[20]. This is good for the reducing potential in the regeneration heat consumption.

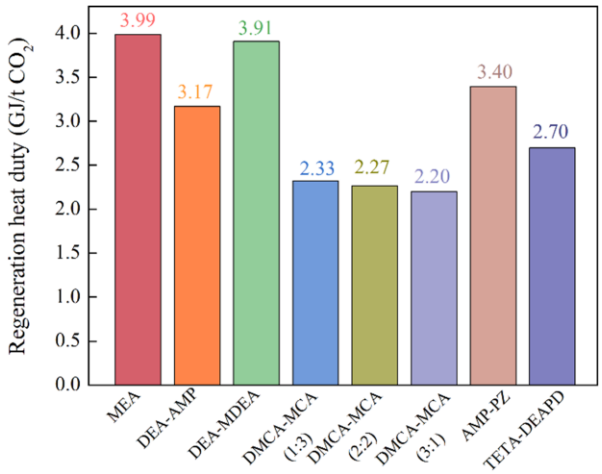

Fig 4 The regeneration heat duty of DMCA/MCA hybrid with different blending ratios, 5M MEA and several hybrid amine absorbents.

The regeneration heat consumptions of DMCA/MCA hybrid with different blending ratios are presented in figure 4. The typical operation condition was used for 5 M MEA while T_{bot} = 110 °C, ΔT = 10 °C, α_{rich} = 0.5 mol CO_2/mol MEA and α_{lean} = 0.25 mol CO_2/mol MEA. The total regeneration heat is turned out to be 3.99 GJ/t CO_2, which agrees well with the reported data[21], indicating this method could predict the regeneration heat for CO_2 desorption accurately. Among these solvent, DMCA-MCA exhibited lower regeneration heat. Tertiary DMCA possesses lower desorption reaction heat than secondary MCA. Thus increasing in the DMCA ratio leads to a decrease in the Q_{rxn} and the final Q_{reg}. Eventually, when the ratio of DMCA to MCA increases

from 1:3 to 3:1, the regeneration heat is decreased from 2.33 to 2.20 GJ/t CO_2.

4. CONCLUSIONS

In this work, a novel hybrid comprising of MCA and DMCA was proposed, while the secondary amine MCA acted as absorption accelerator and the tertiary amine DMCA acted as CO_2 sinker and regeneration promoter. The absorption rate of CO_2 in DMCA-MCA hybrid increased with the secondary amine (MCA) concentration. An overall mass transfer coefficient of 2.02×10^{-10} mol/cm^2·s·Pa was achieved for DMCA-MCA (1M-3M) hybrid, which is 1.2-folder higher than that of 5M MEA. Moreover, the CO_2 absorption capacity reached 3.94 mol/L, substantially higher than 5M MEA (2.70 mol/L). Because of the low reaction heat of DMCA-MCA hybrid and the high CO_2 capacity, the lowest regeneration heat was 2.20 GJ/t CO_2 was achieved, which is 45% lower than that of 5M MEA (3.99 GJ/t CO_2). The study provides a promising hybrid amime to MEA with rapid absorption rate, high capacity and low regeneration heat requirement.

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