

The CO₂ desorption analysis of tri-solvent MEA+BEA+DEEA with several commercial solid acid catalysts

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ABSTRACT

The CO₂ desorption experiments were conducted with tri-solvents MEA+BEA (Butylethanol amine) +DEEA (N, N-diethylethanolamine) at 0.1~0.5+2+2 mol/L, combining with 5 commercial catalysts: blended γ-Al₂O₃/H-ZSM-5, H-beta, H-mordenite, HND-8, and HND-580, to evaluate heat duty. The experiments were conducted in a recirculation process with direct heating at 90 °C or temperature programmed range of 35~85 °C. The results developed two energy efficient tri-solvent of 0.3+2+2 and 0.5+2+2 with various catalysts, which can proceed CO₂ desorption as low as 75~85 °C. After comparison, the 0.3+2+2 and 0.5+2+2 with HND-8 possessed the superior CO₂ desorption performance at very low operation temperatures with low Heat Duty (H) and large Desorption Factor (DF). These results provide a highly energy efficient combination of “tri-solvent + catalysts” as a potential candidate for industrial CO₂ capture pilot plants.

1. Introduction

Though some new energy sources have been developed in recent years, fossil fuel is still the most frequently used one around the world, and this status could continue in next 30-40 years. In fossil fuels combustion, massive CO₂ is generated and can cause the “greenhouse effect” without proper treatment (Yan and Zhang 2019; Hu et al., 2020). Considering the huge fossil fuels consumption in industry, the emission of CO₂ shows an increasing trend in the past decades, which serves as an important reason for global warming and climate changes (Rochelle, 2009). To achieve the goal of The Paris Agreement for controlling the global temperatures rise within 2 °C by the year 2100, the carbon capture, utilization, and storage (CCUS) technology is widely considered as a promising solution, which was classified into three categories, including pre-combustion, post-combustion, and oxy-fuel combustion (Wang et al. 2011; Wang and Mitch. 2015; Wang et al. 2020; Zhang et al., 2020). Among them, post-combustion CO₂ capture (PCC) needs the least refits of current facilities, and thus possesses the strongest feasibility in industrial implementation. Among the several commonly used CO₂ chemisorption technologies, amine liquid-based chemical absorption has become one of the focus because it can achieve high CO₂

adsorption efficiency with relatively low cost, and is applicable in multiple large-scale CO₂ capture projects (Gelowitz et al. 2013; Hu et al. 2020; Liu et al. 2018).

Despite numerous advantages, there are several bottlenecks restricting the further application of amine absorption technology, and among them, the most prominent one was the high energy cost in amine regeneration (Idem et al., 2015; Liang et al., 2015). From repeating publications since 2010, the regeneration process of amine liquid can be improved through solvent improvement, which is to blend different amines to exert their own advantages Liang et al. (2015). Primary amines generally have high CO₂ adsorption efficiency, but the desorption process is very slow, with the enthalpy of CO₂ solubility within the range of 80–90 kJ/mol CO₂. Secondary amines possess lower enthalpy of CO₂ solubility of 70–75 kJ/mol, while tertiary amines further reduce it to 40–55 kJ/mol (Vega et al., 2020). Properly blending different amine blends can significantly reduce heat duty. Bi-blends have been vastly investigated for decades, mostly focused on primary amine monoethanolamine (MEA) blending tertiary amines (MEA+R₃N) (Raphael Idem et al., 2006; Roongrat Sakwattanapong and Amornvaddee, 2005; Shi et al., 2021c). For example, the regeneration performances of MEA-MDEA and MEA-DEAB (4-(diethylamine)-2-butanol))

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were investigated and compared with single MEA solution in our previous study (Shi et al., 2014), and the outcomes showed that heat duty of 5+1.25 mol/L MEA-MDEA was only 73.1% of that of 5 mol/L MEA, while the relative heat duty of 5+1.25 mol/L MEA-DEAB further reduced to 51.4% (Luo et al., 2016). Combined MEA with N, N-diethylethanolamine (DEEA) can improve the property of amine solution, and found that the cyclic capacity of 2.5+2.5 mol/L MEA-DEEA surpassed that of the MEA solution (30 wt%) by 31.8%.

Since 2016, tri-solvent blends, generating from combining primary/secondary amines with tertiary amines, have attracted attentions for further enhancing the adsorption-desorption performances of amine solutions. The study of (Nwaoha et al., 2016) (Zhang et al., 2017) found that the MEA+MDEA+piperazine (PZ) tri-blend attained a significantly lower heat duty than 5 mol/L MEA. They also studied catalytic desorption (Zhang et al., 2019a) (Nwaoha et al., 2017) and investigated the tri-blend of 2-Amino-2-Methyl-1-Propanol (AMP)+PZ+MEA, and found that the heat duty of AMP-PZ-MEA tri-blend was observably lower than that of 5 kmol/m³ MEA. After that, the MEA+PZ+AMP were studied intensively in several publications (Chikezie Nwaoha, 2018; Zhang et al., 2018b). Beside MEA+AMP+PZ (Nwaoha et al., 2017; Nwaoha et al., 2016; Zhang et al., 2018b), other study reported MEA+MDEA+PZ (Zhang et al., 2017; Zhang et al., 2019a) repeatedly. A new tri-solvent of MEA+BEA+AMP was studied with absorption desorption-parameter analysis (Shi et al., 2021a; Shi et al., 2021c). A recent study (Shi et al., 2021b) discovered “coordinative effect” (Liu et al., 2018; Shi et al., 2018b) within MEA and BEA in both CO₂ adsorption and desorption and that additional little MEA can enhance the adsorption and desorption performance of BEA simultaneously. Since DEEA is another energy efficient amine similar to AMP, we hypothesize that MEA+BEA+DEEA act as a promising tri-solvent. Apparently, both MEA-DEEA (Luo et al., 2016) and MEA-BEA (Shi et al., 2021b) bi-blends exhibited good properties in CO₂ desorption.

Besides solvent improvement, heterogeneous catalytic CO₂ desorption is another frequently used method for promoting the regeneration of amine solutions for decades. For example, Zhang et al. (2018a) adopted Al₂O₃/HZSM-5 bifunctional catalyst to improve the regeneration of MEA solvent, and found that the desorption performance was enhanced by 2-3 times in catalytic group. Our recent study of Shi et al. (2021b) also found that the composite γ-Al₂O₃/HZSM-5 blended catalyst showed better desorption effects than solo Al₂O₃ and HZSM-5 in MEA+BEA+AMP solution, which means the synergetic effects were achieved. The study of Zhang et al. (2019a) showed that the heat duty of MEA solution was reduced by 29.5% with the addition of H-beta cata-

(Alivand et al., 2020).

For this study, CO₂ desorption experiments were conducted with tri-solvent MEA+BEA+DEEA at 0.1~0.5+2+2 mol/L, along with 5 commercial solid acid catalysts: blended γ-Al₂O₃/H-ZSM-5, H-beta, H-mordenite, HND-8, and HND-580. The CO₂ desorption profiles, heat duties and desorption factors were investigated in detail. The purposes of this study: (1) Determine the optimized combination of amine blends with catalysts; (2) Compare the optimized amine blend + moderate catalysis and moderate amine blend + optimized catalysis; (3) Study the heat duty and desorption factor of energy efficient combinations under temperature programming increasing; (4) find out the optimized combinations of tri-solvent of MEA+BEA+DEEA within 5 commercial catalysts and compare it to 5.0 M MEA as benchmark.

2. Theory

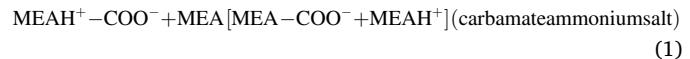
2.1. Mechanism: the coordinative effects within MEA vs BEA

The “coordinative effect” was reported repeatedly to exist in MEA+RR'NH bi-blends, such as MEA+DEA (Shi et al., 2020), MEA+BEA (Shi et al., 2021b) and MEA+BEA+AMP (Shi et al., 2021a). The heat duty of bi-blends was lower than that of single amines (Shi et al., 2021b; Shi et al., 2018b). This phenomenon seems to be contradictory to the well acknowledged concept that MEA enhances CO₂ absorption but sabotages desorption performance in amine blends (Narku-Tetteh et al. 2017).

The principle of coordinative effect works is special: introducing 0.1~0.5 mol/L MEA into 2.0 mol/L secondary amine (RR'NH) increases heat input Q_{input} to 5~10%, but it also boosts CO₂ production to 10~20%. This simultaneous increase reduces heat duty (H = Q_{input}/nCO₂) down to 5~10%. (Shi et al. 2018b) The principle of heat duty reduction has been reported already: reducing heat duty (H) could either reduce Q_{input} as a common method; or increase Q_{input} and nCO₂ simultaneously to a specific ratio (Shi et al., 2018a).

The detailed mechanisms of coordinative effect were listed in Eqs. (1)–(7) in both absorption and desorption with details published repeatedly (Shi et al., 2021a; Shi et al., 2021b).

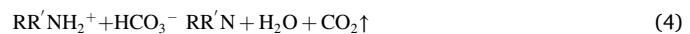
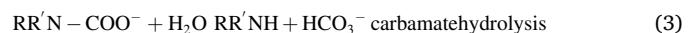
Absorption (298–323 K)



lysts. A recent review reported the catalytic CO₂ desorption of amine solvents, mostly MEA, with various solid acid catalysts, and it reported detailed catalysis, mechanisms and structure-activity correlations (Alivand et al., 2020). This review thoroughly studied most commercial solid acid catalysts and synthesized catalysts in the area, which proposed several similar mechanisms of catalytic carbamate breakdown, along with catalysis and characterization of synthesized solid acid catalysts (Alivand et al., 2020).

Therefore, if the tri-solvent combines with solid acid catalysts, there are only limited studies of “tri-solvent + catalysts” published, (Shi et al., 2021c; Zhang et al., 2019a; Zhang et al. 2018) which are MEA+AMP+PZ (Zhang et al., 2018b), MEA+MDEA+PZ (Zhang et al., 2019a), and MEA+BEA+AMP from the author (Shi et al., 2021c). This study introduced the 4th case of MEA+BEA+DEEA with commercial solid acid catalyst into the field, reflecting the novelty in the area. Other studies mostly focused on MEA and MEA bi-blends with catalysts

Desorption at 363–378 K with lean CO₂ loadings (negligible HCO₃⁻)



The overall desorption reaction with a small amount of free MEA: sum of (3–6) (Shi et al., 2021b):



From absorptions of Eqs. (1) and (2), the primary (RNH₂)/secondary

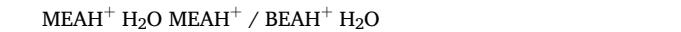
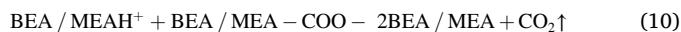
amine ($\text{RR}'\text{NH}$) accepted protons from “carbamate ammonium salt” (Liu et al., 2018) in Eq. (1), and released free MEA molecules to enhance absorption in Eq. (2). The reaction equilibrium of Eq. (2) was determined by pKa of MEA and $\text{RR}'\text{NH}$. At 298K, pKa of MEA was 9.51, pKa of DEA was 8.91, pKa of BEA is 10.0 (Shi et al., 2021b) with the order (basicity) of $\text{DEA} < \text{MEA} < \text{BEA}$. For DEA, since its basicity was weaker than MEA's, it released free MEA out of “carbamate ammonium salt”. For BEA, because its basicity was stronger, it will compete with MEA to accept protons from Zwitterion directly as competition effect (Liu et al., 2018).

The mechanism of CO_2 desorption was listed in Eqs. (3)–(6), and summarized into Eq. (7). The “proton transfer” was a key step from bicarbonate $[\text{HCO}_3^-]$ to MEA to generate carbonate $[\text{CO}_3^{2-}]$ above 363K (Shi et al., 2021b). There was constant heat input during the desorption process. These protons were tightly bounded with $[\text{AmineH}^+]$ and released to $[\text{CO}_3^{2-}]$ with the aid of heat input. At 363K, $[\text{HCO}_3^-]$ released protons to free MEA molecules at small possibility (5~10%) due to comparable pKa. (Bernhardsen and Knuutila, 2017) The short-life intermediate $[\text{CO}_3^{2-}]$ was generated, and it grabbed protons from BEAH^+ spontaneously. Hence, a small number of conjugated pairs of $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ and $[\text{MEA}\text{H}^+]/[\text{MEA}]$ acted as “catalysts” to facilitate $[\text{BEAH}^+]$ regeneration and hydrolysis of carbamate. (Shi et al., 2021b)

The coordinative effect enhanced amine regeneration of BEAH^+ , which resulted in 10~20% increased CO_2 production ($n\text{CO}_2$). Although the Q_{input} increased 10% with blending of MEA, the overall heat duty ($H = Q_{\text{input}}/n\text{CO}_2$) reduced 5~10% (Shi et al., 2018a,b).

2.2. The mechanism of catalytic CO_2 desorption

The reaction pathways of tri-solvent including MEA and R_3N were published repeatedly (Zhang et al., 2018b). The introduction of R_3N provided extra bicarbonate (HCO_3^-) into the system, with much less energy input required. The energy requirement of bicarbonate regeneration was much less than that of carbamate breakdown (Shi et al., 2014). Based on Scheme 1 below, the reaction scheme of MEA- CO_2 was the same as that of BEA- CO_2 , which produced carbamate as the main product. The reaction of DEEA- CO_2 , in which bicarbonate was the only product, was simple. Based on the reaction pathways study, the possible pathways increased from 2 to 6, 4 of which were low energy pathways except 2 for MEA.



A recent review categorized various mechanisms of catalytic CO_2 desorption (Alivand et al., 2020). The mechanisms were published repeatedly with similar diagrams, (Support Information), involving several key steps, such as “Carbamate formation”, “carry protons”, “chemical adsorption”, “isomerization”, “stretching”, “C-N bond cleavage/breaking”, and “desorption / separation” (Alivand et al., 2020). This mechanism was originally proposed by the author in 2011, involving adsorption, surface reaction, desorption of heterogeneous catalysts (Idem et al., 2011). With the aid of various solid acid catalysts, the carbamate breakdown and CO_2 desorption can be possibly proceeded under 80~95 °C, under boiling point of water. Thus, the heat duty can be greatly reduced without latent heat of steam (Alivand et al., 2020) Scheme 2.

2.3. The heat duty and Desorption Factor of CO_2 desorption analysis

The heat duty (H) was the most important parameter of evaluating CO_2 desorption performance. It was calculated with Eq. (12) below. The heat input (Q_{input}) was evaluated with an electrometer, and CO_2 production ($n\text{CO}_2$) was estimated with $(\alpha_{\text{rich}} - \alpha_{\text{lean}}) \times C \times V$. The relative heat duty (RH) was calculated in Eq. (13), with H_{baseline} for 5.0 M MEA.

$$H = \frac{\text{Heat input/time}}{n\text{CO}_2/\text{time}} = \frac{\text{Electricity(kJ)}}{n\text{CO}_2(\text{mol})} \quad (12)$$

$$RH = \frac{H_i}{H_{\text{baseline}}} \times 100\% \quad (13)$$

Recently, the CO_2 desorption performance was evaluated with a desorption parameter (Narku-Tetteh et al., 2017) and a desorption factor (Zhang et al., 2019b). These two are very similar with each other, except Initial Desorption rates (I_{des}) were calculated for desorption parameter (Narku-Tetteh et al., 2017), while Average desorption rates were calculated for desorption factor (Bairq et al., 2020, Gao et al., 2020). The CO_2 desorption was quick in this study, so that the average desorption rates were used to reduce the uncertainty or error.

$$\text{DesorptionFactor} = \frac{\text{Average Desorption Rate} \times \text{Cyclic Capacity}}{\text{Heat Duty}} \quad (14)$$

$$\text{Averagedesorptionrate} = \frac{n\text{CO}_2}{\text{time}} = \frac{(\alpha_{\text{rich}} - \alpha_{\text{lean}}) \times C \times V}{t} \quad (15)$$

3. Experimental apparatus and process

3.1. Chemicals, catalysts and sample analysis

The CO_2 gas was purchased with 99% purity. Different amines (MEA, BEA and DEEA) were purchased from Tansuo Ltd, with a purity of 98.5%, and 99.0%, respectively. The HCl (1.0 mol/L) was used for titration for Amine concentration with methyl orange as the indicator. The CO_2 loading tests were determined by the amine samples with a Chittick apparatus, based on Association of Official Analytical Chemists (AOAC) (Horwitz, 1975).

3.2. Experimental procedures for CO_2 desorption for direct heating

This recirculation process (Support Information) was similar to that in other studies (Shi et al., 2021a; Shi et al., 2021b; Shi et al., 2020). The tri-solvents were prepared for 500 ml and placed at pre-heated oil bath of 363 K. During the heating process, CO_2 desorbed out of the amine solvents continuously. The sample was pipetted at 1~2 ml every 5 min and stored for CO_2 loading tests. After the sample cooled to room temperature, the CO_2 loading tests were conducted and recorded. The dataset of CO_2 loading (α) vs time (t) was plotted to generate CO_2 desorption profiles, from initial overloaded loading 0.75~0.78 mol/mol to lean loading of 0.20~0.25 mol/mol. The rich and lean loading of MEA+BEA+AMP were 0.60 and 0.30 mol/mol, respectively (Shi et al., 2021a). Therefore, the cyclic capacity of MEA+BEA+DEEA was bigger than that of MEA+BEA+AMP under similar conditions.

These CO_2 loadings were repeatedly tested at least twice to ensure the accuracy that AAD = 5%.

The average desorption rates (A_{des}) were calculated with Eq. (15), from the start with fresh solvent (0 mol/mol, 0 min) to the desired time of CO_2 loading tests. The volume decreased with sampling was less than 20 ml (4%), and the volume change was negligible.

Finally, the heat duty was calculated during the first 15 and 30 min with various samples Eq. (14). The heat duties for 15 and 30 min were

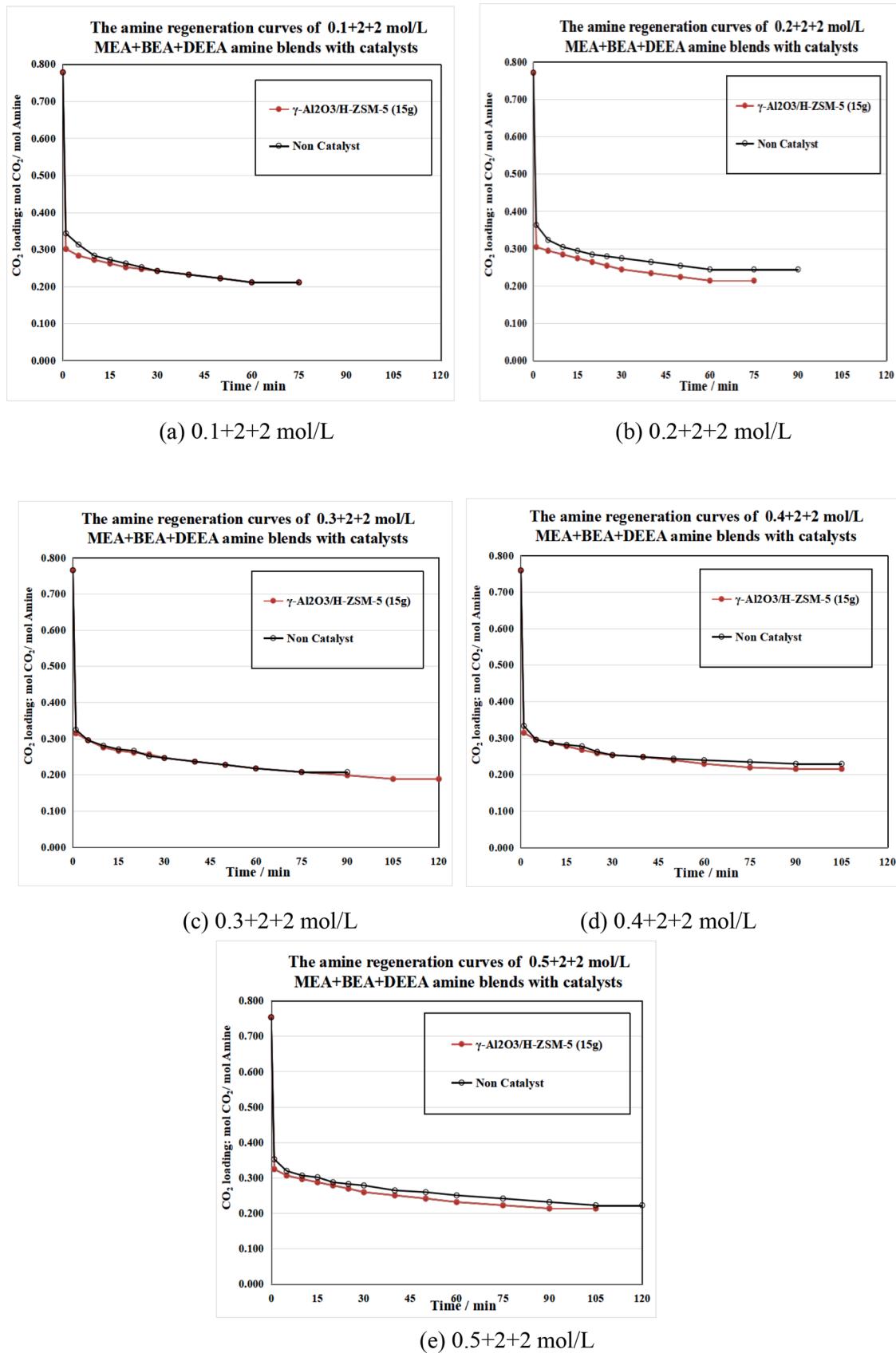


Fig. 1. (a–e) The CO₂ desorption profiles of MEA+BEA+DEEA with catalysts from 0.1+2+2 ~ 0.5+2+2 mol/L.

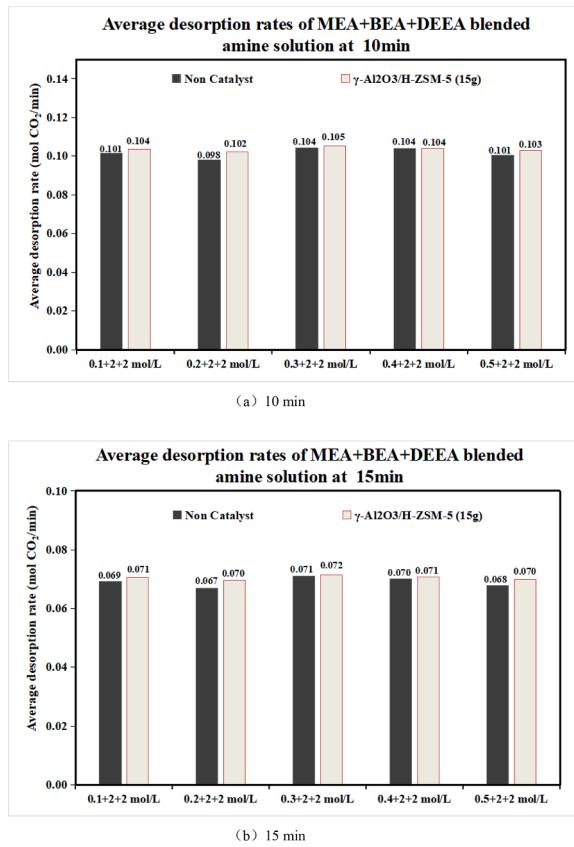


Fig. 2. The average desorption rates of MEA+BEA+DEEA with catalysts: (a) 10 min; (b) 15 min.

indicative since the α_{lean} was reluctant to change at 30–60 min when the carbamate of MEA and BEA was stable. The Desorption Factors derived from heat duty were quite useful in evaluating tri-solvents under a consistent level.

3.3. Experimental procedures for CO₂ desorption for temperature programming

This CO₂ desorption process was similar to that in Section 3.2, except the initial temperature of the oil bath was set at 25 °C, and the initial time was recorded as 35 °C with $t = 0$. Then, the temperate increased with temperature programming (TP) and gradually reached 85–90 °C. The CO₂ desorption curve was also recorded, along with temperature profile labeled in the same plot. This study indicated most CO₂ desorption process was completed at 85 °C.

The desorption under TP was very indicative to two factors: (1) the CO₂ loading α_{lean} under different temperatures at 70, 80 and 90 °C. (2) The CO₂ desorption performance with inadequate heat input. The CO₂ desorption included multiple endo-thermic reactions (Idem et al., 2015). With constant heat input into the amine solvent, T increased to 80–85 °C and stopped, and Q_{input} was converted to continuous reaction heat and CO₂ release/desorption at constant temperature ($Q_{\text{input}} = Q_{\text{output}}$). Therefore, the highest temperature of the desorption was indicative for operation conditions of desorber column for industrial pilot plants.

4. Results and discussion

This study included 3 sets of CO₂ desorption tests: (1) MEA+BEA+DEEA (0.1~0.5+2+2 mol/L) with blended γ -Al₂O₃/HZSM-5 catalysts to find out an energy efficient combination. (2) MEA+BEA+DEEA (0.3+2+2 and 0.5+2+2 mol/L) with 6 commercial

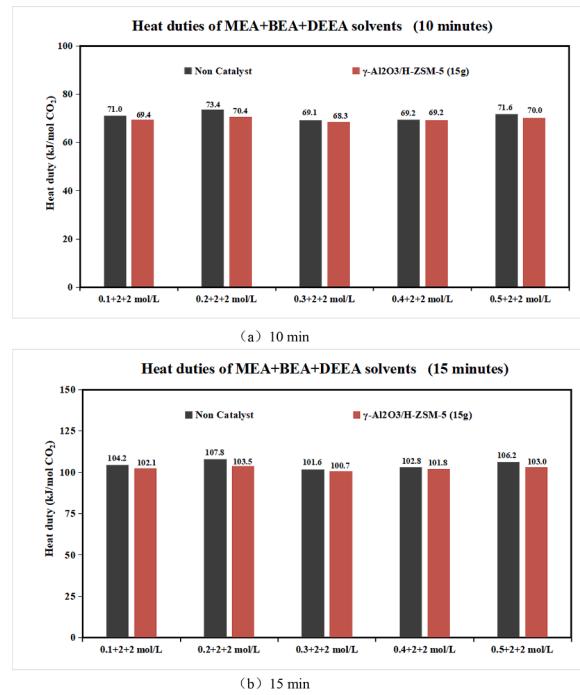


Fig. 3. The heat duties of MEA+BEA+DEEA with blended catalysts at (a) 10 and (b) 15 min.

Table 1

Desorption factors of MEA+BEA+DEEA with various catalysts at 10 and 15 min.

MEA+BEA+DEEA	Desorption Factor (*10 ⁻³ mol CO ₂) ³ /L ² kJ min	
	10 min	15 min
(mol/L)	blank	γ -Al ₂ O ₃ /H-ZSM-5 (15g)
0.1+2+2	2.894	3.100
0.2+2+2	2.618	2.971
0.3+2+2	3.142	3.248
0.4+2+2	3.122	3.130
0.5+2+2	2.824	3.012

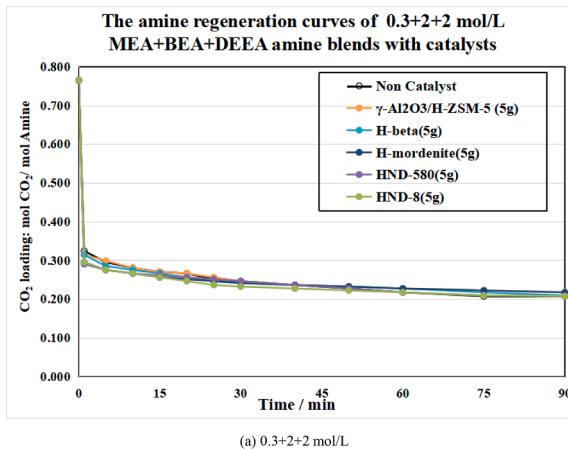
catalysts to find out an energy efficient combination with wider scope of desorption tests. (3) The selected superior combination MEA+BEA+DEEA (0.3+2+2 and 0.5+2+2 mol/L) with HND-8 and H-mordenite with temperature programming to find out a suitable combo for industrial CO₂ desorption pilot plants.

4.1. CO₂ desorption of tri-solvents with blended γ -Al₂O₃/HZSM-5 catalyst

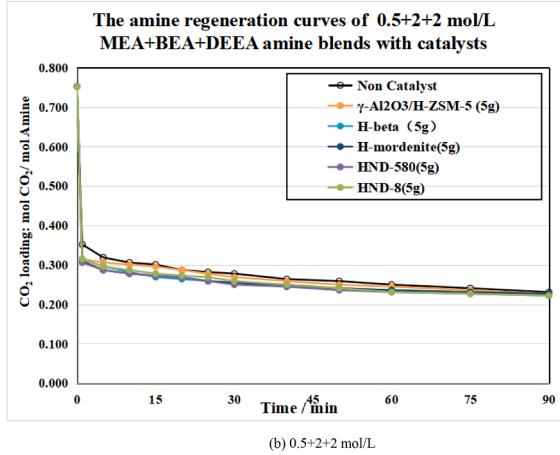
Similar to the previous study (Shi et al., 2021c), the CO₂ desorption tests were firstly conducted within tri-solvent of MEA+BEA+DEEA with blended γ -Al₂O₃/HZSM-5 catalysts. From repeated publications, the catalysis was blended γ -Al₂O₃/HZSM-5=2:1 > HZSM-5 > γ -Al₂O₃ (Shi et al., 2021c). The purpose was to find out the optimized blending ratio of tri-solvent without catalysts, and check the boundary conditions (0.5+2+2 mol/L) of tri-solvent with optimized catalysis.

4.1.1. The CO₂ desorption of MEA+BEA+DEEA

The CO₂ desorption profiles were plotted in Fig. 1 (a–e), with 5 curves of tri-solvents MEA+BEA+DEEA at 0.1~0.5+2+2 mol/L. For the same amine concentration, the catalytic desorption curves were all lower than their non-catalytic counterparts. The average desorption rates were plotted into bar graphs of Fig. 2 (a,b) at 10 and 15 min. The desorption rates with catalysts were higher than those of non-catalytic solvents. The heat duties were plotted into Fig. 3 (a,b), and the figures



(a) 0.3+2+2 mol/L



(b) 0.5+2+2 mol/L

Fig. 4. The CO₂ desorption profiles of MEA+BEA+DEEA with catalysts. (a) 0.3+2+2 mol/L; (b) 0.5+2+2 mol/L.

of amine blends with catalytic desorption were lower than those of non-catalytic solvents. All these figures reflected the similar effect of solid acid catalysis to enhance CO₂ desorption (Alivand et al., 2020).

With comprehensive studies of Figs. 1–3, the mixing ratio with minimum heat duty of MEA/BEA was 0.3/2 mol/L, similar to that of bi-solvent MEA+BEA (Shi et al., 2021b) and tri-solvent MEA+BEA+AMP (Shi et al., 2021a). The coordinative effect was mainly determined by MEA and BEA each other, since MEA+R₃N and MEA+AMP contained negligible coordination (Shi et al., 2021b). The negligible coordination effect was reasonable, since R₃N could not produce carbamate and AMP produced unstable carbamate due to stereo hindrance (Shi et al., 2021b).

From Fig. 3, the trends were similar in both catalytic and non-catalytic cases: H decreased first and reached the minimum value of 0.3+2+2 mol/L before it started to increase generally. To more intuitively exhibit the different performances of 5 tri-solvents in CO₂ desorption, the desorption factor with or without catalysts was calculated, as shown in Table 1. From Table 1, it is clear that the optimized combination of tri-solvent with γ-Al₂O₃/HZSM-5 was 0.3+2+2 mol/L under both noncatalytic and catalytic conditions.

4.1.2. Comparison of MEA +BEA+DEEA vs MEA+BEA+AMP

After the comparison of H and Desorption Factors between MEA+BEA+DEEA and MEA+BEA+AMP, it was found that the order of MEA+BEA+DEEA was similar to that of MEA+BEA+AMP under non-catalytic conditions (Shi et al., 2021c). The optimized ratio was 0.3+2+2 mol/L. However, the 0.5+2+2 mol/L MEA+BEA+AMP with blended catalysts was lower than 0.4+2+2 mol/L due to optimized catalysis onto MEA (Shi et al., 2021c). In the cases of this study,

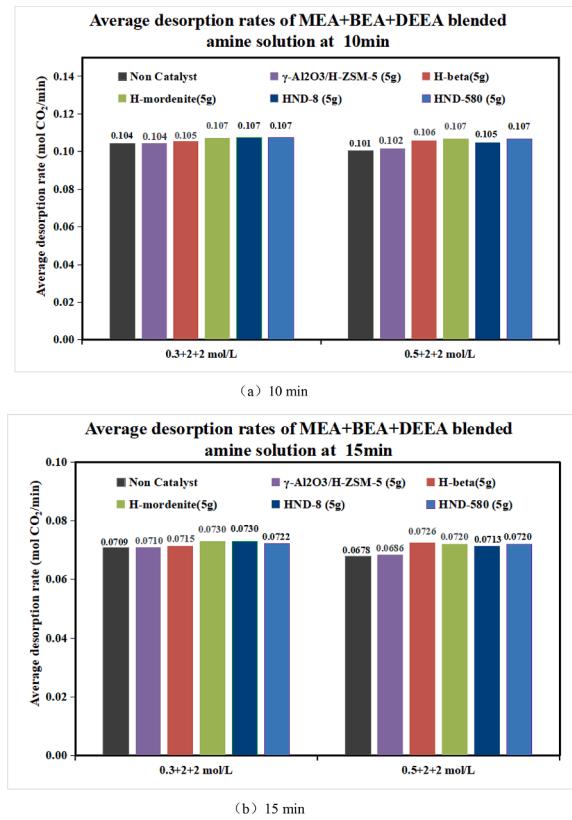


Fig. 5. Average desorption rates of MEA+BEA+DEEA with catalysts at (a) 10 min; (b) 15 min.

0.5+2+2 mol/L MEA+BEA+DEEA with catalyst was worse than that of 0.4+2+2 mol/L.

Such difference was the “competition effect” of increased MEA with enhanced catalysts. With solid acid catalysts being included into the solvent, the “competition effect” may be indicative to either increase or decrease Heat duty with complicated phenomena. The reason was discussed repeatedly with MEA+DEA with catalysts (Shi et al., 2018a). Increased MEA after optimized condition will increase Q_{input} with ΔQ, while increased MEA + catalysts will enhance CO₂ production with ΔnCO₂. However, this tri-solvent was highly energy efficient with very low energy cost, and the increase of nCO₂ with catalysts could not offset the increased Q_{input} in order to facilitate heat duty reduction. For MEA+BEA+DEEA, extra ΔCO₂ released by the catalyst could not offset the ΔQ_{input} into system and H of MEA+BEA+DEEA was bigger than that of 0.3+2+2 mol/L with γ-Al₂O₃/HSM-5.

$$H' = \frac{\text{Heat input/time}}{n\text{CO}_2/\text{time}} = \frac{Q + \Delta Q}{n\text{CO}_2 + \Delta n\text{CO}_2} \quad (12)$$

4.2. Catalytic CO₂ desorption of tri-solvents of 0.3+2+2 and 0.5+2+2 mol/L

Based on Section 4.1, two amine blends were selected for further catalytic CO₂ desorption: 0.3+2+2 for optimized amine blends, 0.5+2+2 for optimized heterogeneous catalysis. It is necessary to study “competition effect” with various heterogeneous catalysts comprehensively Section 4.1, only discussed one type of catalyst, γ-Al₂O₃/HSM-5, which is not representative. It is hard to draw the conclusion that the optimized combination was 0.3+2+2 catalysts without thorough studies of 0.3+2+2 and 0.5+2+2 mol/L with 4~5 catalysts systematically.

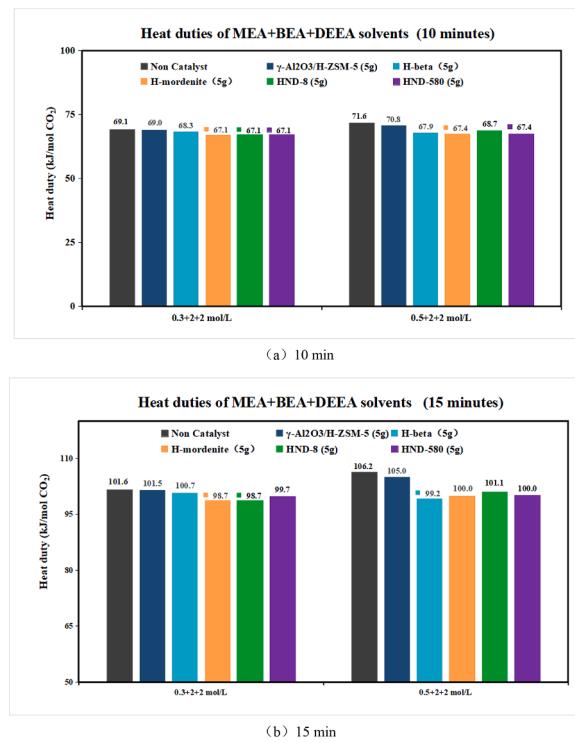


Fig. 6. Heat duties of MEA+BEA+DEEA with various catalysts (a) 10 min (b) 15 min.

4.2.1. The CO_2 desorption of two MEA+BEA+DEEA solvents with 5 commercial catalysts

This section selected two tri-solvent with 5 commercial catalysts to find out the “energy efficient” combination with minimized Heat duty (H) and optimized Desorption Factor (DF). The CO_2 desorption curves were plotted in Fig. 4.(a,b) of two MEA+BEA+DEEA blends with 5 g commercial catalysts, such as: blended $\gamma\text{-Al}_2\text{O}_3/\text{HZSM-5}$, H- β , H-Mordenite, HND-8, and HND-580.

The blended $\gamma\text{-Al}_2\text{O}_3/\text{HZSM-5}$ were reported repeatedly on MEA (Liang et al., 2016), MEA+DEA (Shi et al., 2014), and MEA+BEA+AMP tri-solvent (Shi et al., 2021c), and H- β , H-Mordenite were reported to MEA+MDEA+PZ tri-solvent (Zhang et al., 2019a). However, HND-8, HND-580 were not reported onto heterogeneous catalysis of tri-solvents to the best of our knowledge.

Fig. 5 demonstrated a bar graph of average desorption rates. It is clear that the catalytic desorption has higher rates, and the order was non-cat < blended $\gamma\text{-Al}_2\text{O}_3/\text{HZSM-5}$ < H- β < H-Mordenite. As for the super acid of HND-8 and HND-580, they were always located in relative high levels. For 0.3+2+2 tri-solvent, the average desorption rates of HND-8 and HND-580 were comparable, while for 0.5+2+2 tri-solvent, the HND-8 was lower than HND-580, and HND-580 became the highest rate at both 10 and 15 min. Since the tri-solvents + catalysts were quite energy efficient, the Ades cannot effectively select the better combination. The Heat duty analyses were required in the next step.

Fig. 6 demonstrated heat duty of both tri-solvents, and the results indicated the heat duty was rather small, and catalytic desorption was lower than non-catalytic benchmarks in terms of the heat duty. Among these cases, the 0.3+2+2 was lower than 0.5+2+2 systematically with

direct heating. In the 0.3+2+2 with catalysts, the H-mordenite and HND-8 had the lowest heat duty at both 10 and 15 min.

4.2.2. The comparison of this study with other tri-solvents + catalyst

As stated in introduction, there are only 3 related publications of tri-solvent with solid acid catalysts in the field (Shi et al., 2021c; Zhang et al., 2019a; Zhang et al., 2018b). In this section, we could only compare the catalysis with these publications briefly, since the detailed operation conditions, amine concentrations, desorption temperatures, and catalysts were different from each other. The heat losses were different, either. Direct comparison of heat duty was neither precise nor persuasive to draw the conclusion of “optimized energy efficient combination” of this study. However, the comparison can help to evaluate the advantages of various tri-solvents + catalysts in the field.

Afterward, the catalytic effect of blended $\gamma\text{-Al}_2\text{O}_3/\text{HZSM-5}$ was compared with that of MEA+BEA+AMP with the same blended catalysts (Shi et al., 2021c) at the same concentrations of 0.3+2+2 and 0.5+2+2 mol/L. The absolute heat duty of MEA+BEA+DEEA was lower than that of MEA+BEA+AMP (Shi et al. 2021c), indicating the high energy efficiency of the tri-solvent, and the stronger desorption performance of DEEA over AMP. For MEA+BEA+AMP tri-solvent, the H of 0.5+2+2 with blended catalysts was comparable to that of 0.3+2+2. In this study, the 0.3+2+2 with catalyst was the lowest. The reason is the same competition effect as shown in Section 4.1.2. The increase nCO₂ with 0.2 mol/L MEA can offset the Q_{input} for MEA+BEA+AMP (relative high Heat duty), but cannot offset the Q_{input} of MEA+BEA+DEEA (relative low heat duty) in this study.

Compared with tri-solvent MEA+AMP+PZ (3+2.5+0.5 mol/L) with similar catalyst of $\gamma\text{-Al}_2\text{O}_3$ and HZSM-5 (Zhang et al. 2018b), the cyclic capacity of this study (0.70~0.25 mol/mol) was much bigger than that of MEA+AMP+PZ (3+2.5+0.5 mol/L) of (0.57~0.38 mol/mol). The heat duty of this study at 90 °C was much smaller than that in other works under similar operation conditions of 95 °C (Zhang et al., 2018b). These outcomes indicated the advantages of this tri-solvent with similar catalysis used similar catalysts.

The catalytic effect of MEA+BEA+DEEA with H- β and H-Mordenite was compared with that of MEA+MDEA+PZ at 3+2.5+0.5 mol/L with H- β and H-Mordenite. (Zhang et al., 2019a). With the same catalyst, different tri-solvents also indicated different desorption performances. The cyclic capacity of this study (0.70~0.25 mol/mol) was bigger than MEA+MDEA+PZ (3+2.5+0.5 mol/L) of (0.43~0.23 mol/mol). The α_{lean} were comparable, while the α_{rich} of this study was much bigger, indicating wider operation flexibility. The heat duty was not comparable due to different operation conditions.

The catalytic effect of HND-8 and HND-580 was compared with each other. From Fig. 6, the heat duties of tri-solvent with both acids were very low. The detailed comparison would be discussed in the next section.

4.2.3. The comparison of optimized amine blends vs optimized catalysts

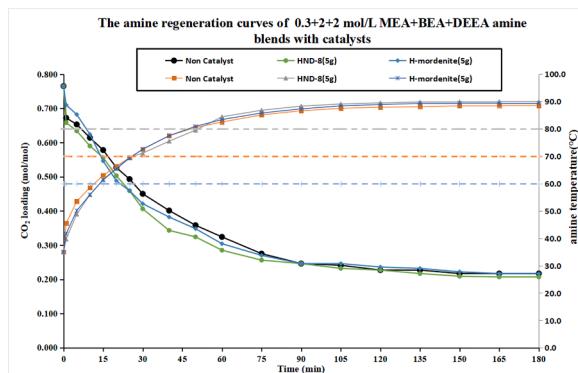
The Heat duties and Desorption Factors were used to compare both cases on a consistent level. Therefore, Table 2 categorized 12 catalytic cases systematically, and some interesting phenomena were discovered. The texture and physical-chemical properties were categorized into Support Information, since most commercial catalyst was characterized, with parameters published repeatedly.

For desorption factor analysis, under blended solid, H-mordenite and HND-8, the tri-solvent 0.3+2+2 was better than the 0.5+2+2

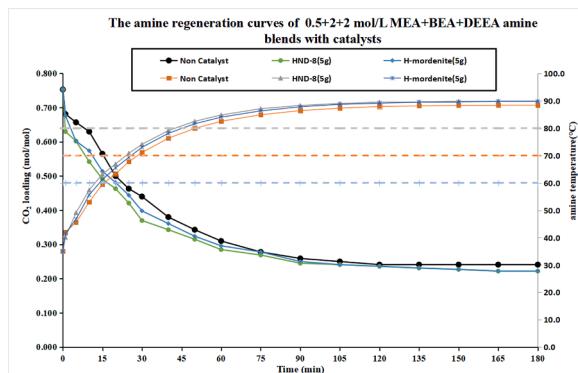
Table 2

The desorption factors of tri-solvent of MEA+BEA+DEEA solvents with 5 g of solid acid catalysts at 15 min.

MEA+BEA+DEEA	Desorption Factor (*10 ⁻³ mol CO ₂)3/L2 kJ min					
(mol/L)	Non Catalyst	$\gamma\text{-Al}_2\text{O}_3/\text{HZSM-5}$	H-beta	H-mordenite	HND-8	HND-580
0.3+2+2	1.485	1.488	1.525	1.618	1.618	1.571
0.5+2+2	1.298	1.342	1.594	1.555	1.507	1.555



(a) 0.3+2+2



(b) 0.5+2+2

Fig. 7. The CO₂ desorption profiles of MEA+BEA+DEEA at (a) 0.3+2+2 mol/L and (b) 0.5+2+2 mol/L with or without catalysts.

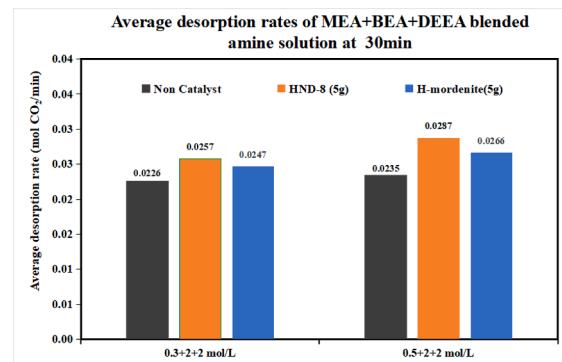
Table 3

CO₂ Loading of tri-solvent of MEA+BEA+DEEA solvents with catalysts at different temperatures.

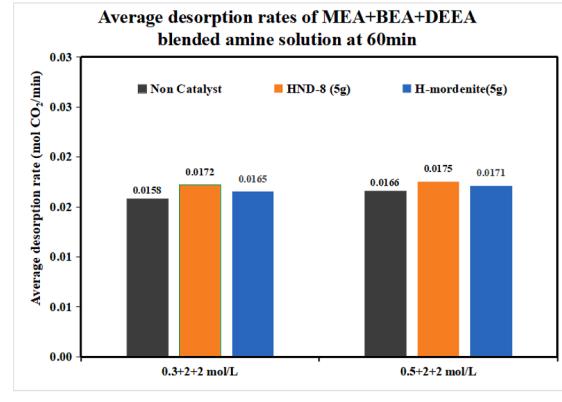
MEA+BEA+DEEA	Temperatures			
	60 °C	70 °C	80 °C	
0.3+2+2	Blank	0.578	0.450	0.358
	HND-8	0.556	0.406	0.324
	H-mordenite	0.546	0.421	0.348
0.5+2+2	Blank	0.565	0.440	0.343
	HND-8	0.491	0.370	0.315
	H-mordenite	0.514	0.398	0.324

counterparts, while 0.3+2+2 with H- β was poorer than 0.5+2+2. From the catalysts characterization (Support Information), the H- β has much bigger total active sites TAS and strong acidity strength over the other catalysts, which was preferred at bigger C_A. The HND-580 was comparable and close to both tri-solvents. Such distribute orders reflected the strong “competition effect” of coordinative effect vs heterogeneous catalysis. For different catalysts used, some catalysts facilitated carbamate effectively on MEA and produced more CO₂ (nCO₂), such as H-mordenite. On the other hand, the other catalysts could not produce extra CO₂ to offset the Q_{input} with 0.2 mol/L MEA introduced, and 0.3+2+2 was better than 0.5+2+2.

The optimized amine blending ratio of 0.3+2+2 mol/L was still dominant with most catalysts. Surprisingly, the case of HND-580 was special, the extra Q_{input} with 0.2 M MEA was offset with extra nCO₂ produced with catalysts, resulting in comparable desorption factors (1.0% difference). The H of tri-solvents of 0.3+2+2 and 0.5+2+2 were applicable. The detailed catalysis awaited further studies of structure-activity of catalyst characterization (Alivand et al., 2020). Last but not least, among 10 cases, the most energy efficient catalysts were



(a) 30 min



(b) 60 min

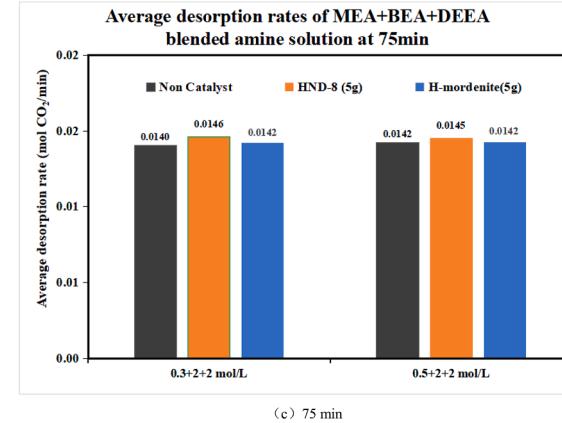


Fig. 8. The average desorption rates of MEA+BEA+DEEA with catalysts at (a) 30 min, (b) 60 min and (c) 75 min.

H-mordenite and HND-8.

The underline represents better performance with same group of catalysts. The bold represent the biggest desorption factors and best desorption performance.

4.3. CO₂ desorption of both tri-solvents with good performance catalysts with temperature programming

From the Review, a new generation of pilot plant for amine scrubbing process of CO₂ capture requires hot water, instead of steam, as heat source (Alivand et al., 2020). Idem's group already reported several steady-state operations with catalytic packing and amine blends (Afari et al., 2018; Akachuku et al., 2019; Narku-Tetteh et al., 2018; Prasongthum et al., 2019). The most important difference was that the process did not use reboiler but a heat exchanger to complete heat transfer, and the operation temperature (85–98 °C) was lower than the boiling point of water, without any steam needed (Prasongthum et al.,

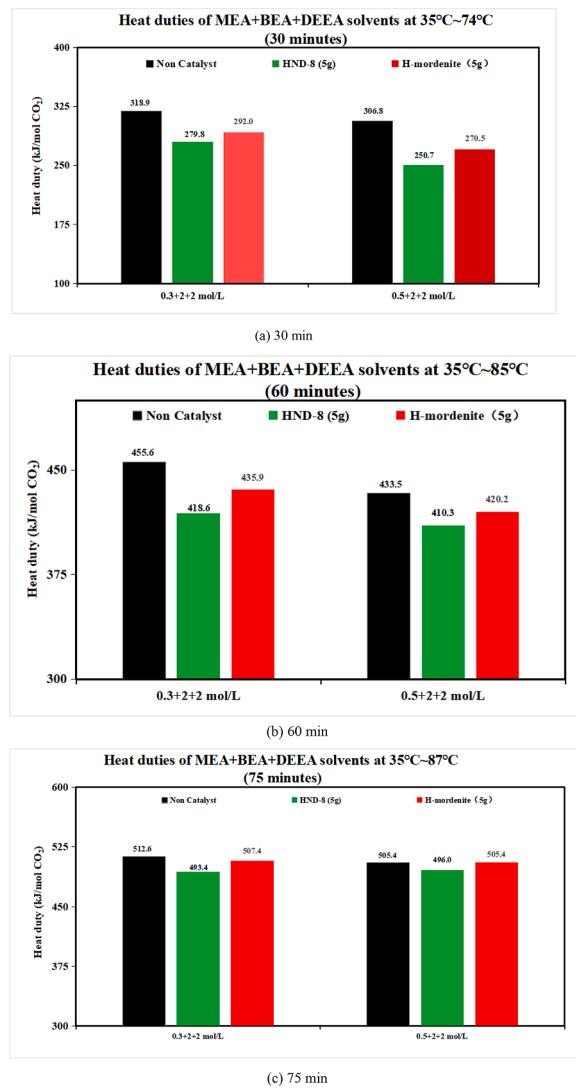


Fig. 9. The heat duties of MEA+BEA+DEEA with various catalysts (a) 30 min (b) 60 min (c) 90 min.

2019). In that case, low “operation temperature” was preferred. As long as the CO₂ desorption was completed at 80~85°C, the heat duty and the input of the entire hot source can be greatly reduced (Alivand et al., 2020). Thus, the temperature programming method was used for this study, similar publications were also reported (Bhatti et al. 2018 a,b).

This section studied both tri-solvents with two good performance catalysts H-mordenite and HND-8 with temperature programming Fig. 7. reported CO₂ desorption curves, with simultaneous tri-solvent temperate plotted into the same plots Table 3. reported the CO₂ loading (α_{lean}) under different temperatures. It is clear that massive CO₂ was released before the operation temperature increased to 85°C. Such results reflected superior performance of low energy efficient combo of tri-solvent MEA+BEA+DEEA with catalysts. The lower desorption temperature reflected much less heat duty (Alivand et al. 2020). As reported, at 90°C, the heat duty of MEA was very high because of carbamate stability. However, this study confirmed that this tri-solvent was quite easy to release CO₂ at the temperature as low as 80°C.

The average CO₂ desorption rates and Heat duties were plotted into bar graphs of Figs. 8 and 9. For both tri-solvents, the order was consistent, which is HND-8 > H-mordenite > non catalyst (A_{des}), and HND-8 < H-mordenite < non catalyst (H) at 30, 60 and 75 min. The higher rates and lower heat duty reflected better desorption performance.

From Fig 9, it was interestingly shown that at 0~30 min with lower

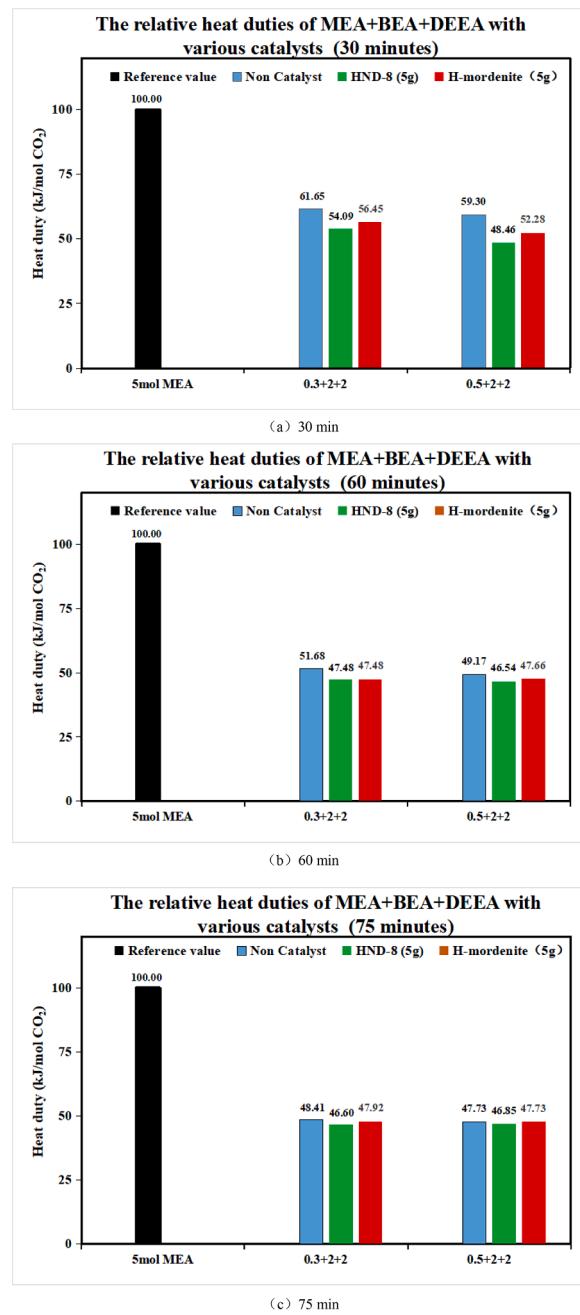
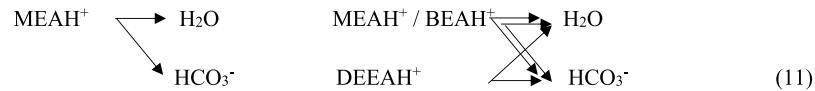
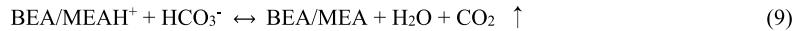
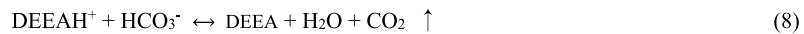


Fig. 10. The relative heat duties (%) of the tri-solvents + catalysts at (a) 30 min, (b) 60 min and (c) 75 min, with MEA with temperature programming heating process as benchmark.

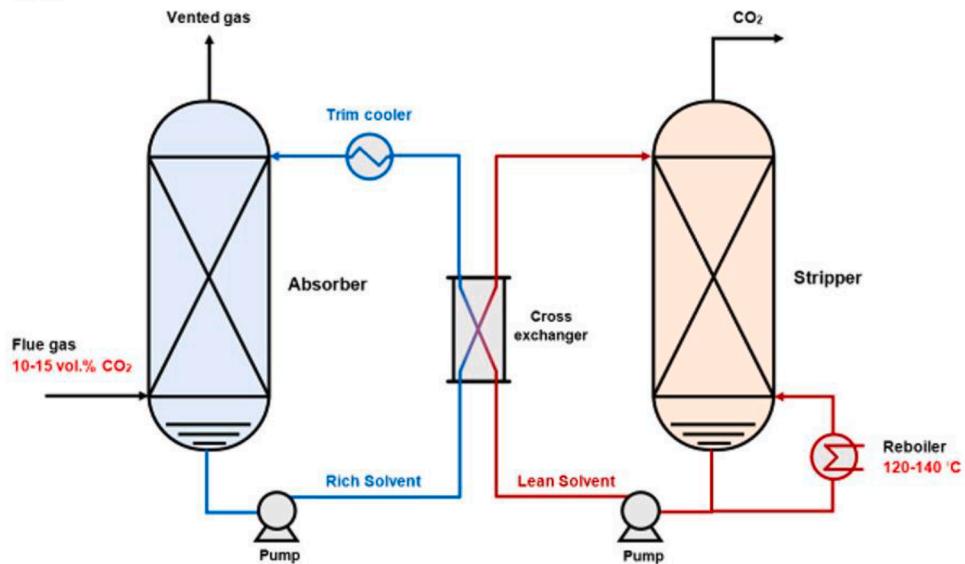
operation temperature (30~70 °C) the 0.5+2+2 with HND-8 was better than 0.3+2+2 with HND-8, with 11.6% less heat duty. However, at 0~60 min, when the operation temperature was 30~82 °C, the 0.5+2+2 with HND-8 was only 2% smaller than 0.3+2+2 with HND-8 in heat duty. Finally, at 0~75 min, when the operation temperature was 30~85 °C, 0.3+2+2 with HND-8 was 0.5% smaller than 0.5+2+2 with HND-8 in heat duty as a reverse. For H-mordenite, the 0.3+2+2 was worse than 0.5+2+2 at 30,60, and 75 min, which reflected the opposite trend of Table 2 that 0.3+2+2 mol/L had better desorption factors than 0.5+2+2 mol/L.

The reverse trend resulted from the different operation temperatures and different amount of heat input. In Table 2, the desorption was conducted with direct heating at 90 °C with pre-heated oil bath. That process involved excessive heat input into the system constantly, and the

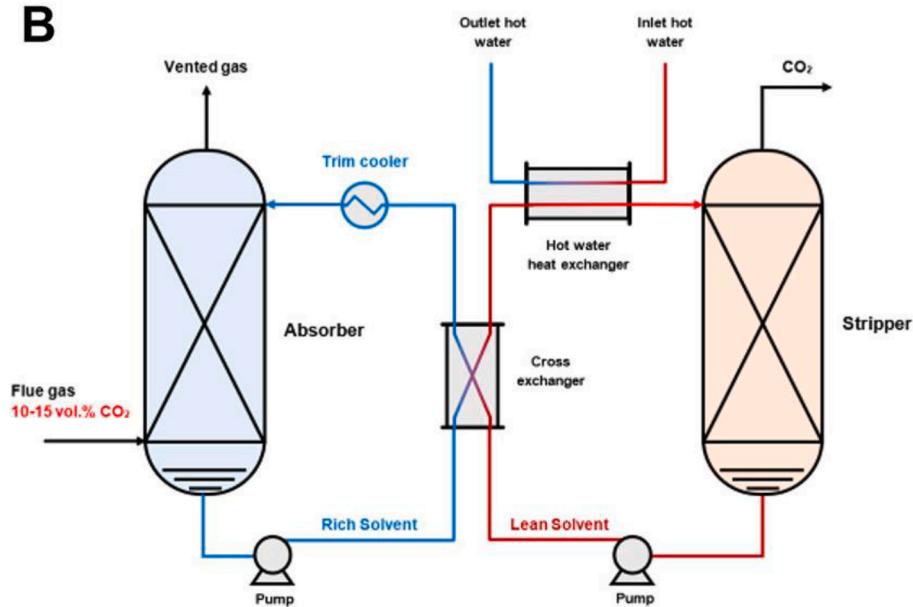


Scheme 1. The reaction pathways of CO₂ desorption for MEA/RR'NH and R₃N (Zhang et al. 2019a).

A



B



Scheme 2. The traditional (A) and new (B) steady-state pilot plant (Alivand et al. 2020).

desorption process completed within 15–30 min. In Fig 9, the Temperature Programming at 30–85 °C reflected desorption process from rich to lean loading regions (Shi et al., 2017), providing inadequate heat input into the system. The HCO₃⁻ was released first at rich loading and

then carbamate breakdown followed at lean loading, since bicarbonate is much easier to regenerate than carbamate (Shi et al., 2014). The nCO₂ of 0.5+2+2 was bigger than that of 0.3+2+2 mol/L with the aid of catalysts at 30–85 °C, resulting smaller H at lower temperature.

Table 4

The desorption factors of tri-solvent of MEA+BEA+DEEA solvents with various catalysts under temperature programming. (30–85 °C).

MEA+BEA+DEEA	Desorption Factor ($\times 10^{-3}$ mol CO ₂) ³ /L ² kJ min								
(mol/L)	30 min	HND-8	H-M	60 min	HND-8	H-M	75 min	HND-8	H-M
0.3+2+2	blank	0.1419	0.0751	blank	0.0848	0.0751	blank	0.0647	0.0595
0.5+2+2	0.1077	0.1974	0.0838	0.0764	0.0900	0.0838	0.0602	0.0637	0.0602

4.4. The optimized combination of tri-solvent of MEA+BEA+DEEA with catalysts

From Fig 10, the energy efficient combinations were investigated with relative heat duty and with MEA as benchmark. This work used temperature programming from 30 to 85 °C. Thus, the absolute heat duties (H) of MEA and tri-solvent were rather high, since limited nCO₂ was released out of the solvent at 30–60°C. With increased time period, the relative H decreased from 50~60 % to 45~50 %. At 30 and 60 min, the energy efficient combination was 0.5+2+2 with HND-8 at temperature programming.

Table 4 reflected the Desorption Factors, under temperature programmed among 30–85 °C. At 30 min, 0.5+2+2 with HND-8 was better than 0.3+2+2 HND-8, while at 60 and 75 min (85 °C), both cases were comparable, but 0.3+2+2 may be slightly better than 0.5+2+2 again. This effect was consistent with the results in Table 2, where 0.3+2+2 with HND-8 > 0.5+2+2 with HND-8 at 90 °C. Therefore, the energy efficient combination under TP was 0.5+2+2 with HND-8 since the first 30 min.

In summary, both 0.3+2+2 and 0.5+2+2 with HND-8 were energy efficient combinations concerning CO₂ desorption performance. For direct heating with excessive heat input at 90 °C, 0.3+2+2 was better than 0.5+2+2 with HND-8. For temperature programming heating with inadequate heat input, where most desorption was conducted at 30–85 °C, 0.5+2+2 was slightly better than 0.3+2+2 with HND-8 at 30 min, and be comparable at 60 and 75 min. Based on the results so far, both combinations were energy efficient solutions for CO₂ desorption in industrial pilot plants. The ultimate choice of the energy efficient solution requires comprehensive analysis of CO₂ absorption-desorption performance of 0.3+2+2 and 0.5+2+2 tri-solvents. The absorption parameters need to be tested with experiments in future to find out the ultimate optimized ratio.

5. Conclusions

This study investigated energy efficient combinations of tri-solvent MEA+BEA+DEEA at 0.1~0.5+2+2 mol/L with 5 commercial catalysts: blended γ -Al₂O₃/H-ZSM-5, H-beta, H-mordenite, HND-8, and HND-580. Experimental results screened out two energy efficient combinations of 0.3+2+2 and 0.5+2+2 mol/L with HND-8 and H-mordenite with very low heat duty. After detailed analysis, both 0.3+2+2 and 0.5+2+2 mol/L with HND-8 turned out to be superior to energy efficient combinations among the others.

- (1) The coordinative effect indicated 0.3+2+2 mol/L was the optimized blending ratio without catalyst and with γ -Al₂O₃/H-ZSM-5.
- (2) With 5 solid acid catalysts tested, the comparison of 0.3+2+2 mol/L with catalysts vs 0.5+2+2 mol/L with catalysts was distributed into different cases. This result was reasonable. The tri-solvent was highly energy efficient with minimized heat duty at the region close to optimized condition. The competition was strong and the difference was quite subtle.
- (3) Under temperature programming method with inadequate heat input, the energy efficient combo was 0.5+2+2 with HND-8 at 30–60 min (lower temperature region) and 0.3+2+2 and 0.5+2+2 with HND-8 after 60 min (higher temperature region).

Both combinations were applicable in an industrial pilot plant, and extra experiments of CO₂ absorption were required to find out the better one.

Nomenclature

C _{A,L}	concentration of solute A in the bulk liquid (k mol/m ³) (mol/L)
H	Heat duty
P	Total system pressure (kPa)
Q _{input}	Heat input
Greek Symbols	
α	CO ₂ loading (mol CO ₂ /mol amine)
α_{eq}	CO ₂ loading of solution in equilibrium with PCO ₂
Abbreviation	
AMP	2-amino-2-methyl-1-propanol
BEA	Butylethanol amine
DEA	Diethanol amine
DEEA	N, N-diethylethanolamine
MEA	monoethanol amine

CRediT authorship contribution statement

Huancong Shi: Conceptualization, Writing – original draft. **Jia-cheng Peng:** . **Xiaofang Cheng:** . **Xuan Yang:** Validation, Data curation. **Jing Jin:** . **Jiawei Hu:** Writing – review & editing, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.ijggc.2022.103647](https://doi.org/10.1016/j.ijggc.2022.103647).

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