

Article

Evaluating CO₂ Desorption Activity of Tri-Solvent MEA + EAE + AMP with Various Commercial Solid Acid Catalysts

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Abstract: The Paris Agreement and one of its goals, “carbon neutrality,” require intensive studies on CO₂ absorption and desorption processes. When searching for ways of reducing the huge energy cost of CO₂ desorption in the amine scrubbing process, the combination of blended amine with solid acid catalysts turned out to be a powerful solution in need of further investigation. In this study, the tri-solvent MEA (monoethanolamine) + EAE(2-(ethylamino)ethanol) + AMP(2-amino-2-methyl-1-propanol) was prepared at: 0.2 + 2 + 2, 0.5 + 2 + 2, 0.3 + 1.5 + 2.5 and 0.2 + 1 + 3 mol/L. The heterogeneous catalytic CO₂ desorptions were tested with five commercial catalysts: blended γ-Al₂O₃/H-ZSM-5, H-beta, H-mordenite, HND-8 and HND-580. Desorption experiments were conducted via a recirculation process with direct heating at 363 K or using temperature programming method having a range of 303–363 K. Then, the average CO₂ desorption rate, heat duty and desorption factors were studied. After comparison, the order of CO₂ desorption performance was found to be HND-8 > HND-580 > H-mordenite > Hβ > blended γ-Al₂O₃/H-ZSM-5 > no catalyst. Among the other combinations, the 0.2 + 1 + 3 mol/L MEA + EAE + AMP with HND-8 had a minimized heat duty (HD) of 589.3 kJ/mol CO₂ and the biggest desorption factor (DF) of 0.0277 × (10⁻³ mol CO₂)³/L² kJ min. This study provided a kind of tri-solvent with catalysts as an energy-efficient solution for CO₂ absorption and desorption in industrial CO₂ capture pilot plants.

Keywords: catalytic CO₂ desorption; carbamate stability; tri-solvent; coordinative effect



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1. Introduction

Effective CO₂ capture, utilization and storage (CCUS) technology is potentially applicable in industry to reach the goals of “Carbon Peak by 2030” and “Carbon Neutrality by 2060”. As an integral part of CCUS technology, post-combustion carbon capture (PCCC) technology is widely applied in power plants, cement plants, etc., to mitigate CO₂ emissions [1–9]. The huge energy costs of CO₂ desorption in carbon capture, accounting for 70% of the overall costs, are a major challenge for PCCC technology [10–14]. This drawback inhibits the implication of PCCC technology, which is of the utmost importance to tackle, since energy-efficient methods are expected to be possible solutions. For decades, several methods have proven to be effective, including solvent improvement, process intensification [1] and heterogeneous catalysis [14].

For solvent improvement, a massive number of studies reported amine blends, mostly bi-blends and some tri-blends. The bi-blends were studied intensively for decades, and we reported 5–6 branches in 2021. The tri-blends of amine A + B + C just started to draw attention in 2016 [15–25]. Most tri-solvents were prepared with combinations of primary

amines or secondary amines and tertiary amines or stereo hindered amines. They had the advantages of enhancing amine solutions' adsorption-desorption performances, fast absorption rates, lower heat duty, the ability to compensate for defects under different operation conditions, and providing a wide operation range of ($\alpha_{\text{lean}}-\alpha_{\text{rich}}$) and cyclic capacity [26]. However, the methodology of preparing amine tri-blends A + B + C at different ratios was much more complicated than that of bi-blends A + B. For a tri-solvent system, primary amine selected as amine A was usually MEA to enhance CO₂ absorption performance. MEA (monoethanol amine) was a commonly used amine, and 5.0 M MEA solvent was the benchmark for CO₂ capture tests in the field. A tertiary amine or stereo hindered amine, such as MDEA, DEEA or AMP, was selected as amine C to enhance CO₂ desorption performance. AMP is a strictly hindered amine which has very good CO₂ desorption performance because of its low carbamate stability. AMP has been widely used in amine blends because of its high desorption factor [26]. Amine B, as a CO₂ converter—A proton acceptor for absorption–desorption—Can be a secondary amine with moderate absorption or desorption abilities to enhance the cyclic capacity. EAE was considered a good candidate for a secondary amine, due to its higher activity of CO₂ absorption and higher pKa. Its desorption is worse than that of DEA because of its stronger carbamate stability. The intrinsic reactions within tri-solvent are complicated, and the sophisticated mechanism results in tri-solvents' overall absorption–desorption performance being better than that of individual amines added together. Thus, tri-solvents are quite attractive.

Table 1 lists a brief literature review, showing several tri-solvents published since 2016, mostly MEA + MDEA + PZ, MEA + AMP + PZ, MEA + BEA + AMP and the recently MEA + EAE + AMP. [15–25]. The tri-solvent MEA + EAE + AMP was published by the author's research group recently [25]. MEA is an activator to enhance CO₂ absorption, whereas AMP was selected to reduce energy costs of desorption. EAE, as a secondary amine, was used to lift the operation region of α_{lean} to α_{rich} and facilitate absorption. However, that study did not involve any catalyst, and the amine concentration was fixed at 2.0 mol/L for EAE and AMP, with a narrow range of MEA concentrations [25]. The tri-solvent MEA + EAE + AMP was far superior according to analysis at various concentrations. The possible improvements in CO₂ desorption brought about by catalysts aroused the authors' strong interests.

Table 1. Studies of various tri-solvents since 2016 [15–25].

Tri-Solvent	Concentration Range	Reference
MEA + MDEA + PZ	3 + 1.5–2.5 + 0.5–1.5 mol/L	[19]
MEA + MDEA + PZ	3 + 2.5 + 0.5 mol/L	[22]
MEA + AMP + PZ	3 + 1.5–2.5 + 0.5–1.5 mol/L	[21]
AMP + PZ + MEA	1.5–2.5 + 0.5–1.5 + 3 mol/L	[15]
AMP + PZ + MEA	1.5–2.5 + 0.5–1.5 + 3 mol/L	[16]
AMP + PZ + MEA	2 + 1 + 2 mol/L	[18,20]
MEA + BEA + AMP	0.1–0.5 + 2 + 2 mol/L	[23,24]
MEA + BEA + DEEA	0.1–0.5 + 2 + 2 mol/L	Accepted in IJGGC
MEA + EAE + AMP	0.1–0.5 + 2 + 2 mol/L	[25]
MEA + EAE + AMP	0.1–0.5 + 1–2 + 2–3 mol/L	This study

Besides tri-solvents, studies since 2010 have shown that heterogeneously catalytic CO₂ desorption is another energy efficient approach to promoting amine regeneration [16]. Solid acid catalysts generally act as both Lewis acids and Brønsted acids. The Lewis acid, with active sites on its surface, reduces the activation energy needed for carbamate breakdown and N–C bond cleavage, and the Brønsted acid provides protons in the basic amine solution to facilitate proton transfer [27,28]. A recent review reported the catalytic CO₂ desorption of MEA solvent with various types of solid acid catalysts, such as H-ZSM-5 [27,28], H β , H-mordenite, MCM-41 [29] and, SO₄²⁻/ZrO₂⁻ supports [12–14,21,22,30–37]. That review focused on heterogeneous catalysis, the physical and chemical texture of the

catalysts, structure–activity correlations and mechanisms [16]. The detailed mechanism was listed in Section 2.1. Based on analyses, the solid acid catalysts were verified to be highly energy efficient. They could significantly reduce the heat duty and decrease the desorption temperature down to 95–98 °C, below the boiling point. Therefore, the latent heat Q_{vap} of steam was negligible, and heat duty was reduced.

Therefore, the combination of “tri-solvent” and heterogeneous catalysts turned out to be a fresh and intriguing research area. With the combination of an improved solvent and heterogeneous catalysts at an optimized ratio, the overall heat duty can be minimized, and the operation temperature of the CO₂ desorber can be decreased down to 80–85 °C. This combination is highly energy efficient and applicable in industrial amine scrubbing. The above-mentioned literature indicates that there have been quite a limited number of studies on “tri-solvent + catalysts” [21,22,24], such as MEA + AMP + PZ [21], MEA + MDEA + PZ [22] and MEA + BEA + AMP [23,24]. Previous studies from the authors’ group have preliminarily revealed several highly energy efficient combinations of tri-solvents with catalysts, which cost only 33–35% as much as 5.0 M MEA—a benchmark [24].

This study introduces the tri-solvent MEA + EAE + AMP with five commercial solid acid catalysts, the combinations of which are highly energy efficient in CO₂ desorption. Compared to MEA + BEA + AMP, EAE was selected to replace BEA. EAE was involved due to its fast absorption rate, which is much better than that of DEA, and larger range of operation tolerance (0.35–0.70 mol/mol) [26,38–45]. However, the lower carbamate stability of EAE is a disadvantage for CO₂ desorption. Therefore, to reduce overall heat duty, we blended EAE with AMP, which is widely blended with various amines to enhance desorption performance [46–54]. The non-catalytic CO₂ absorption and desorption with MEA + EAE + AMP at 0.1–0.5+2+2 mol/L was published recently, revealing the potential of this new tri-solvent [25]. However, this study focused on catalytic CO₂ desorption with MEA + EAE + AMP at different concentrations.

In this study, CO₂ desorption experiments were conducted with tri-solvent MEA + EAE + AMP at amine concentrations of 0.2 + 2 + 2, 0.5 + 2 + 2, 3 + 1.5 + 2.5 and 0.2 + 1 + 3 mol/L with five solid acid catalysts: blended γ-Al₂O₃/H-ZSM-5, H-β, H-mordenite, HND-8 and HND-580. The CO₂ desorption profiles, average desorption rates (AD), heat duties (HD) and desorption factors (DF) were investigated systematically, in detail. The heat duty was the most important index for evaluating the energy costs of various solvent + catalyst combinations, since HD accounts for 70% of the energy costs of carbon capture. The desorption factor (DF) is a comprehensive index that evaluates heat duty, desorption rate and cyclic capacity as an integral. This DF index analysis could avoid mis-selection of some extreme cases with very small heat duty but small cyclic capacity, which is not practical in industry. By focusing on the AD, HD and DF of different tri-solvents with combinations of individual amines varying in concentration under temperature programming, we aimed at finding out the combination of tri-solvent MEA + EAE + AMP with five commercial catalysts that provides the best desorption factor.

The novelties of this manuscript: (1) Testing the CO₂ desorption performance of a tri-solvent of “MEA + EAE + AMP” with four amine concentrations and five commercial solid acid catalysts. (2) The heat duty (HD) and desorption factor (DF) of the tri-solvent with catalysis were evaluated to compare various energy-efficient combinations at a consistent level. (3) One or two energy efficient-combinations were discovered and are highly suitable for the CO₂ desorption process in industrial applications.

2. Theory

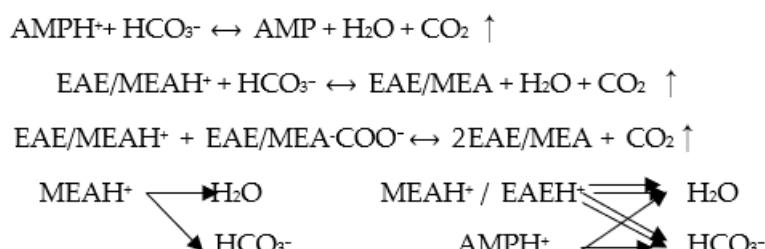
2.1. The Coordinative Effects within MEA vs. EAE

The “coordinative effect” was revealed to exist in MEA + RR'NH bi-blends, such as MEA + DEA [55] and MEA + BEA [56]; and MEA + BEA + AMP [23], MEA + EAE and MEA + EAE + AMP [57]. The heat duty of MEA + RR'NH bi-blends at a narrow but specific ratio is even lower than that of single secondary amines [55,56,58].

This performance seems to be contradictory to the widely acknowledged idea that MEA effectively enhances CO₂ absorption but deteriorates desorption performance in amine blends [26]. After our detailed analysis, we found the above to be maintained by 95% of cases; a narrow but specific range of blending ratios make up the other 5% of cases [23]. The optimized ratio containing the coordinative effect was 0.2/2 for MEA/EAE at CO₂ absorption, whereas it was 0.4/2 for CO₂ desorption [25]. For MEA + EAE + AMP tri-solvents, the optimized ratio containing the coordinative effect of MEA/EAE was consistent as 02/2 for both absorption and desorption. At those specific ratios, the heat duty with the MEA blend was even lower than that of EAE or EAE + AMP alone. The intrinsic principle of the coordinative effect was published and explained repeatedly: introducing 0.1–0.5 mol/L of MEA (a small amount) increased the heat input (Q_{input}) about 5–10%, and it enhanced CO₂ production to 10–20%. This simultaneous increase both Q_{input} and nCO₂ resulted in the reduction of heat duty (HD = $Q_{\text{input}}/\text{nCO}_2$) down to 5–10%. [58]. The principle of heat duty reduction provides two options: (1) reduce Q_{input} directly, as is common; (2) enhance Q_{input} and nCO₂ simultaneously under a specific ratio [58]. The detailed mechanism was published repeatedly, to indicate extra nCO₂ production with blending of MEA [23,55,56,59–61].

2.2. The Mechanism of Catalytic CO₂ Desorption

The reaction schemes of MEA-CO₂ and EAE-CO₂ are the same, as listed in Scheme 1. The carbamate is the main product of CO₂-amine for MEA (primary amine) and EAE (secondary amine). The reaction of AMP-CO₂ produces unstable carbamate, which converts to bicarbonate finally. Based on Scheme 1, the possible reactions of proton transfer from AmineH⁺ to Lewis Base increase from two to six, tripling; there are four more low energy pathways than for MEA.



Scheme 1. The reaction pathways of CO₂ desorption for MEA/RR'NH and R₃N [22].

A recent review (2020) categorized several similar catalytic CO₂ desorption mechanisms [16] with similar diagrams, which involved several consecutive key steps, such as (1) “carbamate formation”, (2) “carry protons”, (3) “chemical adsorption”, (4) “isomerization”, (5) “stretching”, (6) “C–N bond cleavage/breaking” and (7) “desorption/separation” [16]. This mechanism was proposed by the author first in 2011, involving three steps: heterogeneous adsorption, surface reaction and heterogeneous desorption [62]. The mechanism was plotted in Figure S1 in Supplementary Materials. With solid acid catalysts introduced into the amine solvent or packed in a desorber, the carbamate breakdown and CO₂ desorption can proceed under 80–95 °C, which is below the boiling point of water. Therefore, the heat duty (HD) is reduced with negligible latent heat of steam, H = Q_{reac} + Q_{sensi} [63].

2.3. The Average Desorption Rate, Heat Duty and Desorption Factor of CO₂ Desorption

The CO₂ desorption was too fast to analyze accurately, so the average desorption rates were calculated with Equation (1). The heat duty (HD) was calculated with Equation (2) below, which is the most important parameter of evaluating CO₂ desorption performance. The heat input (Q_{input}) was evaluated with an electrometer (E), and CO₂ production (nCO₂) was estimated with $(\alpha_{\text{rich}} - \alpha_{\text{lean}}) \times C \times V$ at different time periods. The absolute heat duty (HD) was not indicative, since different studies adopted different operation conditions

(C, V, T, Q_{loss}, etc.), so the H is not comparable. The relative heat duty (RH) was calculated by Equation (3), with H_{baseline} for various benchmarks. The RH can help to find the most energy efficient combinations.

$$\text{Average desorption rate} = \frac{n\text{CO}_2}{\text{time}} \quad (1)$$

$$\text{HD} = \frac{\text{Heat input/time}}{n\text{CO}_2/\text{time}} = \frac{\text{Electricity(kJ)}}{n\text{CO}_2(\text{mol})} \quad (2)$$

$$\text{RH} = \frac{H_i}{H_{\text{baseline}}} \times 100\% \quad (3)$$

Recently, the CO₂ desorption was evaluated comprehensively with a desorption factor [22]. The average desorption rates, cyclic capacity and heat duty were calculated for desorption factor with Equation (5) [32,33]. Cyclic capacity was calculated from α_{rich} / α_{eq} to α_{lean} along different time periods and the results were included into the desorption factor as an integral.

$$\text{Cyclic Capacity} = (\alpha_{\text{rich}} - \alpha_{\text{lean}}) \times C_A \quad (4)$$

$$\text{Desorption Factor} = \frac{\text{Average Desorption Rate} \times \text{Cyclic Capacity}}{\text{Heat Duty}} \quad (5)$$

3. Results and Discussion

This study involved CO₂ desorption tests of the following three sets of tri-solvents for various purposes: (1) MEA + EAE + AMP (0.1–0.5 + 2 + 2 mol/L) with blended γ-Al₂O₃/HZSM-5 catalysts with direct heating to find out suitable blending ratios. (2) MEA + EAE + AMP (0.2 + 2 + 2 and 0.5 + 2 + 2 mol/L) with five commercial catalysts with temperature programming to discover energy efficient combinations. (3) MEA+EAE+AMP (0.3 + 1.5 + 2.5 and 0.2 + 1 + 3 mol/L) at different EAE/AMP ratios with five commercial catalysts with temperature programming to find out other potential energy efficient combinations.

3.1. CO₂ Desorption of Tri-Solvents MEA + EAE + AMP with Blended γ-Al₂O₃/HZSM-5 Catalyst

Similarly to those studies [25,56], the CO₂ desorption tests were performed within tri-solvent of 0.1–0.5 + 2 + 2 mol/L MEA + EAE + AMP with blended γ-Al₂O₃/HZSM-5 catalysts. Existing reports have proved repeatedly that the efficiency ranking of catalysis was: blended γ-Al₂O₃/HZSM-5 in the ratio 2:1 > HZSM-5 > γ-Al₂O₃ [24]. The purpose of this part of the study was to discover the optimized blending ratio of tri-solvent within 0.1–0.5 + 2 + 2 mol/L with catalysts, and compared with the boundary conditions (0.5 + 2 + 2 mol/L) of tri-solvent with best catalysis.

The Catalytic CO₂ Desorption of MEA + EAE + AMP with Direct Heating

Figure 1a–e plots five CO₂ desorption profiles of tri-solvents MEA + EAE + AMP at 0.1–0.5 + 2 + 2 mol/mol with the blended solid acid catalyst γ-Al₂O₃/H-ZSM-5. For non-catalytic tests, the desorption period was consistently 150 min. In comparison, the catalytic desorption took 120–150 min, about 15–30 min shorter. The CO₂ loading decreased from equilibrium loading to α_{lean} of 0.35 mol/mol. After 150 min, the CO₂ loading could hardly further decrease under the desorption temperature of direct heating, and most of the lifecycle of CO₂ desorption was completed. For tri-solvents with the same amine concentration, the catalytic desorption curves are below those of their non-catalytic counterparts.

The average desorption rates at 15 and 30 min were plotted into bar graphs in Figure 2a,b. Higher average desorption rates were seen in catalytic tests compared with their non-catalytic counterparts. Figure 3a,b displays the heat duties of amine blends with catalysts. In Figure 3a, the trends are similar for both catalytic and non-catalytic cases. Absolute heat duty (HD) decreased first and reached the minimum value at 0.2 + 2 + 2 mol/L, and then increased in the range of 0.3–0.5 + 2 + 2 mol/L. In Figure 3a, the relative heat duty (%) of catalytic desorption vs. that of non-catalytic counterparts ranged from 71.3%

at $0.2 + 2 + 2 \text{ mol/L}$ to 92.4% at $0.3 + 2 + 2 \text{ mol/L}$; it was 85.3% at the boundary condition of $0.5 + 2 + 2 \text{ mol/L}$. With increased amine concentration, the catalysts started to work on MEA to desorb extra CO_2 , which made the H of $0.5 + 2 + 2 \text{ mol/L}$ lower than that of $0.3 + 2 + 2 \text{ mol/L}$. In Figure 3b, the relative heat duty (%) ranges from 83.6% at $0.2 + 2 + 2 \text{ mol/L}$ to 96.6% at $0.4 + 2 + 2 \text{ mol/L}$; it is 84.3% at the boundary condition of $0.5 + 2 + 2 \text{ mol/L}$. In both periods, the absolute heat duty reached the minimum value when the ratio was $0.2 + 2 + 2 \text{ mol/L}$ and catalysts were added; the maximum heat duty was reached when the ratio was $0.5 + 2 + 2 \text{ mol/L}$ and catalysts were excluded. In Figure 3, the difference in absolute HD between catalytic desorption and non-catalytic desorption at $0.2 + 2 + 2 \text{ mol/L}$ is -170 kJ at 15 min, and -127 kJ at 30 min. After thorough comparisons, Figures 1–3 verified repeatedly that solid acid catalysis could enhance CO_2 desorption, and $0.2 + 2 + 2 \text{ mol/L}$ MEA + EAE + AMP with catalyst was the best solution among the above-mentioned options [14].

The findings in Figures 1–3 can be summarized as this. The mixing ratio $0.2/2 \text{ mol/L}$ for MEA/EAE contributed to minimum heat duty. This result is consistent with findings from previous studies in tri-solvent MEA + EAE + AMP [57]. The coordinative effect mainly resulted from MEA and EAE, since MEA + R_3N and MEA + AMP contained negligible coordination [56]. In Figure 3b, the heat duty of catalytic CO_2 desorption is the lowest at $0.2 + 2 + 2 \text{ mol/L}$, and the boundary condition of $0.5 + 2 + 2 \text{ mol/L}$ is the second lowest value. This phenomenon was explicable, since the optimized blending ratio of $0.2/2$ with solid acid was slightly better than the biggest blending ratio $0.5/2$ with optimized catalysis. This result and academic explanation are similar to those of another test on MEA + BEA + DEEA + $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ [64]. The comparison of optimized ratio plus catalysts with boundary ratio plus optimized catalysis needs to be further studied case by case.

In order to compare different amine blends under a consistent level, the CO_2 desorption factors (DF) of five tri-solvents without and with $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ were categorized in Table 2. Table 1 shows that the optimized ratio of individual amines in tri-solvent with $\gamma\text{-Al}_2\text{O}_3/\text{HZSM-5}$ was $0.2 + 2 + 2 \text{ mol/L}$, due to its higher desorption rate and relatively lower heat duty among the rests. The desorption factor was mainly determined by heat duty, followed by the average desorption rate. The heat duties were different based on different desorption periods, so that the desorption factors were different. The heat duty of catalytic tri-solvent with the ratio of $0.2 + 2 + 2 \text{ mol/L}$ was the lowest of all sets, indicating its optimized DF.

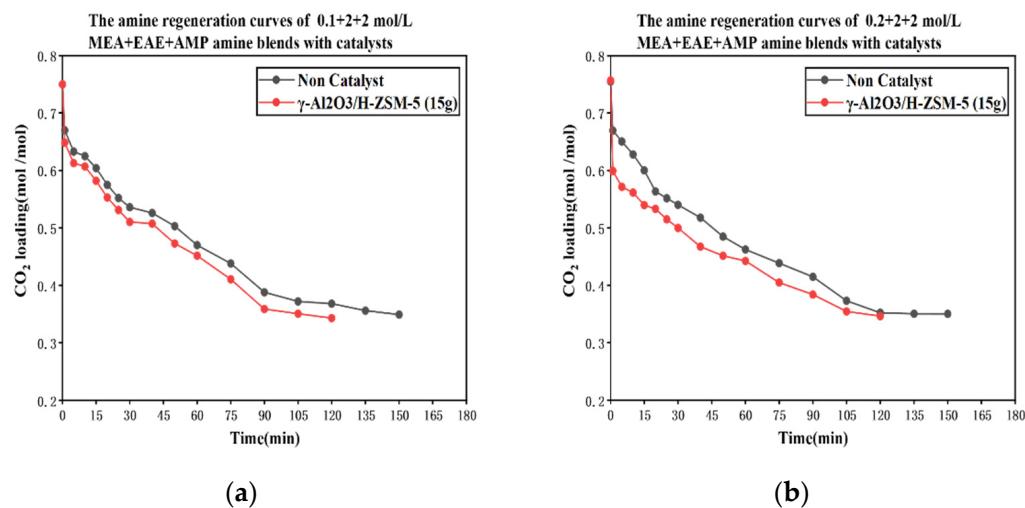


Figure 1. Cont.

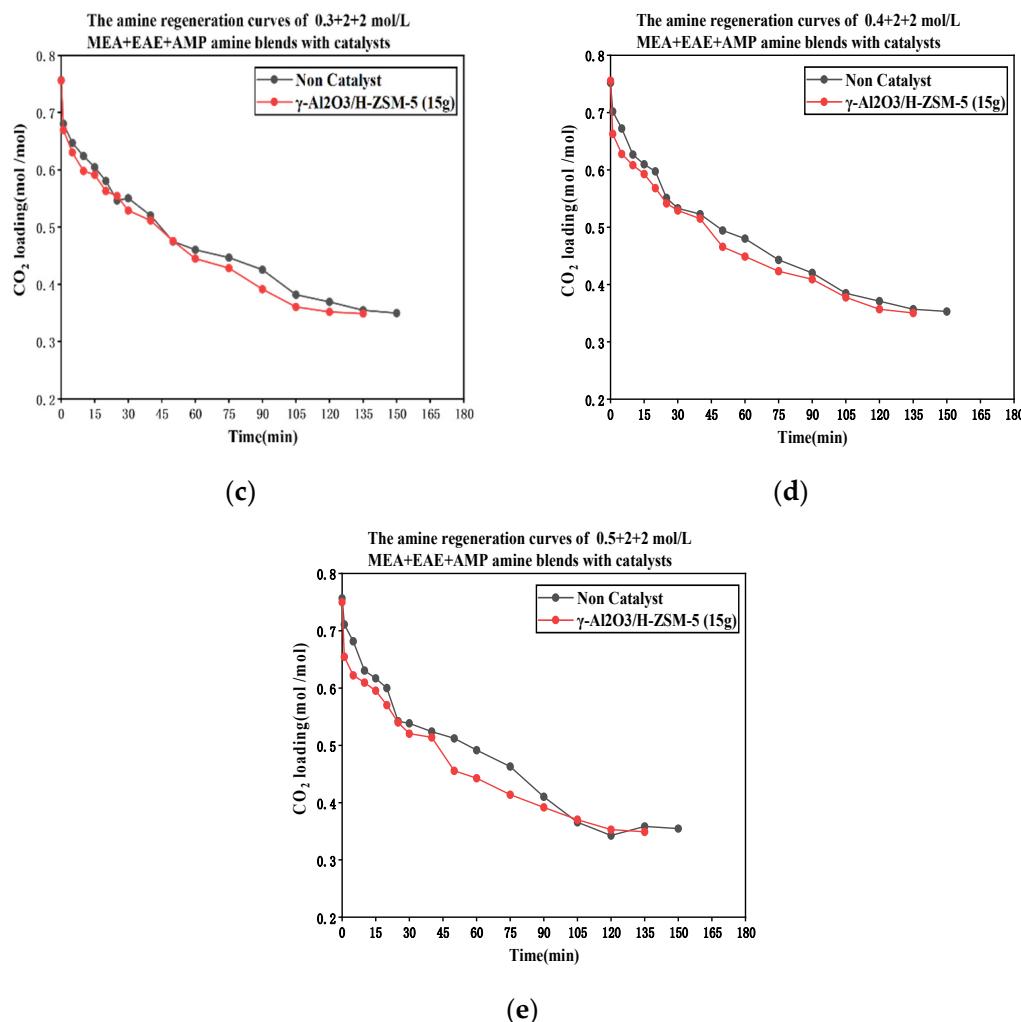


Figure 1. The CO₂ desorption profiles of MEA + EAE + AMP with catalysts within 0.1 + 2 + 2 mol/L–0.5 + 2 + 2 mol/L. (a) 0.1 + 2 + 2 mol/L, (b) 0.2 + 2 + 2 mol/L, (c) 0.3 + 2 + 2 mol/L, (d) 0.4 + 2 + 2 mol/L, (e) 0.5 + 2 + 2 mol/L.

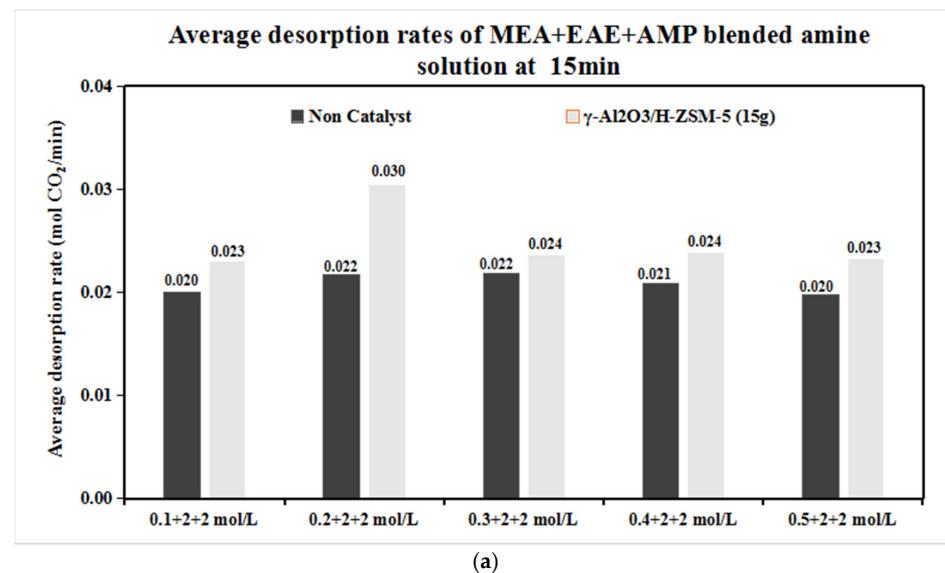


Figure 2. Cont.

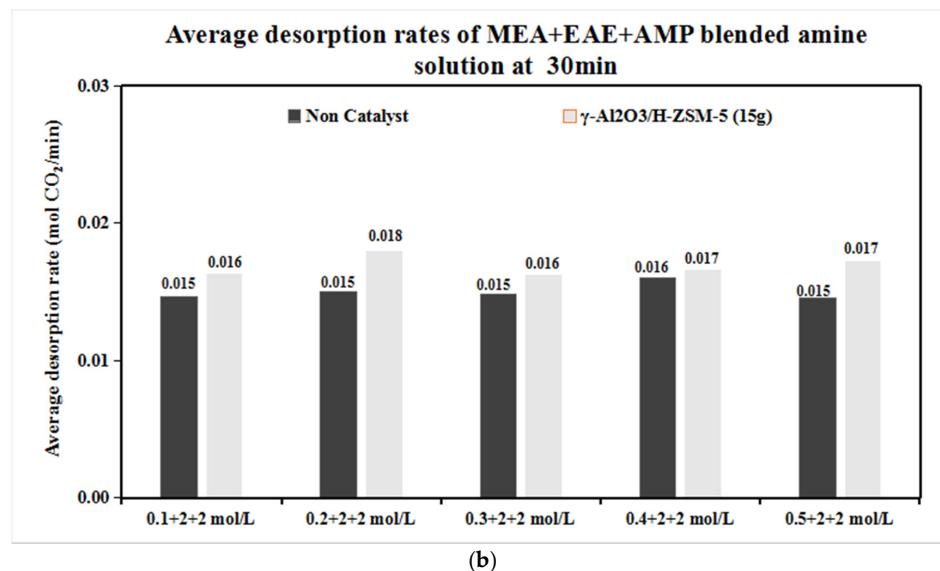


Figure 2. The average desorption rates of MEA + EAE + AMP at 0.1–0.5 + 2 + 2 mol/L with catalysts at (a) 15 min and (b) 30 min.

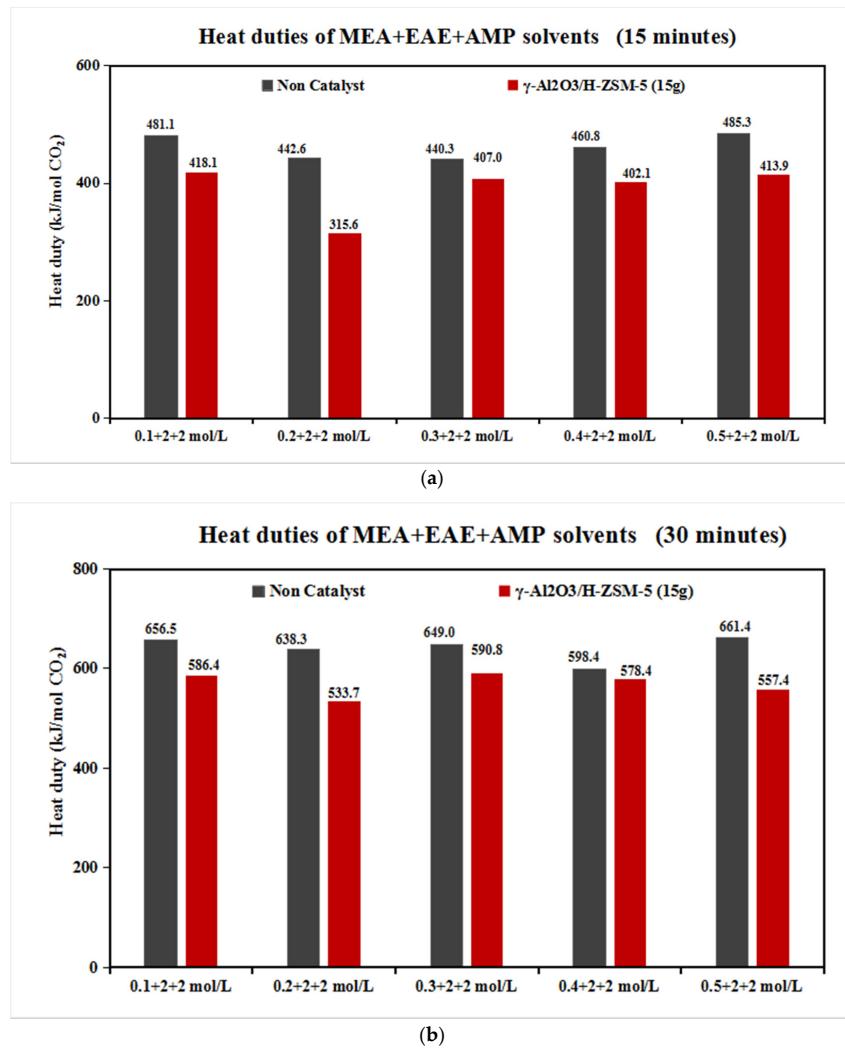


Figure 3. The heat duties of MEA + EAE + AMP at 0.1–0.5 + 2 + 2 mol/L with various catalysts: (a) 15 min, (b) 30 min.

Table 2. The desorption factors of tri-solvent of MEA + EAE + AMP solvents with various catalysts: 15 min and 30 min.

MEA + EAE + AMP	Desorption Factor (10^{-3} mol CO ₂) ³ /L ² kJ min			
	15 min		30 min	
(mol/L)	Blank	$\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ (15 g)	Blank	$\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ (15 g)
0.1 + 2 + 2	0.025	0.038	0.020	0.027
0.2 + 2 + 2	0.032	0.088	0.021	0.036
0.3 + 2 + 2	0.032	0.041	0.020	0.027
0.4 + 2 + 2	0.029	0.043	0.026	0.029
0.5 + 2 + 2	0.027	0.039	0.019	0.032

3.2. Catalytic CO₂ Desorption of Tri-Solvents with Temperature Programming

Only one type of catalyst, $\gamma\text{-Al}_2\text{O}_3/\text{HSM-5}$, was not adequate for this study. Four amine conditions were selected for further catalytic CO₂ desorption tests with the ratios of 0.2 + 2 + 2 and 0.5 + 2 + 2 again. Additionally, various EAE/AMP ratios of 0.3 + 1.5 + 2.5 and 0.2 + 1 + 3 mol/L were set, and five commercial solid acid catalysts were involved. It was necessary to investigate the four solid acid catalysts systematically.

3.2.1. The CO₂ Desorption of 0.2 + 2 + 2 and 0.5 + 2 + 2 mol/L Solvents with Five Catalysts

Recently, a new type of pilot plant using hot water as the heat source instead of steam was designed and developed for CO₂ capture [16]. Several publications reported steady-state operations with the aid of catalytic packing [65–68]. The new process used a heat exchanger, instead of a reboiler, to conduct heat transfer, with operation temperatures lower than 100 °C [69]. As long as the CO₂ desorption process was completed at 75–95 °C, the heat input Q_{input} could be greatly reduced. The heat duty will certainly decrease. Based on these publications, the similar temperature programming was adopted in this study [32,70–72].

Studies in this section were carried out in two tri-solvents with several commercial catalysts under temperature programming. Figure 4 reports CO₂ desorption curves with tri-solvent at two temperatures. It shows that massive CO₂ was released at 30–70 °C. The temperature topped 90 °C for 0.2 + 2 + 2 mol/L and 95 °C for 0.5 + 2 + 2 mol/L, which was mainly determined by α_{lean} of various tri-solvents. The TP reflected a desorption temperature scope of superior performance for tri-solvent MEA + EAE + AMP with catalysts [14]. This study confirmed that tri-solvent MEA + EAE + AMP could release CO₂ at a temperature as low as 90 °C, with operation temperature reaching 85–95 °C.

The average CO₂ desorption rates (AD) and heat duties (HD) were plotted into bar graphs in Figures 5 and 6. For 0.2 + 2 + 2 and 0.5 + 2 + 2 mol/L, the order of AD was the same: HND-8 > HND-580 > H-mordenite > H β > blended $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ > no catalyst; the order of HD was HND-8 < HND-580 < H-mordenite < H β < blended $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ < no catalyst at 30 and 60 min. The whole sets of 0.2 + 2 + 2 mol/L + catalysts also performed slightly better than 0.5 + 2 + 2 mol/L + catalysts. The higher rates and lower heat duty contributed to better desorption performance. After comparison, the heat duty of 0.2 + 2 + 2 mol/L with HND-8 was the optimized combination with minimized heat duty at 0.1–0.5 + 2 + 2 mol/L.

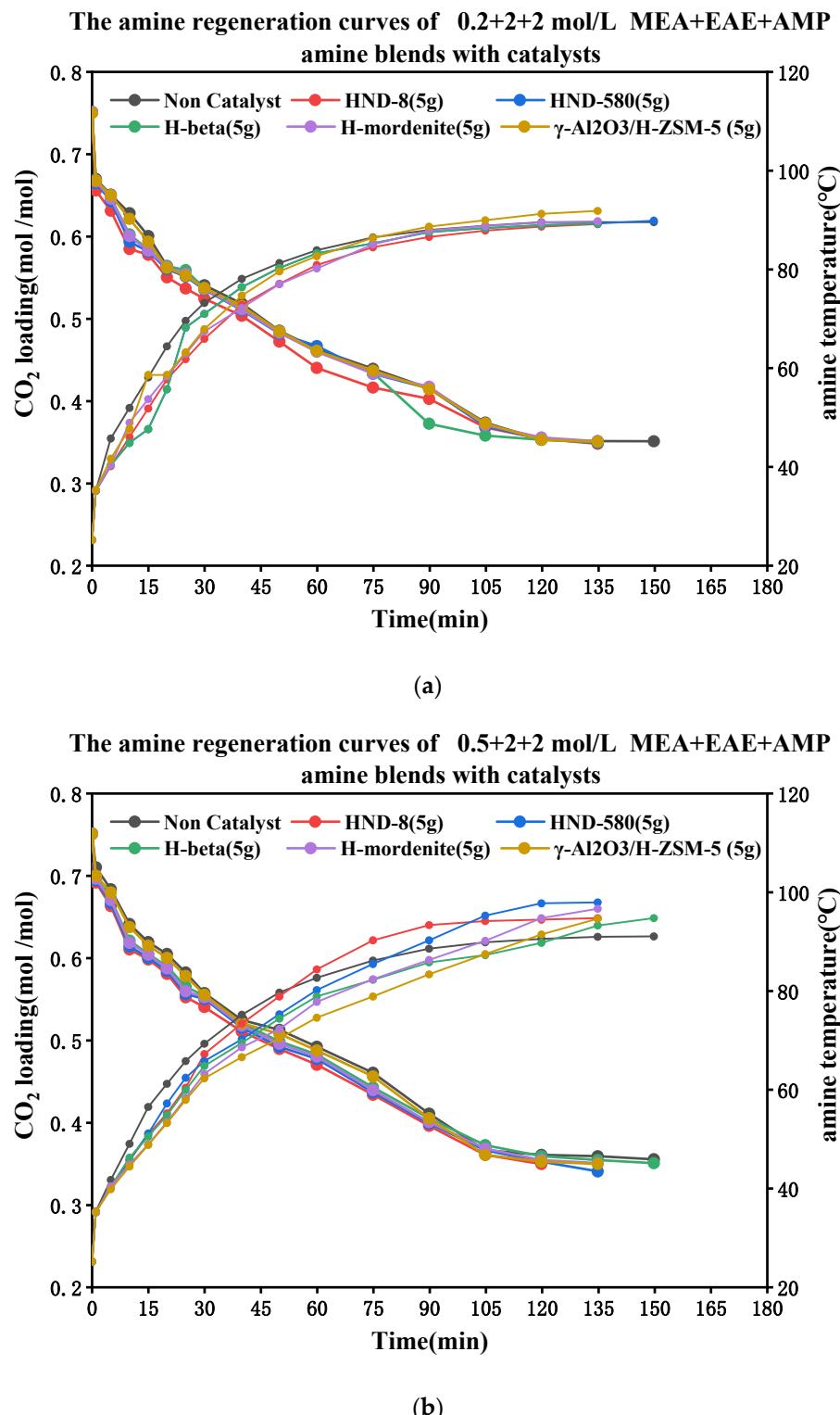


Figure 4. The CO₂ desorption profiles of MEA + EAE + AMP with catalysts at (a) 0.2 + 2 + 2 mol/L and (b) 0.5 + 2 + 2 mol/L.

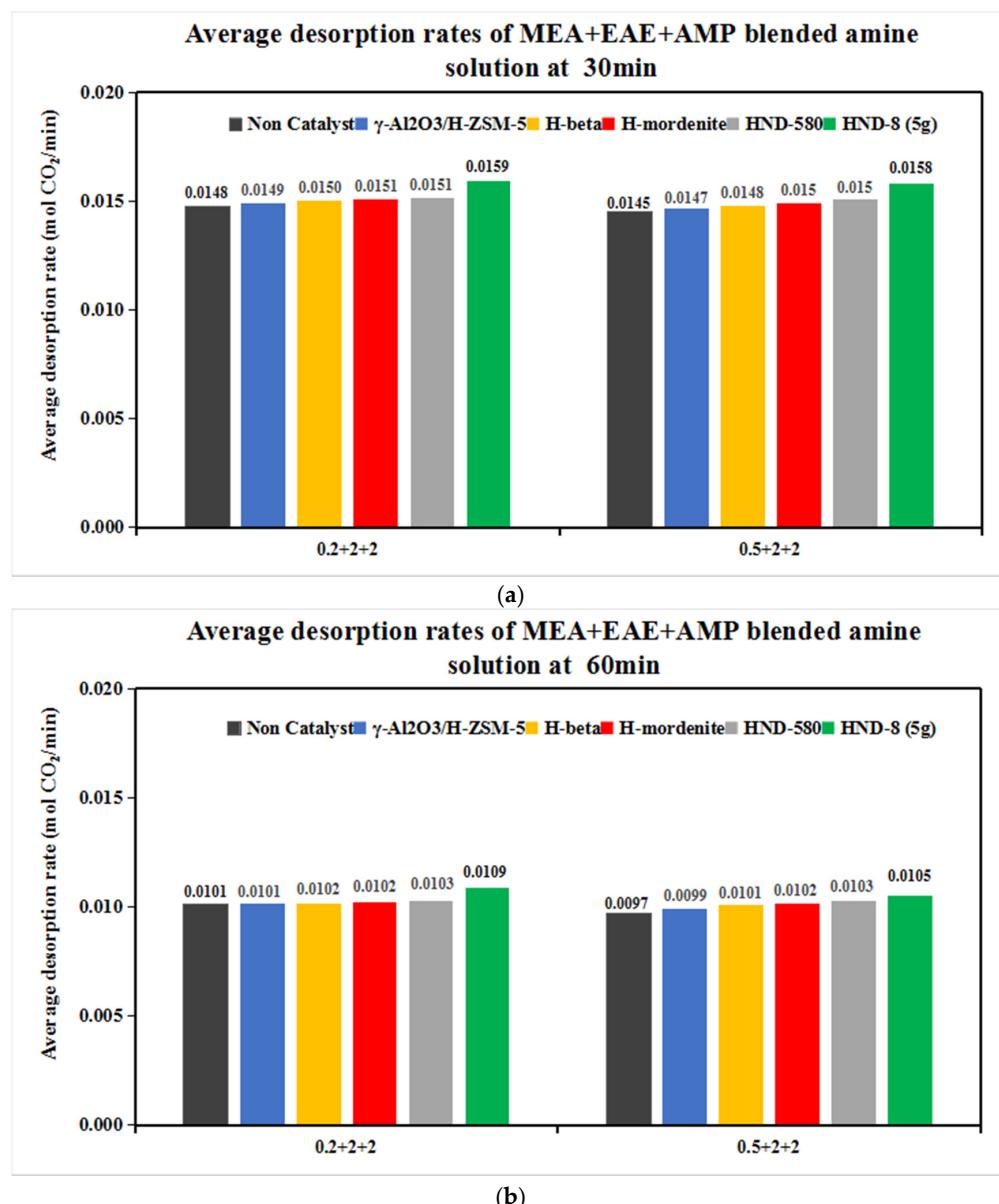


Figure 5. The average desorption rates of MEA + EAE + AMP with catalysts at (a) 30 min and (b) 60 min.

Comparing Figure 6 with Figure 3, the authors found that heat duty of TP in the non-catalytic process was higher than that in direct heating. This can be explained by the lesser amount of CO_2 desorption resulting from a lower temperature and inadequate heat input. In Figure 6, the heat duties of the first 30 min are around 200 kJ/mol CO_2 , smaller than those of the first 60 min. This effect resulted from the complex interaction of CO_2 released under the operation temperature range. With temperature programming from rich to lean loading regions, heat inputted into the system from unique operation process became inadequate. Firstly, there was more CO_2 released in the first 30 min than in the second 30 min, since HCO_3^- was released first at rich loading and then followed by its carbamate breakdown at lean loading. According to reaction enthalpy analyses, compared with carbamate, it is much easier for bicarbonate to convert CO_2 . On the other hand, the temperature range of the first 30 min was smaller than that of the second 30 min, which indicated weaker catalysis and reactivity of endothermic reaction. After calculating the exact amount of CO_2 released during the two periods, the first 30 min of TP reflected less

heat duty compared with the first 60 min. The large amount of bicarbonate conversion was dominant under inadequate heat input.

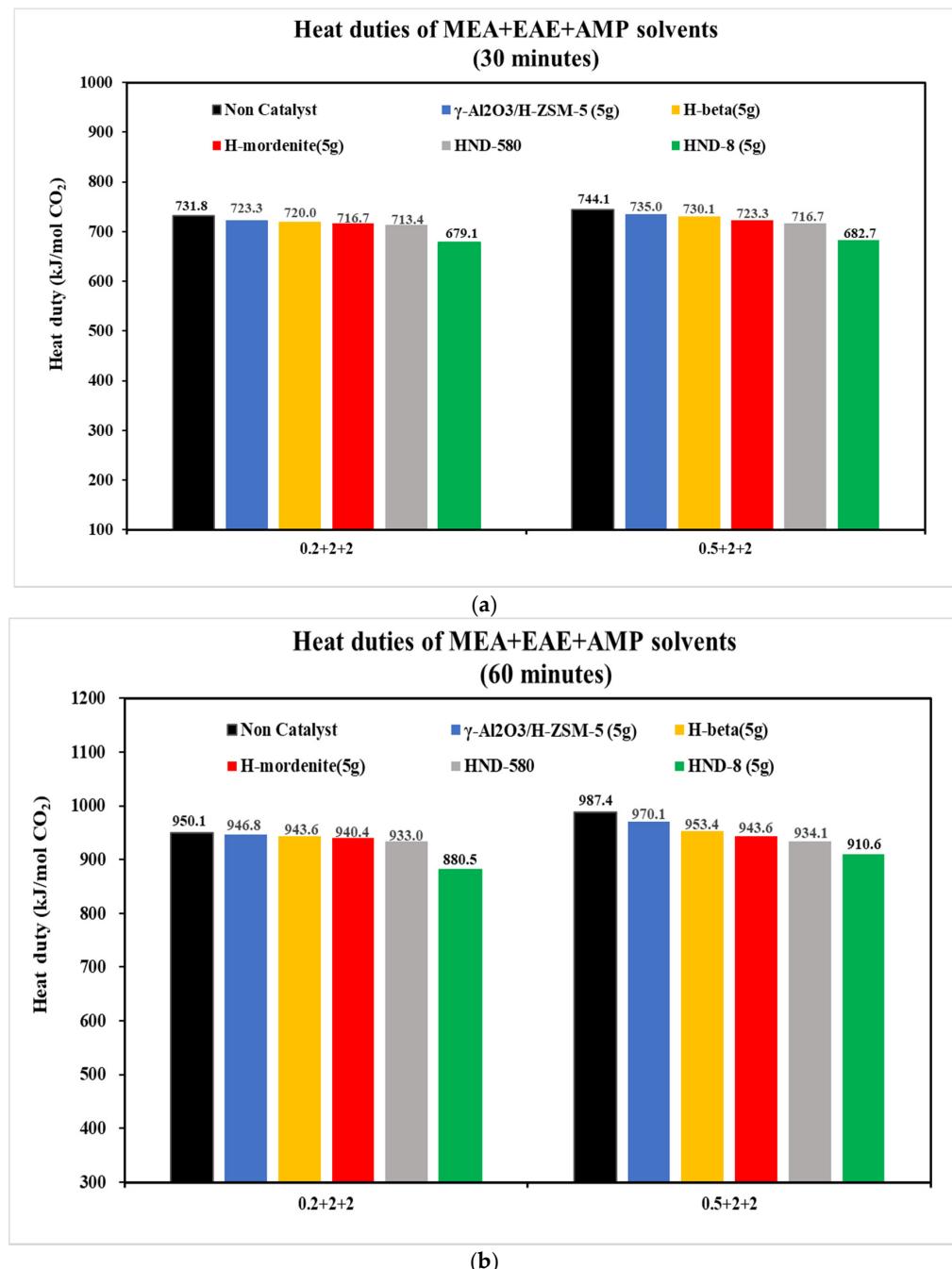


Figure 6. The heat duties of MEA + EAE + AMP with various catalysts at (a) 30 min and (b) 60 min.

The desorption factors of $0.2 + 2 + 2$ and $0.5 + 2 + 2$ mol/L were categorized in Table 3. Among five commercial catalysts, HND-8 was the best, and the factors of $0.2 + 2 + 2$ and $0.5 + 2 + 2$ mol/L were comparable with each other using the TP method. The desorption factor should take heat duty, average desorption rate and cyclic capacity into consideration. The HD of $0.5 + 2 + 2$ mol/L was slightly lower than that of $0.2 + 2 + 2$ mol/L, and the AD of $0.5 + 2 + 2$ mol/L was slightly higher than that of $0.2 + 2 + 2$ mol/L because of its slightly higher amine concentration with catalysts. After calculation, the desorption factors for the two cases were very close to each other. Both combinations were applicable for

an industrial desoerber, and CO₂ absorption tests were required to further determine the better one.

Table 3. The desorption factors of tri-solvent of MEA+EAE+AMP solvents at 0.2 + 2 + 2 and 0.5 + 2 + 2 mol/L with 5 g solid acid catalysts at 30 min.

MEA + EAE + AMP (mol/L)	Non Catalyst	Desorption Factor (10 ⁻³ mol CO ₂) ³ /L ² kJ min				
		γ-Al ₂ O ₃ /H-ZSM-5	H-Beta	H-Mordenite	HND-8	HND-580
0.2 + 2 + 2	0.0179	0.0185	0.0188	0.0190	0.0223	0.0193
0.5 + 2 + 2	0.0170	0.0176	0.0180	0.0185	0.0220	0.0190

3.2.2. The CO₂ Desorption of 0.3 + 1.5 + 2.5 and 0.2 + 1 + 3 mol/L Solvents with Catalysts

After the above-mentioned studies, two other combinations were selected and tested. The amine concentration for EAE + AMP was fixed at 4 mol/L again, but with different ratios of 1.5/2.5 and 1/3 instead. The different ratios of EAE/AMP resulted in various desorption performances, because AMP facilitated desorption, whereas EAE was good at absorption [25]. The AMP concentrations were increased to 2.5 and 3.0 mol/L to enhance the desorption performance, and the fixed concentrations of EAE + AMP were used to maintain the similar cyclic capacity, making them comparable towards 0.2 + 2 + 2 and 0.5 + 2 + 2 mol/L. Furthermore, the ratio of MEA/EAE was fixed at 1/5, which was the optimized value for coordinative effect in CO₂ desorption [25]

Figure 7 reflects the CO₂ desorption curves of 0.3 + 1.5 + 2.5 mol/L with five commercial catalysts under TP, and their average absorption rates are plotted in Figure 8. Their heat duties are plotted in Figure 9. Among five solid acid catalysts, HND-8 possessed the highest rates and lowest heat duty in general. The ranking of heat duty performance was: no catalysis > blended γ-Al₂O₃/H-ZSM-5 > H β > H-mordenite > HND-580 > HND-8. The lower, the better. The order was consistent with conclusions in the previous two cases.

The amine regeneration curves of 0.3+1.5+2.5 mol/L MEA+EAE+AMP amine blends with catalysts

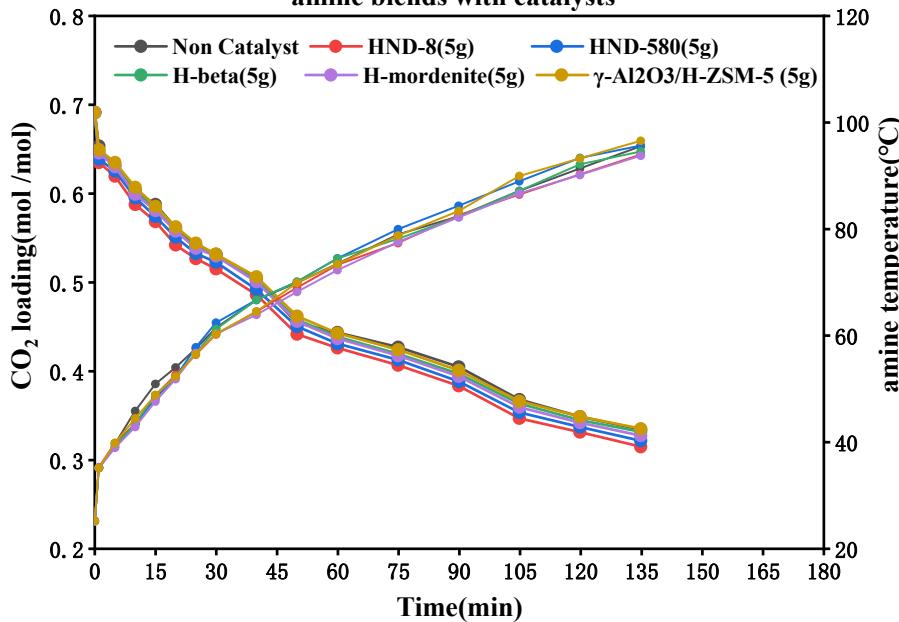


Figure 7. The CO₂ desorption profiles of MEA + EAE + AMP at 0.3 + 1.5 + 2.5 mol/L with catalysts of 0.3 + 1.5 + 2.5 mol/L.

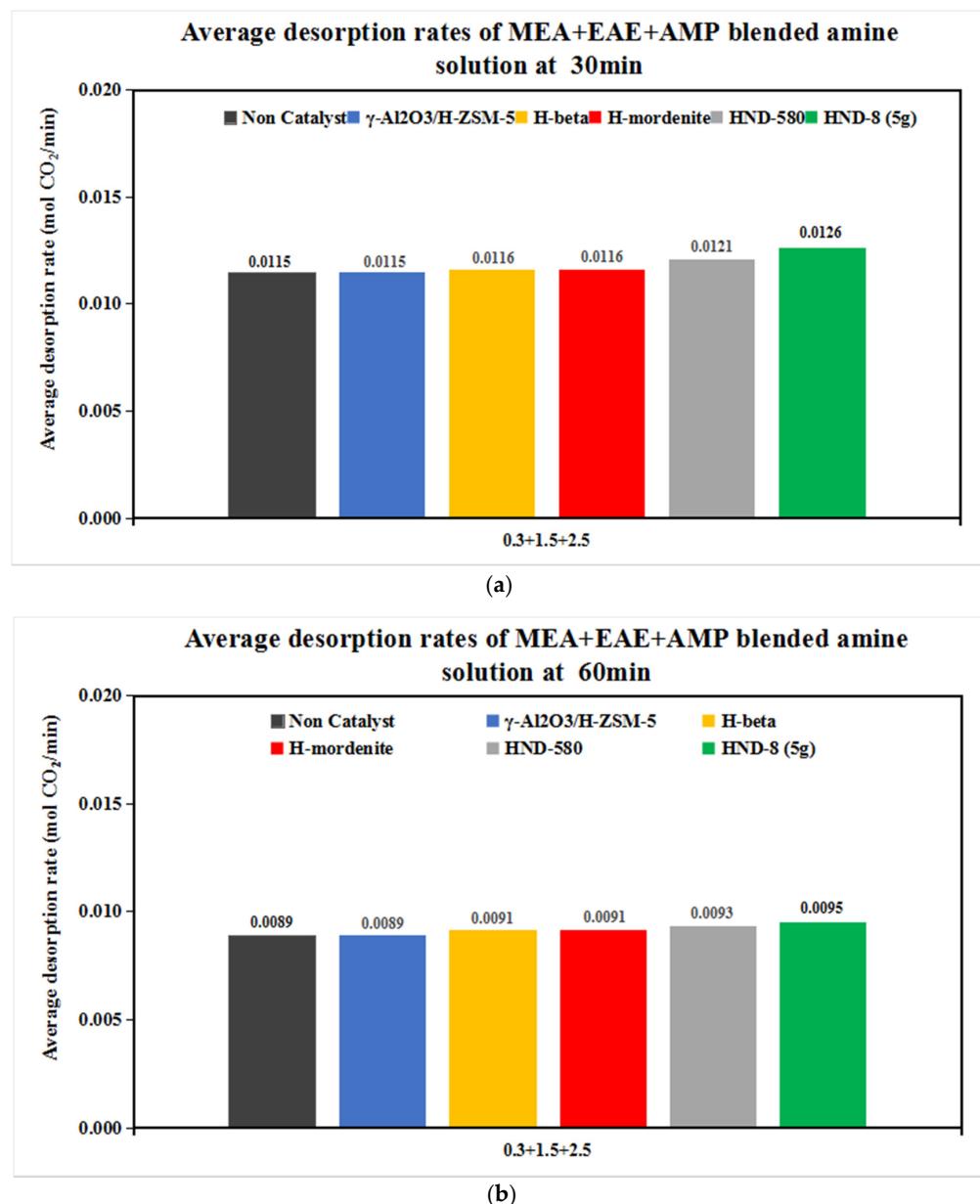


Figure 8. The average desorption rates of MEA + EAE + AMP at 0.3 + 1.5 + 2.5 mol/L with catalysts at (a) 30 min, (b) 60 min.

The absolute value of heat duty of 0.3 + 1.5 + 2.5 mol/L was slightly higher than that of 0.2 + 2 + 2 mol/L. The ratio of 1.5/2.5 for EAE/AMP produced worse performance than that of 2/2 with the temperature programming method. This seems to be contradictory to the better desorption, and less heat duty was achieved through higher ratio of AMP/EAE. However, it can still be explained by comparing Figures 4a and 7 carefully. The main reason turned out to be its operation temperatures. The operation temperature at the first 30 min only reached 60 °C at 0.3 + 1.5 + 2.5 mol/L, and it reached 70 °C at 0.2 + 2 + 2 mol/L. Lower temperature resulted in weaker catalysis and less CO₂ desorption, giving rise to higher heat duty. The intrinsic reasons await further analyses.

Finally, the tri-solvent of 0.2 + 1 + 3 mol/L was tested, and the ratio of EAE/AMP was reduced to 1/3 to make full use of AMP's advantages in CO₂ desorption. The concentration of MEA + EAE was narrowed down to 1.2 mol/L in total. Figure 10 reports the CO₂ desorption profile. Figure 11 reports the average desorption rates. Additionally, Figure 12 reports heat duties. Figure 10 indicates that the operation region of α_{lean} to α_{rich} could

achieve 0.25–0.70 mol/mol, which is a relatively wide range that is suitable for industrial applications. The temperature reached 70 °C at 30 min and 78–85 °C at 60 min, which are comparable to those of 0.2 + 2 + 2 in Figure 4a.

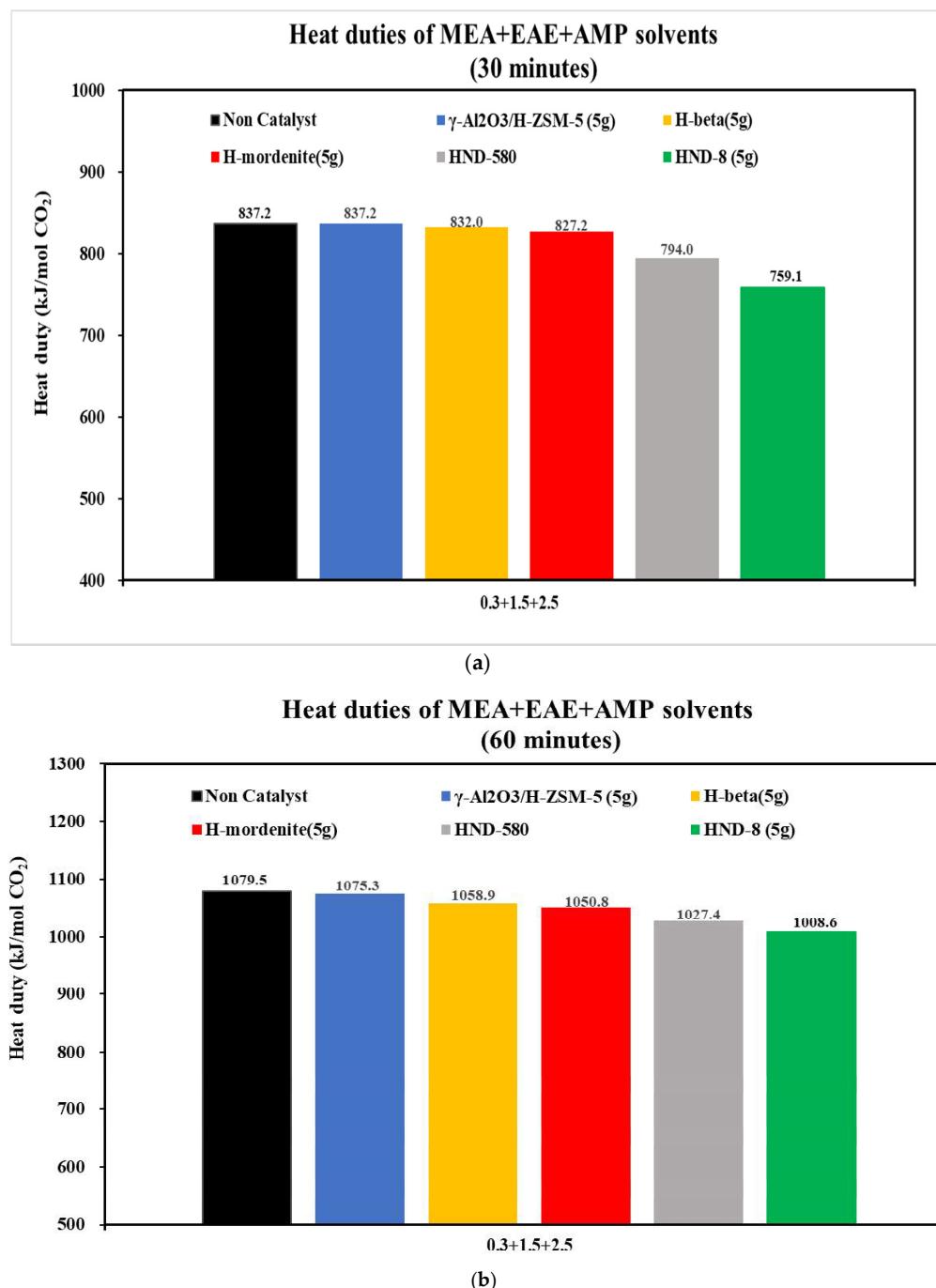


Figure 9. The heat duties of MEA + EAE + AMP at 0.3 + 1.5 + 2.5 mol/L with various catalysts at (a) 30 min, (b) 60 min.

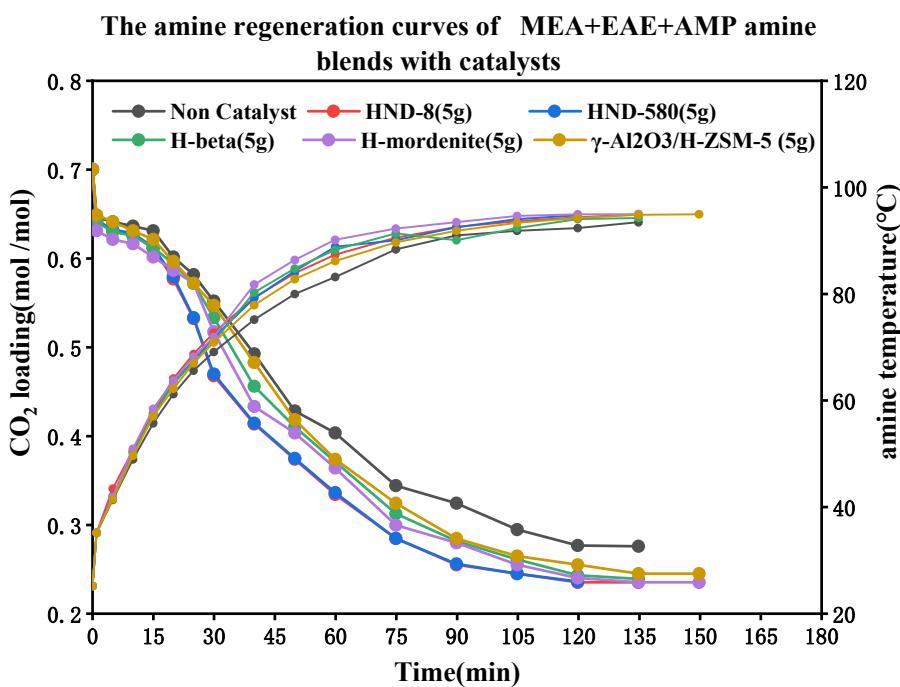


Figure 10. The CO₂ desorption profiles of MEA + EAE + AMP at 0.2 + 1 + 3 mol/L with catalysts.

Figures 11 and 12 reflected the ranking of heat duty as follows: blank > blended γ-Al₂O₃/H-ZSM-5 > H_β > H-mordenite > HND-580 > HND-8. The smaller, the better. This outcome was not only similar to those in the other three cases, but also accorded with previous studies in tri-solvent MEA + BEA + DEEA [64]. The heat duty of HND-8 was the lowest among the five types of solid acid catalysts.

Compared Figure 12 with Figure 6, the heat duty of 0.2 + 1 + 3 mol/L was less than that of 0.2 + 2 + 2 mol/L at both 30 and 60 min. The HD was 589.3 kJ/mol CO₂ at 30 min and 748.1 kJ/mol CO₂ at 60 min, which were the minimum values among the five sets of tri-solvents. Under comparable operation temperatures, the larger AMP/EAE ratio reflected less energy costs of desorption and lower heat duty.

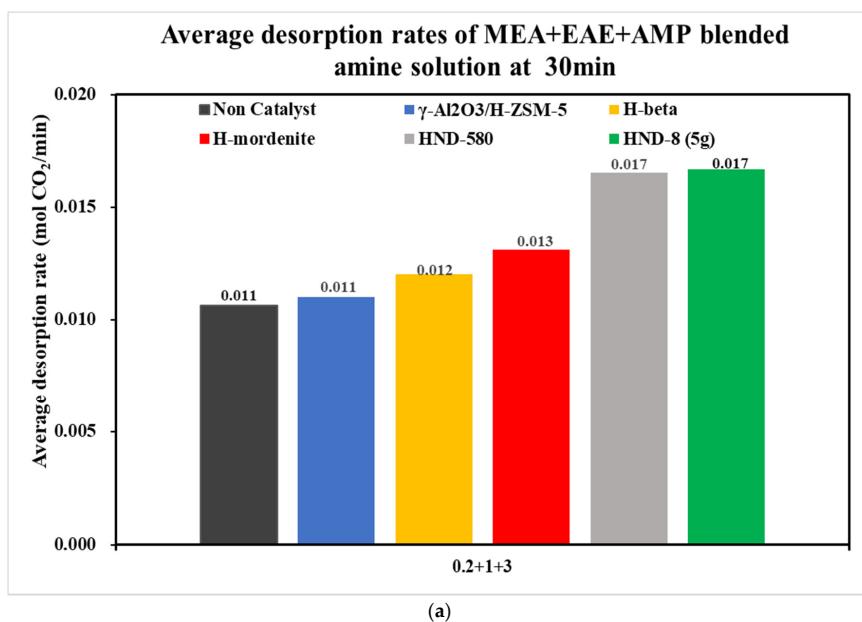


Figure 11. Cont.

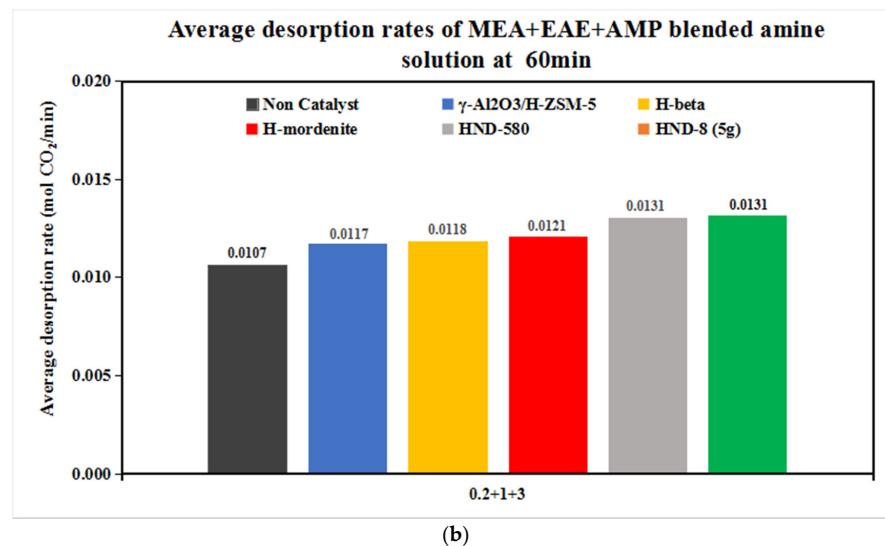


Figure 11. The average desorption rates of MEA + EAE + AMP at 0.2 + 1 + 3 mol/L with catalysts at (a) 30 min and (b) 60 min.

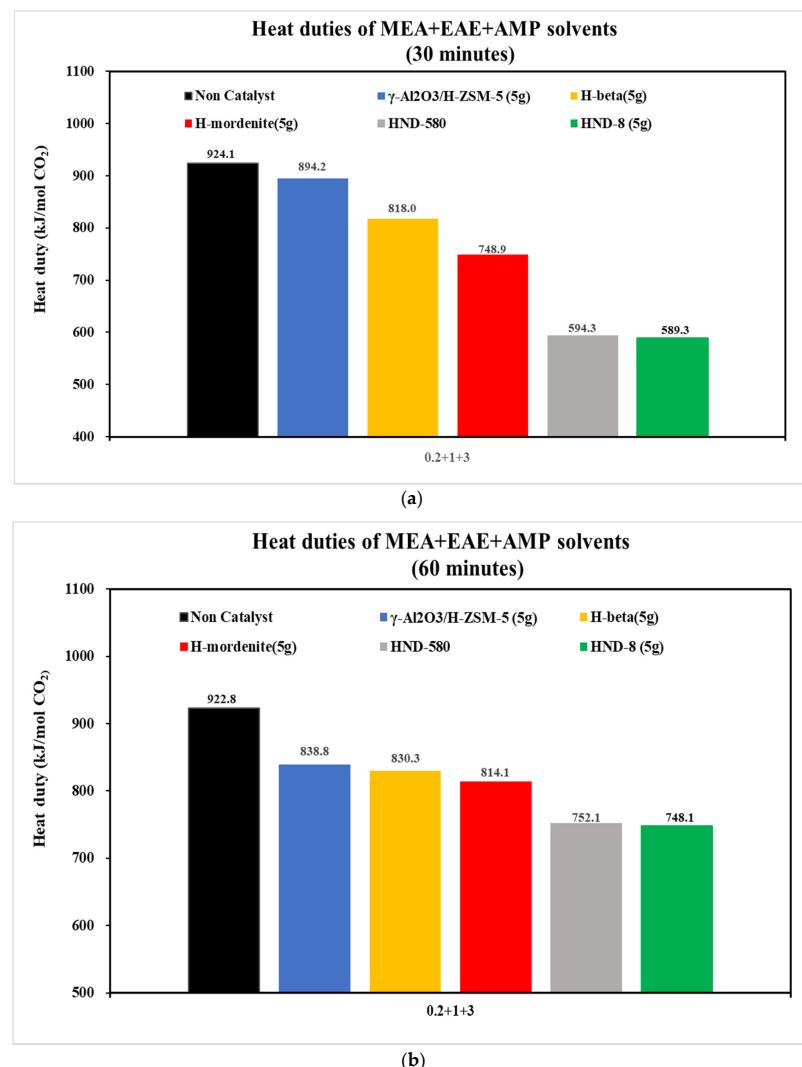


Figure 12. The heat duties of MEA + EAE + AMP at 0.2 + 1 + 3 mol/L with various catalysts at (a) 30 min and (b) 60 min.

The results that the ranking of heat duties $1/3 > 2/2 > 1.5/2.5$ EAE/AMP followed those of temperature programming were quite indicative. The intrinsic reason for the abnormal case of $1.5/2.5$ was mainly its lower operation temperature. The temperature was $60\text{ }^{\circ}\text{C}$ at 30 min, and it was $70\text{ }^{\circ}\text{C}$ at 60 min for $0.3 + 1.5 + 2.5\text{ mol/L}$, which was the lowest among these three sets. The CO_2 desorption of MEA + EAE + AMP tri-solvents required desorption temperatures of at least $70\text{ }^{\circ}\text{C}$ to maintain catalysis and desorption rates up to threshold. The reaction kinetics for this await further studies. Table 3 reflected the desorption factors for the first 30 min, and $0.2 + 1 + 3\text{ mol/L}$ was much better than $0.3 + 1.5 + 2.5\text{ mol/L}$ given the much lower heat duty.

3.3. The Optimized Combination of Tri-Solvent MEA + EAE + AMP with Catalysts at Four Different Concentrations

The heat duty (HD) was one of the most important parameters with which to evaluate energy efficiency for various combinations [58]. For this study, combinations with various HD could be compared because of their similar amine concentrations. For each set with the same concentration, the lowest HD was discovered when each type of amine was blended with HND-8. If the heat duties of different amine concentrations are compared based on Figures 6, 9 and 12, we can see that the heat duties of HND-8 followed the order of $0.2 + 1 + 3 < 0.2 + 2 + 2 < 0.5 + 2 + 2 < 0.3 + 1.5 + 2.5\text{ mol/L}$. The lower, the better.

As shown in Tables 3 and 4, the desorption factors of all the systems followed the same order as that of HND-8: $0.2 + 1 + 3 > 0.2 + 2 + 2 > 0.5 + 2 + 2 > 0.3 + 1.5 + 2.5\text{ mol/L}$. The bigger, the better. The $0.2 + 1 + 3 + \text{HND-8}$ was the most energy efficient combination in this study. The operation temperature was better if it was higher up to $90\text{ }^{\circ}\text{C}$. The AMP concentration in this combination was the biggest, which resulted in extra bicarbonate in the amine solution. The explanation for the worst case of $0.3 + 1.5 + 2.5\text{ mol/L}$ may be the lower desorption temperature, which inhibited CO_2 desorption. Therefore, the operation temperature of desorption for MEA + EAE + AMP tri-solvent needed to be at least $70\text{ }^{\circ}\text{C}$. The threshold temperature was $70\text{--}75\text{ }^{\circ}\text{C}$, which is quite practical for its application.

Table 4. The desorption factors of tri-solvent of MEA + EAE + AMP solvents with various catalysts at 30 min.

MEA + EAE + AMP		Desorption Factor ($10^{-3}\text{ mol CO}_2^3/\text{L}^2\text{ kJ min}$)				
(mol/L)	Non Catalyst	$\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$	H-Beta	H-Mordenite	HND-8	HND-580
$0.5 + 1.5 + 2.5$	0.0094	0.0094	0.0097	0.0098	0.0126	0.0110
$0.2 + 1 + 3$	0.0072	0.0079	0.0103	0.0135	0.0277	0.0270

3.4. The Structure–Activity Correlations of Various Catalysts

These five commercial solid acid catalysts have similar properties, as they contain both Lewis acid and Brønsted acid sites. According to recent studies [16], an intensive characterization method was used on these catalysts via XRD, SEM, BET, $\text{NH}_3\text{-TPD}$, Py-TPD, etc. Based on plenty of existing publications, the structure–activity correlation was mainly due to the MSA (mesopore surface area), TAS (total active sites), B/L ratio (Brønsted/Lewis acid ratio) and BAS (Brønsted acid sites). The solid catalysts with optimized performance were mainly due to TAS, BAS and in most cases, the product of MSA*TAS for different types of amine [14]. However, there is not a universal structure–activity correlation for various solid acid catalysts, yet. Even for single amine MEA, it is challenging to work out a concise structure–activity correlation for various types of solid acid catalysts because of different surface areas, pore volumes and sizes, acidity and other possible physico-chemical properties.

This study did not design characterization experiments catering for five catalysts because all these catalysts are commercially available and have similar data. The characteristics of catalysts $\gamma\text{-Al}_2\text{O}_3$, H-ZSM-5, H β and H-mordenite were published repeatedly and

categorized in a recent review [16]. The characteristics of HND-8 and HND-580 catalysts are provided in Table 5 herein. The HND-8 contains 24.75 mmol/g acidity by strength, and this advantage results in its super desorption ability compared with the rest of the catalysts in this study. The structure–activity correlations of these catalysts may require further study.

Table 5. The characteristics of super solid acid catalysts HND-8 and HND-580.

Parameters	Catalyst	
	HND-8	HND-580
Acidity by strength (mmol/g)	24.75	≥ 4.95
Wet apparent density (g/mL)	0.75–0.85	0.55–0.65
Wet true density (g/mL)	1.18–1.28	1.18–1.28
Average pore diameter (nm)	≥ 15	≥ 15
Surface area (m^2/g)	>20	≥ 20
Pore volume (cm^3/g)	0.2–0.4	0.2–0.45
Particle size between 0.315–1.25 mm (%)	>90	≥ 90
Water content (%)	≤ 3 (dry), 50–57 (wet)	≤ 3
Maximum service temperature (°C)	150	170

4. Materials and Methods

4.1. Chemicals, Solid Acid Catalysts and CO_2 Loading Tests

The 99% pure CO_2 gas was purchased. Different amines (MEA, EAE and AMP) were purchased from Sigma Aldrich to prepare the tri-solvent. The solid acid catalysts were commercially available for this study. The HCl (1.0 mol/L) was a standard solution for titration for the amine concentration C_A of the tri-solvent; methyl orange was the indicator. The main experimental data, CO_2 loading α , of various samples were determined with a special Chittick apparatus. The CO_2 loading analysis method was based on the standard of the Association of Official Analytical Chemists (AOAC). [72]. Each sample experienced a CO_2 loading testing 2–3 times to maintain error less than 3%.

4.2. Experimental Procedures for CO_2 Desorption for Temperature Programming

This CO_2 desorption process was similar to that of other study [19,61] with a recirculation process and an oil bath [23–25,56,57,61]. The diagram and photos of the process are provided in the Figure S2 in Supplementary Materials. From repeated publications, the mass balance of CO_2 desorption in gas phase and difference in CO_2 loading in the liquid phase are relatively small, within 5% [16]. The tri-solvent MEA + EAE + AMP of this study is highly energy efficient; the desorption process was completed at 85–90 °C. The difference in catalytic CO_2 desorption under direct heating was quite narrow. Therefore, this study used temperature programming (TP) to distinguish various desorption tests. This study set the initial temperature of the oil bath to 298 K. Then, the temperate increased gradually with temperature programming to reach 85–95 °C. The CO_2 desorption curve was plotted based on CO_2 loading, along with the simultaneous temperature profiles in the same figure.

The desorption periods were around 120–150 min for this study, from α_{rich} close to 0.70 mol/mol to α_{lean} nearing 0.35 mol/mol. After loading reached 0.35 mol/mol, the CO_2 loading can hardly decrease based on the heating input and operation temperature. The desorption period was not a fixed value. As soon as the CO_2 loading reached 0.35 mol/mol for the tri-solvents, the desorption process was completed. Usually, the process took 120–150 min.

The desorption process under TP was indicative of: (1) Various CO_2 loading levels α_{lean} at 30 and 60 min. (2) Special CO_2 desorption, performed with inadequate heat input. The CO_2 desorption process included multiple endo-thermic reactions based on Scheme 1. The kinetics of CO_2 release can be discovered carefully. (3) The suitable operation temperature and threshold of the desorber column. Under steady state process with constant heat input (Q_{input}), the heat was mostly converted to continuous reaction heat

Q_{reac} , heat loss Q_{loss} and CO_2 release/desorption; little was used for temperature increase ΔT and sensible heat Q_{sensi} . Therefore, the steady-state temperature of the desorption was indicative of an industrial amine scrubbing process.

5. Conclusions

This study evaluated multiple energy efficient combinations of tri-solvent MEA + EAE + AMP under four different concentrations with five commercial catalysts: blended $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$, $\text{H}\beta$, H-mordenite, HND-580 and HND-8. The heat duty (HD) and desorption factor (DF) were major indexes of evaluation of the energy efficient combinations.

- (1) The coordinative effect of MEA and EAE indicated that $0.2 + 2 + 2 \text{ mol/L}$ was the best among $0.1 - 0.5 + 2 + 2 \text{ mol/L}$ scenarios with blended catalyst $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$.
- (2) With the aid of five commercial solid acid catalysts, the tri-solvents at various concentrations ($0.2 + 1 + 3$, $0.2 + 2 + 2$, $0.5 + 2 + 2$ and $0.3 + 1.5 + 2.5 \text{ mol/L}$) were consistent in the order of heat duty performance: blank > $\gamma\text{-Al}_2\text{O}_3/\text{H-ZSM-5}$ > H-mordenite > $\text{H}\beta$ > HND-580 > HND-8. The lower, the better. HND-8 was the best solid acid catalyst due to its super acidity by strength. The structure–activity correlations of these catalysts await further studies.
- (3) With HND-8 as an energy efficient catalyst, the order of DF with various amine concentrations was: $0.2 + 1 + 3 > 0.2 + 2 + 2 > 0.5 + 2 + 2 > 0.3 + 1.5 + 2.5$. The bigger, the better. The optimized desorption condition was $0.2+1+3 \text{ MEA+EAE+AMP}$ with HND-8 at 95°C . This combination of $0.2 + 1 + 3 + \text{HND-8} + 95^\circ\text{C}$ is quite applicable for industrial CO_2 capture processes.
- (4) The order of HD with different ratios of EAE/AMP was: $1/3 > 1/1 > 1.5/2.5$. Generally, higher AMP concentration resulted in better desorption performance. The abnormal case happened when EAE/AMP was $1.5/2.5$, which resulted from its lower operation temperature with inadequate heat input, which led to much less CO_2 desorption.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12070723/s1>, Figure S1: The mechanism of catalytic CO_2 desorption and carbamate breakdown. Figure S2: The picture of CO_2 desorber process.

Author Contributions: Conceptualization, H.S. and B.Z.; methodology, J.P.; software, Y.L.; validation, J.H.; formal analysis, B.Z.; investigation, H.S.; resources, S.L.; data curation, J.P.; writing—original draft preparation, B.Z. and H.S.; writing—review and editing, H.S.; supervision, H.S.; funding acquisition, H.S. and J.J. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

$C_{\text{A:L}}$	concentration of solute A in the bulk liquid (k mol/m^3) (mol/L)
DF	Desorption Factor
HD	Heat duty
P	Total system pressure (kPa)
Q_{input}	Heat input

Greek Symbols

A	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
EAE	2-(ethylamino)ethanol
MEA	monoethanol amine
PZ	Piperazine

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