



A comparative study of the effects of aqueous mixed amines on biogas upgrading based on ^{13}C nuclear magnetic resonance (NMR) analysis

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ABSTRACT

As a key technology for biogas upgrading, mixed amines scrubbing can meet the world's demand for renewable energy by ensuring high methane (CH_4) purity while achieving low energy regeneration. In this paper, several monoamines with excellent performance in biogas upgrading process were selected to study the effectiveness of their blends for biogas upgrading and compared with 30 wt% monoethanolamine (MEA). The biogas upgrading effect, carbon dioxide (CO_2) loading, regeneration effect and CO_2 desorption heat of mixed amines were determined by batch experiments. ^{13}C NMR was used to mechanistically interpret and quantify the carbocation trend of the amine solution before and after the reaction and regeneration. The results showed that the biogas upgrading and regeneration effect of the mixed amines combined with methyl monoethanolamine (MMEA) and N-methyldiethanolamine (MDEA) was the best, and its initial methane purity, saturated CO_2 loading, regeneration rate and CO_2 desorption heat after upgrading were 100%, 0.617 mol CO_2 /mol amine, 54.3% and 64.91 kJ/mol CO_2 , respectively. Except for the saturated loading which was second only to MMEA/dimethyl monoethanolamine (DMMEA) with 0.624 mol CO_2 /mol amine, all the performances are optimal and the CO_2 desorption heat is 19.01% lower than that of 30 wt% MEA, which can effectively reduce the regeneration energy consumption of the reaction. The results of ^{13}C NMR showed that the increase of bicarbonate content could effectively reduce the regeneration energy consumption and enhance the initial regeneration rate, and the increase of carbamate could accelerate the initial uptake rate and methane purity, which could provide theoretical support for the subsequent screening of mixed amines to achieve different reaction purposes.

1. Introduction

With global carbon dioxide (CO_2) levels rising year by year and the extraction of fossil energy sources facing imminent depletion (Li et al., 2016), it is essential to urgently realize the energy transition and accelerate the exploitation of renewable energy sources in order to achieve climate change mitigation and solve the energy shortage on the basis of carbon emission reduction (Jiang et al., 2020). In addition, as urbanization levels increase and population numbers continue to rise, the amount of waste generated by people's lives will also increase, which may likewise pose a threat to global climate change and the environment (Anto et al., 2021). Biogas, a product of anaerobic digestion of waste, has received a lot of attention from researchers due to its high content of methane (CH_4) and carbon dioxide, which can cause considerable carbon emissions and safety hazards if not properly treated (Vilardi et al., 2020). However, if biogas can be upgraded to remove CO_2 and other impurities, its low-level calorific value will be greatly

increased (Abdeen et al., 2016), resulting in a cleaner and renewable energy source that will be of great value in achieving carbon reduction and renewable energy strategies worldwide (Mondal and Samanta, 2020).

Amine scrubbing is a simple and proven CO_2 capture technology with a high selectivity (Muchan et al., 2017) and uptake of CO_2 (Chowdhury et al., 2013) and is widely used by the CO_2 capture industry worldwide (Rochelle et al., 2011). Zhang et al. (2022) investigated the equilibrium solubility of carbon dioxide in aqueous 2-(dimethylamino)-2-methyl-1-propanol (2DMA2M1P) solutions and proposed a new extended model to predict the equilibrium solubility of carbon dioxide. Although this technology is widely accepted by the CO_2 capture industry, its commercialization is hampered by its high regeneration energy consumption (Zhang et al., 2016). Currently there are three main types of amines in common use: primary, secondary and tertiary amines (Rivera-Tinoco and Bouallou, 2010). Primary and secondary amines have faster CO_2 absorption rates than tertiary amines (Singh et al., 2011), but do not absorb as much as tertiary amines and

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Abbreviations	
CO ₂	Carbon Dioxide
CH ₄	Methane
MEA	Monoethanolamine
MDEA	N-methyldiethanolamine
MMEA	Methyl Monoethanolamine
DMMEA	Dimethyl Monoethanolamine
BMEA	Butyl Monoethanolamine
α_{abs}	Carbon Dioxide Absorption
α_{des}	Carbon Dioxide Desorption
N ₂	Nitrogen
T _{abs}	Absorption Temperature
R	General Gas Constant
Δh_{abs}	Carbon Dioxide heat of absorption
P _{CO₂}	Partial Pressure of Carbon Dioxide
CH ₃ CN	Acetonitrile
CH ₃	Methyl
NMR	Nuclear Magnetic Resonance
JEOL	Liquid Nuclear Magnetic Resonance Spectrometer
T _{96%}	Duration to Reach 96% Export Methane Purity
T _{85%}	Duration to Reach 85% Export Methane Purity
2DMA2M1P	2-(dimethylamino)-2-methyl-1-propanol
PA	Price of Amines
CCR	Cycling Rate of Amines
DC	Cost of Desorption
RG	Regeneration Gain
TRC	Total Relative Energy Consumption

have much higher regeneration energy consumption than tertiary amines (Rayer et al., 2014). In order to solve the problems of monoamines in CO₂ absorption and to develop amine absorbers with high CO₂ absorption and low regeneration energy consumption (Li et al., 2021), the research of mixed amines has received a lot of attention from researchers (Pasha et al., 2021). Zhang et al. (2019) investigated the regeneration performance of the MEA/MDEA/PZ triple solution mixture of amines with four different solid acid catalysts and found that the kinetics of CO₂ desorption was greatly improved compared to the MEA solution.

It has been shown that the addition of tertiary amines to primary amines can effectively reduce their CO₂ desorption energy consumption while ensuring a high CO₂ absorption effect (Gong et al., 2018). Liu et al. (2021) compared the CO₂ absorption performance of MEA and MDEA monoamine solutions with that of a mixture of the two and found that the absorption rate of the mixture was slightly lower than that of the mono-MEA solution but the regeneration performance was much higher than that of the MEA solution. Teerawat et al. (Sema et al., 2012) investigated in depth the mechanism and performance parameters of MEA/MDEA mixed amines in the CO₂ absorption process and successfully explained the reasons for their superior absorption performance compared to single component MEA. Hamidi et al. (2018) investigated the CO₂ uptake rate and absorption capacity of a MEA/MDEA mixed amines at different concentration ranges in an isothermal batch reactor and found both high CO₂ uptake rates and low regeneration energy consumption. Liu et al. (2016) investigated the effect of MEA/MDEA amine mixture on the absorption effect of flue gas and found that the addition of MDEA led to a large improvement in the absorption and regeneration effect. Therefore, continued research into blending between monoamines with higher CO₂ absorption rates and those with lower regeneration energy consumption is an important process to drive the development of mixed amines.

There are also many choices in the screening process of mixed amines (Bajpai and Mondal, 2013), mainly because different amines have different advantages and disadvantages in the process of CO₂ capture (Sharif et al., 2020). In order to categorize the amines, some scholars have explored their effects on CO₂ absorption performance starting from the effects of functional groups. Nabil et al. (El Hadri et al., 2017) investigated the effect of the structure of 30 amines on CO₂ absorption properties and found that both methyl and butyl on MMEA and monoethanolamine (BMEA) can be used as electron donors to effectively increase the CO₂ absorption of secondary amines, while the hydroxyl and methyl groups on MDEA and DMMEA can substantially reduce the CO₂ absorption heat when increasing the CO₂ absorption of tertiary amines. Francesco et al. (Barzaghi et al., 2016) found that MMEA and BMEA, which possess methyl and butyl groups, are expected to be alternatives to aqueous MEA due to their larger CO₂ absorption and lower regeneration energy consumption during their study. Diwakar and

Folgueira et al. (Folgueira et al., 2014; Pandey and Mondal, 2020) found that MMEA outperformed MEA in terms of CO₂ loading, recycling capacity and heat absorption. Yu et al. (Dong et al., 2022) in the course of their study found that BMEA possesses better CO₂ solubility than MEA and was expected to be an alternative to non-aqueous amine fluids. Many papers also showed that MDEA can effectively reduce the energy consumption of amine regeneration (Akachuku et al., 2017) and was an amine with excellent CO₂ regeneration performance (Akachuku et al., 2019; Decardi-Nelson et al., 2017; Nwaoha et al., 2016). However, there are still few studies on the direct use of the above amines for simulating biogas penetration curves.

In summary, the amine washing technology, as a relatively mature CO₂ capture technology, on one hand is not ideal for CO₂ capture because of the large differences in absorption, absorption rate and regeneration rate of different amine solutions in the process, and on the other hand, its commercial application is greatly limited by the high regeneration energy required in the regeneration process. In addition, there is a lack of mechanistic analysis of mixed amines and few studies on the use of this technology for biogas upgrading. Based on this, the paper investigated the blending between several different types of selected amines, analyzed the CO₂ absorption, biogas upgrading effect, regeneration energy consumption and CO₂ selectivity, prepared a mixed amine solution with high CO₂ absorption, fast CO₂ absorption rate, high CH₄ purity, low regeneration energy consumption and fast regeneration rate at the same time, and investigated the reaction mechanism to provide a reference and technical guidance for selecting the suitable amine solutions for mixing in subsequent industrial production.

2. Experimental

2.1. Materials

Monoethanolamine (MEA), methyl monoethanolamine (MMEA), dimethyl monoethanolamine (DMMEA), butyl monoethanolamine (BMEA) and N-methyldiethanolamine (MDEA) were obtained from Macklin, mass flow meters were produced from Beijing Seven Star Company, CH₄, CO₂ and nitrogen (N₂) cylinders were supplied by Tianjin Air Liquide Company, and all materials were not further purified. The molecular structure diagrams of the materials used are shown in Table 1.

2.2. Measurement of the effectiveness of biogas upgrading

The biogas upgrading process is mainly carried out by the absorption equipment and desorption equipment (Naquash et al., 2022). The biogas first enters the absorption equipment and reacts with the amine solution, the upgraded biomethane is discharged from the absorption equipment, the reacted rich amine solution enters the desorption equipment and

Table 1
Chemical structure of amines.

Abbreviations	Molecular weight
MEA	61.08 g/mol
MDEA	119.16 g/mol
DMMEA	89.14 g/mol
MMEA	75.11 g/mol
BMEA	117.19 g/mol
Purity	Molecular structures
99.0%	
99.0%	
98.0%	
99.0%	
99.0%	

regenerates under high temperature, the regenerated CO₂ is discharged from the desorption equipment, and the obtained lean amine solution is cooled down by the lean/rich amine solution heat exchanger and then enters the absorption equipment again for biogas upgrading (Yoro et al., 2021). The absorption effect of biogas upgrading of amine was tested as shown in Fig. 1(a). 800 ml of fresh amine solution with a concentration of 4.9 mol/L was first placed in the reactor, and then simulated biogas with 65% methane purity was delivered to the reactor for stirring at a flow rate of 580 ml/min after passing through a saturated water device, and the temperature of the reactor was set at 298.15 K by the action of a water bath. The upgraded biogas was dewatered and then analyzed by a non-spectrophotometric infrared biogas analyzer, and the resulting gas components were recorded. The reaction was stopped until the concentration of the upgraded gas matched that of the incoming gas, and the dissolved CO₂ content (α_{abs}) in the amine solution was calculated by titration with a Chittick titrator, and the results were averaged over three titrations.

Subsequently, amine desorption experiments were performed in the apparatus shown in Figs. 1(b), 500 ml of the amine rich solution obtained after upgrading the biogas was placed in a reactor equipped with mechanical stirring at 363.15 K. The outlet of the reactor was equipped with a condensing device to prevent the loss of amine and water. The CO₂ content of the amine solution was calculated by Chittick titration every 10 min and the final residual CO₂ loading (α_{des}) of the regenerated amine was obtained as shown in Fig. 1(b).

2.3. Calculation of the heat of desorption of CO₂

The energy consumption of amine in regeneration process is mainly divided into the sensible heat of amine solution from absorption temperature to regeneration temperature (Barzagli et al., 2018), the desorption heat of CO₂ desorption and the latent heat of water in evaporation process (El Hadri et al., 2017), among which the CO₂ desorption heat is an important index to judge whether the amine solution has economic feasibility (Zhang et al., 2017). Since the heat of CO₂ desorption is numerically consistent with the heat of absorption (Li et al., 2021), it can be estimated by the Gibbs-Helmholtz equation (Rayer and Henni, 2014), and the calculation formula is shown in Eq. (1).

$$\frac{d(\ln P_{CO_2})}{d\left(\frac{1}{T_{abs}}\right)} = \frac{\Delta h_{abs}}{R} \quad (1)$$

where T_{abs} , R and Δh_{abs} are the absorption temperature of the amine (K), CO₂ heat of absorption of the amine (J/mol) and general gas constant (8.314 J/mol·K).

The CO₂ desorption heat measurement apparatus was also shown in Fig. 1(a). The partial pressure of CO₂ (P_{CO_2}) was kept constant by changing the flow rates of N₂ and CO₂ at the gas inlet, and the stable gas mixture was passed into 800 ml of fresh amine solution for the reaction, and the reaction temperatures were set at 298.15 K, 308.15 K and 318.15 K, and the P_{CO_2} was 10.1, 35.5, 50.7, 82.8 and 101 kPa, respectively, and finally the saturated CO₂ loading in the amine solution was obtained by titration.

2.4. The selective measurement of CO₂ in biogas upgrading with amines

The determination of CO₂ selectivity was carried out by means of a homemade reaction vessel as shown in Fig. 2. The reaction vessel was equipped with two stirring paddles acting on the gas and liquid phases respectively. The reaction vessel was continuously filled with CO₂ and CH₄ at 1 atm respectively by pumping from a vacuum pump and inlet from a CH₄/CO₂ cylinder, and the temperature was stabilized at about 298.15 K by a thermostatic device. Fresh amine solution was injected into the reactor for reaction by a homemade constant pressure titration device, and JYB-KO-HAA Digital pressure (absolute pressure) and temperature sensors transfer the data in the reaction vessel to a computer and record them.

2.5. ¹³C NMR spectroscopy of reaction solutions

¹³C NMR spectroscopy is a well-established technique that can be used to determine the concentration of each component in a solution (Barzagli et al., 2019; Zhang et al., 2018), and the results in this paper were obtained using a liquid NMR spectrometer (JEOL) JNM-ECA600 at a relaxation time of 20 s and a sampling count of 128. In order to accurately quantify the content of amines and their reaction products

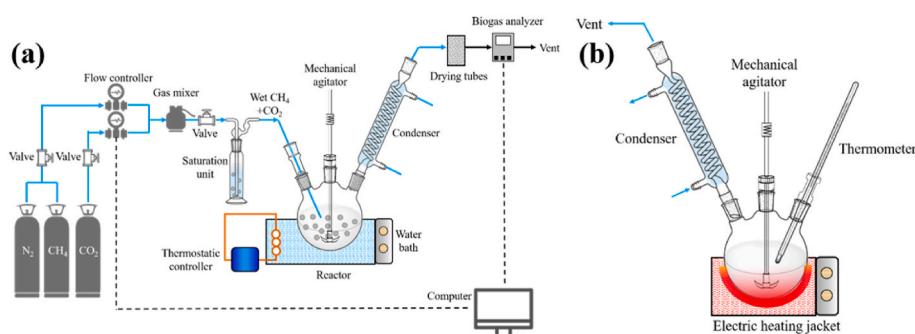


Fig. 1. Measuring device for biogas upgrading effect: (a) Absorption effect of amines, (b) Desorption effect of amines.

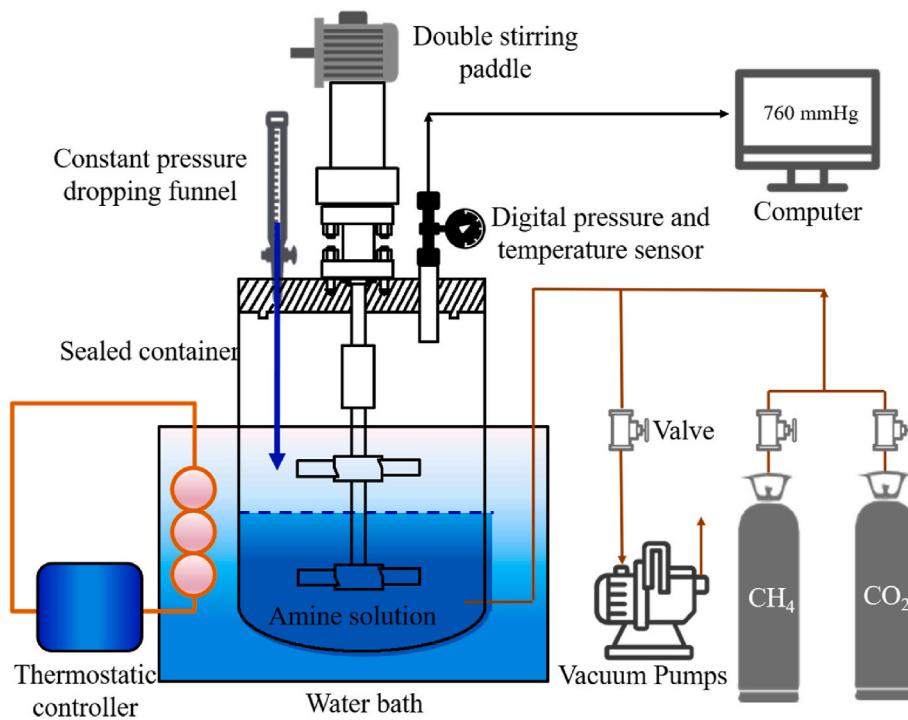


Fig. 2. Gas selectivity determination device for amines.

with CO_2 , 20 μl of acetonitrile (CH_3CN) was added as an internal standard (CH_3 , $\delta = 0.643$; CN , $\delta = 178.781$) to 400 μl of the solution to be measured. In addition, 100 μl of D_2O reagent was also added to the solution to be tested in order to make the test results more accurate. JEOL Delta v6.0 software was used to perform data processing.

The total content of bicarbonate/carbonate ions which are in rapid exchange can also be quantitatively calculated from the NMR results, but it is not possible to quantitatively analyze one of the components alone. In this paper, the bicarbonate content at this chemical shift was estimated by fitting the chemical shifts obtained from the NMR results of Na_2CO_3 and NaHCO_3 solutions with different concentrations precisely dissolved in D_2O to their admixture ratios, and the error could be controlled within 5% (Barzaghi et al., 2018).

3. Results and discussion

3.1. Biogas upgrading experiments with mixed amines

In this paper, firstly, the biogas upgrading effect and regeneration effect of the four screened amines and MEA were studied under the same molecular weight conditions, as shown in Fig. 3(a). From Fig. 3(a), it can be preliminarily found that the methane purity of biogas upgraded by MMEA, BMEA and MEA can reach 96% and 85% for about 175 and 200 min respectively, meeting the standards of China (Methane purity $\geq 96\%$) and some EU countries (Netherlands, France, Spain and Switzerland of methane purity requirements $\geq 85\%$, 86%, 95% and 96% respectively) where biomethane is used for grid and vehicle applications, respectively (Awe et al., 2017). In addition, MMEA and BMEA maintained methane purity per mole longer than MEA per mole and have better regeneration rates and volumes than MEA, as shown in Fig. 3(b). MDEA and DMMEA maintained methane purity above 85% for a long time despite not reaching the 96% threshold required for methane purity, and in addition having much better regeneration rates and volumes than MEA, MMEA, and BMEA. Therefore, this paper decided to further investigate the effect of biogas upgrading of these amines after blending, to screen the best combination of the four amines and to elaborate the reaction mechanism.

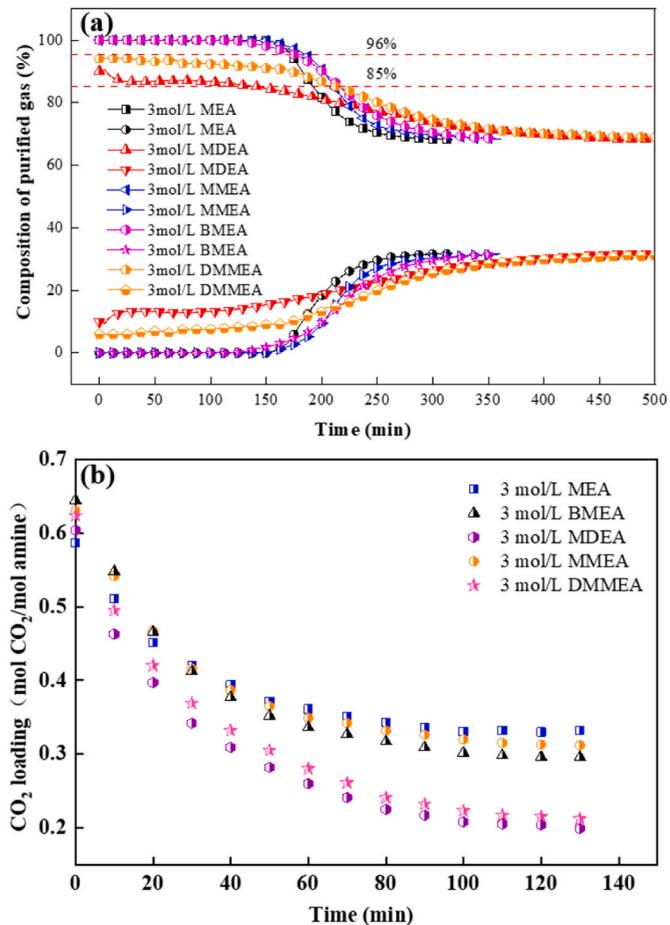


Fig. 3. Biogas upgrading and desorption curves for monoamines: (a) Absorption process, (b) Desorption process.

In order to better compare the biogas upgrading performance with the 30 wt% MEA widely used in engineering, the total molar concentration of amine was set to 4.9 mol/L in the experiment, and the specific mixing ratio, the CO₂ saturation absorption of amine and the residual CO₂ loading after regeneration are shown in Table 2. In addition, the penetration curves of the biogas upgrading process of amines in different combinations and their regeneration curves are also shown in Fig. 4. The results of Fig. 4(a) showed that by adding appropriate amounts of MDEA and DMMEA to MMEA and BMEA, the initial purity of methane at the outlet could still be maintained above 96%, with the penetration curves of MMEA/MDEA and MMEA/DMMEA mixed amines were second only to 30 wt% MEA. The biogas upgrading effect of MMEA/MDEA and MMEA/DMMEA mixed amines was 11.06% and 7.08% lower than 30 wt% MEA, respectively, if the duration to reach 96% export methane purity ($T_{96\%}$) was used as a measure, but the same upgrading effect as 30 wt% MEA could be achieved by adjusting the retention time of aqueous amines in the reaction vessel. It is worth noting that the biogas upgrading effect of MMEA/MDEA and MMEA/DMMEA amine blends was 2.65% and 6.73% higher than that of 30 wt% MEA, respectively, as measured by the duration to reach 85% export methane purity ($T_{85\%}$), which is mainly due to the lower initial uptake rate but higher saturated CO₂ loading of the mixed amines than MEA. Since MEA, MMEA, and BMEA have hydrogen bonds in their chemical structures, they will break during the reaction and quickly form structurally stable carbamates with CO₂, while the broken hydrogen bonds will combine with another amine to form protonated amines, so the reaction rate is fast but the absorption is low. In contrast, MDEA and DMMEA do not produce carbamate without hydrogen bonding but will directly obtain hydrogen bonding from water or other amines with hydrogen bonding in the structure to produce protonated amine and at the same time produce bicarbonate or carbamate, so the reaction rate is slower but the absorption is higher. Therefore, in terms of biogas upgrading effect, the combination of MMEA with MDEA and DMMEA, respectively, could achieve better results than MEA.

The regeneration effect of the mixed amines is also a key parameter for its ability to be used as an alternative to MEA, and the variation of CO₂ loading with regeneration time is shown in Fig. 4(b). By observing the regeneration curve within 40 min, it was clear that MMEA/MDEA had the fastest regeneration rate, in addition to a regeneration rate of 54.30% (over 24% for 30 wt% MEA). This should be mainly due to the fact that MMEA/MDEA generates more substances like bicarbonate with lower heat of CO₂ desorption than other absorbents during the reaction process and the slower generation rate of these substances like bicarbonate rate than carbamates reduced the efficiency of biogas upgrading appropriately. Further analysis will be conducted separately.

3.2. Calculation of CO₂ desorption heat of mixed amines

In this section, the energy consumption of regeneration of mixed amines is evaluated by performing the calculation of CO₂ desorption heat. The variation curves of saturated CO₂ loading with absorption temperature and CO₂ partial pressure for different mixed amines and MEA are shown in Fig. 5. It could be roughly found from the figure that the variation of CO₂ loading with CO₂ partial pressure was basically linear, while the rate of decrease of CO₂ loading tended to accelerate as the absorption temperature increases. By substituting different P_{CO₂} and

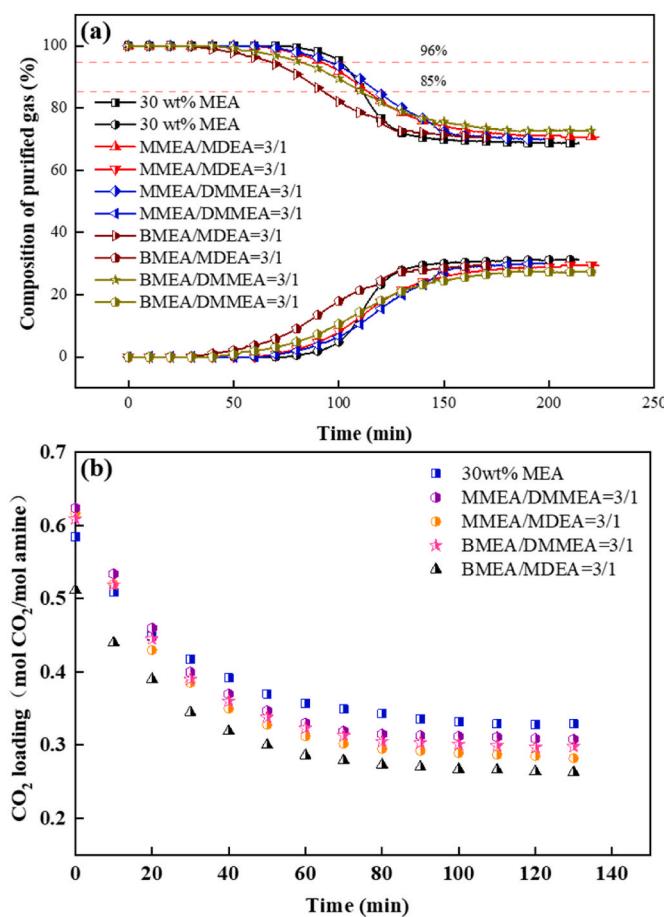


Fig. 4. Biogas upgrading and desorption curves for mixed amines: (a) Absorption process, (b) Desorption process.

Tabs with the same CO₂ loadings screened into the Gibbs equation for fitting, the results are shown in Fig. 6. The CO₂ desorption heat of different amine blends could be estimated from the fitted equations, as shown in Table 3, where the lowest CO₂ desorption heat of MMEA/MDEA amine blend reached 64.91 kJ/mol CO₂, which was 19.08% less than the CO₂ desorption heat of 30 wt% MEA, greatly reducing the regeneration energy consumption. The results of CO₂ desorption heat were consistent with the regeneration rate and regeneration amount in the previous paper, further indicating that a large of products with lower CO₂ desorption heat were produced during the reaction.

In addition, cost factors are also one of the important factors that must be considered in the process of biogas upgrading. In this paper, the economic analysis of each of the screened mixed amine systems was performed using the method used by Chen et al. (2022) and Hu et al. (2022) for cost analysis of amine solutions. This method takes into account the price of amines (PA, \$/dm³), the cycling rate of amines (CCR, dm³/min), the cost of desorption (DC, \$/min) and the regeneration gain (RG, \$/min). The calculated price values for aqueous 30 wt% MEA, MMEA/DMMEA = 3/1, BMEA/DMMEA = 3/1, MMEA/MDEA = 3/1 and BMEA/MDEA = 3/1 are 4.84, 6.95, 32.33, 7.84 and 33.21 \$/dm³,

Table 2

Physical properties of aqueous amines and carbon dioxide loading.

Name	Concentration(M)	ratio	T _{96%} (min)	T _{85%} (min)	α _{abs} (mol CO ₂ /mol amine)	α _{des} (mol CO ₂ /mol amine)	Regeneration rate(%)
30 wt% MEA	4.9 M	/	98.15	111.5	0.585	0.329	43.76%
MMEA/DMMEA	4.9 M	3/1	91.20	119.0	0.624	0.308	50.64%
BMEA/DMMEA	4.9 M	3/1	75.50	111.45	0.609	0.298	51.07%
MMEA/MDEA	4.9 M	3/1	87.30	114.45	0.617	0.282	54.30%
BMEA/MDEA	4.9 M	3/1	62.15	93.45	0.512	0.263	48.63%

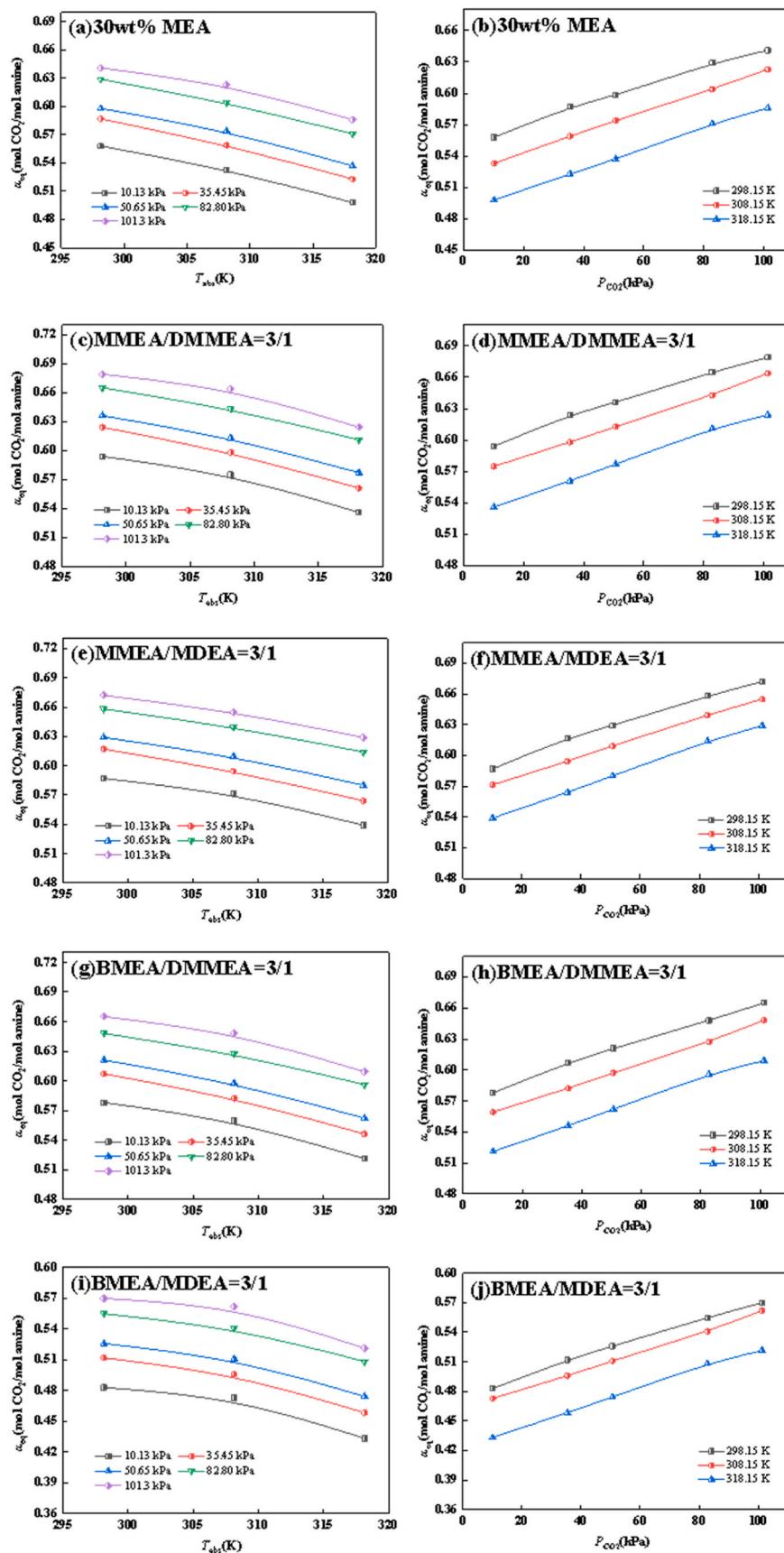


Fig. 5. The trends in equilibrium CO₂ solubility with absorption temperature and CO₂ partial pressure: (a) and (b) are the variation of CO₂ equilibrium solubility of 30 wt% MEA with absorption temperature and CO₂ equilibrium partial pressure respectively, (c) and (d) are the variation of CO₂ equilibrium solubility of MMEA/DMMEA with absorption temperature and CO₂ equilibrium partial pressure respectively, (e) and (f) are the variation of CO₂ equilibrium solubility of MMEA/MDEA with absorption temperature and CO₂ equilibrium partial pressure respectively, (g) and (h) are the variation of CO₂ equilibrium solubility of BMEA/DMMEA with absorption temperature and CO₂ equilibrium partial pressure respectively, (i) and (j) are the variation of CO₂ equilibrium solubility of BMEA/MDEA with absorption temperature and CO₂ equilibrium partial pressure respectively.

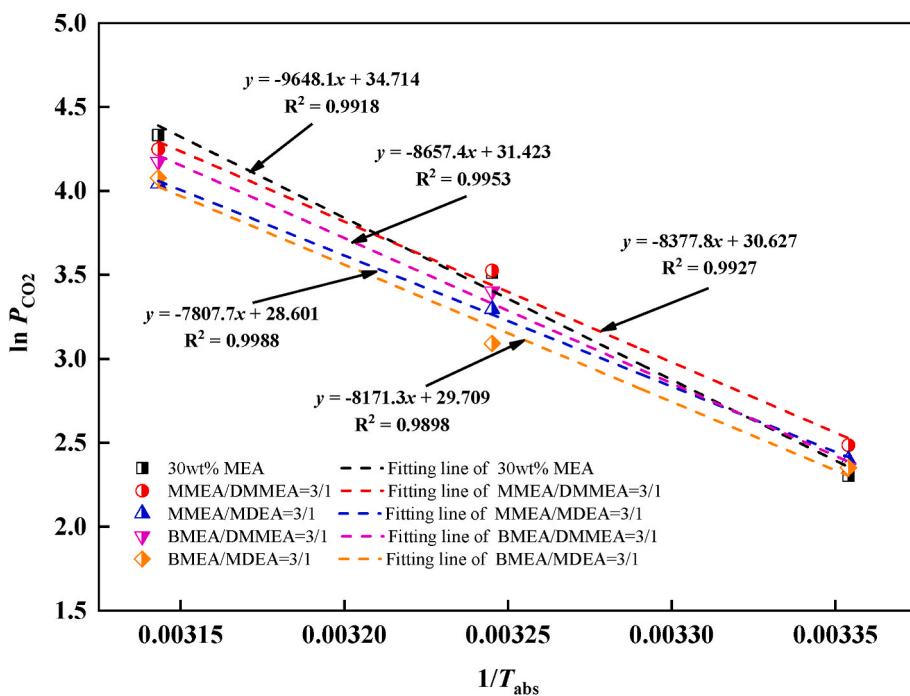


Fig. 6. Fitting curves for the heat of CO_2 desorption of amines.

Table 3
 CO_2 absorption heat of mixed amines.

Name	CO_2 absorption heat
30 wt%MEA	80.21 kJ/mol CO_2
MMEA/DMMEA = 3/1	69.65 kJ/mol CO_2
BMEA/DMMEA = 3/1	71.98 kJ/mol CO_2
MMEA/MDEA = 3/1	64.91 kJ/mol CO_2
BMEA/MDEA = 3/1	67.94 kJ/mol CO_2

respectively. The total relative energy consumption (TRC , \$/min) of each amine during the biogas upgrading process was calculated as shown in Fig. 7, where the TRC of MMEA/MDEA = 3/1 was slightly lower than that of aqueous 30 wt% MEA. The detailed calculation procedure can be found in the supporting information.

3.3. Mechanistic analysis of biogas upgrading and regeneration process

The ^{13}C NMR of the different mixed amines during the biogas upgrading process when the CO_2 saturation load was reached and the

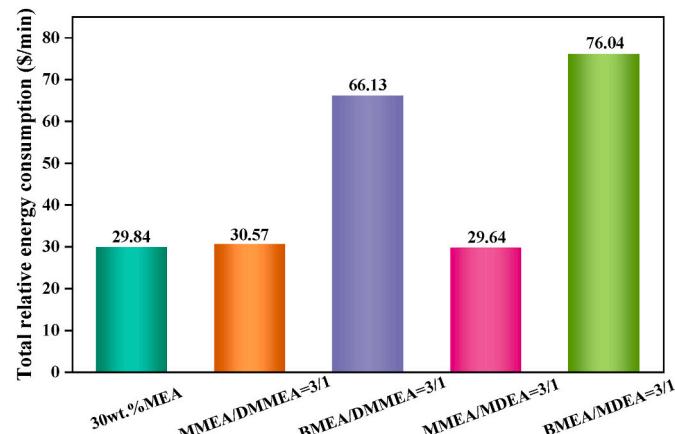


Fig. 7. Total relative energy cost of different amines.

regeneration time reached 20 min is shown in Fig. 8. The ratio between the peak areas of the internal standards in the different tested solutions was 1. It was clear from the graph that the CO_2 reacts with several amine mixtures screened in this study to form mainly carbamates, carbonates and bicarbonates. By comparing the plots of the amines before and after regeneration it could be clearly observed that the content of carbonate and bicarbonate decreased rapidly while only a small amount of CO_2 was released from the carbamate, which indicated that more heat was required for the carbamate desorption. In order to compare the relative contents of bicarbonate and carbonate more directly, we fitted the empirical values that have been obtained for their contents as well as for their chemical shifts, as shown in Fig. 11(a). Fig. 9 showed the changes in the content of each substance in the amine before and after regeneration, from which it was clear that the amount of carbamate regenerated during the initial regeneration was very small and dominated by carbonate and bicarbonate. The larger amount of carbamate in the MEA reaction product led to higher regeneration energy consumption and higher heat of CO_2 desorption, echoing the previous results. The mixed amine had a lower regeneration energy consumption due to the introduction of two tertiary amines, MDEA and DMMEA, which resulted in a relatively small amount of carbamate with stable chemical structure in the reaction product and a large amount of easily decomposed carbonate and bicarbonate. In the MMEA/MDEA mixed amines, more bicarbonate was produced in the reaction product than carbonate, which resulted in lower heat of desorption and better regeneration.

Based on the excellent biogas upgrading effect of MMEA/MDEA, we analyzed the NMR spectra of the mixed amines at different stages of the reaction process. It could be seen from Fig. 10 that the early stage of the reaction was dominated by the production of carbamate, which indicated that the mixed amines with higher production of carbamate during the reaction process tends to have faster initial absorption rate and relatively better biogas upgrading effect to obtain higher methane purity. As the reaction proceeded, the content of carbonate and bicarbonate gradually increased, and it was also mainly generated at the end of the reaction. The specific changes of the content are shown in Fig. 11(b). The results in the graph clearly showed that the CO_2 loading was basically linear, where the content of MMEA decreased sharply before 80 min and the content of carbamate and protonated MMEA increased

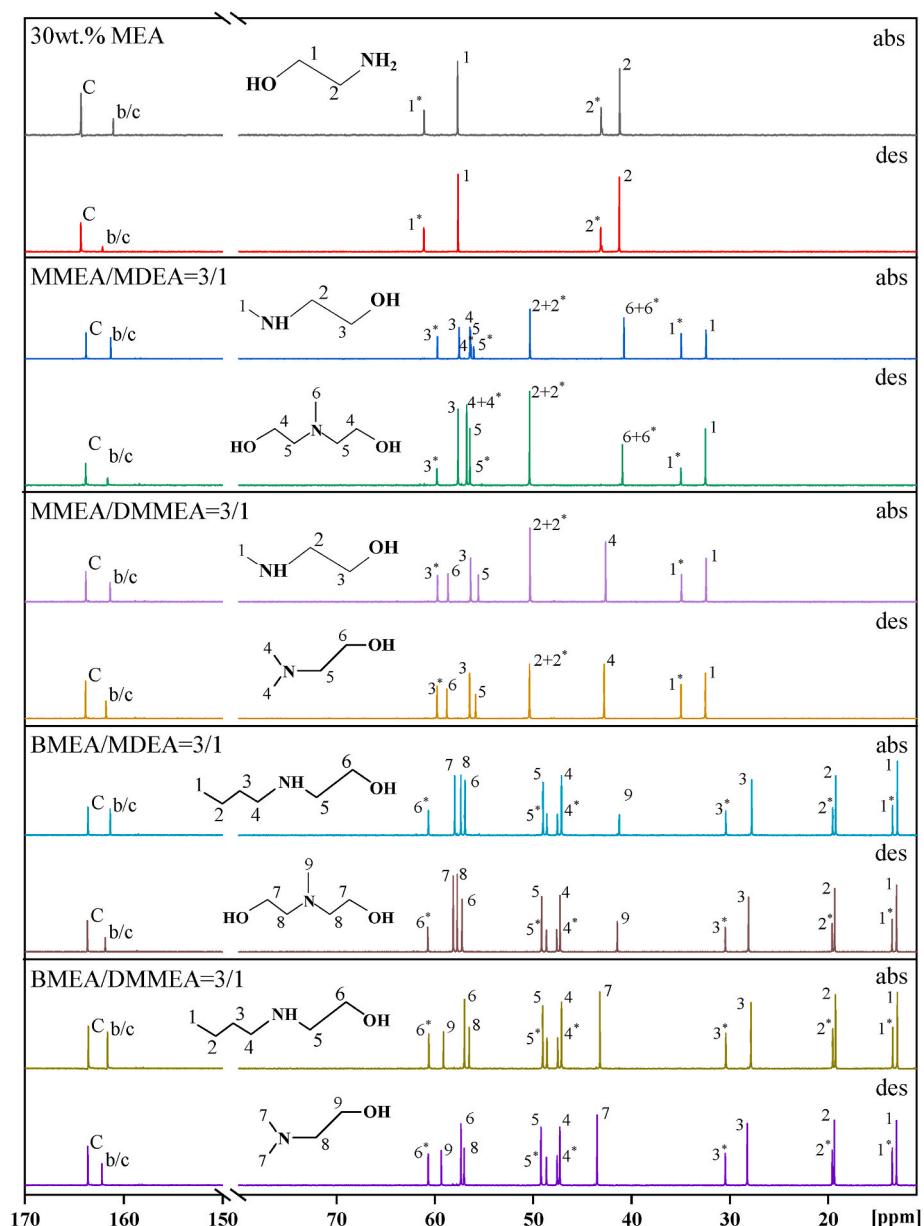


Fig. 8. ^{13}C NMR spectra of mixed amines reaching CO_2 saturation loadings during biogas upgrading and after 20 min of regeneration. Numbers refer to the carbon atoms rapidly exchanged between free and protonated amines in the NMR measurement range. Asterisks refers to the carbon skeleton of the carbamate. C indicates the carbonyl atom on the carbamate. b/c refers to the rapidly exchanging bicarbonate/carbonate ion.

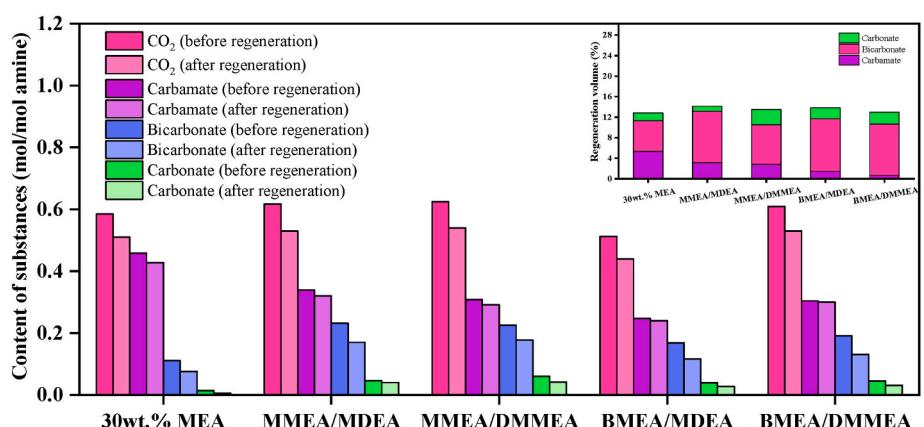


Fig. 9. Changes in the content of each substance before and after 20 min of regeneration of different amines.

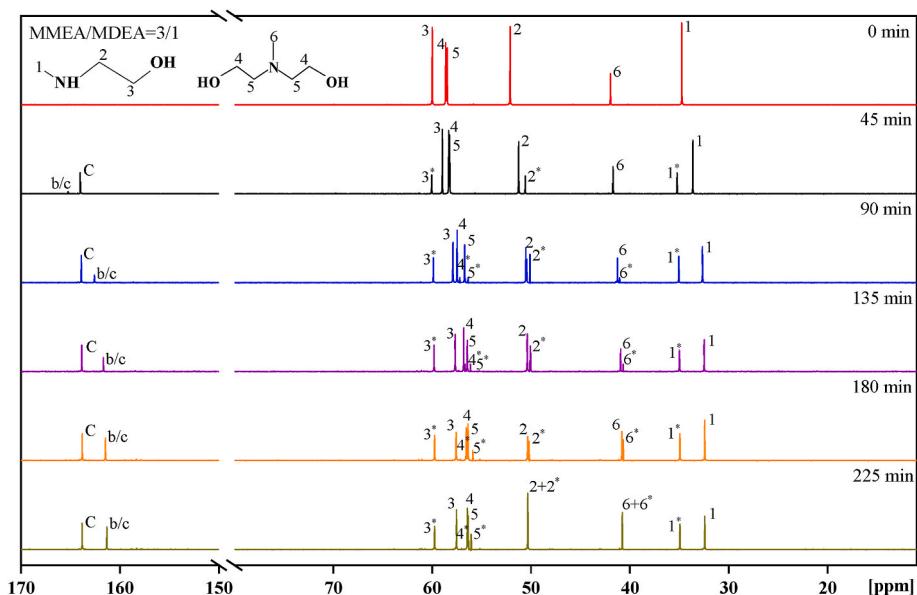


Fig. 10. ^{13}C NMR spectra of MMEA/MDEA mixed amines in biogas upgrading process. Numbers refer to the carbon atoms rapidly exchanged between free and protonated amines in the NMR measurement range. Asterisks refers to the carbon skeleton of the carbamate. C indicates the carbonyl atom on the carbamate. b/c refers to the rapidly exchanging bicarbonate/bicarbonate ion.

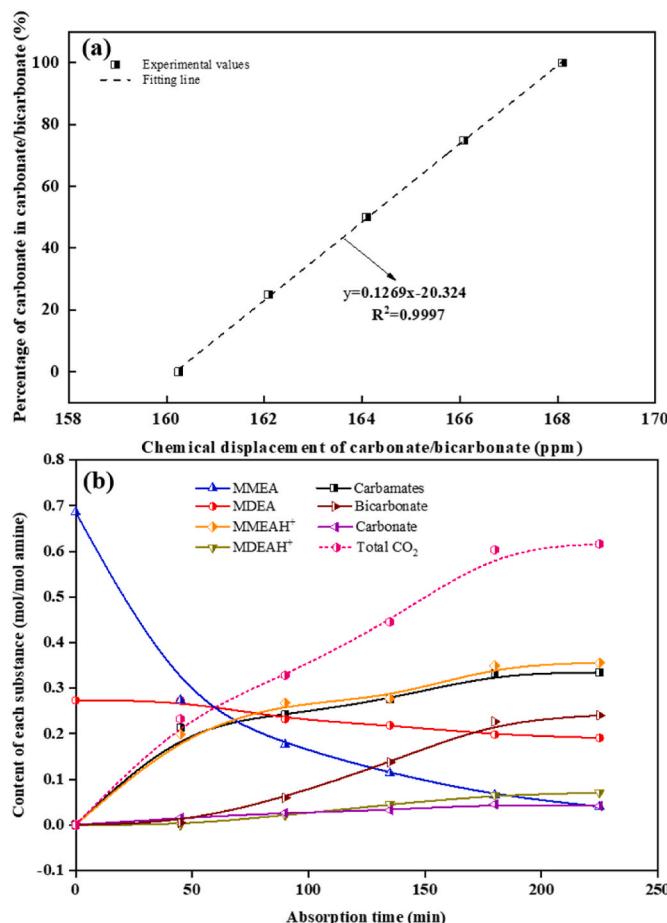
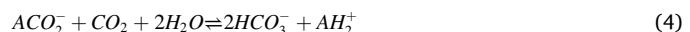
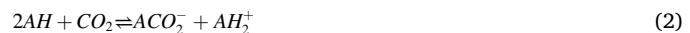


Fig. 11. Quantitative analysis based on ^{13}C NMR spectra: (a) Fitted curve of relative bicarbonate/bicarbonate content with chemical shift, (b) Trend of each content during MMEA/MDEA biogas upgrading.

sharply, which indicated that the presence of MMEA could effectively increase the initial CO_2 uptake rate. As the reaction time increased, the content of MDEA began to gradually decrease and the content of protonated MDEA and bicarbonate slowly increased, which indicated that MDEA started to join the reaction. It was worth noting that the bicarbonate content increases much faster than the carbonate content, which would greatly improve its regeneration energy consumption, and the reason for this phenomenon could be explained by Eqs. (2)–(5). It was also noteworthy that there was basically no production of carbonate and bicarbonate at the beginning of the reaction, but there was a significant consumption of MDEA, which was due to the fact that MMEA replaces part of the water to react with MDEA, but the reaction product was not bicarbonate but carbamate, as shown in Eqs. (6) and (7). This process was beneficial to speed up the initial absorption rate but increased the regeneration energy consumption, so choosing the right ratio through different targets is also a key factor for biogas upgrading.



where AH, AH_2^+ and ACO_2^- denotes the free amine, protonated amine and amine carbamate, respectively.



where A_T and A_TH^+ indicates the tertiary amine and protonated tertiary amine, respectively.

3.4. Selective analysis of CO_2/CH_4

The trend of CO_2 uptake with time for the mixed amines shown in Fig. 12(a) could give a good indication of the initial uptake rate of different amines with time, and the partial pressure of CO_2 when the uptake reaches equilibrium also clearly illustrated the trend of the

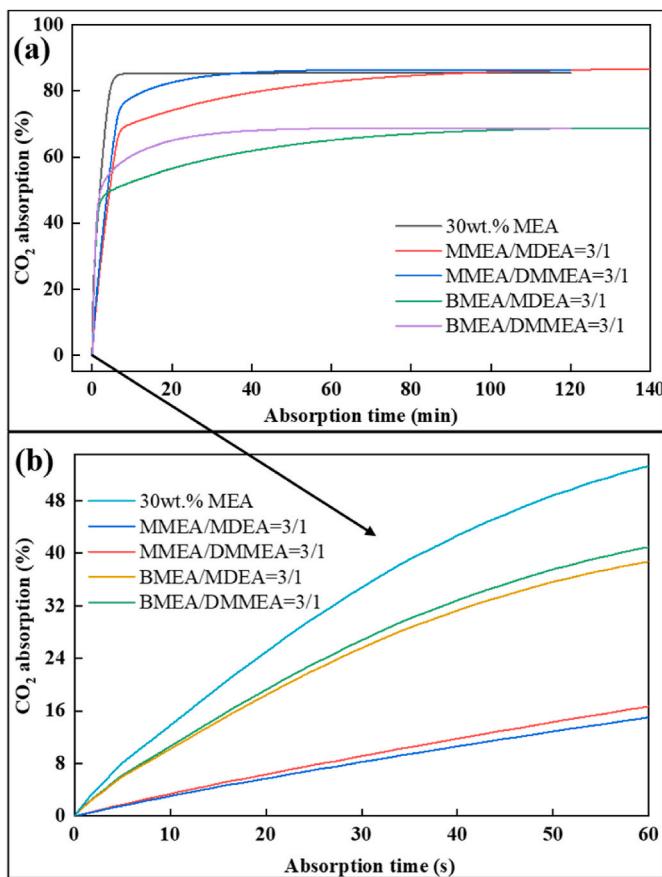


Fig. 12. CO₂ absorption rate curve of amine: (a) CO₂ equilibrium partial pressure calculation, (b) Initial CO₂ absorption rate of amine.

reaction between the amine and CO₂ in solution. Among them, MEA, MMEA/MDEA and MMEA/DMMEA had smaller CO₂ partial pressures when they reached equilibrium, indicating that they reacted with CO₂ more easily than the two mixed amines BMEA/MDEA and BMEA/DMMEA. This is mainly due to the reaction of MEA, MMEA/MDEA and MMEA/DMMEA with CO₂ to form a large amount of chemically stable carbamates, which corresponds to the results shown in Fig. 9. As can be seen from Fig. 12(b), although their initial reaction rates were not very different and both can reach the expected 96% methane purity, the initial CO₂ uptake rates of MMEA/MDEA and MMEA/DMMEA were slightly lower than the remaining two amine blends, which was mainly influenced more by the amount of carbamate produced at the beginning of the reaction. In addition, we also investigated the CH₄ absorption performance of different amine blends, as shown in Fig. 13, and found that the methane absorption was very low or even negligible. Therefore, the screened amine blends all also have high upgrading efficiency and high CO₂/CH₄ selectivity.

4. Conclusions

The results showed that the mixed amines consisting of MMEA/MDEA had the best biogas upgrading effect under the same experimental conditions, and the MMEA/MDEA = 3/1 was able to simultaneously achieve a saturation absorption of 0.617 mol CO₂/mol amine, an initial 100% methane purity and a regeneration rate of 54.3%. In addition, the ¹³C NMR results of this amine further indicated that the presence of MDEA could reduce the production of carbamate and promote the production of bicarbonate during the reaction process thus significantly reducing the heat of CO₂ desorption (19.01% lower than 30 wt% MEA under the same reaction conditions) while ensuring its high upgrading

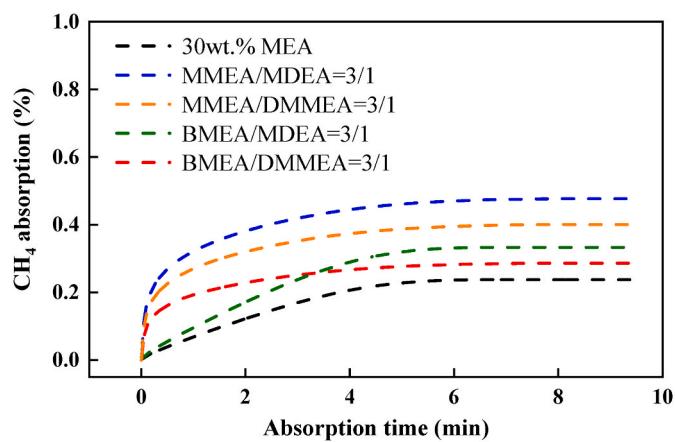


Fig. 13. Trend of methane equilibrium partial pressure.

effect. CO₂/CH₄ selectivity experiments can also be found that mixed amines have a low absorption of CH₄, which can ensure the upgrading efficiency of biomethane during biogas upgrading.

In conclusion, the mixed amines produced by blending MMEA with MDEA could have both higher upgrading performance of biogas, lower regeneration energy consumption and higher CO₂/CH₄ selectivity, and is expected to be a replacement for 30 wt% MEA. Finally, it is reasonable to believe that further research on the variation of reaction products with time or CO₂ loading during the reaction process of different amines and its effect on the regeneration process will be beneficial to guide the screening and preparation of mixed amines and lay the foundation for the continued improvement of renewable energy utilization in the future.

CRediT authorship contribution statement

Fanzhi Meng: Investigation, Writing – original draft. **Siyu Han:** Methodology. **Yuan Meng:** Conceptualization, Writing – review & editing. **Tongyao Ju:** Conceptualization, Writing – review & editing. **Li Lin:** Conceptualization, Writing – review & editing. **Jianguo Jiang:** Investigation, Conceptualization, Methodology, Writing – review & editing.

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.

Data availability

I have put all the data in the article

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2022.133288>.

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