

Effects of Alkyl Groups on Monoethanolamine Derivatives for Biomethane from Biogas Upgrading

Fanzhi Meng, Siyu Han, Yuan Meng, Tongyao Ju, Li Lin, and Jianguo Jiang*

Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 7299–7308

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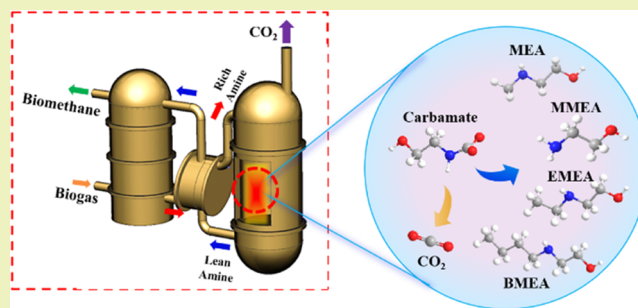
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ABSTRACT: Amine scrubbing is one of the key technologies for biogas upgrading to biomethane, which can be used to increase the calorific value of biomethane by separating out CO₂ to meet the global demand for renewable energy. In this paper, several monoethanolamine (MEA) derivatives with alkyl groups as variables are screened as sorbents for the biogas upgrading process. The effect of alkyl groups on the efficiency of biogas upgrading, the effectiveness of sorbent regeneration, and the selectivity of CO₂/CH₄ during biogas upgrading are investigated. The analysis of biogas upgrading experiments with different MEA derivatives shows that methyl and butyl are more favorable for improving CO₂ absorption and meeting the biogas upgrading effect of methane purity for a long period of time applicable in some countries, and ethyl is more conducive to the regeneration efficiency of amines. The results of the CO₂ desorption heat calculations show that the CO₂ desorption heat of ethyl monoethanolamine (EMEA) (66.67 kJ/mol CO₂), formed by replacing a hydrogen near the nitrogen with an ethyl group, is significantly lower than those of methyl monoethanolamine (MMEA) (73.04 kJ/mol CO₂) and butyl monoethanolamine (BMEA) (73.27 kJ/mol CO₂), formed by replacing a hydrogen near the nitrogen with a methyl group and a butyl group, respectively. The CO₂ desorption heats were significantly lower than those of MEA (82.12 kJ/mol CO₂), suggesting that ethyl can significantly reduce the CO₂ desorption heat of the amine compared to other alkyl groups. In the CO₂/CH₄ selectivity experiments, BMEA showed the fastest initial CO₂ absorption rate of 0.83%/s, while dimethyl monoethanolamine (DMMEA) showed the lowest initial CO₂ absorption rate of 0.16%/s. All amine solutions showed less than 1% absorption of CH₄ and had high CO₂/CH₄ selectivity.

KEYWORDS: amine scrubbing, biogas upgrading, alkyl groups, CO₂ desorption heat, CO₂/CH₄ selectivity



1. INTRODUCTION

Energy is the physical basis for human existence, and with the ongoing use of fossil fuels, in addition to the fact that they are a nonrenewable energy source, they also exert huge pressure on the ecological environment.^{1,2} To decrease the percentage of fossil fuels in the use of energy around the world and to further improve the environmental problems caused by the greenhouse effect, bioenergy has become a hot topic of concern for various countries and regions.^{3–5} Biogas, as a renewable bioenergy source, is being increasingly valued worldwide for its high low-level calorific value, which can substitute some fossil fuels for the generation of electricity, heating, and civil transport, and can help the EU to meet the future energy targets of the Renewable Energy Policy document (32% of total energy demand from renewable sources by 2030).^{6–10} Biogas consists of two main components, methane and carbon dioxide, and the presence of carbon dioxide can greatly hinder the energy efficiency of biogas, therefore upgrading biogas to prepare a high purity biomethane is a crucial step toward biogas for energy substitution.^{6,11–14}

As the demand for CO₂ capture continues to grow, new technologies for CO₂ capture are being developed by

researchers. The new gas treatment technology, OASE sulfexx, jointly introduced by BASF and ExxonMobil, is capable of selectively removing hydrogen sulfide while reducing CO₂ coabsorption in the gas stream. This technology helps eliminate bottlenecks in the Kraus tail gas treatment, acid gas concentration, and high-pressure acid gas removal units, resulting in a product hydrogen sulfide volume fraction of less than 10 μL/L, reducing both energy consumption and CO₂ emissions.^{15,16} Li et al. showed the direct conversion of CO₂ to valuable light olefin products by photocatalysis with high selectivity for C₂–C₄ conversion.¹⁷ Shen et al. prepared a solid amine material for biogas upgrading based on fly ash and polyethyleneimine, which significantly improved the cyclic stability by inhibiting the formation of urea compounds and

Received: February 6, 2022

Revised: April 26, 2022

Published: May 23, 2022

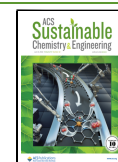


Table 1. Basic Information on the Molecular Structure of Amines

Name	Mass	Purity	Structure
MEA	61.08 g/mol	99.0 %	
MMEA	75.11 g/mol	98.0 %	
EMEA	89.14 g/mol	99.0 %	
BMEA	117.19 g/mol	99.0 %	
IPA	75.11 g/mol	99.0 %	
BA	89.14 g/mol	99.0 %	
DMMEA	89.14 g/mol	99.0 %	

has promising applications.¹⁸ The aqueous amine scrubbing technology, as a mature and high-efficiency chemical absorption technology with organic solvents, is considered the best option for capturing CO₂ from mixed gases, but it is limited by the high energy consumption for regeneration during its usage.^{19–22} In the biogas upgrading process, besides considering the regeneration effect of the amine solution, it is also important to ensure that the biogas upgrading effect, that is the methane purity of the upgraded biogas, meets the standards for use in different countries and industries.^{23–25} Among them, aqueous amines with higher CO₂ absorption can greatly reduce the circulation rate of lean amine liquids, aqueous amines with faster CO₂ absorption rates can significantly improve the methane purity of upgraded biogas, and aqueous amines with lower CO₂ desorption heat can greatly reduce the regeneration energy consumption of rich amine liquids and ultimately improve the carbon capture efficiency during the biogas upgrading process.^{26–28} Therefore, the development of amines with high CO₂ capture efficiency, high CO₂ loading, and low CO₂ desorption heat is an important part of biogas upgrading technology.^{29–31}

The screening of amines is an expensive and time-consuming process, and many studies have demonstrated that the CO₂ capture capacity of different structural amines varies.^{32–35} Muchan et al. studied the experiments of mixing several amines, such as 2-amino-2-methyl-1-propanol (AMP), 2-(ethylamino) ethanol (EAE), and 2-(dimethylaminoethanol) (DMAE), and found that the presence of steric hindrance resistance led to a significant improvement in CO₂ absorption by the absorbers.³⁶ Pandey et al. studied the experiments of mixing 2-(ethylamino) ethanol (EAE) and aminoethyl ethanolamine (AEEA) and found an enhancement in the heat of CO₂ desorption, the initial CO₂ absorption rate, and the amount of CO₂ absorbed by the mixed solutions.⁶ Sharif et al. showed that the presence of piperazine (PZ) increased the CO₂ uptake in the absorption system but decreased the solvent circulation rate in the trapping device.³⁷

The differences in dissociation constants and desorption heats of 14 amines (primary, secondary, and tertiary) were summarized by Rayer et al.³⁸ Ye et al. found that the heat of regeneration of mixed triethylenetetramine (TETA) and 2(diethylamino)-ethanol (DEEA) solutions was 50% lower than that of MEA solutions.¹¹ Although a large number of scholars have worked on amine solutions with better CO₂ absorption performance than 30 wt % aqueous MEA solutions, there is no systematic assessment of the effect of different amine structures on CO₂ absorption performance and the effectiveness of biogas upgrading.^{36,39–42} Therefore, it is necessary to establish the relationship between the molecular structure of amines and the biogas upgrading effect to better guiding the synthesis and screening of amines in the future.

In this work, all MEA derivatives with alkyl groups as variables are screened to study the effects of amines with different molecular structures on CO₂ uptake capacity, purity of methane, heat of CO₂ desorption, and initial CO₂ absorption rate in the biogas upgrading process to provide theoretical support for the selection and design of mono/hybrid amines to be subsequently used in the biogas upgrading process with amine scrubbing technology as the core and further promote the future increase of the percentage of renewable energy in the total energy demand.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Monoethanolamine (MEA), methyl monoethanolamine (MMEA), dimethyl monoethanolamine (DMMEA), ethyl monoethanolamine (EMEA), butyl monoethanolamine (BMEA), isopropylamine (IPA), and butylamine (BA) were purchased from Macklin and without further purification. The basic structural information of these amines is shown in Table 1, and the concentration was set at 3 mol/L during the experiment. The initial concentration of simulated biogas and the partial pressure of CO₂ are regulated by means of mass flow controllers purchased from Seven Star Flow Meters Ltd. The purity of CH₄, N₂, and CO₂ gases purchased from Air Liquide is greater than 99.9%.

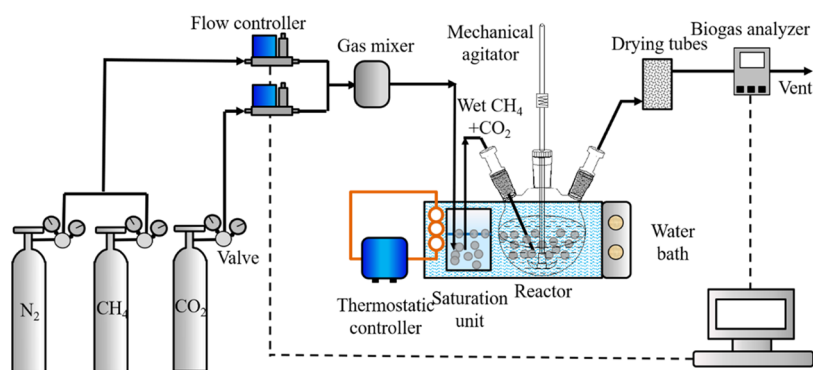


Figure 1. Diagram of the biogas upgrading plant.

2.2. Biogas Upgrading for Biomethane Preparation Experiments. The experimental setup for simulating biogas upgrading is shown in Figure 1, where the simulated biogas and methane purity are set at 580 mL/min and 65%, respectively, by adjusting the gas flow rate at the inlet via a computer and a mass flow controller. After passing through a saturated water device to compensate for the loss of outlet moisture, the gas mixture is fed into a reactor with mechanical stirring and reacted with 800 mL of fresh amine solution at a concentration of 3 mol/L in a water bath at 298.15 K. The purified gas is dehydrated through a drying tube and then fed into a nonspectrophotometric infrared biogas analyzer, where the calculated gas composition of the exit gas is transmitted back to the computer and recorded.

When the methane purity of the purified gas corresponds to the methane purity of the inlet simulated biogas, the reaction is stopped and the CO₂ absorption of the amine solution (α_{abs}) is determined by the Chittick titration apparatus with the results calculated three times and averaged.^{35,43}

2.3. Regeneration Experiments with Aqueous Amine Solutions. The reaction unit for regeneration through the desorption of CO₂ from aqueous amine solutions is shown in Figure 2. Five

desorption temperature, the CO₂ desorption heat required to desorb CO₂ from the rich amine solution and the evaporation heat from the evaporation of water under high temperature conditions, of which the CO₂ desorption heat is a key indicator of whether the amine solution is available for biogas upgrading under economically viable conditions. The heat of CO₂ desorption and the heat of absorption are considered to be numerically identical, and a number of studies have shown that the Gibbs–Helmholtz equation can be used to estimate the heat of CO₂ absorption of an amine solution without the use of a calorimeter, as shown in eq 1.^{6,44–47}

The experimental apparatus for the determination of the heat of CO₂ desorption is also shown in Figure 1. The flow ratio between N₂ and CO₂ at the gas inlet is varied by means of a mass flow controller, and the gas mixture is fed into a mechanically stirred reactor with 100 mL of fresh amine solution at a constant CO₂ partial pressure (P_{CO_2}) and simulated gas flow rate. The specific experimental parameters are shown in Table 2. The CO₂ loading of the amine solution during the reaction

Table 2. Experimental Parameters in the Determination of the CO₂ Desorption Heat

experimental parameters	numerical values
reaction temperature (K)	298.15, 308.15, 318.15
flow rate of the mixture (mL/min)	600
CO ₂ partial pressure (kPa)	10.1, 35.5, 50.7, 82.8, 101

was also measured using the Chittick titration apparatus. When the CO₂ loading of the samples taken for two consecutive periods remained constant, the aqueous amine solution was considered to be saturated and the reaction was stopped.

$$\frac{d(\ln P_{\text{CO}_2})}{d\left(\frac{1}{T_r}\right)} = \frac{\Delta h_r}{R} \quad (1)$$

where T_r is the reaction temperature (K), Δh_r is the CO₂ heat of absorption of the amine (J/mol), and R is the universal gas constant (8.314 J/mol·K).

2.5. CO₂ Selectivity Analysis of Aqueous Amines. The CO₂ selectivity of the aqueous amine in the biogas upgrading process is an important indicator to evaluate whether the gas upgraded by the aqueous amine can meet the requirements of the industry. A sealed pressure vessel with a two-phase stirrer was repeatedly pumped and injected by a vacuum pump and a CO₂ cylinder, respectively, to fill the vessel with CO₂. The prepared aqueous amine was injected into the reactor through a constant voltage device at a constant water bath temperature (298.15 K), and the temperature and pressure inside the pressure vessel were transmitted to the computer and recorded via an HAA digital pressure and temperature sensor. The aqueous amine absorption experiments for CH₄ are in agreement with the CO₂ absorption experiments (Figure 3).

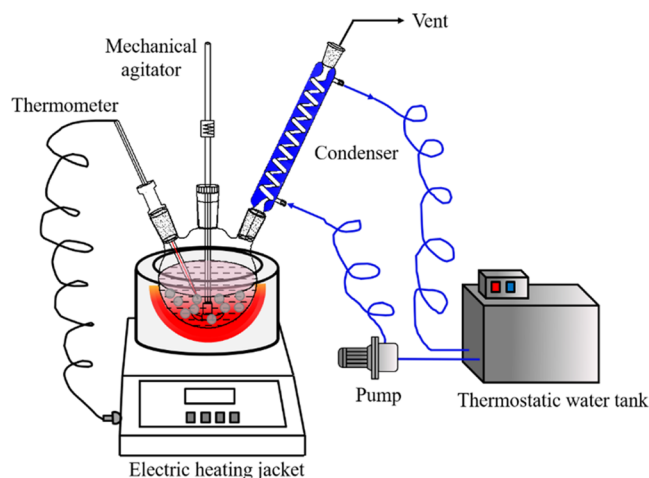


Figure 2. Diagram of the regeneration unit for amine-rich liquids.

hundred milliliters of the reaction solution was placed in a reactor with mechanical stirring and heated by an electric heating jacket with a thermometer and a condensation device at the outlet of the reactor to prevent excessive amine loss and water evaporation during the desorption process. The duration of the reaction is controlled to 130 min and samples are taken at 10 min intervals. The CO₂ loading of the amine solution (α_{des}) is then determined by the Chittick titration apparatus at various times of desorption.

2.4. CO₂ Desorption Energy Analysis. The energy consumption of aqueous amines during regeneration is mainly the sensible heat of increasing the amine solution from absorption temperature to

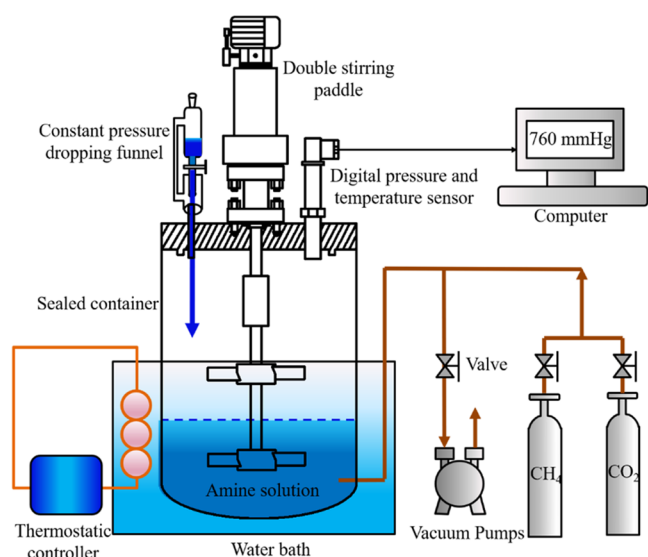


Figure 3. CO₂ selective determination device for amines.

3. RESULTS AND DISCUSSION

3.1. Experimental Series of Biogas Upgrades. Biomethane has been used in China and some EU countries for grid and vehicle applications, and the required biomethane purity is above 95 and 85%, respectively.²⁶ The calorific value of biomethane is mainly determined by the purity of methane after biogas upgrading; therefore, the composition of the upgraded gas is the key to determine whether this aqueous amine can be applied to the biogas upgrading technology by amine scrubbing. The purity of biomethane produced by the aqueous amine selected for biogas upgrading under the same operating conditions as a function of time is shown in Figure 4.

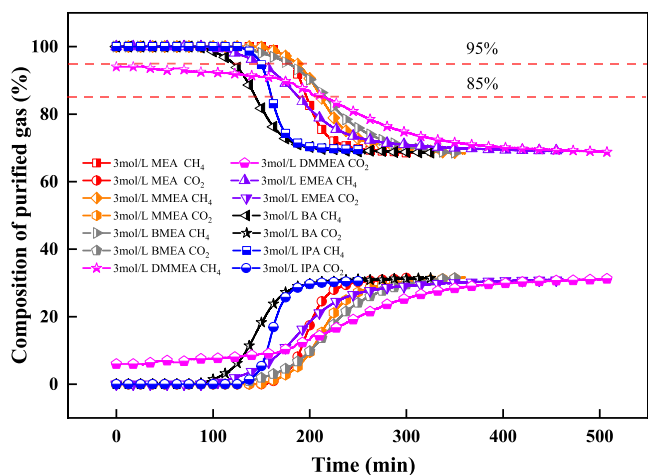


Figure 4. Effect of alkyl groups on MEA derivatives in biogas upgrading experiments.

The experimental results show that, if the purity of methane in the purified gas is 95%, the relationship between the biogas upgrading effect of the selected aqueous amine is MMEA > MEA > BMEA > EMEA > IPA > BA > DMMEA, and if the purity of methane in the purified gas is 85%, the relationship between the biogas upgrading effect of the selected aqueous amine is BMEA > DMMEA > MMEA > MEA > EMEA > IPA > BA, and the values of the specific upgrading time are shown in Figure 5.

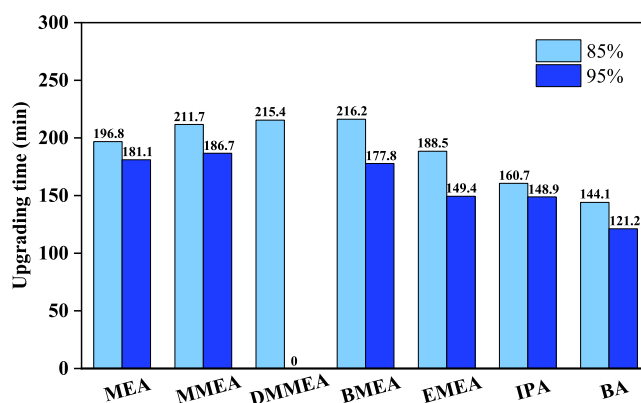


Figure 5. Upgrading time for different amines at 85 and 95% exported methane purity.

The presence of alkyl groups essentially reduces the effectiveness of upgrading biogas to 95% methane purity, especially when the two hydrogen bonds linked to nitrogen in the MEA structure are replaced by methyl groups, the methane purity of the upgraded biogas will not reach 95%. This is mainly because although methyl can increase the upgrading effect by increasing CO₂ uptake with the same high CO₂ capture rate when both H-bonds of MEA (primary amine) are replaced by methyl, it becomes DMMEA (tertiary amine) and cannot continue to react with CO₂ to form carbamate, which greatly reduces the CO₂ capture rate and thus makes the upgrading effect significantly lower.^{21,48,49} It is worth noting that the biogas upgrading effect of MMEA, IPA, and BMEA does not decrease significantly compared to the other MEA derivatives, suggesting that methyl and butyl have a lower weakening effect on biogas upgrading than the other alkyl groups. However, the absolute majority of the amines are able to achieve 85% methane purity in the upgraded gas over a longer period of time, with MMEA and BMEA surprisingly outperforming MEA for biogas upgrading, again suggesting that methyl and butyl have less of a weakening effect on biogas upgrading than the other alkyl groups. Combined with the data in Figures 4 and 5, it is likely that this enhanced biogas upgrading is the result of methyl and butyl significantly increasing the total CO₂ loading of the amine in addition to appropriately weakening the 100% methane purity of the amount of upgraded biogas. The results of DMMEA further confirm this conjecture, as shown in Figure 4, where the peak methane purity of the upgraded gas is significantly reduced after the introduction of the two methyl groups but still remains above 85%, and the extension of the curve due to the significant increase in CO₂ absorption leads to a longer time to 85% methane purity. This is also mainly due to the fact that methyl as an electron donor is effective in increasing the alkalinity of the solution and thus the CO₂ absorption but not in biogas upgrading, which is influenced by the absorption rate. Therefore, the biogas upgrading of MMEA and BMEA is more effective in terms of the methane purity of the upgraded gas. It is also worth noting that the biogas upgrading effect of aqueous EMEA with hydrogen bonds near the nitrogen replaced by ethyl is always in the middle part of the ranking results for 85 and 95% methane purity, respectively, and is also a relatively effective and stable amine solution.

3.2. Study of the Desorption Rate and Regeneration Characteristics of Amines. The regeneration effect of an amine is always the key to evaluate whether amine can be used in an amine washing technology, as it is directly related to the

economic cost of applying the technique and the recycling rate of the amine solution. The CO₂ loading of the amine-rich solution formed after the use of the different MEA derivatives at 363.15 K as a function of time is shown in Figure 6. The results

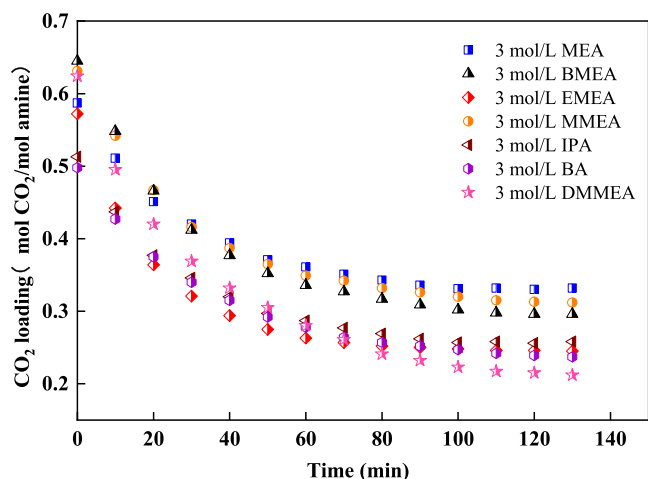


Figure 6. Desorption curve of amine-rich solution at 363.15 K.

show that the CO₂ loading of the amine solution decreases rapidly with increasing desorption time and then plateaus at around 120 min. Combining the CO₂ loadings and regeneration rates of the different amines before and after desorption in Table 3, it can be seen that all of the MEA derivatives introduced with

Table 3. Regenerative Properties of Different Amines

amine aqueous solution	molar volume (mol/L)	α_{abs} at 298.15 K	α_{des} at 363.15 K	regeneration rate (%)
MEA	3.0	0.587	0.332	43.44
MMEA	3.0	0.631	0.312	50.55
BMEA	3.0	0.645	0.296	54.11
BA	3.0	0.498	0.237	52.41
EMEA	3.0	0.572	0.245	57.17
IPA	3.0	0.513	0.258	49.71
DMMEA	3.0	0.624	0.212	66.03

alkyl groups have improved regeneration results compared to MEA, indicating that alkyl groups can effectively reduce the energy required for the desorption process of MEA. In addition, the results in order of regeneration rate are DMMEA > EMEA > BMEA > BA > MMEA > IPA > MEA, where DMMEA and EMEA show the fastest desorption rate and the best regeneration effect (66.03 and 57.17%, respectively), which, on the one hand, indicates that the regeneration effect of the amine solution is more favorable for ethyl than for other alkyl groups and, on the other hand, that the change in nature of the amine from secondary to tertiary amine significantly affects its regeneration effect more than primary to secondary amine in the process of continuous methyl substitution of hydrogen bonds close to the nitrogen. This is mainly due to the fact that tertiary amines only form substable carbamate hydrogens rather than stable carbamates during the reaction with CO₂.

In the upgrading process of biogas, the CO₂ loading of the amine-rich liquid before and after regeneration is also an important indicator to determine the performance of the amine liquid. The α_{abs} and α_{des} of different aqueous amines are shown in Figure 7. Only EMEA and DMMEA exhibit both relatively

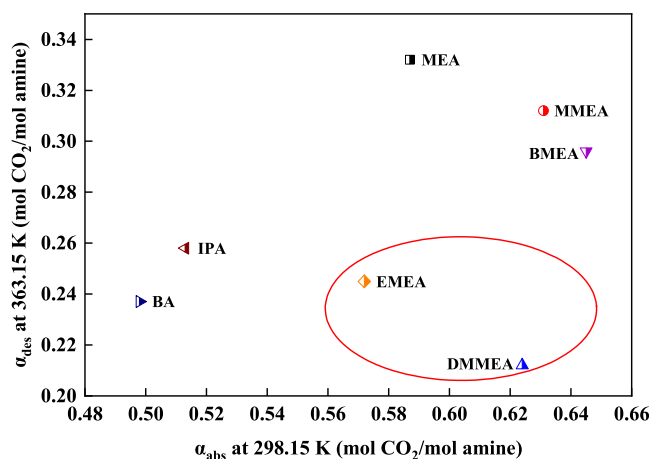


Figure 7. CO₂ loading before and after desorption of the amine solution.

high α_{abs} and low α_{des} , so the combination of desorption rate and regeneration efficiency suggests that EMEA and DMMEA have a high CO₂ loading and can quickly complete desorption and achieve a high regeneration effect.

3.3. Effects of Hydroxyethyl Groups in MEA Derivatives on the Biogas Upgrading. To further establish the relationship between the molecular structure and the biogas upgrading performance of the amine, we have summarized the situation of MEA derivatives with different molecular structures in terms of CO₂ absorption and desorption, as shown in Figures 8 and 9. The MEA derivatives in Figure 8 are dominated by the replacement of hydrogen bonds near the nitrogen by alkyl groups, whereas the MEA derivatives shown in Figure 9 are mainly dominated by the replacement of hydrogen bonds near the carbon by alkyl groups. It is clear from the results in these figures that the substitution of alkyl groups on top of the MEA structure has a significant effect on the absorption and desorption properties of CO₂.

From the data in Figure 8, it can be seen that after the hydrogen on MEA near the nitrogen was replaced by methyl, ethyl, and butyl to form MMEA, EMEA, and BMEA, respectively, the CO₂ absorption also increased from 0.587 to 0.631, 0.572 and 0.645 mol CO₂/mol amine, respectively. This indicates that methyl and butyl are favorable for increasing the CO₂ absorption of amine during the biogas upgrading process, while ethyl has almost a noneffect on the increase of CO₂ absorption. The CO₂ loadings of MMEA, EMEA, and BMEA after desorption also increased from 0.332 to 0.312, 0.245 and 0.296 mol CO₂/mol amine, respectively, indicating that the presence of ethyl facilitated the regeneration of the amine process. When the other hydrogen bond near the nitrogen in MMEA was also replaced by methyl, the CO₂ loading of the amine during the biogas upgrading process did not change significantly, but the CO₂ loading after desorption decreased significantly again, indicating that the presence of the H-bond increases the energy required for the amine during desorption and thus does not facilitate the regeneration of the rich amine.

As shown in Figure 9, the replacement of hydrogen bonds close to the carbon in the molecular structure of MEA by alkyl groups resulted in a decreasing trend in CO₂ loading during biogas upgrading. The replacement of hydrogen bonds near the carbon in MEA by methyl and ethyl groups to form IPA and BA reduced the CO₂ loading from 0.587 to 0.513 mol CO₂/mol amine and 0.498 mol CO₂/mol amine, respectively, indicating

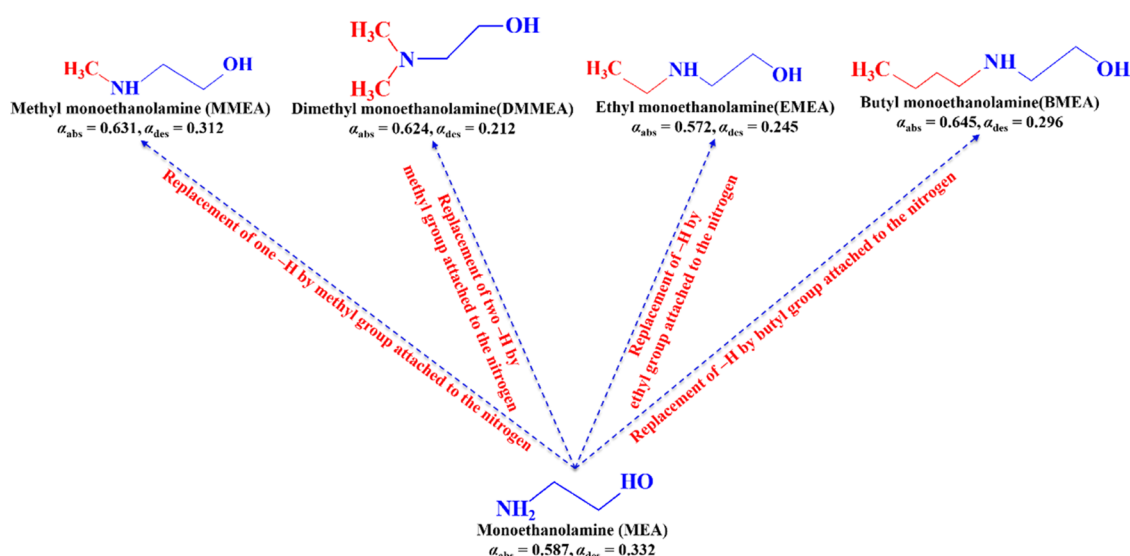


Figure 8. Changes in the chemical structure of MEA after modification to MMEA, DMMEA, EMEA, and BMEA.

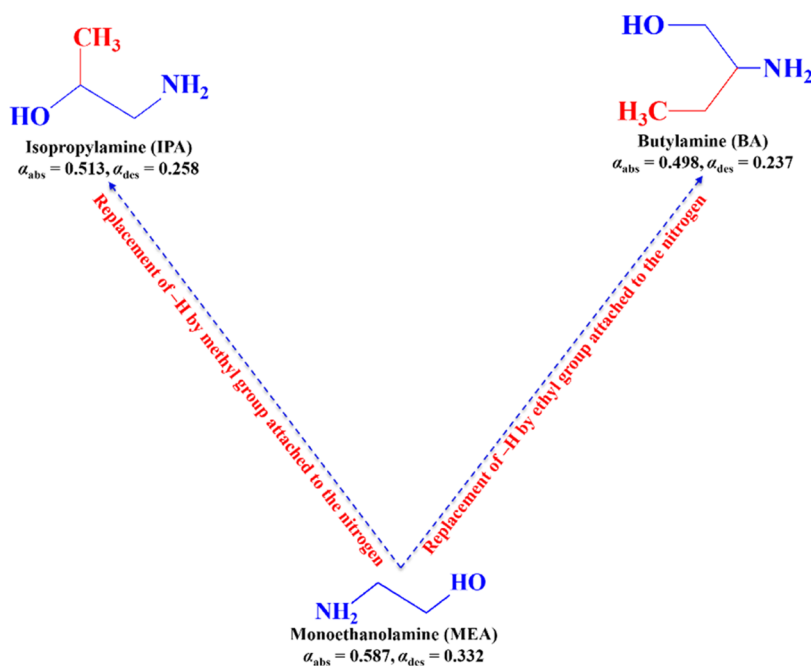


Figure 9. Changes in the chemical structure of MEA after modification to IPA and BA.

that C–H bonds play a more important role in CO₂ uptake than N–H bonds. In addition, IPA was able to achieve a CO₂ loading of 0.513 mol CO₂/mol amine during biogas upgrading compared to 0.498 mol CO₂/mol amine for BA, further suggesting that methyl is more beneficial than ethyl in improving CO₂ absorption during biogas upgrading. The CO₂ loading of IPA after desorption of the amine-rich solution was 0.258 mol CO₂/mol amine, while that of BA dropped to 0.237 mol CO₂/mol amine, again suggesting that ethyl is more favorable for amine regeneration, echoing the previous results.

3.4. Analysis of Energy Consumption of Aqueous MEA Derivative Desorption. To further analyze the energy consumption for the desorption of different MEA derivatives with alkyl groups as variables, we calculated the heat of CO₂ desorption of the selected amines to assess the energy required for the reaction products of the amines with CO₂ during the

thermal decomposition of the amines to release CO₂. Following the calculation method and experimental parameters mentioned in Section 2.4, we calculate the equilibrium CO₂ absorption (α_{eq}) of the different amines and its trend with CO₂ partial pressure and absorption temperature, as shown in Table S1 and Figure S1 of the supporting information, respectively.

Figure S2 represents a plot of the partial pressure of CO₂ versus absorption temperature for different amines when the same equilibrium solubility of CO₂ is obtained. From the results in the graph, it can be found that the experimentally obtained data have a good fit to the Gibbs–Helmholtz equation, and therefore, the heat of CO₂ desorption of the amine solution can be calculated from the respective slopes of the fitted equations, and the specific values of which are shown in Figure 10. The results show that DMMEA and EMEA have the lowest heat of CO₂ desorption of 61.68 and 66.67 kJ/mol CO₂, respectively,

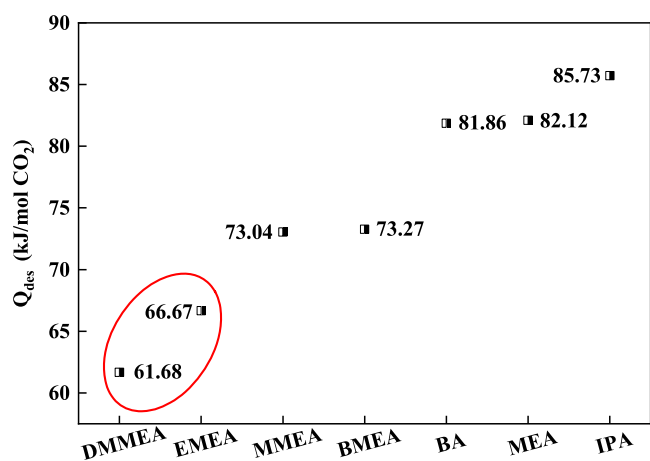


Figure 10. Values of the heat of CO_2 desorption for different MEA derivatives.

indicating that they require the lowest energy for the desorption process and have the fastest desorption rates, which echoes the findings in Section 3.2. The higher heat of CO_2 desorption of 85.73, 82.12, and 81.86 kJ/mol CO_2 for IPA, MEA, and BA, respectively, indicates that they absorb more energy to destroy the products of the reaction between amine and CO_2 during the desorption process, which is also consistent with the results of the analysis in Section 3.2 and is not conducive to the regeneration process of the amine solution. This experiment therefore further confirms the importance of the heat of CO_2 desorption for the amine regeneration process.

3.5. Initial Absorption Rate and Selectivity of CO_2 . The initial CO_2 absorption rate is one of the key factors in determining the purity of methane after biogas upgrading. The trend of CO_2 absorption with time for different MEA derivatives is shown in Figure 11. It is clear from Figure 11b that the initial absorption rates of amines within 1 min are $\text{BMEA} > \text{MEA} > \text{IPA} > \text{MMEA} > \text{EMEA} > \text{BA} > \text{DMMEA}$. Although the initial CO_2 absorption rates vary in magnitude, all of the MEA derivatives in this paper, except DMMEA, achieve 95% methane purity at export for the effect of initial biogas upgrading. This also indicates that they all have excellent initial CO_2 absorption rates.

In addition, CO_2/CH_4 selectivity is also an important factor to focus on in the biogas upgrading process. Figures 11a and 12 show the effect of different types of MEA derivatives on CO_2 and CH_4 capturing alone under the influence of equilibrium partial pressure, respectively. The results show that the screened amines have a high CO_2 capture capacity (over 60% CO_2 capture for BMEA and close to 85% CO_2 capture for the other amines) and a low CH_4 uptake capacity (less than 1% CH_4 absorption), indicating that these MEA derivatives have negligible CH_4 absorption in the biogas upgrading process and have a high CO_2/CH_4 selectivity.

3.6. Comprehensive Evaluation of MEA Derivatives. To make a comprehensive evaluation of the performance of the MEA derivatives mentioned in this paper with alkyl groups as variables in the biogas upgrading process, several essential data have been selected for comparison, as shown in Table 4, where the initial absorption rate refers to in this paper is the average absorption rate over one minute in Figure 11b, which will determine the methane purity of the upgraded gas at the beginning of the biogas upgrading. On the one hand, the biogas upgrading time of the amine solution used in this paper is usually

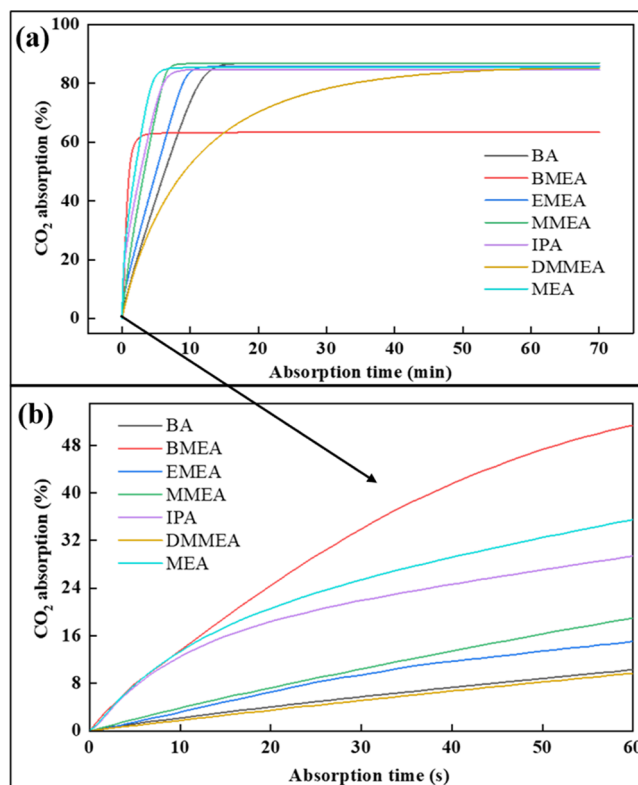


Figure 11. Variation of CO_2 absorption rate with time: (a) determination of the equilibrium partial pressure of CO_2 and (b) initial CO_2 absorption rate in 1 min.

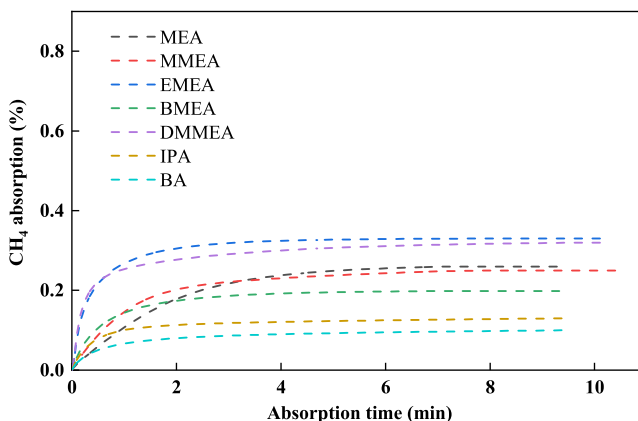


Figure 12. Variation of CH_4 absorption rate with time.

Table 4. List of Main Properties of Amines

amine aqueous solution	molar volume (mol/L)	initial absorption rate (%/s)	α_{abs} at 298.15 K	Q_{des} (kJ/mol CO_2)
MEA	3.0	0.53	0.587	82.12
MMEA	3.0	0.27	0.631	73.04
BMEA	3.0	0.83	0.645	73.27
BA	3.0	0.17	0.498	81.86
EMEA	3.0	0.24	0.572	66.67
IPA	3.0	0.47	0.513	85.73
DMMEA	3.0	0.16	0.624	61.68

200–500 min much longer than 1 min, and on the other hand, to reduce the error caused by the initial external disturbance, the

absorption rate within 1 min is chosen as the initial absorption rate. In addition, the CO₂ absorption load and the heat of CO₂ desorption, mentioned in the previous analysis, play an important role in the upgrading time during the biogas upgrading process and the regeneration energy consumption during the desorption process, respectively.

The distribution of the data is shown in Figure 13. In the selection process of amines for biogas upgrading, the amines

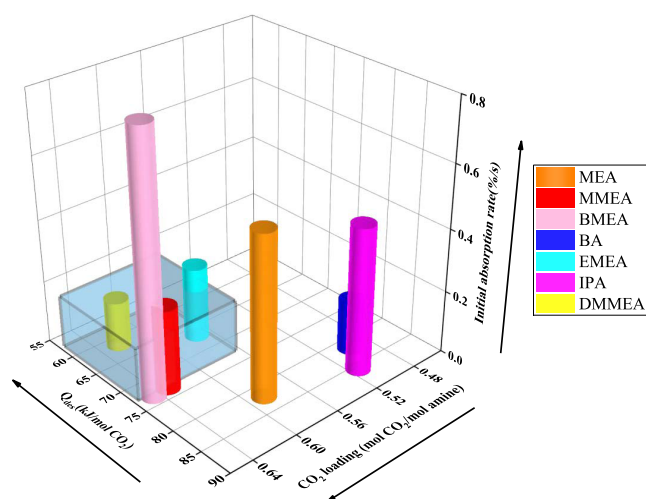


Figure 13. Comprehensive evaluation of the effectiveness of biogas upgrading with different amines.

with faster initial absorption rates, higher CO₂ loading, and lower CO₂ desorption heats are preferred. The distribution of the different amines in the graph shows that BMEA and MMEA have the best CO₂ loading and initial absorption rates, with intermediate values for the heat of CO₂ desorption. DMMEA has the best heat of CO₂ desorption and a high CO₂ loading with the lowest initial absorption rate (still achieving 85% methane purity for a long time, see Section 3.2). EMEA has a slightly lower CO₂ absorption and initial absorption rate than the previous three but with a lower heat of CO₂ desorption. From these results, it can be concluded that DMMEA performs best when the methane purity of the upgraded biomethane is required to be as low as 85%. If the methane purity of the upgraded biomethane is very high and close to 100%, BMEA, MMEA, and EME have good biogas upgrading performance; however, if the process is optimized to achieve the required methane purity within the time limit by adjusting the process parameters such as circulation rate and biogas residence time, then EMEA with a lower heat of CO₂ desorption is the best performer.

4. CONCLUSIONS

The results show that the effect of different alkyl groups on MEA derivatives in biogas upgrading varies, with methyl and butyl groups not significantly weakening the upgrading effect and even improving it significantly at 85% methane purity at export. The introduction of alkyl groups also facilitates the regeneration of aqueous amines and effectively reduces the energy consumption during the desorption of MEA derivatives, with ethyl groups having a better energy reduction effect than other alkyl groups. The amine used in this paper also has a negligible effect on the capture of CH₄ with a high CO₂/CH₄ selectivity.

On balance, DMMEA performs best when the methane purity of the biomethane from the upgraded biogas is required to be as low as around 85%. If the methane purity of the upgraded biomethane is significantly higher, even close to 95%, BMEA, MMEA, and EME have good performance for biogas upgrading, and on this basis, EMEA with its lower heat of carbon dioxide desorption is the best choice for optimizing the process so that the methane purity can be successfully achieved within the specified time by adjusting the process parameters, such as the amine circulation rate and biogas residence time. Finally, it is reasonable to believe that further research into the relationship between the functional groups of different amines and the effectiveness of biogas upgrading and amine liquid regeneration will be more beneficial in guiding the screening and preparation of blended and synthetic amines, laying a solid foundation for increasing the share of renewable energy in total energy in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c00728>.

Methyl and butyl are more effective in increasing the effective time of biogas upgrading; Methyl and butyl are effective in increasing the CO₂ loading of amines; Ethyl is effective in reducing the CO₂ desorption heat and energy consumption; Alkyl groups have little effect on CO₂/CH₄ selectivity; DMMEA and EMEA are best when 85 and 95% CH₄ purity is required respectively (Highlights) (PDF)

Data table and trend of equilibrium CO₂ uptake for 3 mol/L MEA, MMEA, BMEA, BA, EMEA, IPA, and DMMEA at different reaction temperatures (298.15, 308.15, and 318.15 K) and CO₂ partial pressures (10.1, 35.5, 50.7, 82.8, and 101 kPa) and fitting curves for the heat of CO₂ desorption of MEA, MMEA, BMEA, BA, EMEA, IPA, and DMMEA (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jianguo Jiang — School of Environment, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-0074-040X; Phone: (+86) 010 62783548; Email: jianguoj@tsinghua.edu.cn

Authors

Fanzhi Meng — School of Environment, Tsinghua University, Beijing 100084, China
 Siyu Han — School of Environment, Tsinghua University, Beijing 100084, China
 Yuan Meng — School of Environment, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-9591-0052
 Tongyao Ju — School of Environment, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-5629-8921
 Li Lin — School of Environment, Tsinghua University, Beijing 100084, China

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c00728>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are thankful for the financial support from the National Natural Science Foundation of China (Grant 22176108).

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