

Full Length Article

Effects of hydroxyethyl group on monoethanolamine (MEA) derivatives for biomethane from biogas upgrading

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ABSTRACT

Upgrading of biogas to produce biomethane is an essential way to increase the calorific value of biogas by separating CH₄ and CO₂ to satisfy the global renewable energy demand. In this study, the efficiency of carbon dioxide (CO₂) trapping in aqueous monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), and triethanolamine (TEA) solution during biogas upgrading for biomethane was determined. Effects of hydroxyethyl groups on MEA derivatives were investigated in terms of biogas upgrading and regeneration, CO₂ desorption heat, initial CO₂ absorption rate and CO₂/CH₄ selectivity. The duration of upgraded biogas meeting certain European Union (EU) application standards for methane purity during upgrading was reduced by 70, 78 and 200 mins for DGA, DEA and TEA respectively compared to MEA due to the partial substitution of H-bonds by hydroxyethyl groups, and the absorption rate was also reduced, whereas TEA was not suitable for biogas upgrading as it was inefficient for biogas upgrading effect and absorption rate. The calculated results from the Gibbs-Helmholtz equation showed that MEA had the largest CO₂ desorption heat (82.47 kJ/mol CO₂) and the other MEA derivatives had lower desorption heat than MEA, indicating that MEA consumes more energy in the desorption process. As for the equilibrium partial pressure, all amine solutions absorbed less than 0.4% of the total volume of CH₄ and had a high CO₂/CH₄ selectivity.

1. Introduction

With the growing global environmental and energy problems, the development and utilization of renewable energy sources has attracted great attention from governments in order to meet our future energy requirements [1]. To promote energy innovation, the European Union's Renewable Energy Policy (EU) 2018/2001 clearly states that renewable energy must account for 32% of total energy demand by 2030. Biogas, as a renewable bioenergy produced by biodegradation of organic matter in landfill and anaerobic digester, has four characteristics including cleanness, high efficiency, safety and renewability [2,3]. Biogas is mainly composed of methane (45–70%), carbon dioxide (30–55%) and other trace substances such as hydrogen sulfide, water, nitrogen, oxygen, ammonia, siloxane, etc., and due to its high calorific value (15–30 MJ/Nm³), it can partly replace gasoline, diesel or natural gas as engine fuel and then solve the problem of global energy crisis, which has attracted more and more attention from all over the world [4–6]. As the main impure component of biogas, CO₂ seriously reduces the applicability and calorific value of biogas [7]. It is necessary to upgrade biogas

to biomethane through upgrading technology which will increase the volume concentration of CH₄ and achieve higher low-calorific value (LHV) [8,9].

The main purpose of biogas upgrading is to remove carbon dioxide and obtain high-purity methane. The existing decarbonization technologies mainly include: (1) pressure swing adsorption (PSA) technology, which utilizes the differences of adsorption capacity, adsorption capacity and adsorption speed of adsorbents for different gas components, and the characteristics of adsorption capacity changing with pressure [10,11]; (2) Water washing and organic solvent physical absorption technologies, which is in feature of different solubility of methane and carbon dioxide in water and organic solvent; (3) Organic solvent chemical absorption technology which is used for separation and absorption of carbon dioxide and methane by amine solution [12,13]; (4) The membrane separation technology, which is based on the different permeability of gas through polymer membrane [14,15]; (5) Low temperature upgrading technology, which achieves the goal of selective condensation and separation of carbon dioxide by cooling mixed gas with refrigeration system. As a mature CO₂ capture technology, amine

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scrubbing technology has many advantages, such as high upgrading efficiency (>97% methane), powerful absorption capacity, little methane loss, renewable lean solution and low operation cost [16–19]. However, this technology still has some inherent defects, such as high regeneration energy consumption, easy oxidation and degradation. For amine scrubbing biogas upgrading technology, larger absorption capacity can effectively reduce the circulation rate and sensible heat loss, while fast absorption rate can significantly improve the upgrading efficiency of biogas and reduce capital consumption [20,21]. The most important point is that the faster desorption rate can greatly reduce the regeneration energy consumption and improve the carbon capture efficiency. Therefore, the development of a solvent with high CO₂ absorption capacity, fast absorption rate and fast desorption rate is the key to upgrading technology of biogas by amine method [21–24].

Primary amines and secondary amines have a fast CO₂ absorption rate, but the CO₂ absorption capacity (theoretical value is greater than 0.5 mol CO₂/mol amine) and desorption rate are insufficient. Compared with the former, tertiary amines have higher CO₂ absorption capacity (theoretical value can reach 1 mol CO₂/mol amine) and lower regeneration energy consumption, but the CO₂ absorption rate is slower [16,25,26]. Mixed amines can combine the advantages of each amine, so that the reaction solution has both a higher CO₂ absorption capacity and a fast absorption rate. Some studies on the decarbonization of mixed amines have been reported [27–29]. For example, Mohamad et al. have studied the different compositions of the mixture of methyldiethanolamine (MDEA) and diethanolamine (DEA) by simulation, analysis and numerical simulation, in order to reduce the exergy loss, energy loss and CO₂ emission in the deodorization process [5]. Xiao et al. found that adding piperazine to MDEA aqueous solution can effectively improve the decarbonization process of amine absorption method [30]. Zhang et al. studied the competitive and cooperative reaction of primary and secondary amino groups in the process of CO₂ absorption, and proposed the competitive and cooperative reaction mechanism [31]. Although there are still good prospects for the development of mixed amines, the screening of amines is a very time-consuming and expensive task. It is necessary to further understand the relationship between the molecular structure of amines and their carbon capture characteristics, and develop a pre-evaluation method that links its molecular structure with the decarbonization performance of amines, which can better guide the screening and design of mixed amines in the future [9,32–35].

In this work, we screened all monoethanolamine (MEA) derivatives with hydroxyethyl group as a variable to investigate the effects of amine molecular structure on CO₂ absorption during biogas upgrading, regeneration, CO₂ desorption heat and CO₂/CH₄ selectivity, in order to provide theoretical guidance and support for the further mixing amine selection and design, which is important for raising the percentage of renewable energy in future energy consumption.

2. Experimental section

2.1. General information

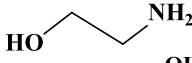
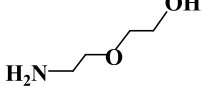
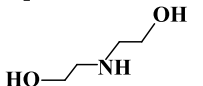
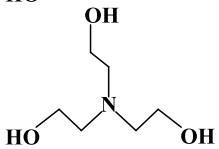
MEA, diglycolamine (DGA), DEA, and triethanolamine (TEA) were purchased from Macklin and used without further upgrading. The detailed structures of these amines are shown in Table 1. CH₄ (>99.9%), N₂ (>99.9%) and CO₂ gases (>99.9%) were purchased from Air Liquide. The mass flow controller (CS200) was purchased from Beijing Sevenstar Flowmeter Co., Ltd. The pH value of all samples was measured by WTW pH 3310 m at 298.15 K. During the experiment, the concentration of amine aqueous solution was set at 3 mol/L.

2.2. Biogas upgrading experiments

The experimental device shown in Fig. 1(a) was used for the experiment of CO₂ removal from biogas. The device was mainly composed of gas cylinder, gas flow controller, gas mixer, saturation unit, water bath,

Table 1

The information of Amines in this work.

Acronym	Molecular weight	Purity	Boiling point	Molecular structure of alkanolamines
MEA	61.08 g/mol	99.0 %	443.15 K	
DGA	105.14 g/mol	98.0 %	494.15 K	
DEA	105.14 g/mol	99.0 %	490.15 K	
TEA	149.19 g/mol	99.0 %	608.55 K	

flask, mechanical agitator, condenser and biogas analyzer. By adjusting the flow ratio of CH₄ and CO₂, the biogas under different CO₂ partial pressure was simulated. In the experiment of CO₂ removal from biogas, 800 ml fresh amine aqueous solution with certain concentration was injected into a round bottom reactor and stirred in a water bath at 298.15 K (±2 K). The mixing flow of methane and carbon dioxide was controlled by mass flow controller and mixing tank, and the partial pressure of carbon dioxide was set to 35.5 kPa. The mixture gas flow rate of 580 ml/min was introduced into the saturator to obtain wet CH₄ and CO₂ to compensate the loss of water at the outlet. Then the mixture gas entered the reactor to react with amine liquid, and the purified biogas gas passed through the condensing device to recover the evaporated water and amine. The content of methane and carbon dioxide in outlet gas was analyzed by Gas-borad 2000 plus non spectroscopic infrared biogas analyzer, and the resolution and accuracy of the instrument are 0.01% and ±2% FS, respectively.

2.3. Experiments on regeneration of amine-rich solutions

The experimental device for amine regeneration by CO₂ desorption from rich amine solution was shown in Fig. 2, which was similar to that mentioned in the literature [36,37]. 400 ml of rich amine solution was placed in a 1000 ml three necked round bottom flask and heated by an electric heating jacket at the bottom of the flask. The desorption temperature was measured by a thermometer placed in the desorption sample and between the value of the thermometer and the set value with 1 K error. The top of the three necked flask was equipped with a mechanical stirrer, and a condenser was connected at one outlet of the flask to prevent amine loss and water evaporation during desorption. The solutions reaching different desorption times (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 and 130 mins) were taken for CO₂ loading measurement.

2.4. Desorption energy consumption

CO₂ desorption heat is an important index to evaluate the CO₂ removal ability of a new solvent, because it is closely related to the energy consumption in the solvent regeneration process. Firstly, the equilibrium solubility of CO₂ was measured by the equipment in Fig. 1 (a) and the partial pressure of CO₂ was controlled by adjusting the flow ratio of N₂ and CO₂. Secondly, during the reaction, 60 ml of fresh amine aqueous solution with definite concentration was placed in the reactor and immersed into the water bath with mechanical agitation. The water bath temperature was set at 298.15 K, 308.15 K and 318.15 K respectively, and the partial pressure of CO₂ was set at 10.13, 35.45, 50.65, 82.8 and 101.3 kPa respectively. Then the mixed gas was successively

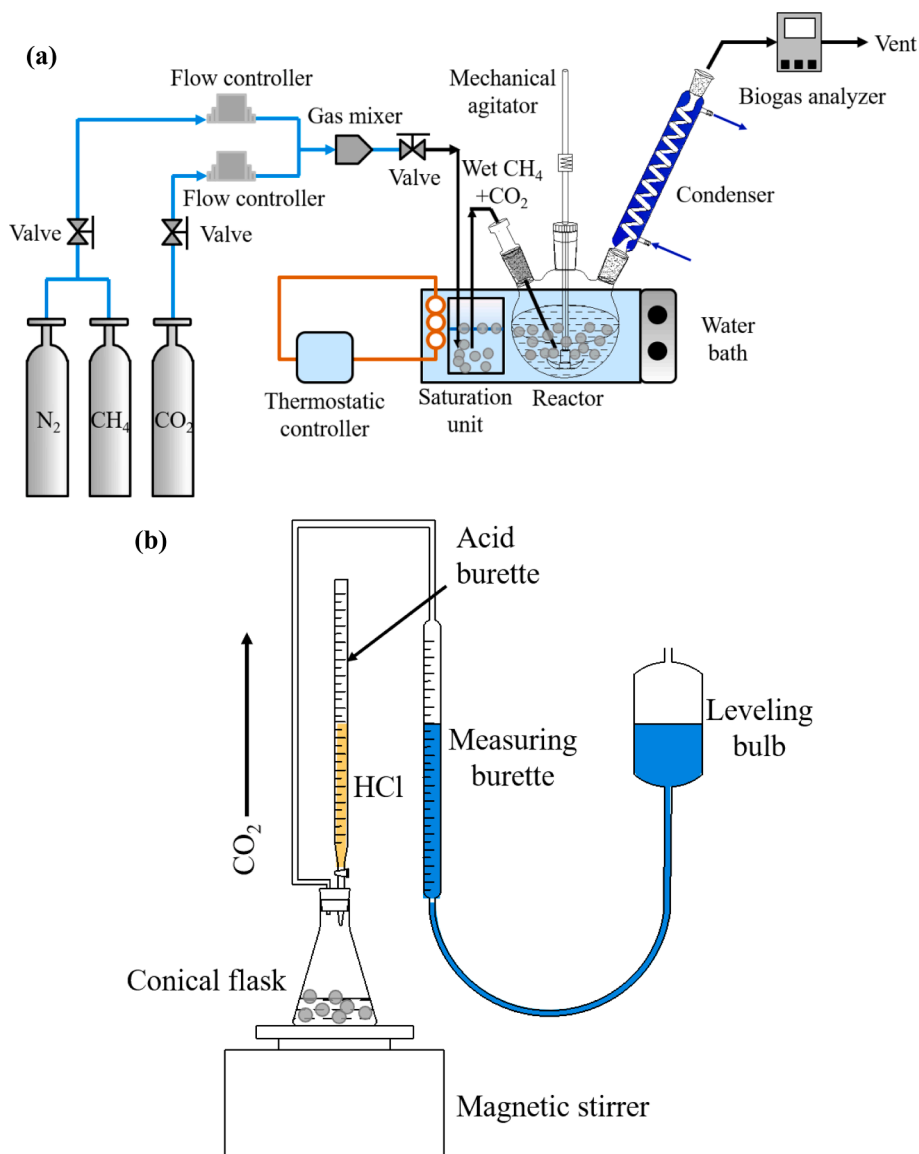


Fig. 1. Device diagram used in biogas upgrading experiment: (a) The schematic diagram of biogas upgrading device, (b) The schematic diagram of titration device.

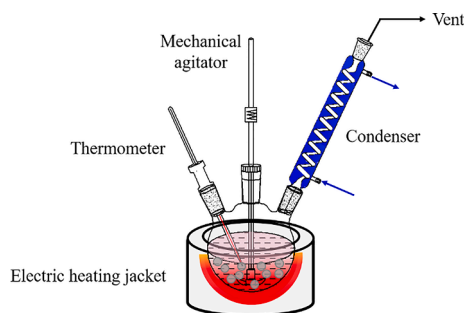


Fig. 2. Schematic diagram of amine regeneration device.

passed through the saturation unit, fresh amine solution and condensing unit at the gas speed of 800 ml/min according to the method shown in Section 2.2. After the reaction reached a certain extent, 5 ml sample was taken for titration. When the titration results for two consecutive times were basically unchanged, it was considered that the CO_2 absorption of the amine solution had reached saturation and the reaction was stopped. Finally, the heat of CO_2 desorption was calculated by the CO_2 loading

obtained at different absorption temperatures and CO_2 partial pressures. The biogas analyzer was used to analyze the composition of the purified gas and the CO_2 equilibrium solubility of amine solution was obtained by hydrochloric acid titration.

2.5. Selectivity of CO_2 in amine solution

The equilibrium partial pressure of CO_2 in amine solution is another important factor to evaluate whether a new absorbent can replace the traditional absorbent, because it will directly affect the CO_2 selectivity of amine solution in the process of biogas upgrading. The schematic diagram of CO_2 equilibrium partial pressure measuring device was shown in Fig. 3. Before the experiment of measuring the equilibrium partial pressure of CO_2 , the gas in the sealed pressure vessel was pumped out with a vacuum pump and filled with pure CO_2 or CH_4 gas, and repeated three times. The prepared fresh amine solution (See Section 2.1 for details) was injected into the container through the pressure equalizing dropping funnel. The reaction vessel was equipped with a gas-liquid two-phase mechanical stirrer, and the temperature was controlled by a 298.15 K circulating water bath. The change of pressure and temperature in the vessel with time were transmitted to the computer through

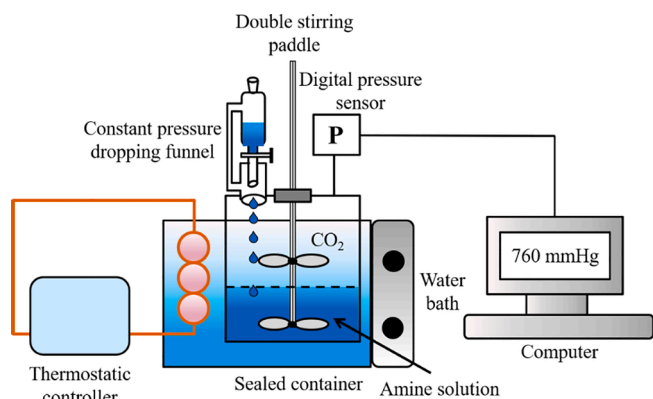


Fig. 3. Equilibrium partial pressure measurement.

the internal JYB-KO-HAA pressure sensor (-20 °C–85 °C, 0–100 MPa, $\pm 0.1\%$ FS) and recorded.

3. Data analysis

3.1. CO₂ loading

Determination of CO₂ loading in amine solutions using the Chittick apparatus by Eq. (1) according to the standard method given by the Association of Official Analytical Chemists (AOAC). The schematic diagram of titration device was shown in Fig. 1(b). The device was mainly composed of conical flask, acid burette, measuring burette and leveling bulb. HCl was titrated to the conical flask to react with the amine solution, and the amount of CO₂ produced was calculated by draining the volume of water. The calculation results were calculated three times and the average value was taken. The amount of CO₂ absorbed in amine solution was expressed by the amount of CO₂ loading, that is, the ratio of one mole of CO₂ to one mole of amine.

$$\alpha_{\text{abs}} = \frac{V_{\text{CO}_2} - V_{\text{HCl}}}{22.4 \times M_{\text{amine,abs}} \times V_{\text{amine,abs}}} \times \frac{273.15}{273.15 + T_R} \quad (1)$$

where, α_{abs} is the CO₂ loading of absorption solution (mol CO₂/mol amine), $M_{\text{amine,abs}}$ is the molarity of amine sample (mol/L), $V_{\text{amine,abs}}$ is the volume of amine solution (ml), V_{CO_2} is the displacement volume of liquid in the measuring burette (ml), V_{HCl} is the volume of hydrochloric acid used in the acid burette (ml), T_R is the room temperature during titration (K).

The CO₂ loading of desorption solution at different desorption time (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 and 130 mins) was also obtained by hydrochloric acid titration based on Eq. (2).

$$\alpha_{\text{des}} = \frac{V_{\text{CO}_2} - V_{\text{HCl}}}{22.4 \times M_{\text{amine,des}} \times V_{\text{amine,des}}} \times \frac{273.15}{273.15 + T_R} \quad (2)$$

where, α_{des} is the CO₂ loading of desorption solution (mol CO₂/mol amine).

3.2. Heat of CO₂ desorption

The heat of absorption at constant pressure is equal to the change of enthalpy of absorption, as shown in Eq. (3). It has been reported in the literature that the Gibbs-Helmholtz equation in Eq. (4) can be directly used to estimate the CO₂ absorption heat of solution without calorimeter, that is, to analyze the data of CO₂ partial pressure under different temperatures and the same CO₂ loading [21,38–41]. The key is that CO₂ desorption heat is considered to be numerically the same as the heat of CO₂ absorption [22,37,39].

$$\Delta H = \Delta U + \Delta(PV) \quad (3)$$

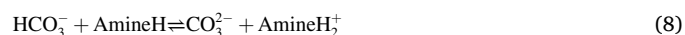
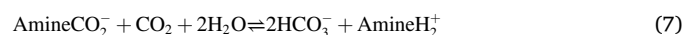
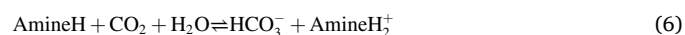
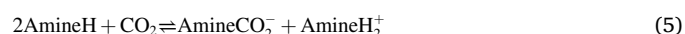
$$\frac{d(\ln P_{\text{CO}_2})}{d\left(\frac{1}{T_{\text{abs}}}\right)} = \frac{\Delta h_{\text{abs}}}{R} \quad (4)$$

where ΔH and ΔU are the enthalpy change and heat change in the reaction process, respectively. P_{CO_2} is the equilibrium partial pressure of CO₂ in biogas (kPa), T_{abs} is the reaction temperature in biogas upgrading process (K), Δh_{abs} is the heat of CO₂ absorption in biogas upgrading process (J/mol), R is the universal gas constant (8.314 J/mol·K). Under the condition of similar CO₂ solubility, P_{CO_2} and T_{abs} were selected, and the slope between $(\ln P_{\text{CO}_2})$ and $(1/T_{\text{abs}})$ was multiplied by R to obtain the heat of CO₂ absorption.

4. Results and discussion

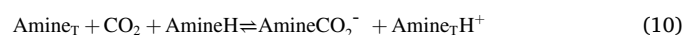
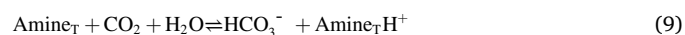
4.1. Series of biogas upgrading experiments

In order to analyze the difference of upgrading performance of amine solution in biogas, we decided to study the purity of methane after upgrading of simulated biogas. The process of CO₂ capture by amine aqueous solution in biogas upgrading could be described by the following equation:



where AmineH denotes the free amine, AmineCO₂⁻ denotes the amine carbamate and AmineH₂⁺ indicates the protonated amine.

In the absence of water, only primary and secondary amines can react directly with CO₂ to form carbamates, as shown in Eq. (5). Therefore, the theoretical CO₂ absorption of primary amine and secondary amine is 0.5 mol CO₂/mol amine. However, in aqueous amine solution, as shown in Eq. (5)–(8), the theoretical values of CO₂ absorption of primary amine and secondary amine are greater than 0.5 mol CO₂/mol amine. The tertiary amine can react with CO₂ in the presence of water, and the theoretical CO₂ absorption is close to 1 mol CO₂/mol amine, as shown in Eq. (9). In addition, in the process of biogas upgrading with mixed amine solution, primary amine and secondary amine can also be used as the bases for deprotonation of tertiary amine, as shown in Eq. (10).



where Amine_T indicates the tertiary amine, Amine_TH⁺ denotes the protonated tertiary amine.

According to the results in Table 2, it can be clearly concluded that in the simulated biogas upgrading process with CO₂ partial pressure of 35.5 kPa, the CO₂ saturated absorption of primary and secondary amines

Table 2
CO₂ loading of amine solution measured during biogas upgrading.

Amine aqueous solution	Mass fraction (wt.%)	Molar volume (mol/L)	α_{abs} at 298.15 K	α_{des} at 363.15 K	pH ^a	
					initial	end
MEA	18.4	3.0	0.589	0.332	12.3	8.3
DGA	30.9	3.0	0.553	0.308	12.1	8.2
DEA	30.8	3.0	0.541	0.293	11.9	8.2
TEA	42.7	3.0	0.297	0.185	11.4	8.7

^a The pH value of prepared fresh amine aqueous solution at the beginning (initial) and at the time of reaching the saturated absorption of CO₂ (end).

such as MEA (0.589 mol CO₂/mol amine), DGA (0.553 mol CO₂/mol amine) and DEA (0.541 mol CO₂/mol amine) was similar and close to the theoretical value (0.5 mol CO₂/mol amine). However, the CO₂ solubility of TEA (0.297 mol CO₂/mol amine) as a tertiary amine was much lower than that of MEA, DGA and DEA in addition to not reaching the theoretical uptake (1 mol CO₂/mol amine).

In addition to the amount of CO₂ absorbed by amine solution, the purity of methane in the upgrading process of biogas will directly affect the calorific value of biomethane, so the purity of biogas upgrading was another important index to measure whether amine solution can be used as upgrading reagent. The variation of the composition of the purified gas obtained in the process of biogas upgrading with the upgrading time was shown in the Fig. 4(a). Several EU countries such as the Netherlands require methane purity $\geq 85\%$ for the use in vehicles and grids [8]. The experimental results showed that the aqueous MEA solution had excellent biogas upgrading effect, and under the simulated biogas inlet rate of 580 ml/min, the purity of biomethane could be maintained 100% and above 85% for 170 and 210 mins, respectively. The effect of biogas upgrading with DGA was slightly lower than with MEA, with the purity of upgraded methane below 100% and 85% at 95 and 140 min, respectively. The biogas upgrading effect of the DEA was lower than that of the DGA, and although 100% methane purity was achieved for only 25 min of the initial upgrading process, it remained above 85% methane purity until the 132 min mark due to the slower CO₂ capture rate. The results indicated that MEA, DGA and DEA all showed favorable effects for biogas upgrading, which was mainly due to their rapid reaction with

CO₂ for the formation of carbamates, as shown in Eq. (5). As a product of TEA with 3 hydroxyethyl groups, the biogas upgrading was extremely inefficient, with initial methane purity of 89% and the purity of methane dropping below 85% in less than 10 min. Moreover, the rate of decrease in methane purity after upgrading could be used to approximately estimate the CO₂ absorption rate of the samples during the biogas upgrading process. It was therefore tentatively concluded that the CO₂ absorption rates of MEA and DEA during the biogas upgrading process were basically identical and slightly higher than that of DEA. The CO₂ absorption rate of TEA was too slow and the purity of the biogas failed to meet the application requirements, making it unsuitable as an absorbent for biogas upgrading.

4.2. Experiments on regeneration performance of amine solution

The regeneration effect of rich amine solution is a very important part in the process of biogas upgrading, which is directly related to the upgrading rate of biogas and the economic cost of carbon capture industry. In order to further analyze the differences in the regeneration rates of different MEA derivatives with hydroxyethyl as a variable, we studied the desorption effect of amine solution. The loading amount of CO₂ in the desorption process of rich amine solution was shown in Fig. 4 (b). The data in Fig. 4(b) showed that with increasing desorption time the residual CO₂ loadings of the MEA, DGA and DEA solutions were essentially stable at 0.332, 0.308 and 0.292 mol CO₂/mol amine respectively at around 100 mins, where the desorption rates of MEA and DGA were essentially identical and the initial desorption rate of DEA was slightly greater than that of MEA and DGA until 20 mins. In addition, the CO₂ loading of TEA was not significantly lower than the initial value due to the low CO₂ uptake of the amine-rich solution, although the CO₂ loading decreased from 0.297 mol CO₂/mol amine to 0.177 mol CO₂/mol amine after 80 mins of desorption, which was much lower than that of the final CO₂ loading after desorption of MEA, DGA and DEA solutions, and the desorption rate was relatively slow.

The regeneration performance of MEA derivatives could be evaluated from the data in Fig. 5. The regeneration rates of MEA, DGA and DEA solutions were basically consistent at a desorption temperature of 363.15 K and the values were 43.6%, 44.3% and 45.8% respectively, while the TEA solution showed a lowest regeneration rate of 37.7%. The analysis of the absorption, desorption and regeneration performance of these MEA derivatives showed that MEA has the fastest CO₂ absorption rate, the best biogas upgrading effect and the highest absorption amount, while TEA was not suitable for the biogas upgrading process as the other indicators were rather weak except for the relatively complete desorption.

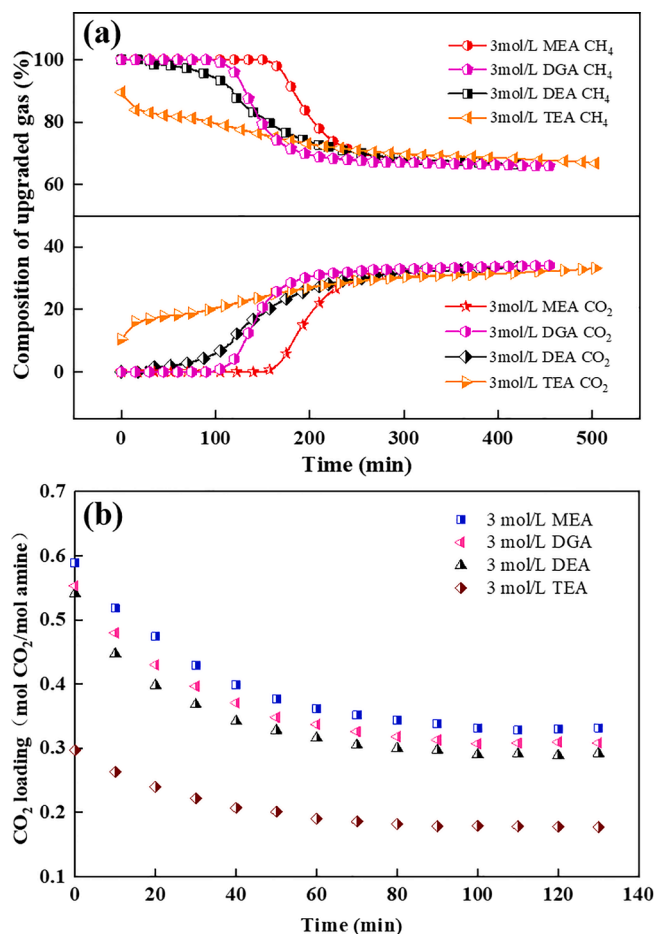


Fig. 4. Biogas upgrading performance curve of amines: (a) The variation of upgraded gas composition with upgrading time of simulated biogas with a CO₂ partial pressure of 35.5 kPa at 298.15 K and 1 atmospheric pressure, (b) The change of CO₂ loading with time in the desorption process of MEA derivatives at 363.15 K.

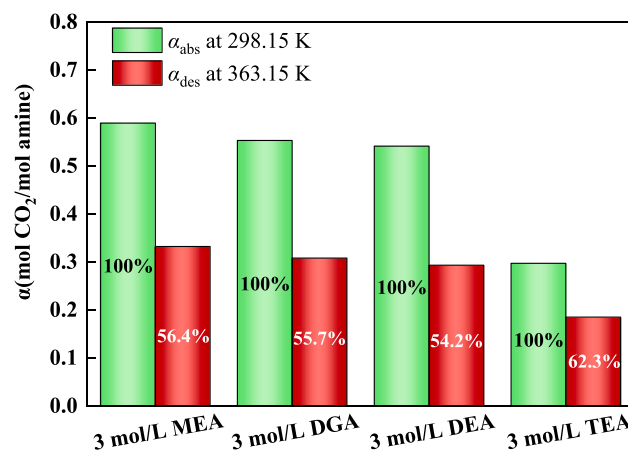


Fig. 5. The changes in CO₂ loading of MEA derivatives before and after desorption at a desorption temperature of 363.15 K.

4.3. Effects of hydroxyethyl groups in MEA derivatives on the biogas upgrading

In order to further evaluate the relationship between hydroxyethyl groups and CO₂ absorption/desorption performance, the structure of MEA was used as a basic reference structure to evaluate the absorption and desorption effects of the addition of hydroxyethyl groups to it. A graphical representation of the effect of changes in MEA structure on CO₂ loading was shown in Fig. 6. It can be clearly seen from the graph that the addition of functional groups to the MEA structure has a significant effect on the absorption and desorption of CO₂. In the chemical structure of MEA, one hydrogen of the amino group was replaced by a hydroxyethyl group to obtain DEA, two hydrogens of the amino group are exchanged by two hydroxyethyl group to obtain TEA, and one hydrogen on the hydroxyl group was substituted by a hydroxyethyl group to obtain DGA. The modification showed that when the substitution of one hydrogen by one hydroxyethyl group or two hydrogens by two hydroxyethyl group on the amine group of the MEA molecule produced DEA and TEA, respectively, the carbon dioxide loadings went from 0.589 mol CO₂/mol amine to 0.541 mol CO₂/mol amine and 0.297 mol CO₂/mol amine, respectively. This indicated that the hydroxyethyl group was a powerful electron attractor which reduced the CO₂ loading in the amine solution. Furthermore, when a hydrogen on the hydroxyl group of the MEA molecular structure was replaced by a hydroxyethyl group to produce DGA, the carbon dioxide loading was similarly reduced from 0.589 mol CO₂/mol amine to 0.533 mol CO₂/mol amine, which further suggested that the hydroxyethyl group was more detrimental to the CO₂ capture process relative to the hydrogen bond. In addition, the saturated CO₂ loading of the DGA solution was slightly higher than that of DEA, suggesting that hydrogen bonding on the amine group was more conducive to CO₂ capture than on the hydroxyl group during the upgrading of biogas.

From the analysis of the relationship between upgrading effect and CO₂ absorption rate of different structures of amines in Section 3.1 of this paper, it could be obtained that with the increasing of hydroxyethyl group in the molecular structure, the methane purity of biogas after upgrading gradually decreased from 100% for 170 min and above 85% for 210 min to 100% for 0 min and above 85% for less than 10 min, and

the reaction rate also showed a decreasing trend. This indicated that the presence of hydrogen bonds effectively increased the upgrading of biogas and the production rate of reaction products between amines and CO₂, while the presence of hydroxyethyl groups reduced the efficiency of biogas upgrading of aqueous amines. In addition, the methane purity of the biogas upgraded by the DGA solution lasted 70 mins and 8 mins more than DEA at 100% and above 85% respectively, again indicating that hydrogen bonding on the amino group was more useful than hydrogen bonding on the hydroxyl group in improving the biogas upgrading of the amine solution.

4.4. Analysis of energy consumption of aqueous MEA derivatives desorption

In order to evaluate the regeneration energy consumption of MEA derivatives with hydroxyethyl as a variable, we measured the CO₂ desorption heat of samples according to the method provided in the literature [41]. The energy consumption of aqueous amine solution in the regeneration process (Q_T) is mainly divided into three parts, which are the sensible heat of increasing the temperature of amine solution from absorption to desorption temperature (Q_S), the evaporation heat of water evaporated due to heating in the desorption process (Q_V) and the CO₂ desorption heat needed for CO₂ released from amine solution (Q_{des}), as shown Eq (11). The key is that Q_{des} is considered to be numerically the same as the heat of CO₂ absorption.

$$Q_T = Q_S + Q_V + Q_{des} \quad (11)$$

The equilibrium carbon dioxide absorption (α_{eq}) data tables and trend graphs for aqueous MEA derivatives at different absorption temperatures (T_{abs}) and partial pressures of carbon dioxide (P_{CO_2}) were shown in Table S1 and Fig. S1 in the supporting information, respectively.

From the results in Fig. S1, it could be seen that the CO₂ equilibrium solubility of the amine solution showed a decreasing and increasing trend with the increasing absorption temperature and partial pressure of CO₂ during the reaction, respectively. In addition, the decreasing rate of CO₂ equilibrium solubility tended to accelerate as the absorption temperature increased, while the growth of CO₂ equilibrium solubility

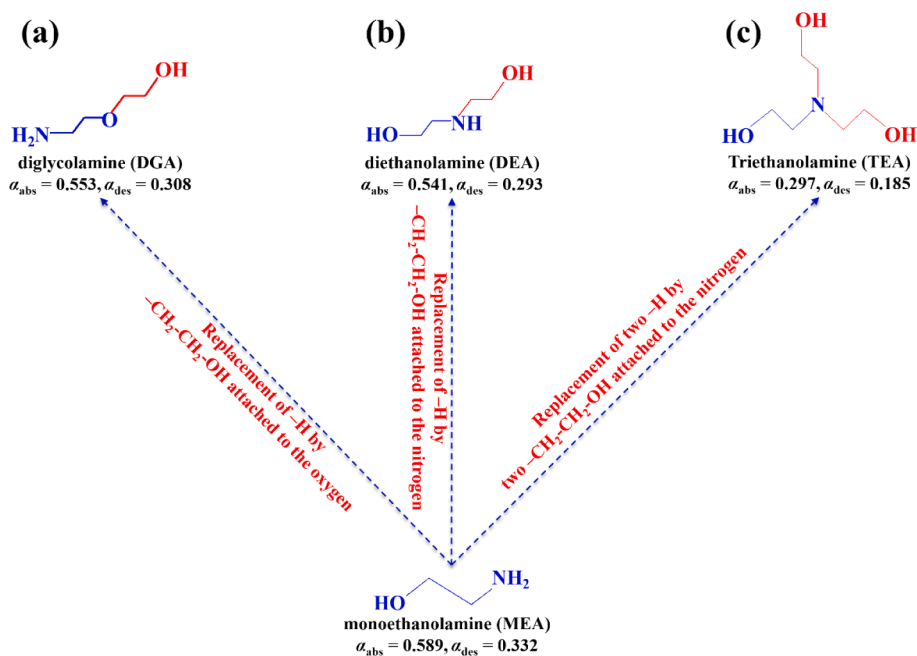


Fig. 6. The changes in the chemical structure of MEA after modification to DGA, DEA and TEA: (a) A hydrogen bond near oxygen on the MEA structure is replaced by a hydroxyethyl group to form DGA, (b) A hydrogen bond near nitrogen on the MEA structure is replaced by a hydroxyethyl group to form DEA, (c) Two hydrogen bond near nitrogen on the MEA structure is replaced by two hydroxyethyl group to form TEA.

basically showed a linear change with the increasing partial pressure of CO₂ equilibrium.

A plot of the equilibrium partial pressure of CO₂ versus absorption temperature for each of the different amine solutions selected from the same equilibrium solubility of CO₂ was shown in Fig. S2. From the graphs, it could be found that the experimentally obtained results have a relatively strong fitness to the Gibbs Helmholtz equation with the fits (R^2) all being above 0.99. Therefore, the slope of the fitted equation allowed the calculation of the value of the heat of desorption of CO₂ in the amine solutions, which was shown in Table 3. The data in the table showed that MEA had the greatest heat of CO₂ desorption (82.47 kJ/mol CO₂), indicating that MEA had to absorb more of the heat during the desorption process to decompose its reaction products with CO₂. TEA has the lowest heat of CO₂ desorption (65.72 kJ/mol CO₂), which means that it requires less heat to destroy the CO₂ trapped products during the desorption process, making it more conducive to reducing the energy consumption of amine regeneration. The CO₂ desorption heat of DGA (79.58 kJ/mol CO₂) was relatively equivalent to that of MEA, while the CO₂ desorption heat of DEA (71.54 kJ/mol CO₂) was lower than that of MEA. The heat of desorption would therefore directly affect the desorption rate and the thoroughness of the desorption of the amine solution. These heat of desorption results were also generally consistent with the relevant data in the literature and echoed the results of the analysis based on the desorption curve of the amine-rich solution in this work.

4.5. Selectivity of CO₂ in biogas upgrading with amine solution

Since the reaction in the sealed vessel was a constant volume reaction, the amount of gas absorbed during the reaction at a known temperature and pressure could be obtained from the ideal gas equation. By comparing the initial CO₂ or CH₄ absorption rates of amine liquids, the biogas upgrading effect of amine solutions with CO₂/CH₄ selectivity can be further investigated more deeply, as shown in Fig. 7. From the data in Fig. 7(a), the initial absorption rates of MEA, DGA and DEA were very fast, requiring only 10 mins to reach the equilibrium partial pressure of CO₂, with the fastest absorption rate for MEA, requiring only about 5 mins to complete the reaction, further indicating that the presence of H-bonds could greatly increase the absorption rate, echoing the previous results. As for the TEA, the initial reaction was quite slow, taking more than two hours to reach the equilibrium partial pressure of carbon dioxide, which echoed the results of the previous analysis of the biogas upgrading effect of the amine solution.

In addition, under the premise of ensuring that the purity of biogas was up to standard, the yield of biomethane is another important factor in the process of upgrading biogas to prepare biological natural gas. The initial CH₄ uptake rates of TEA was comparatively higher, while the initial CH₄ rates of MEA, DGA and DEA were relatively lower, but

Table 3
Heat of CO₂ desorption from amine solution.

Amine solution	T_{abs} (K)	P_{CO_2} (kPa)	Q_{des} (kJ/mol CO ₂)	Sources
MEA	298.15, 308.15,	10.13, 35.45, 50.65,	82.47	This work
MEA	318.15	82.80, 101.3		
	303, 318, 333	8, 15, 30, 60, 100	82.00	[41]
DEA	298.15, 308.15,	10.13, 35.45, 50.65,	71.54	This work
DEA	318.15	82.80, 101.3		
	303.15, 313.15,	9.67–101	69.00	[42]
	318.15			
TEA	298.15, 308.15,	10.13, 35.45, 50.65,	65.72	This work
	318.15	82.80, 101.3		
TEA	298.15, 303.15,	/	66.59	[22]
	308.15, 313.15			
DGA	298.15, 308.15,	10.13, 35.45, 50.65,	79.58	This work
	318.15	82.80, 101.3		

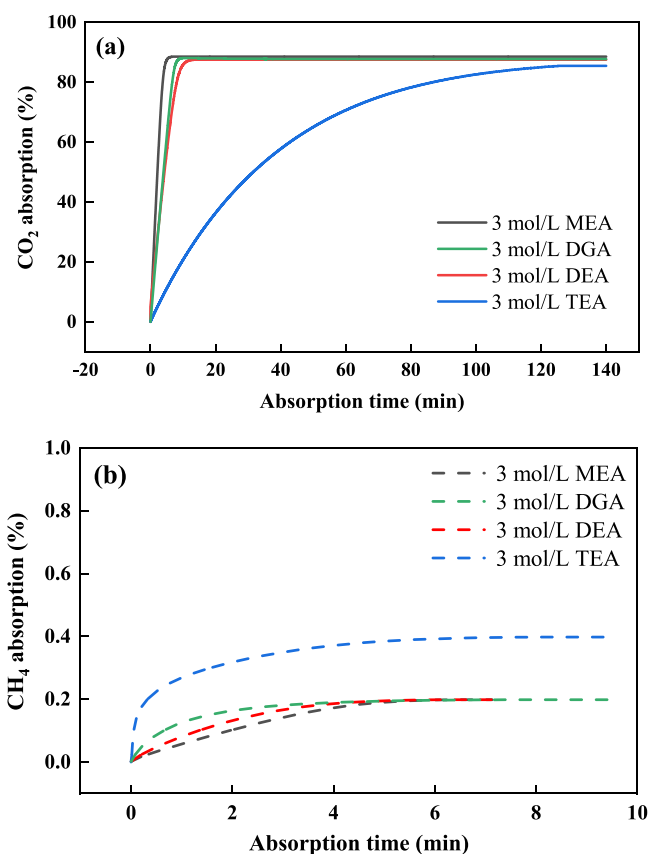


Fig. 7. The initial absorption rates of CO₂ and CH₄ by samples at room temperature as a function of time.

overall they were all below 0.4% of the CH₄ content in the reaction vessel, indicating that the amine solutions possessed a high CO₂/CH₄ selectivity in the biogas upgrading process for the preparation of biomethane, which was conducive to ensuring the maximum upgrading effect and upgrading efficiency, as shown in Fig. 7(b).

5. Conclusions

The results showed that with the change of the molecular structure of MEA derivatives with hydroxyethyl group as the variable, the biogas upgrading efficiency and the upgraded methane purity of the samples showed a more obvious decreasing trend, especially after both hydrogen bonds on the amino group were replaced by hydroxyethyl group to generate TEA, the methane purity of the upgraded biogas was only maintained above 85%, which could not meet the requirements of biogas upgrading. However, the introduction of hydroxyethyl group is beneficial to reduce the CO₂ desorption heat of amine in the regeneration process, which is important to reduce the energy loss in the desorption process. In addition, the CH₄ uptake of each amine solution is less than 0.4% at the equilibrium partial pressure of CH₄, which has a high CO₂/CH₄ selectivity. We have reason to believe that continued research on the relationship between the molecular structure of amines and the effect of biogas upgrading will be beneficial to guide the screening and preparation of subsequent mixed and synthetic amines, and provide effective support for the early realization of carbon neutral and 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, Review.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2022.124874>.

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