

Absorption and Desorption of Carbon Dioxide from Biogas Using Amines

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Abstract: To study the effect of the amino group number of amine on the absorption and desorption performance, monoamine MEA, polyamine EDA and DETA were selected for absorption-desorption-cycle experiments, and the results showed that under the same absorption conditions, polyamines have stronger absorption performance than monoamine, but with effective amine as the absorption evaluation system, increasing the number of amino groups in the molecule could not enhance the absorption capacity of the absorbents, and the effective amine absorption capacity of the three absorbents is MEA>EDA≈DETA. Under the condition of 100°C desorption, the highest desorption efficiency within 90 min is still MEA solution. In addition, compared with DEA and DETA absorbents, the saturation solubility of MEA solution is more sensitive to partial pressure and its cycling stability is stronger.

Keywords: Amine, CCS, CO₂.

1. Introduction

With the reduction of fossil fuels, the development and utilization of biomass energy has attracted the attention of carbon emission reduction and renewable resources research. Among them, biomass energy with carbon capture and storage can offset the carbon emissions of the global energy system and is considered to be one of the most potential negative carbon emission technologies. As a biomass energy source, biogas is mainly composed of methane (45%~70%), CO₂ (30%~55%), and other trace substances such as hydrogen sulfide, water, nitrogen, ammonia, and siloxane, which is clean, efficient, and renewable^[1]. However, the non-flammability of carbon dioxide gas reduces the combustion efficiency of biogas and limits the further use of biogas, and capturing and utilizing carbon dioxide from biogas is an effective way to achieve negative carbon emissions. In addition, the preparation of biomass natural gas from biomass biogas after upgrading and decarbonization can be used as a substitute for petrochemical natural gas and expand the application field of biomass biogas, which has good environmental and economic benefits^[2-4]. Therefore, how to remove CO₂ from biogas is the key to improve the utilization performance of biogas and achieve negative carbon emissions.

With the continuous expansion of the scale of bio-natural gas in the world, the decarbonization of biogas to obtain high-purity CH₄ has been gradually emphasized, and the existing decarbonization technologies mainly include (1) absorption in liquids, (2) adsorption on solid surfaces, (3) membrane separation, (4) cryogenic separation and (5) methanation.^[5] Among them, the organic amine capture method is suitable for large-scale biogas purification projects due to its large absorption capacity and renewability, but the organic amine capture method generally has problems such as high desorption temperature, high energy consumption, high water consumption and poor cycling absorption, resulting in high capture costs and water waste.

Studies have shown that different types of amino groups have different capacities for the absorption and desorption of CO₂^[6, 7]. The primary amino group and secondary amino

group have strong binding ability to carbon dioxide, and the absorption rate is fast but the temperature required for desorption is high, resulting in low desorption efficiency at low temperature and high desorption energy consumption at high temperature. The tertiary amino group reacts with carbon dioxide to form unstable bicarbonate, which has a fast desorption rate and a low temperature required for desorption. However, the tertiary amino group reacts slowly with carbon dioxide, resulting in a slow absorption rate and a small circulating capacity. Different single absorbents have different advantages and disadvantages^[8]. In order to make up for the shortcomings of single amine solutions, in recent years, attention has been paid to dual-amine aqueous blends, by mixing absorbents containing different kinds of amino groups in a certain proportion to prepare highly efficient absorbents with low energy consumption. The results show that the absorbent containing dual-amine had improved absorption and desorption performance compared with the single amine solution. Xinwei He et al.^[9] mixed tertiary amines with different primary amines and secondary amines to prepare mixed absorbents, which showed good absorption performance and better desorption performance than traditional absorbent MEA. Studies have found that both 1-methylpiperazine and piperazine have a promoting effect on the absorption of DETA, and piperazine has a stronger promoting effect^[10]. Dechen Zhu et al.^[11] investigated the absorption and desorption capacity of dual-amine aqueous blends based on MEA. W. Conway et al.^[12] introduced CO₂ into aqueous amine blended solutions containing monoethanolamine (MEA), N,N-dimethylethanolamine (DMEA), N,N-diethylethanolamine (DEEA) and amino-2-methyl-1-propanol (AMP). Several studies have also explored the trapping capacity of dual-amine aqueous absorbents based on MDEA^[13, 14]. For example, MDEA is mixed with PZ as a dual-amine absorbent^[15]. It is worth noting that some studies have used primary or secondary amines as absorbents and tertiary amines as phase splitting agents to prepare mixed dual-amine phase change absorbents^[16]. Shihan Zhang et al.^[17] prepared a mixed system with triethyltetraamine as the absorbent and tertiary amine as the phase splitting agent,

which significantly reduced the energy consumption of the system regeneration compared with the MEA aqueous solution. Yao Shen et al.^[18] investigated the relationship between absorbent properties and capture performance of different mixed diamine phase change absorbents. Yaoyao Li et al.^[19] found that aqueous solutions of triethyltetramine (TETA) and N,N-diethylethanolamine (DEEA) are effective CO₂ biphasic absorbents. X. Zhou^[20] proposed a novel two-phase solvent of PMDETA and DETA for CO₂ capture and explored the interaction between PMDETA and DETA. Some studies have mixed sterically hindered amines such as AMP with monoamines to facilitate the absorption process and reducing desorption energy consumption. F. Liu, et al.^[21] compared the trapping performance and mechanism of triethylenetetramine (TETA) and 2-amino-2-methyl-1-propanol (AMP) in aqueous/non-aqueous solutions. Y. Du et al.^[22] investigated the synergistic trapping effect of piperazine with tertiary amines and sterically hindered amines. S. K. Dash et al.^[23] found that the mixed absorbent of 1 MPZ and AMP had the advantages of good thermodynamic equilibrium capacity of AMP and good rate kinetics of 1 MPZ, and the overall performance was better than that of the MEA benchmark absorbent. There are also studies that have focused on ionic liquid absorbents, such as Fan Liu et al.^[24] who investigated AMP-activated Switchable ionic liquids (SILs) to increase the capture rate and reduce viscosity.

Recent studies have focused on the interaction of three or more amine mixtures of absorbents and their interaction in the absorption and desorption process.^[25] For example, piperazine + EMEA + DEEA mixed solution^[26], MEA + MDEA + AMP mixed solution^[27], MDEA + AMP + PZ mixed solution^[28]. C. Nwaoha et al.^[29] investigated the regenerative heat of MDEA, DETA, and AMP mixed absorbent. C. Nwaoha et al.^[30] found that the MEA+AMP+PZ three-solvent blend has a higher cycle capacity, a larger initial desorption rate, and a lower heat load than MEA.

In our study, the absorption and desorption capacity and cycle stability of MEA, EDA, DETA on CO₂ in biogas were explored. The properties of three different absorbents were compared, and the performance differences between monoamines and polyamines were studied.

2. Materials and Methods

2.1. Chemicals

Monoethanolamine, ethylenediamine, diethylenetriamine and sulfuric acid were purchased from Sinopharm Chemical

Reagent Co., Ltd., and CH₄ (> 99.99%) and CO₂ (> 99.99%) were provided by Air Liquide (Kunshan) Gas Technology Co., Ltd. All the chemicals for experiments were used without any further purification.

2.2. Absorption and desorption

Carbon dioxide absorption experiment was carried out in a bubbling experimental setup at one atmosphere. The absorption solution is prepared by dissolving 45g of amine in 105g of deionized water. The simulated biogas contains 40% CO₂ and 60% CH₄, and the mass flow controller (D08) (purchased from Beijing Seven Star Electronics Co., Ltd) controls the total flow rate of the mixed gas to 200ml/min. After passing through the water saturation device, the gas mixture enters a 250 ml four-neck flask which containing 150 g absorbent solution (one neck is connected to the air intake device, one neck is connected to the condenser tube, and one neck is connected to the thermometer). A constant temperature magnetic stirrer (DF-101T-10L, ±2K, Gongyi Yuhua Instrument Co., Ltd.) was used to control the reaction temperature of 25 °C and the rotation speed of 150 r/min. After the mixed gas is fully mixed with the absorption liquid, the remaining gas enters the mass flow meter through the condenser tube and drying pipe to measure the instantaneous flow rate of the remaining gas. The installation diagram is shown in Figure 1. The duration of absorption is 3.5h. The acidolysis of sampling at certain intervals is used to determine the CO₂ load.

The desorption experiment was carried out in a thermostatic magnetic stirrer equipped with a condensing device. The absorbed rich liquid was heated to 100 °C pyrolysis in a thermostatic magnetic stirrer for a duration of 90min. The carbon dioxide gas produced by pyrolysis is absorbed by the NaOH solution after passing through the drying tube and mass flow meter. Acidolysis is taken at regular intervals to determine the carbon dioxide load.

The mixed gas is introduced into the absorption liquid to start the absorption process, and the absorbed rich liquid pyrolysis partially or completely releases carbon dioxide, which is a cycle. Four cycles were carried out sequentially. The carbon dioxide load of the absorbent solution was measured before and after each cycle, and the changes in the absorption and desorption capacity of the solution during the recycling process were explored. In this way, the stability and feasibility of Amine absorbents in the practical application of carbon capture were verified.

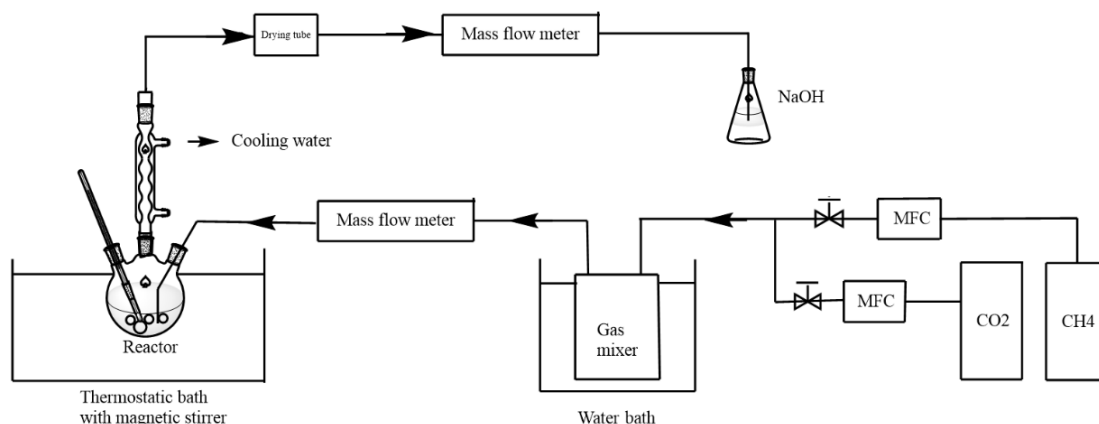


Figure 1. Absorption installation diagram

2.3. Equilibrium CO₂ loading

This study investigate the saturated solubility of carbon dioxide at different partial pressures by changing the ratio of the mixed gas to control the partial pressure. The specific operation process is to put 50g of the configured 30% absorption solution in the absorption device, control the absorption temperature to 25 °C, and the total flow rate of the mixed gas is 500ml/min. After a certain period of absorption, the carbon dioxide load is measured by acidolysis until the titrated carbon dioxide load no longer changes, at which point the system is considered to be in equilibrium. In this study, the saturated solubility of 3M MEA solution at 298 K was determined and compared with the literature. The results are shown in Figure 4 (a), and the data are basically in agreement, which proves the reliability of the method.

3. Results & Discussion

3.1. Absorption

In order to compare the absorption capacity of different absorbents, the mixed gas was continuously introduced into the mixture for 210 min under the same experimental conditions (amine mass fraction 30%, 298K). The results show that the absorption performance of different absorbents is different, as shown in Figures 2 and 3. As the absorption time increases, the CO₂ load of the aqueous solution of the three amines increases. Among them, the carbon dioxide load of DETA aqueous solution was significantly higher than that of other absorbent solutions, followed by EDA>MEA. This is determined by the number of amino groups on different molecules. However, it is worth noting that the amide group does not work on absorption, and tertiary amines do not directly absorb carbon dioxide. If only the absorption of the available amino group on the amine molecule is considered. The difference in CO₂ load between EDA and DETA aqueous

solution is small, and it is always smaller than that of MEA aqueous solution. At 210 min, the carbon dioxide load on the available amino group of MEA reached 0.52 molCO₂ / mol-NH₂, EDA and DETA were 0.42 molCO₂ / mol-NH₂ and 0.39 molCO₂ / mol-NH₂, respectively.

As can be seen from Figure 2, the absorption rate of MEA aqueous solution decreased rapidly in the 210 min, and the load was basically stable at 210 min. The absorption rate of EDA and DETA aqueous solutions was stable, and the load still showed an upward trend at 210 min. On the basis of this experiment, the absorption time was increased until the load of the three absorbent liquids was stable. As shown in Figure 3, the CO₂ load of the three absorbents increased to varying degrees as the absorption time continued to increase. Moreover, the maximum absorption capacity of DETA is greater than that of other two absorption solutions, the maximum carbon dioxide load of MEA、EDA、DETA is 0.72 mol CO₂/mol amine、0.97 mol CO₂/mol amine、1.47mol CO₂/mol amine , respectively. The maximum absorption capacity of MEA evaluated with available amino group is greater than that of EDA and DETA. the carbon dioxide load on the available amino group of MEA reached 0.72 molCO₂ / mol-NH₂, EDA and DETA were 0.49 molCO₂ / mol-NH₂ and 0.49 molCO₂ / mol-NH₂, respectively. It can be seen that increasing the number of amino groups in the absorbent molecule does not increase the effective amine load.

In summary, within 210 min, DETA absorption load was the highest, but the effective amine load was the lowest. The absorption load of MEA is basically the same as that of EDA, and the highest available amine load is much greater than that of EDA and DETA, but the absorption rate decreases faster after long-term absorption. Among the three absorbents, the highest absorption load was DETA>EDA>MEA, and the highest effective amine load was MEA>EDA≈DETA.

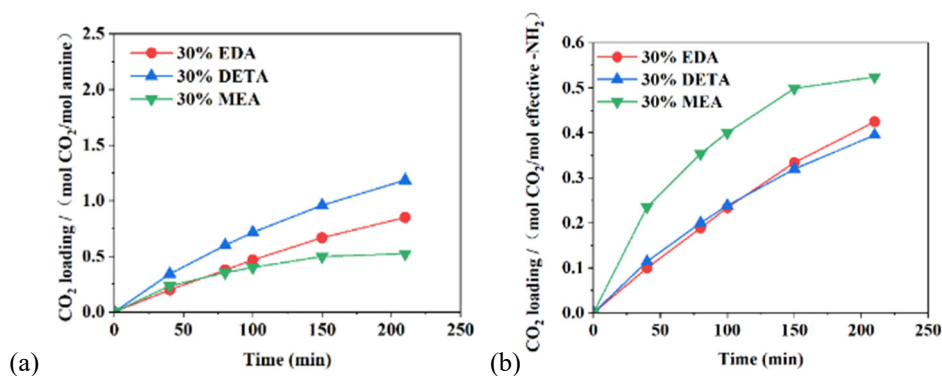


Figure 2. Absorption load of each absorbent at different absorption time

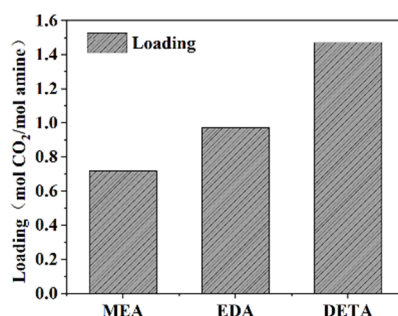


Figure 3. Saturation solubility at different partial pressures

3.2. Equilibrium solubility of CO₂

The equilibrium solubility of carbon dioxide reflects the maximum absorption load of the absorbent under different absorption conditions. In this study, the saturated solubility of MEA solution at 298K and partial pressures of 4.9, 6.9 and 9.8 KPa was determined. The results are in good agreement with the literature, as shown in Figure 4(a). Secondly, the saturated solubility of the absorbent solution with 30% mass fraction was prepared and measured under the condition of 0-100 Kpa, and the results are shown in Figure 4(b). With the increase of carbon dioxide partial pressure, the saturated solubility of the three absorbents increased. This is due to the increase in the partial pressure of carbon dioxide that causes the reaction to move forward, the concentration of carbamate in the solution increases, and the saturated solubility also increases accordingly. However, it is worth noting that the

saturation solubility of different absorbents has different increasing trends. Among them, MEA is more sensitive to pressure changes. As the pressure increased from 20 kPa to 100 kPa, the saturated solubility of MEA increased from 0.61 mol CO₂/mol amine to 1.08 mol CO₂/mol amine. The saturated solubility of EDA and DETA changed little with the increase of carbon dioxide partial pressure. The EDA increased from 0.96 mol CO₂/mol amine to 1.02 mol CO₂/mol amine and the DETA increased from 1.44 mol CO₂/mol amine to 1.76 mol CO₂/mol amine. At a partial pressure of carbon dioxide below 80kpa, the saturation solubility is always MEA<EDA<DETA. It can be seen that the partial pressure of carbon dioxide has different effects on the saturation solubility of different absorbents, and it is not that the higher the number of amino groups, the greater the saturated solubility, which is related to the physicochemical properties of the absorbents themselves.

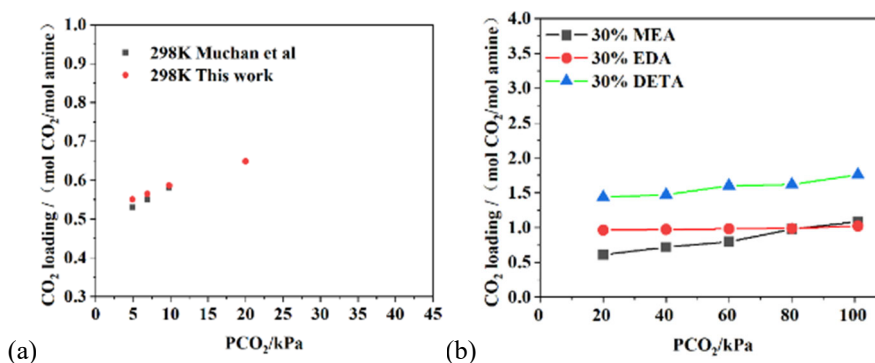


Figure 4. Saturation solubility at different partial pressures

3.3. Desorption

In this study, the rich liquid of MEA, EDA and DETA solutions after 210 min of absorption is heated in a 373K oil bath for 90 minutes, and compare their desorption performance. The results are shown in Figure 5(a). The CO₂ load of the three absorbents changes flat. The load of DETA changed greater than MEA and EDA, from the initial 1.18 mol CO₂/mol amine to 0.64 mol CO₂/mol amine. The desorption efficiency of MEA can reach 64% within 90 min, which is greater than the resolution efficiency of EDA (34%), and DETA (46%). From the desorption curve, it can be seen that the desorption rate of DETA remained at a low level in the first 15 min, and decrease to reached a stable level at 60-90 min. If the load is calculated based on the number of effective amino groups, the result is shown in Figure 3(b). The

strongest desorption capacity at the same desorption time is MEA aqueous solution, followed by DETA>EDA. Within 90 minutes of desorption time, the available amine load decreased from 0.52 mol CO₂/mol -NH₂ to 0.19 mol CO₂/mol -NH₂, the DETA effective amine load decreased from 0.39 mol CO₂/mol -NH₂ to 0.21 mol CO₂/mol -NH₂, and the EDA effective amine load decreased from 0.42 mol CO₂/mol -NH₂ to 0.28 mol CO₂/mol -NH₂. MEA has the highest initial effective amine load and the lowest effective amine load after desorption. This phenomenon is caused by the different types and numbers of amino groups on the molecule. The carbamate formed by primary and secondary amino groups is very stable and not easily pyrolyzed. Therefore, the increased number of primary and secondary amino groups in EDA and DETA molecules does not improve desorption efficiency compared to MEA.

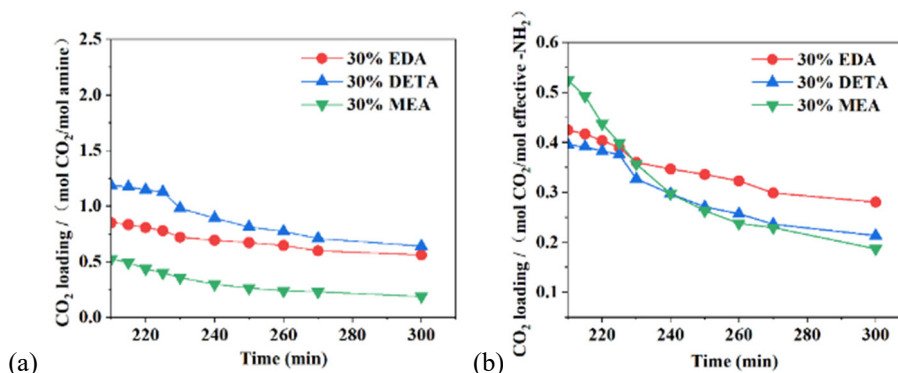


Figure 5. Desorption load of each absorbents at different desorption times

3.4. Cycles of Absorption–Desorption

In order to evaluate the performance of different absorbents more completely and verify its cycling stability, Multiple cycles of absorption-desorption experiments were performed on the three absorbents. No reagents were added to compensate for the evaporation during the experiment. The results are shown in Figure 6. The circulating capacity of DETA is significantly larger than that of the other two basal absorbents. As can be seen from Figure 6, compared with the

MEA aqueous solution, the maximum absorption load of the aqueous solution of DETA showed a slight decreasing trend during multiple cycles. This is due to the volatile nature of DETA, and the pyrolysis process will cause the loss of absorbent, resulting in a decrease in the maximum absorption load, while MEA is not easy to volatilize compared with DETA, and only water is lost in the circulation process, so the maximum absorption load in the circulation process shows a slight upward trend. As a result, MEA has better industrial availability than the two amine absorbents.

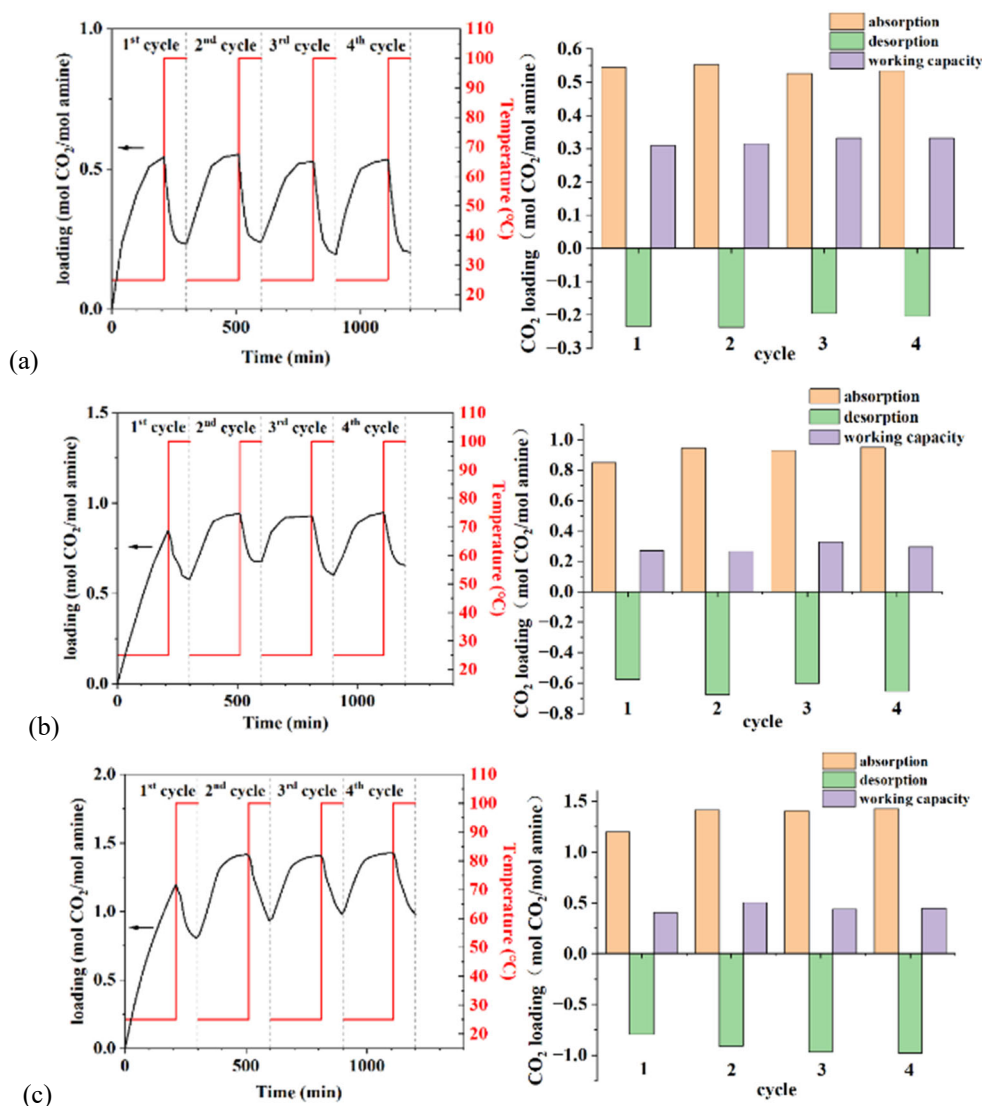


Figure 6. Cycle diagram: (a) MEA; (b) EDA; (c) DETA;

4. Conclusion

From the results of this work, it was found that all MEA have better absorption and regeneration performance than EDA and DETA. Under the condition of 25°C and 101kPa, the effective amine load of MEA can reach 0.52 mol CO₂/mol -NH₂ within 210min, EDA and DETA were 0.42 mol CO₂/mol -NH₂ and 0.39 mol CO₂/mol -NH₂, respectively. MEA is more sensitive to pressure changes. As the pressure increased from 20 kPa to 100 kPa, the saturated solubility of MEA increased from 0.61 mol CO₂/mol amine to 1.08 mol CO₂/mol amine. At a desorption temperature of 100°C and a desorption time of 90 minutes, MEA has the maximum

desorption efficiency. The desorption efficiency of MEA can reach 64% within 90 min, which is greater than the resolution efficiency of EDA (34%), and DETA (46%). In addition, the results of cycling experiments show that MEA has better cycling stability due to the different physicochemical properties of different absorbents.

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