Removal of Carbon Dioxide from Biogas with Pilot Chemical Absorption System at Different Operating Conditions

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In this work, a large amount of removal of carbon dioxide from biogas could be achieved on a pilot absorption system using monoethanolamine solution as an absorbent. The important parameters influencing on the CO₂ removal were investigated. The optimized CO₂ removal efficiency could be achieved at the monoethanolamine solution flow of 20 L h⁻¹ and the gas flow of 350 L h⁻¹ when the volume of CO₂ was 45 %. The purity of biogas of the resulting gas could be as high as 97-100 %. Moreover, the CO₂ removal efficiency reduced with increasing CO₂ content of the input gas. The pressure in the absorption tower varying in 0.05 MPa to 0.1 MPa has no significant influence on the CO₂ removal. The CO₂ removal efficiency could be improved when the volume of the input CO₂ was reduced or the content of the monoethanolamine was increased.

Keywords: Carbon dioxide, Monoethanolamine, Absorption, Regeneration, Mixed gas.

INTRODUCTION

Nowadays, with the growth of environmental pollutions and energy crisis, the development of clean and renewable energy has received great deals of attention in both the scientific and technological fields¹. As an important biomass energy, the use of biogas can not only reduce the discharge of the house refuse, city sludge and other waste, but also it can play a positive role in the remission of the severe "greenhouse gas"². Although the technologies of anaerobic digestion for biogas production in China have gradually been in mature, the use of the biogas still remains in its original ways^{3,4}. Normally, the biogas resources are mainly used for living energy for the rural families with low efficiency^{5,6}. Therefore, the high value and efficient utilization of the biogas has not been achieved. Theoretically, the application of the biogas can be used efficiently including vehicle fuel, fuel cell besides heating and cooking as an energy source⁷⁻⁹.

Moreover, the calorific value of biogas is in the range of 22000-25000 kJ m⁻³. As one of main components¹⁰, calorific value of methane is as high as 39000 kJ m⁻³. Therefore, it is necessary to purify the biogas to maximize the utilization efficiency of biogas. As for the biogas purification, removal of CO₂ is the first and the most important step. Furthermore, in recent years, the effective separation and regeneration of CO₂ also became important for the recycling and utilization of energy¹¹. Although great efforts¹²⁻¹⁶ have been devoted to

design and develop new physical and chemical methods to increase absorption of CO₂. Generally, there are three methods to separate CO₂ from the biogas¹⁷. One is water treatment, whereas such method needs complicated operating conditions and cannot usually achieve a high level separation¹⁸. The second one is membrane separation method which suffers high cost and short lifetime of membrane¹⁹⁻²⁰. The third one is Pressure-Swing-Adsorption method involving a physical absorption process, which is beneficial to the environment²¹.

However, this method also needs complicated equipments. Therefore, it is prime importance to find an effective method to achieve an easy, safe and stable process for a large scale separation with low cost. As comparison, the chemical absorption method can run in low costs with high stability and security and potentially overcome the above difficulties in the mentioned methods.

In this work, we have put forward new designed equipment, which could separate a large amount of CO₂ from simulated biogas and regenerate absorption solution effectively. The removal of CO₂ was investigated on this pilot system at various parameters including the gas flow, liquid flow, pressure, initial CO₂ content, monoethanolamine content and absorption tower height. The aims of this work are to clarify the effects of the mentioned parameters on the CO₂ removal, which could offer a theoretical reference for the biogas purification in application.

EXPERIMENTAL

In order to simplify the experiments on the CO₂ removal, N₂ was used to take place of methane, which was further mixed with CO₂ in a certain ratio to simulate the biogas. Because the solubility of N₂ in the water is very small, the whole process could be more accurately described for the gas purification.

We designed a pilot-scale plant which contained an absorption tower (height 260 cm), a desorption tower (height 190 cm) and two liquid storage tanks (40 L for each) (Fig. 1). The inner and outer diameters for both of absorption tower and desorption tower, both were 46 mm and 50 mm, respectively. There were four wall wiper redistributing sets which were welded in the inner wall of the absorption tower and desorption tower to avoid the liquid wall flowing. Two types of stainless steel θ -rings (height of 4 mm with diameter of 4 mm and height of 6 mm with diameter of 6 mm) were filled in both the absorption tower and desorption tower to create a large surface between gas and liquid. Specially, the θ -rings with height of 6 mm were filled in the every wall wiper redistributing sets to make the reaction of liquid and gas effectively. The heat insulation layer (thickness of 40 mm) was covered around the desorption tower through the electricity relay control to ensure the desorption temperature constant. The condense unit was stalled at the top of desorption tower for condensing absorption liquid steam. The electric heating device was stalled at the bottom of desorption tower for heating the absorption liquid. We designed a preheating equipment before the desorption tower to raise the temperature of absorption liquid and make the process of the desorption process much easier.

Fig. 1. Equipments for the absorption of CO₂ from the mixed gas by the chemical method (1. CO₂ cylinder 2. N₂ cylinder 3. Absorption tower 4. Lean solution storage tank 5. Pump 6. Preheating equipment 7. Desorption tower 8. Pump 9. Rich solution storage tank)

The CO₂ gas (99.99 %) and the N₂ gas (99.99 %), were both purchased from Beijing Orient Medical Gas Co. Ltd.. They were mixed as simulated biogas before being transferred to the absorption tower. The simulated biogas and absorption liquid were then channeled into the absorption tower with a stable pressure. The absorption liquid used in the process was

monoethanolamine solution which was sprayed from the top of the absorption tower. monoethanolamine was purchased from Tianjin Fuchen Chemical Reagents Factory. The mixed gas was channeled from the bottom of the tower. After the absorption, the monoethanolamine solution was pumped into the preheating equipment, then pumped into the desorption tower. In this tower, the monoethanolamine solution was regenerated in the conditions of the pressure of 50 kPa and the temperature of 95 ± 5 °C. The surplus gas was released from the tower.

General procedure: According to the actual content of CO₂ in the biogas, the volume fraction of CO₂ in the simulated biogas was controlled at 25, 35 and 45 %. Based on the experimental conditions, the pressure in the absorption tower was controlled in the range from 0.05 to 0.1 MPa. The liquid flow of 30 L h⁻¹ and the gas flow of 590 L h⁻¹ were the maximum operating flows for this system. Therefore, the gas inflow in the absorption tower was controlled in the range 230-590 L h⁻¹ and the flow of absorption solution was in the range of 15-30 L h⁻¹. The volume fractions of monoethanolamine were selected as 5, 10 and 20 % in the absorption solution. The monoethanolamine solution with the absorbed CO₂ was heated up to 90 °C in the desorption tower, for regeneration. In this system, a closed monoethanolamine solution cycle was applied in order to protect the environment and to save the energy and monoethanolamine consumption.

Detection method: The gas samples were taken from the inlet and outlet of the system. The purified gas was obtained from the pilot-plant without drying. We used a syringe to get gas samples, then put them into the gas chromatograph (GC) (SP-2100, Beifen Ruili Co., Beijing) which equipped with a 2 m × 3 mm stainless-steel column and a thermal conductivity detector (TCD) to measure the content of N₂ and CO₂. The temperatures of oven, injector and detector were controlled at 100, 120 and 120 °C, respectively. Argon was used as the carrier gas at a flow rate of 30 mL/min. The standard gas (Beifen Ruili Co., Beijing) composed of 60.1 % N₂ and 39.9 % CO₂ was used for the calibration.

RESULTS AND DISCUSSION

Effect of the ratio of liquid/gas: Herein, we set the flow of monoethanolamine solution as 15 L h⁻¹, 20 L h⁻¹, 25 L h⁻¹ and 30 L h⁻¹. The pressure in the absorption tower was fixed at 0.1 MPa and the CO₂ content in the simulated biogas was selected as 45 %. The gas flow was in the range of 230-590 L h⁻¹. The height of the absorption tower was 2.6 m. The CO₂ removal ratio with the change of the ratio of liquid/gas was illustrated in Fig. 2. When the monoethanolamine solution flow was in the range of 15-25 L h⁻¹, the CO₂ removal ratio decreased as the gas flow increasing. With increasing the flow of the monoethanolamine solution, the CO₂ removal ratio significantly increase. Taking the condition of the gas of 530 L h⁻¹ as an example, when the monoethanolamine solution flow increased from 15 L h⁻¹ to 20 L h⁻¹, the CO₂ removal ratio was increased at 98 %. When the flow increased to 25 L h⁻¹, the content of CO₂ was reduced by 21.3 %. When the flow was 30 L h⁻¹, the CO₂ could be totally removed under the condition of the gas flow of 230-590 L h⁻¹.

Fig. 2. CO₂ removal ratio with different ratio of liquid/gas

According to Fig. 2, it could be obviously found that the CO₂ removal ratio could be increased with the increase of the ratio of liquid/gas. It could be increased from 62.9 to 100 % when the liquid/gas ratio varied from 20/590 to 20/350. When the liquid/gas ratio was in the range of 20/350-20/230 L h⁻¹, the 100 % CO₂ removal ratio could be achieved.

When the flow of the input gas was reduced to 350 L h⁻¹, the 100 % CO₂ removal ratio also could be achieved. Considering the flow of the input gas was less than 350 L h⁻¹ in practical process, we kept the flow of the input gas at the range of 230-350 L h⁻¹. It was found that the CO₂ removal ratio could keep at 100 % for three months, which demonstrated the method was highly effective for absorption of CO₂ for applications.

Effects of pressures in the absorption tower: All of the experiments above were performed with the constant pressure in the absorption tower of 0.1 MPa. To study the influence of the pressure in the absorption tower on the CO₂ absorption, we further adjusted the pressure to 0.05, 0.075 and 0.1 MPa. The gas flow rate, monoethanolamine solution flow rate and the CO₂ content were controlled at 350 L h⁻¹, 20 L h⁻¹ and 45 %, respectively. The results are shown in Fig. 3. As the pressure of the absorption tower decreased from 0.1 to 0.05 MPa, the 100 % CO₂ removal ratio could be kept. Thus it is concluded

that the pressure of the absorption tower was not a key factor to affect the CO₂ removal efficiency.

Fig. 3. CO₂ removal ratio with different pressure

Effects of the initial CO₂ content: For the practice, it is necessary to investigate the CO₂ absorption effects once the input CO₂ content changed. According to the composition of the real biogas, we set the initial CO₂ content in the range of

25-45 %. The flow of the monoethanolamine solution was 20 L h⁻¹ and the gas flow was in the range 230-590 L h⁻¹. Fig. 4 presented the CO₂ removal ratio at different CO₂ concentration. It was shown that the CO₂ removal ratio presented increase with the decrease of the initial CO₂ content when the liquid/gas ratio was lower than 20/350. When the liquid/gas ratio was 20/530, the initial CO₂ content increased from 25 to 35 %, the CO₂ removal ratio was decreased by 15.8 %. When the initial CO₂ content kept increasing from 35 to 45 %, the CO₂ removal ratio was correspondingly decreased by 13.8 %. Therefore, it could be concluded that the input CO₂ concentration played a key role to the CO₂ removal efficiency by using the monoethanolamine solution as the absorbent.

Fig. 4. CO₂ removal ratio with different CO₂ concentration

Effects of the content of the monoethanolamine: According to literatures²², the concentration of the monoethanolamine was usually in the range of 5 to 15 %. Once the concentration increased to more than 15 %, the absorption efficiency decreased and the equipment was potentially corroded. If the concentration was less than 5 %, the absorption was not obvious. Therefore, we set the concentration of monoethanolamine of 5, 10 and 15 % to investigate their influences on the CO₂ absorption efficiency. As shown in Fig. 5, increasing concentration of monoethanolamine, the CO₂ removal ratio was correspon-

Fig. 5. CO₂ removal ratio with different monoethanolamine concentration

dently increased. When the liquid/gas ratio was kept constant at 20/470, the CO₂ removal ratio increased by 33.1 % and 18.7 % as the concentration of the monoethanolamine solution increased from 5 to 10 % and 15 %.

Effects of the padding layer height in the absorption tower: Due to other researchers' work²³, there was no need to build a high absorption tower when using the chemical absorption method. We further investigated the CO₂ absorption efficiency when the height of the absorption tower was reduced by 0.7 m. Taking the condition with the liquid/gas ratio of 20/410 as an example, the CO₂ removal ratio could be decreased by 20.6 % once the height of the padding layer in absorption tower was reduced by 0.7 m (Fig. 6). This result suggested that the height of the padding layer was important to the CO₂ removal efficiency.

Fig. 6. CO₂ removal ratio with different absorption tower height

Conclusion

In this work, the absorption of CO₂ in the simulated biogas was investigated at the pilot system by the use of monoethanolamine as the chemical absorbent. The main parameters influencing on the CO₂ removal were investigated. The results indicated that increasing initial CO₂ content, the CO₂ removal efficiency could be reduced. The optimized efficiency occurred at the liquid/gas ratio of 20/350, when the initial CO₂ content was 45 %. It was also found that the pressure in the absorption tower in the range of 0.05 MPa-0.1 MPa had no obvious influence on the CO₂ removal. Meanwhile, the CO₂ removal could be improved once the volume of the input CO₂ was reduced. The CO₂ removal could be significantly increased with the increase of monoethanolamine content. Finally, increasing the height of absorption tower was also benefit to the removal efficiency. In summary, the work supplied a good method to absorb a large amount of CO₂ in the biogas.

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