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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 CO_2 removal were investigated. The optimized CO_2 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 CO_2 was 45 %. The purity of biogas of the resulting gas could be as high as 97-100 %. Moreover, the CO_2 removal efficiency reduced with increasing CO_2 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 CO_2 removal. The CO_2 removal efficiency could be improved when the volume of the input CO_2 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 fields[1]. 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 efficently including vehicle fuel, fuel cell besides heating and cooking as an energy source[7-9].

Moreover, the calorific value of biogas is in the range of 22000-25000 kJ m^{-3}. As one of main components[10], 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 CO_2 is the first and the most important step. Furthermore, in recent years, the effective separation and regeneration of CO_2 also became important for the recycling and utilization of energy[11]. Although great efforts[12-16] have been devoted to design and develop new physical and chemical methods to increase absorption of CO_2. Generally, there are three methods to separate CO_2 from the biogas[17]. One is water treatment, whereas such method needs complicated operating conditions and cannot usually achieve a high level separation[18]. The second one is membrane separation method which suffers high cost and short lifetime of membrane[19-20]. The third one is Pressure-Swing-Adsorption method involving a physical absorption process, which is beneficial to the environment[21].

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 CO_2 from simulated biogas and regenerate absorption solution effectively. The removal of CO_2 was investigated on this pilot system at various parameters including the gas flow, liquid flow, pressure, initial CO_2 content, monoethanolamine content and absorption tower height. The aims of this work are to clarify the effects of the mentioned parameters on the CO_2 removal, which could offer a theoretical reference for the biogas purification in application.

EXPERIMENTAL

In order to simplify the experiments on the CO_2 removal, N_2 was used to take place of methane, which was further mixed with CO_2 in a certain ratio to simulate the biogas. Because the solubility of N_2 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.

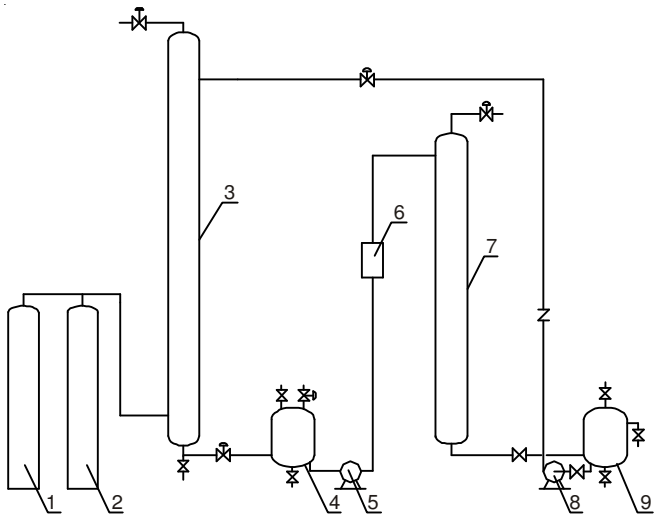

Fig. 1. Equipments for the absorption of CO_2 from the mixed gas by the chemical method (1. CO_2 cylinder 2. N_2 cylinder 3. Absorption tower 4. Lean solution storage tank 5. Pump1. 6. Preheating equipment 7. Desorption tower 8. Pump 2 9. Rich solution storage tank)

The CO_2 gas (99.99 %) and the N_2 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 CO_2 in the biogas, the volume fraction of CO_2 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 CO_2 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 N_2 and CO_2. 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 % N_2 and 39.9 % CO_2 was used for the calibration .

RESULTS AND DISCUSSION

Effect of the ratio of liquid/gas: Herein, we set the flow of monoethanolamine solution as15 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 CO_2 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 CO_2 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 CO_2 removal ratio decreased as the gas flow increasing. With increasing the flow of the monoethanolamine solution, the CO_2 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 CO_2 removal ratio was increased at 98 %. When the flow increased to 25 L h^{-1}, the content of CO_2 was reduced by 21.3 %. When the flow was 30 L h^{-1}, the CO_2 could be totally removed under the condition of the gas flow of 230-590 L h^{-1}.

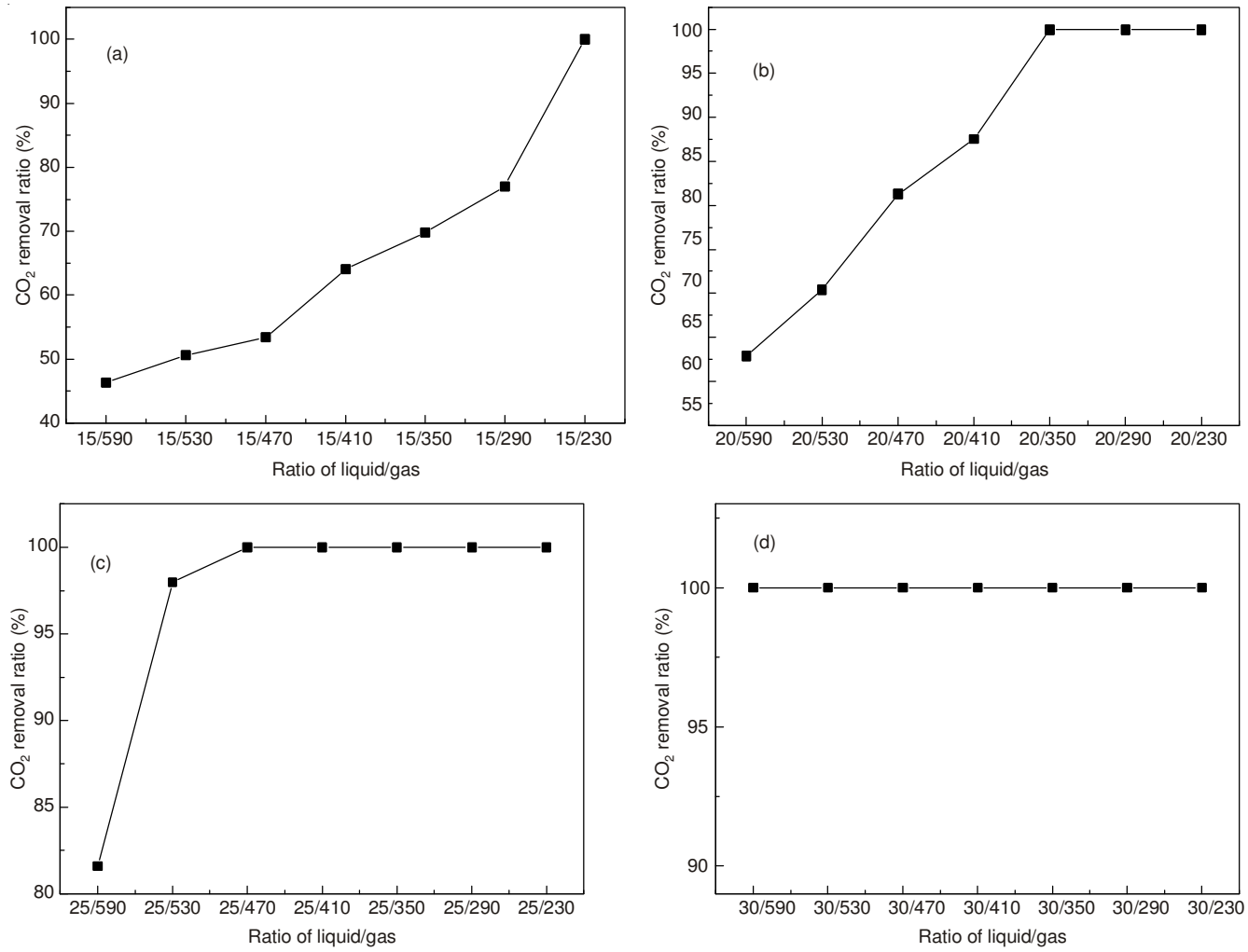

Fig. 2. CO_2 removal ratio with different ratio of liquid/gas

According to Fig. 2, it could be obviously found that the CO_2 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}, the100 % CO_2 removal ratio could be achieved.

When the flow of the input gas was reduced to 350 L h^{-1}, the100 % CO_2 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 CO_2 removal ratio could keep at 100 % for three months, which demonstrated the method was highly effective for absorption of CO_2 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 CO_2 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 CO_2 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 % CO_2 removal ratio could be kept. Thus it is concluded that the pressure of the absorption tower was not a key factor to affect the CO_2 removal efficiency.

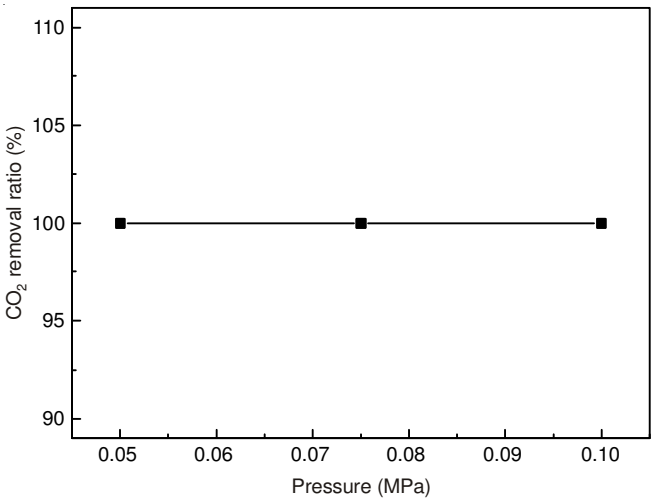

Fig. 3. CO_2 removal ratio with different pressure

Effects of the initial CO_2 content: For the practice, it is necessary to investigate the CO_2 absorption effects once the input CO_2 content changed. According to the composition of the real biogas, we set the initial CO_2 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 CO_2 removal ratio at different CO_2 concentration. It was shown that the CO_2 removal ratio presented increase with the decease of the initial CO_2 content when the liquid/gas ratio was lower than 20/350. When the liquid/gas ratio was 20/530, the initial CO_2 content increased from 25 to 35 %, the CO_2 removal ratio was decreased by 15.8 %. When the initial CO_2 content kept increasing from 35 to 45 %, the CO_2 removal ratio was correspondingly decreased by 13.8 %. Therefore, it could be concluded that the input CO_2 concentration played a key role to the CO_2 removal efficiency by using the monoethanolamine solution as the absorbent.

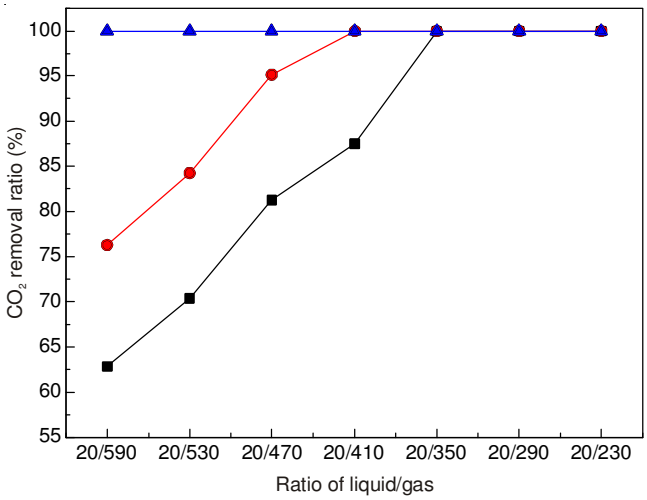

Fig. 4. CO_2 removal ratio with different CO_2 concentration

Effects of the content of the monoethanolamine: According to literatures[22], the concentration of the monoethanolamine was usually in the range of 5 to15 %. 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 CO_2 absorption efficiency. As shown in Fig. 5, increasing concentration of monoethanolamine, the CO_2 removal ratio was correspondingly increased. When the liquid/gas ratio was kept constant at 20/470, the CO_2 removal ratio increased by 33.1 % and 18.7 % as the concentration of the monoethanolamine solution increased from 5 to 10 % and 15 %.

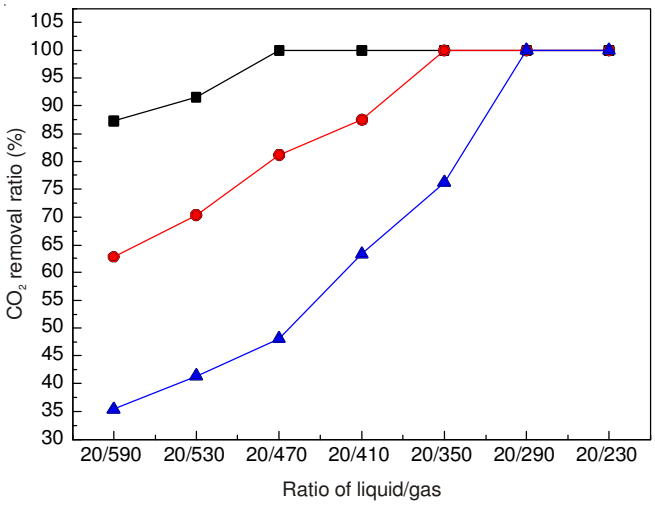

Fig. 5. CO_2 removal ratio with different monoethanolamine concentration

Effects of the padding layer height in the absorption tower: Due to other researchers' work[23], there was no need to build a high absorption tower when using the chemical absorption method. We further investigated the CO_2 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 CO_2 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 CO_2 removal efficiency.

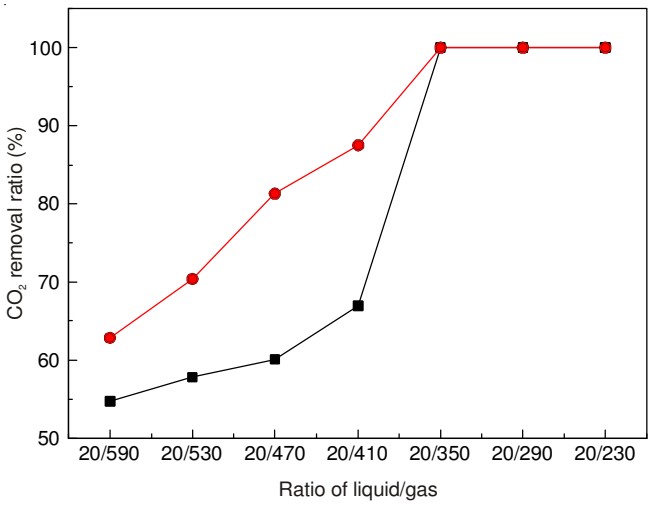

Fig. 6. CO_2 removal ratio with different absorption tower height

Conclusion

In this work, the absorption of CO_2 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 CO_2 removal were investigated. The results indicated that increasing initial CO_2 content, the CO_2 removal efficiency could be reduced. The optimized efficiency occurred at the liquid/gas ratio of 20/350, when the initial CO_2 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 CO_2 removal. Meanwhile, the CO_2 removal could be improved once the volume of the input CO_2 was reduced. The CO_2 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 CO_2 in the biogas.

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REFERENCES

1. S. Chu, *Science*, **325**, 1599 (2009).
2. Y. Pang and X. Li, *Trans. Chinese Soc. Agric. Eng*., **22(S1)**, 53 (2006).
3. X. Jiang, S.G. Sommer and K.V. Christensen, *Sustainab. Biofuels*, **39**, 6073 (2011).
4. X. Li, B. Zhou and H. Yuan, *Trans. Chinese Soc. Agric. Eng*., **S2**, 352 (2011).
5. X.J. Li, Solid Waste Engineering, China Environmental Science Press, Beijing (2003).
6. H. Katuwal and A.K. Bohara, *Renew. Sustain. Energy Rev*., **13**, 2668 (2009).
7. J.L. Walsh, C.C. Ross, M.S. Smith and S.R. Harper, *Biomass*, **20**, 277 (1989).
8. M.H. Praßl, Biogas Purification and Assessment of the Natural Gas Grid in Southern and Eastern Europe, Leibnitz (2008).
9. A. Wellinger and A. Lindberg, IEA Bioenergy Task 24: Biogas Upgrading and Utilization (2006).
10. X.J. Yao and Y.S. Tian, Clean Conversion of Biomass Resource Utilization Technology, Chemical Industry Press, Beijing (2005).
11. IPCC, Carbon dioxide Capture and Storage, Cambridge, Cambridge University Press, United Kingdom (2005).
12. A. Aroonwilas, P. Tontiwachwuthikul and A. Chakma, *Sep. Purif. Technol*., **24**, 403 (2001).
13. S. Rasi, J. Läntelä, A. Veijanen and J. Rintala, *Waste Manage*., **28**, 1528 (2008).
14. H. Xu and L. Cui, *Environ. Sci. Manage.*, **31**, 79 (2006).
15. S. Yan and M. Fang, *Chem. Ind. Eng. Progr.*, **25**, 1018 (2006).
16. Q.Y. Zeng, Y.J. Bai and C.J. Yang, *Gas Chem*., **35**, 23 (2010).
17. A. Kohl and R. Nielsen, Gas Purification, Gulf Publishing Company, Houston, Texas (1997).
18. J. Läntelä, S. Rasi, J. Lehtinen and J. Rintala, *Appl. Energy*, **92**, 307 (2012).
19. R. Wang, D.F. Li and D.T. Liang, *Chem. Eng. Process.*, **43**, 849 (2004).
20. P.H. Feron and A.E. Jansen, *Sep. Purif. Technol*., **27**, 231 (2002).
21. L. Tian, Z. Deng and Z. Xia, *Environ. Eng*., **28**, 78 (2010).
22. S.Y. Zhu, The Environmental and Industrial Gas Purification Technology, Chemical Industry Press, Beijing (2001).
23. J.T. Yeh, H.W. Pennline and K.P. Resnik, *Energy Fuels*, **15**, 274 (2001).