CO₂ chemical absorption by using membrane vacuum regeneration technology

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Abstract

The novel regeneration process by using membrane vacuum technology was put forward to reduce the regeneration energy consumption in the chemical absorption process for CO₂ separation from flue gas. The rich MEA solution was flowed in the lumen of the hydrophobic PP hollow fiber membrane contactors, and the shell side was maintained at a reduced pressure by a vacuum pump. In addition, the additional low temperature steam whose temperature is the same to rich MEA solution was also provided to act as the sweep gas to improve the regeneration performance and to prevent the water loss of the lean solution. Results showed that this membrane vacuum regeneration process can regenerate rich MEA solution to reach a relatively better regeneration performance and can effectively utilize the low temperature energy or waste heat in the power plants.

Keywords: Desorption; Hollow fiber membrane; Membrane stripping; Separation; Regeneration energy consumption; Carbon dioxide; Flue gas

1. Introduction

Among the applicable CO₂ capture technologies, CO₂ chemical absorption technology based on monoethanolamine (MEA) is considered as the currently most promising technology for CO₂ separation from flue gas [1,2]. But in fact, this CO₂ removal process is not as straightforward as it could be expected because of its higher separation cost and energy penalty [3]. In the CO₂ chemical absorption process, CO₂-rich solution must be heated to reach or exceed the boiling temperature because the chemical kinetics of regeneration increases with temperature [4]. So, high pressure or high temperature steam coming from the steam turbine must be applied to provide the regeneration heat. So, the regeneration energy consumption is estimated to be 15%-30% of the net power production of a coal-fired power plant when 90% CO₂ is captured [5]. Therefore, determining how to reduce the energy consumption, especially the regeneration energy consumption of the CO₂ chemical absorption process would be the

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Gibbins et al. [6] formulated that the low-grade heat or waste heat other than the high-grade steam from the steam cycle had better be used for solvent regeneration in order to reduce the energy consumption. So, the low regeneration temperature of solvent must be adopted. That is because that if the CO₂ absorption process has the lower regeneration temperature, more low temperature energy or waste heat which are not recovered now because of low temperature or technical difficulty [7] can be largely utilized in the power plants. In addition, the MEA degradation rate is approximately in inverse proportion to the regeneration temperature [8,9]. So, the decrease of regeneration temperature can contribute to reduce the MEA degradation rate. But, as for the single solvents like MEA, if the regeneration temperature (e.g. 80 °C) is decreased to be less than the boiling temperature at the ambient pressure in the conventional heating regeneration process, the regeneration performance will become worse [5]. So, some alternative solvents must be developed to replace the single MEA to capture CO₂. The development of these solvents should provide the equivalent or greater CO₂ absorption rate, higher CO₂ loading capacity and lower regeneration temperature or energy consumption than MEA [10]. The study on the alternative solvents includes the improvement of the conventional amines [11,12], the research of mildly hindered amines [13,14] and the investigation of new solvents [15-17].

In addition, the development of new regeneration process will be favorable for the reduction of regeneration energy consumption. For example, using vacuum regeneration technology rather than conventional heating method may lead to lower the regeneration temperature [7,18,19]. Nii et al. [19] successfully investigated the vacuum regeneration method to regenerate the CO₂-loaded carbonate solution. A capillary-type facilitated transport membrane module was put forward by Teramoto et al. [18] to absorb CO₂ and simultaneously regenerate the CO₂-rich solution by vacuum technology. And this process can reduce the CO₂ recovery energy consumption in a great extent. Based on it, Okabe et al. [7] developed a new CO₂ recovery process called a membrane flash process to reduce the CO₂ recovery energy consumption, in which some types of ultrafiltration membranes were used to regenerate the rich diethanolamine (DEA) solution under the reduced pressure. In this new process, the maximum regeneration temperature is only about 70 °C, which means that much low grade heat can be utilized to provide the heat of regeneration. Koonaphapdeeelert et al. [20] used pure N₂ gas as the sweep gas to strip CO₂ from rich MEA solution at 80 °C-100 °C in the ceramic hollow fiber membrane contactors. The researches discussed above showed that the membrane vacuum regeneration technology may be used to regenerate CO₂ from the CO₂-rich solution.

So, the feasibility of CO₂ regeneration method by using hollow fiber membrane contactors and vacuum technology was investigated in this study. In addition, some operating parameters influencing the regeneration performance were experimented in detail.

2. Experimental

2.1. Desorption apparatus

In this experiment, the hydrophobic microporous polypropylene (PP) hollow fiber membrane module, which was provided by Zheda Kaihuua Membrane Technology Co., Ltd., was used as the stripper. The specifications of hollow fiber and membrane module are listed in Table 1. Two serial cylindrical modules were used to regeneration CO₂ from CO₂-rich solution in this study.

2.2. Experimental procedure

The experimental setup is schematically shown in Fig. 1. Before each experiment, aqueous MEA solutions with the desired concentration were firstly prepared. And then pure CO₂ gas was directly introduced to the solutions for about 1-2 h to form the CO₂-rich MEA solutions.
Table 1 Specifications of hollow fiber and membrane module

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Module I.D. (m)</td>
<td>0.02</td>
</tr>
<tr>
<td>Fiber I.D. (µm)</td>
<td>344</td>
</tr>
<tr>
<td>Fiber O.D. (µm)</td>
<td>442</td>
</tr>
<tr>
<td>Fiber Length (m)</td>
<td>0.26</td>
</tr>
<tr>
<td>No. of fibers</td>
<td>500</td>
</tr>
<tr>
<td>Average pore size (µm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Fiber porosity (%)</td>
<td>&gt;45</td>
</tr>
<tr>
<td>Contact area (inner, m²)</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Fig. 1. Experimental setup of CO₂-rich solution regeneration by using membrane vacuum technology: (1) condenser; (2) CO₂-rich solution tank; (3) heaters; (4) heater band; (5) liquid pump; (6) liquid flow meter; (7) pressure gauge; (8) thermocouple; (9) hollow fiber membrane contactors; (10) vacuum pressure gauge; (11) trap; (12) thermostat water batch; (13) deionized water tank; (14) vacuum pressure control valve; (15) vacuum pump; (16) temperature controller.

Then, the leakage test of the experimental system was carried out under the vacuum produced by vacuum pump (15) (VCH1028-24V; Maximum absolute vacuum pressure: 10 kPa; Pumping rate: 28 L/min; Chendu Weicheng Electromechanical Company, PR China). The perfect air tightness performance was indicated by a constant vacuum pressure gauge (10) (-0.1-0 MPa, ±2 kPa). If the pressure was steady, the regeneration pressure was then regulated to reach the desired value in the experiments by regulating the valve opening of the vacuum pressure control valve (14). After the leakage test and pressure regulation, the CO₂-rich MEA solution was added into the rich solution tank (2) and heated to the desired temperature by heaters (3). The liquid temperature was controlled by the temperature controller (16). Then the rich solution was introduced by liquid pump (5) to the fiber lumen of the top of membrane contactors (9) where the thick-layer rich solution was partitioned into the continuous thin-layer rich solutions. When the membranes were completely filled with liquids, the reduced pressure produced by (15) was applied through the shell side of (9). At this point, time was recorded. In this study, steam coming from the deionized water tank (13) heated by thermostat water bath (12) was also flowed through the shell side of (9) to act as the sweep gas during the course of regeneration. Then, CO₂ would be regenerated from rich solution due to the favorable effect of reduced pressure and the sweep gas, and then CO₂ would permeate the gas-filled membrane pores to reach the shell side of (9). CO₂ and the steam were extracted from the shell side of (9) into the trap (11) where the sweep gas was condensed. Then the enriched CO₂ was vented by vacuum pump.

During the course of regeneration, all the pipelines and membrane modules were heated by the heater bands (4) in order to prevent the heat loss of rich solution before entering (9). The temperature of sweep gas, temperature of the heater bands and solution temperature were simultaneously controlled by (16) in order to get the same temperature to inhibit the water loss of lean solution. After a given time, the lean solution samples were taken from
the liquid outlet to assess the regeneration performance. And the CO₂ loading ratio of samples would be determined by the standard method described by Aroonwilas and Tontiwachwuthikul [21].

After each experiment, (13) were weighed before and after regeneration by an electronic balance (PL2002; Maximum measurement range: 2100 g; Accuracy: ±0.01; Mettler-Toledo Instruments (Shanghai) Co., Ltd.), and the amount of vaporized water (Δm) was determined from the difference of these weights. In addition, the condensate in (11) was weighed to estimate the amount of water loss during the course of regeneration. And the pH value of condensate was also measured by pH-meter (Delta 320; Measurement range: 0.00-14.00; Accuracy: ±0.01; Mettler-Toledo Instruments (Shanghai) Co., Ltd.) to assess the amount of MEA loss because pH value is a function of CO₂ loading ratio, temperature, and MEA concentration [22].

2.3. Data analysis

In this study, the average mass transfer rate of CO₂ regeneration (JR) was mainly used to evaluate the regeneration performance. In addition, the mass concentration difference of MEA between before and after regeneration (∆C) was used to reflect the water loss based on the assumption that MEA loss can be ignored.

\[
J_R = \frac{(Q_R \times \alpha_R \times M_R - Q_L \times \alpha_L \times M_L) \times 60}{1000 \times A}
\]

\[
\Delta C = \frac{Q_R \times t \times \rho \times C_0}{Q_R \times t \times (m_c - \Delta m) - C_0}
\]

where \( J_R \) is the mass transfer rate of CO₂ regeneration, mol/(m² h); \( Q_R \) and \( Q_L \) denote the flow rate of rich and lean solutions, respectively, ml/min; \( \alpha_R \) and \( \alpha_L \) denote the CO₂ loading ratio of rich and lean solution, respectively, mol/mol; \( M_R \) and \( M_L \) are the molar concentration of rich and lean solution, respectively, mol/L; \( A \) represents the gas-liquid interfacial area, m²; \( t \) is the regeneration time, min; \( C_0 \) denotes the mass concentration of rich solution, %; \( \rho \) is the density of rich solution, g/ml; \( m_c \) is the weight of condensate in (11), g; \( \Delta m \) represents the amount of additional steam during the course of regeneration, g.

3. Results and discussion

3.1. Feasibility of CO₂-rich MEA solution using vacuum technology

Fig. 2. Regeneration performance of thick-layer MEA solution using vacuum technology (\( C_0 =6.1\% \), \( \alpha_R =0.691 \) mol/mol; 10 kPa; 284 K).

Fig. 3. Effect of MEA solution thickness on regeneration performance (\( C_0 =6.1\% \), \( \alpha_R =0.691 \) mol/mol; 10 kPa; 284 K).
The CO₂ amount regenerated from aqueous rich MEA solution by using vacuum technology as the function of sampling sectional positions (Z) is shown in Fig. 2. The apparatus and procedure can be found in our previous work [23]. These curves clearly show that a gradient of CO₂ loading ratio along the liquid depth is formed, and the smaller Z leads to the higher regeneration performance. The possible reason may be that CO₂ molecules released from the solution sections far from the liquid-gas interface must be diffused from the sections to the interface, and then to the interface based on the “two-film” theory. Then, the regeneration performance may be directly proportional to the mass transfer distance which is equivalent to the distance between the solution section and interface, Z. Based on these experimental phenomena, it can be hypothesized that the diffusion of CO₂ molecules within the liquid phase may be the major factor controlling the regeneration performance under the same operating conditions. Therefore, the decrease of total mass transfer distance, i.e., the rich solution thickness (H) will be favorable to the improvement of total regeneration performance. The hypothesis is validated by the experimental results shown in Fig. 3. It can be clearly seen from Fig. 3 that the regeneration performance of rich solution is improved greatly when the total solution thickness was decreased from 51.6 to 10 mm. And it is also worthy to be noticed that it must take about at least 4 times regeneration time to reach the same CO₂ regeneration ratio for the solution of 51.6-mm thick compared to that with 10-mm thick at Z = 2 mm. This result strongly suggests that the vacuum regeneration performance also depends on the amount of CO₂ contained in the rich solution. In addition, it is shown from Fig. 2 and Fig. 3 that the increase of regeneration time can improve the regeneration performance.

So, under the same conditions such as temperature, pressure, CO₂ loading ratio, and time, it can be deduced that the vacuum technology may be theoretically feasible to regeneration rich solution, and it is very crucial to reduce the thickness of rich solution in the course of regeneration in order to get the better regeneration performance. And the hydrophobic hollow fiber membrane may be used to reduce the thickness of rich solution because of its smaller membrane inner diameter.

3.2. Regeneration performance of MEA rich solution using membrane vacuum technology

3.2.1. Effect of rich solution flow rate

In Fig. 4, the regeneration performance is plotted as a function of rich solution flow rate. It can be seen that αₜ value decreases with rich solution flow rate. That is because that when the thickness of rich solution, the liquid surface facing the vacuum and sweep gas, and CO₂ loading ratio are the same, the regeneration mass transfer driving force is same. So, the regeneration performance will be controlled by the regeneration time. The decrease of liquid flow rate can increase the liquid-gas contact time, and consequently improve the regeneration performance. But, the rich solution flow rate can not be decreased without limitation because lower flow rate will result in the lower Jₚ value, hence the smaller CO₂ regeneration amount, and consequently the higher vacuum pump energy consumption per kg of CO₂, as shown in Fig. 4. So, an appropriate rich solution flow rate must be carefully designed in order to get the better regeneration performance and lower regeneration energy consumption. If both the lower αₜ value and higher regeneration mass transfer rate can be required, the increase of membrane length may be used to increase the liquid-gas contact time.

Fig. 5 shows the losses of water and MEA from the rich MEA solution during the course of vacuum regeneration. Based on the ΔC value, the changes of MEA mass concentration due to the water loss can be controlled to be less than 0.6% except 10 ml/min liquid flow rate. The result means that the additional low temperature steam acting as the sweep gas whose temperature is the same to the rich solution can not only improve the vacuum regeneration performance, but also inhibit the water loss. Fig. 5 also shows the amount of MEA loss. Because the CO₂ loading ratio of the condensate collected by (11) can be neglected in the experiments, MEA concentration in the condensate can be estimated by using the difference of pH value between the condensate and the 0.0005 mol/L MEA aqueous solution. Apparently, it is seen from Fig. 5 that the pH value of condensate is less than that of 0.0005 mol/L MEA solution whatever liquid flow rate is used, which means that the MEA concentration in the condensate is less than
0.0005 mol/L. When liquid flow rate is 8 ml/min, the MEA loss is less than 0.89 kgMEA/t CO₂, which is lower than that in the heating regeneration process (about 1.6 kgMEA/t CO₂ [24]).

3.2.2. Effect of regeneration pressure

Effect of regeneration pressure on \( J_R \) value is shown in Fig. 6. It is evident that as the vacuum pressure decreases, \( J_R \) value increases, which represents the improvement of regeneration performance. That is because that the decrease of pressure can decrease the CO₂ partial pressure in the gas phase, hence increase the regeneration mass transfer driving force. On the other hand, the decrease of total pressure also leads to the increase of additional steam flow rate, as shown in Fig. 6. For example, when the water temperature is 338 K, the water vapor pressure is about 25 kPa. When the regeneration pressure is less than 25 kPa, the deionized water in (13) will boil and large amount of water vapor will be generated to act as the sweep gas to sweep the liquid surface facing the vacuum during the course of regeneration, which then results in the great decrease of the CO₂ partial pressure in the gas phase, and consequently the distinct increase of CO₂ regeneration mass transfer rate. If the pressure is higher than 25 kPa, the amount of additional steam acting as the sweep gas will greatly decrease with the increase of regeneration pressure, which will lead to the considerable decrease of CO₂ regeneration mass transfer rate.

3.2.3. Effect of rich solution temperature

Effect of rich solution temperature on \( J_R \) and additional steam flow rate is plotted in Fig. 7. It is clearly seen that regeneration performance improves with the solution temperature. Nii et al. [19] also reported the similar results.
It is well known that the reversible reaction constant in the stripper increases with the liquid temperature [3], which leads to the improvement of regeneration performance. In addition, in our experimental system, the increase of rich solution temperature also leads to the increase of additional steam flow rate acting as the sweep gas to regenerate CO2, as shown in Fig. 7. So, the increase of sweep gas amount will lead to the decrease of CO2 partial pressure in the gas phase, and consequently result in the increase of regeneration mass transfer driving force and the improvement of regeneration performance.

3.2.4. Effect of MEA concentration

Fig. 8 demonstrates the relation between MEA concentration and regeneration performance under the same conditions. It is clearly observed that the amount of CO2 regenerated, \((\alpha_r - \alpha_l)\), decreases with the increase of MEA concentration. It is also worthy to be noticed that in the first region where \(C_0\) is below 20 w.t.%, the effect of MEA concentration on \((\alpha_r - \alpha_l)\) values is not remarkable. But in the second region where \(C_0\) is above 20 w.t.%, \((\alpha_r - \alpha_l)\) values decrease considerably with the increase of MEA concentration. The reason is that when the liquid facing the vacuum, pressure, CO2 loading ratio and liquid flow rate are the same, the solution having the higher concentration, hence the larger amount of CO2 contained in the rich solution will be regenerated slowly. In addition, when \(C_0\) is less than 20 w.t.%, the molecular diffusion coefficient of CO2 in aqueous MEA solution \(D\) decreases slightly, but the viscosity of MEA solution \(\eta\) increases slightly with the increase of MEA concentration [25]. So, the change of \(D\) and \(\eta\) will lead to the slight decrease of \((\alpha_r - \alpha_l)\). But, when \(C_0\) is 30 w.t.%, \(D\) decreases greatly and \(\eta\) increases considerably compared to 20 w.t.%, which will lead to the enormous decrease of \((\alpha_r - \alpha_l)\). Fig. 8 also shows that the \(J_R\) value increases considerably with MEA concentration. So, a compromise has to be taken between higher \((\alpha_r - \alpha_l)\) and higher \(J_R\) when what concentration is determined.

3.2.5. Effect of initial rich CO2 loading ratio

The effect of \(\alpha_r\) on regeneration performance is plotted in Fig. 9. It is shown that the relatively lower \(\alpha_r\) value should be used in order to get the lower \(\alpha\) value. But, it is also indicated that the increase of \(\alpha_r\) leads to the increase of \(J_R\) value, which means that the decrease of energy consumption per kg of CO2 under the same conditions. So, it is important to select an appropriate \(\alpha_r\) value in order to get the lower \(\alpha\) value and lower regeneration energy consumption.
4. Conclusion

(1) Vacuum regeneration may be viable if the thick-layer rich solution can be easily portioned into the continuous thin-layer solutions with the appropriate thickness, on which vacuum is pulled. And the hydrophobic hollow fiber membrane contactor can be selected to reduce the rich solution thickness.

(2) When the PP hollow fiber membrane contactors and vacuum technology were used to regenerate the continuous CO₂-rich MEA solution, water and MEA losses from the rich solution are very small. And the great decrease of rich solution flow rate and regeneration pressure, and increase of rich solution temperature can improve the regeneration performance based on the \( \alpha_L \) value. But, the decrease of rich solution flow rate can lead to the decrease of \( J_R \) value, whereas can result in the increase of vacuum pump energy consumption per kg of CO₂. In addition, the appropriate MEA concentration and CO₂ loading ratio of rich solution must be carefully designed due to the contradiction between the CO₂ loading ratio of lean solution and \( J_R \) value.

(3) In order to ensure the long-term stable operation of membrane vacuum regeneration process, some novel hollow fiber membranes which have the stronger hydrophobicity, the better thermal and chemical stabilities must be developed in the future. And the porous ceramic hollow fiber membranes which can be modified to be hydrophobic reported by Koonaphapdeeelert [20] may be the alternative to replace the conventional polymeric membranes to regenerate CO₂ from rich solution under vacuum.

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