Membrane stripping technology for CO₂ desorption from CO₂-rich absorbents with low energy consumption

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Abstract

CO₂ membrane stripping is a novel method for CO₂ desorption at low temperature (around 348K) for amine-based CO₂ capture, which has the potential to reduce regeneration energy requirement. In this work, we investigated CO₂ membrane stripping with two different commercial hollow fiber membranes, polypropylene (PP) and Polyvinylidene fluoride (PVDF). CO₂ membrane stripping in PVDF membrane showed a faster CO₂ desorption rate than in PP membrane, but PP membrane presented a better stability on long-term running. Energy consumption for CO₂ membrane stripping with 20 wt% MEA solvent was evaluated. Compared with conventional thermal regeneration, 28% energy can be saved if regeneration pressure of CO₂ membrane stripping operated at 20 kPa.

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Keywords: CO₂; Membrane stripping; Absorbent; Desorption; Energy consumption;

1. Introduction

Fossil fuel combustion in power generation and industrial sectors is considered as the largest stationary source of CO₂ emission, which accounts for 60% of global CO₂ emission [1,2]. At present, solvent based post-combustion capture (PCC) technology, which typically separates CO₂ from flue gas in packing columns, is believed to be one of the most mature technologies [3,4]. Nevertheless, the main challenge for this technology is its energy-intensive stripper for rich-solvent regeneration. Significant amounts of heat for rich-solvent regeneration are required, with reducing the power plant efficiency by as much as 30% [5]. Therefore, it has been proposed to develop novel...
regeneration technology with lower energy consumption in recent years.

Hollow fiber membrane contactors were proposed as a promising separation unit than conventional packed columns for CO₂ separation [6,7]. Therefore, membrane stripping technology, which has the potential to reduce energy requirement of CO₂ separation, is a novel method for CO₂ desorption [8-11]. In this process, CO₂ is desorbed in a hollow fiber membrane contactor instead of packed column. The regeneration temperature, which is usually around 353K, is much lower than conventional thermal regeneration temperature. Kosaraju et al. [8] firstly demonstrated the feasibility of CO₂ membrane stripping using commercial PP membrane contactors by long term running for 55 days. Fang et al. [12] further studied CO₂ membrane stripping comprehensively with using monoethanolamine (MEA) as absorbent. Besides MEA absorbent, Wang et. al. [13,14] screened the different amine-based absorbent for CO₂ membrane stripping process.

In this work, we studied the CO₂ membrane stripping with two different commercial hollow fiber membranes, polypropylene (PP) and Polyvinylidene fluoride (PVDF). The effects of membrane materials on CO₂ membrane stripping performance were compared by investigating their regeneration efficiencies, CO₂ desorption rates and long-term stabilities. In addition, to evaluate the advantages of membrane stripping technology, energy consumption for CO₂ membrane stripping with 20 wt% MEA solvent was estimated.

2. Experimental

2.1. Materials

The MEA absorbent (purity > 99%) we used in this work were provided by Sinopharm Company. The pure CO₂ gas (purity > 99.9%), provided by Hangzhou Jingong Gas Co., Ltd., was used to prepare the CO₂ loaded solvent by introducing to the fresh solvent in a bubbling reactor. The CO₂-loading of solutions can be determined by the standard method described in our previous work [12].

The hydrophobic micro-porous polypropylene (PP) and Polyvinylidene fluoride (PVDF) hollow fiber membrane modules were provided by the Zheda Kaihua Membrane Technology Co., Ltd. and Tianjin Fengke Membrane Technology Co., Ltd., respectively. The detail specification of the membrane modules is listed in Table 1. It should be noted that for PP membrane, we used two identical membrane modules by connecting each other in series.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>PVDF</th>
<th>PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber I.D.</td>
<td>µm</td>
<td>700</td>
<td>344</td>
</tr>
<tr>
<td>Fiber O.D.</td>
<td>µm</td>
<td>1000</td>
<td>424</td>
</tr>
<tr>
<td>Thickness of membrane wall</td>
<td>µm</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>Porosity</td>
<td></td>
<td>85%</td>
<td>45%</td>
</tr>
<tr>
<td>Average micropore size</td>
<td>µm</td>
<td>0.16</td>
<td>0.1</td>
</tr>
<tr>
<td>Active length of module</td>
<td>cm</td>
<td>40</td>
<td>26×2</td>
</tr>
<tr>
<td>Module O.D./I.D.</td>
<td>cm</td>
<td>2.5/2.2</td>
<td>2.4/2</td>
</tr>
<tr>
<td>NO. of fibers</td>
<td></td>
<td>130</td>
<td>500</td>
</tr>
<tr>
<td>Contact area</td>
<td>m²</td>
<td>0.068</td>
<td>0.14×2 m²</td>
</tr>
</tbody>
</table>

2.2. Apparatus and procedure

The experimental setup of CO₂-rich solution by using membrane stripping technology is shown in Fig. 1. The prepared CO₂-rich solution was added into the rich-solvent tank, and then heated to desired temperature before membrane module. After pre-heating, CO₂ rich solution was continuously pumped into the tube side of the hollow fiber membrane contactor by a peristaltic pump. Liquid flow rate was controlled by adjusting the rotation speed of the peristaltic pump, the liquid phase temperatures and pressures are both metered in inlet and outlet of membrane module. Low-temperature water steam coming from the steam generator flowed through the shell side of the
membrane contactor to act as the sweeping gas by the driving force of vacuum pump during the course of regeneration. The reduced pressure in the shell side of membrane contactor was controlled by a vacuum pump located at end of module. Hence, the CO₂ would be regenerated from the rich solution due to the positive effects of reduced pressure and sweeping gas, and permeated the gas-filled membrane pores to the shell side. Then the CO₂ and steam were extracted together from the shell side of membrane contactor into the condenser in which sweeping steam was condensed. Finally, the CO₂ was enriched and could be collected from the vacuum pump.

Fig. 1. Schematic diagram of CO₂ membrane stripping experimental set-up

In CO₂ membrane stripping process, the average CO₂ stripping rate and regeneration efficiency are usually used to evaluate the performance of membrane stripping. Average CO₂ stripping rate ($N_{CO₂}$) can be identified by following equation,

$$N_{CO₂} = \frac{nπR^2VL (α_{rich} - α_{lean})}{S}$$

(1)

Regeneration efficiency ($η$) can be calculated by Eq. 2,

$$η = (1 - \frac{α_{lean}}{α_{rich}})×100\%$$

(2)

in which $V_L$ is liquid velocity, m/s; $n$ is fibre number; $R$ is radius of membrane, m; $C$ is the concentration of solvent, mol/m³; $α_{rich}$ and $α_{lean}$ are CO₂ rich loading and CO₂ lean loading of solvent in mole of CO₂ per mole of absorbent; $S$ is the membrane contact area, m².

3. Results and discussion

3.1. Comparison of different membrane materials

To evaluate the CO₂ membrane stripping with different membrane materials, we chose two types of commercial membrane (PP and PVDF) modules to compare their effects on CO₂ membrane stripping. 20 wt % MEA solvent with CO₂ loading of 0.535 mol CO₂/mol MEA was used as the CO₂-rich solvent and flowed through the tube side of membrane contactor. The regeneration temperature was 343K. The stripping pressure was controlled at 20 kPa. Fig.
2 presents the comparison of regeneration efficiencies of PP membrane and PVDF membrane modules at different solvent velocities. It shows that regeneration efficiency is a decreasing function of solvent velocity for both membrane modules. This is expected since a lower liquid velocity leads to an increase in residence time (reaction time) in membrane module. The similar result was also reported by Wang et al. [10] and Fang et al. [12]. Additionally, PP membrane module presents a better performance than PVDF membrane module. This could be explained by the difference of effective gas-liquid contact area of different membrane modules. Due to the smaller diameter of PP fiber membranes, as shown in Table 1, PP membrane module can provide higher gas-liquid contact area than that of PVDF module. PP membrane with smaller diameter will also shorten the diffusion time of CO₂ molecule from the inside of membrane fiber to the external gas/liquid interface.

Fig. 2. The change of regeneration efficiencies under different solvent velocities for PP and PVDF membrane modules (Rich CO₂ loading: 0.553 mol CO₂/mol MEA, MEA concentration: 20 wt%, regeneration temperature:343K, regeneration pressure = 20kPa)

Fig. 3 compared the average CO₂ desorption rate at different liquid velocities in PP and PVDF membrane modules. Opposite to regeneration efficiency, Fig. 3 reveals that a faster liquid velocity favors a higher CO₂ desorption rate. This indicates that, as the liquid velocity increases, the loading change becomes small, but to a lesser extent of the increase of liquid velocity. As a result, the net impact of increase of liquid velocity is an increase in CO₂ desorption flux under the conditions studied. In terms of CO₂ desorption rate, PVDF membrane module presented a better performance than PP membrane module. This is mainly due to the structural differences of different membranes. PVDF membrane has higher porosity than PP membrane, which means that the mass transfer resistance of PVDF membrane is lower than that of PP membrane.

Fig. 3. The change of average CO₂ desorption rate under different solvent velocities for PP and PVDF membrane modules (Rich CO₂ loading: 0.553 mol CO₂/mol MEA, MEA concentration:20 wt%, regeneration temperature:343K, regeneration pressure = 20kPa)
3.2. Stability of different membrane materials in membrane stripping

In order to investigate the stability performances of membrane, the continuous running experiments of different membrane modules were also carried out for a period of time up to 120 h. The long-term membrane stripping was operated at temperature of 343K, pressure of 30 kPa. 20 wt% MEA solvent with CO₂ loading of 0.5 mol CO₂/mol MEA was used as CO₂-rich solvent. The liquid flow rate was kept constant at 1.5 mL/min.

Fig. 4. Long-term performance of PP membrane in CO₂ membrane stripping for a period of time up to 120 h. (MEA concentration: 20 wt%, regeneration temperature: 343K, regeneration pressure = 30kPa, liquid flow rate: 1.5 mL/min)

Fig. 4 shows that CO₂ membrane stripping performance was quite stable for PP membrane module. The regeneration efficiency only reduces by only 24% in PP membrane module after 120 hours running. The change of regeneration efficiency of membrane stripping with operating time in PVDF membrane module is presented in Fig. 5. We can find a significant drop on regeneration efficiency with time for PVDF membrane. The regeneration ratio was reduced by 83% after 120 hours running. The results indicated that PP membrane was much more stable than PVDF membrane in membrane stripping process.

Membrane wetting is the main reason that results in the reduction on regeneration efficiency [7,14]. For the fresh membrane, the pores of the membrane remain completely gas-filled. If membranes are wetted, the membrane pores will be filled by the liquid instead gas, which will considerably increase the mass transfer resistance on membrane phase. Although both PP and PVDF membranes are hydrophobic membrane, the extents of hydrophobicity for PP
and PVDF membranes are different. The extent of hydrophobicity can be measured by investigating the water contact angle of membrane surface. The contact angle of PP membrane was usually larger than that of PVDF membrane, it means that PP is more hydrophobic than PVDF membrane, which will lead to less membrane wetting after long term contact of liquid. In addition, the micropore size of PP membrane is smaller than PVDF membrane in this work, as shown in Table 1. Membrane with smaller pore size will be more difficult to suffer membrane wetting based on Young-Laplace equation [14]. Therefore, PP membrane is a better choice than PVDF in the process of membrane stripping.

3.3. Energy evaluation of CO2 membrane stripping process

Membrane stripping process has the potential to reduce the regeneration temperature, but also bring about the additional energy cost, such as vacuum pump and compressor to further compress CO2 stream after membrane stripper. Therefore, in order to evaluate the advantages of membrane stripping technology, we estimated the total energy consumption of 20 wt% MEA in CO2 membrane stripping process based on following assumptions:

1. CO2 lean loading is 0.26 mol CO2/mol MEA;
2. CO2 stream after membrane stripper is further compressed to 2 bar which is usually considered as outlet pressure of typical packing column stripper;
3. Only the latent heat of sweeping steam and work for vacuum pump & compressor are considered, energy for gas stream and vacuum pump cooling are ignored;
4. Compression process is isentropic.

Energy consumption of vacuum pump and compressor

The work required for vacuum pump and compressor is estimated by the following equation [15],

\[ W = \frac{GRTZ\kappa}{(1-\kappa)\eta} \left[ \left( \frac{P_{in}}{P_{out}} \right)^{1/(\kappa-1)/\kappa} - 1 \right] \]  

(3)

In which \( G \) is molar flow rate of feed gas saturated with water vapour; \( Z \) is the number of compression stage, \( \kappa \) is adiabatic constant for feed gas, \( T \) is gas stream temperature after condensation, \( P_{in} \) and \( P_{out} \) are pressures in suction port and exhaust port of vacuum pump or compressor, respectively. \( \eta \) is the efficiency of vacuum pump or compressor.

The latent heat of sweeping steam can be calculated by following equation,

\[ Q_{steam} = q_{vapor} G_{H2O} \]  

(4)

In which \( G_{H2O} \) is the sweeping steam mass flow rate, kg/s; \( q_{vapor} \) is latent heat of vaporization for water, kJ/kg.

Sensible heat of solvent is the heat that elevates the solvent temperature to stripping temperature before going into the membrane stripper, which can be estimated by

\[ Q_{sens} = G_{ab} C_p \Delta t \]  

(5)

\( C_p \) is the specific heat of solvent at constant pressure, kJ/(kg K); \( G_{ab} \) is the mass flow rate of solvent, kg/s, \( \Delta t \) is the temperature difference of lean/rich heat exchanger, which is 10K commonly.

Due to the lower desorption temperature for CO2 membrane stripping than conventional thermal regeneration, therefore, it will be more reasonable to compare energy consumption with thermal regeneration by total equivalent work [16], which is described as

\[ E_{eq} = \left[ \frac{Q_{total} (T_{reb} + 10) - 313}{T_{reb} + 10} + W_{ip} + W_{com} \right] / G_{CO2} \]  

(6)
In which $Q_{\text{total}}$ is the total heat required for CO$_2$ desorption, which includes sensible heat and latent heat, kJ/s; $T_{\text{reb}}$ is regeneration temperature, K; $W_{\text{VP}}$ and $W_{\text{com}}$ are electrical power of vacuum pump and compressor, kJ/s; $G_{\text{CO}_2}$ is the CO$_2$ desorption rate, kg CO$_2$/s.

Fig. 6 is the regeneration energy consumption for 20 wt% MEA at different regeneration pressure in CO$_2$ membrane stripping process. With the decreasing of regeneration pressure, overall equivalent work for CO$_2$ desorption decreases initially before reaching a minimum value, and then increases sharply after this point. The minimum overall equivalent work is 0.78 MJ/kg CO$_2$ as pressure is about 20 kPa. As regeneration pressure is lower than 20 kPa, further decrease on regeneration pressure will result in considerable increase on the energy consumption of vacuum pump and compressor. As regeneration pressure is higher than 20 kPa, more sweeping steam is required to reach CO$_2$ lean loading of 0.26 mol CO$_2$/mol MEA with increasing regeneration pressure.

![Fig. 6 The regeneration energy consumption of 20 wt% MEA solvent in CO$_2$ membrane stripping process (regeneration temperature: 353K, regeneration pressure: 30kPa)](image)

In Fig. 6, the red dash line is the equivalent work required for conventional thermal regeneration of MEA solvent. It has been found that about 28% equivalent work can be saved if CO$_2$ membrane stripping is operated at regeneration pressure of 20 kPa. However, if the regeneration pressure is higher than 50 kPa or lower than 5 kPa, CO$_2$ membrane stripping will lose its advantage on energy consumption. Furthermore, due to the low regeneration temperature of membrane stripping, the energy for generating sweeping steam and sensible heat could be substituted by waste heat. Therefore, if abundant less valuable heat or waste heat were available nearby the power plant, membrane stripping will be a promising technology with lower energy required for CO$_2$ desorption.

4. Conclusions

PP and PVDF commercial hollow fiber membrane modules were used in this study to investigate the CO$_2$ membrane stripping of 20 wt% MEA at 343K. CO$_2$ membrane stripping in PVDF membrane showed a faster CO$_2$ desorption rate than in PP membrane, but PP membrane presented higher regeneration efficiency and a better stability on long-term running, which concluded that PP membrane is a better choice than PVDF in the process of membrane stripping. Energy consumption for CO$_2$ membrane stripping with 20 wt% MEA solvent was also evaluated. With the decreasing of regeneration pressure, overall equivalent work for CO$_2$ membrane stripping decreases initially before reaching a minimum value, and then increases sharply after this point. The optimal operating pressure for CO$_2$ membrane stripping was 20 kPa in this work. Compared with conventional thermal regeneration, 28% of energy consumption can be reduced for CO$_2$ membrane stripping as regeneration pressure operated at 20 kPa.
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References