Hindawi Publishing Corporation
Journal of Chemistry
Volume 2016, Article ID 5729503, 9 pages
http://dx.doi.org/10.1155/2016/5729503

Research Article

Optimization of CO_2 Absorption Characteristic under the Influence of SO_2 in Flue Gas by Hollow Fiber Membrane Contactor

Ziyi Qu,[1,2,3] Li Zhang,[1,2] Yunfei Yan,[1,2] and Shunxiang Ju[1,2]

[1]*Key Laboratory of Low-Grade Energy Utilization Technologies and Systems, Ministry of Education, Chongqing University, Chongqing 400030, China*
[2]*College of Power Engineering, Chongqing University, Chongqing 400030, China*
[3]*Chongqing Electric Power College, Jiulongpo District, Chongqing 400053, China*

Correspondence should be addressed to Li Zhang; lizhang@cqu.edu.cn

Received 9 August 2016; Accepted 6 November 2016

Academic Editor: Naoki Haraguchi

Hollow fiber membrane contactor is a new, highly efficient, and the most promising technology for CO_2 absorption in flue gas. There is still SO_2 that exists in the flue gas after desulfurization tower of power plant. This paper studied the influence of SO_2 on CO_2 absorption characteristic in flue gas by hollow fiber membrane contactor with absorbent of EDA, EDA + MEA (0.6 : 0.4), and EDA + MEA + PZ (0.4 : 0.4 : 0.2). The influences of SO_2 concentration, cycle absorption and desorption characteristic of absorbent, absorbent concentration, and liquid-gas flow rate ratio are studied to analyze the influence of SO_2 on CO_2 absorption characteristic. The appropriate absorbent composition ratio and appropriate parameter range that can inhibit the influence of SO_2 are proposed by studying the hybrid sorbent with activating agent, appropriate absorbent concentration, and ratio of liquid-gas flow rate. Among the three kinds of absorbents, EDA + MEA + PZ (0.4 : 0.4 : 0.2) had the best tolerance ability to SO_2 and the highest efficiency. With comprehensive consideration of CO_2 removal efficiency and operating cost, under the condition of 1000 ppm SO_2, the appropriate concentration and liquid-gas flow rate ratio of EDA, EDA + MEA, and EDA + MEA + PZ are proposed.

1. Introduction

In recent years, energy consumption has been increasing with the rapid growth of the world economy. The greenhouse effect of CO_2 became increasingly serious, and hence energy conservation is urgent [1]. The hollow fiber membrane contactor is a new technology for the CO_2 absorption process [2]. The membrane does not participate in the reaction, which isolates gas and liquid. In a hollow fiber membrane contactor, the absorbent flows in one side while the flue gas flows in the other side. The flue gas diffuses through the gas-liquid interface initially, and then CO_2 reacts with the absorbent. Because of the CO_2 concentration gradient in the gas and liquid phases, CO_2 transfers from the gas phase to liquid phases through the membrane pores and continues to react with the absorbent. Because of the high reaction rate, simple operation, small volume membrane absorption technology, and low cost, the hollow fiber membrane contactor is one of the most promising decarburization technologies.

The alcohol amine absorbent used in CO_2 absorption has been used in SO_2 removal by many researchers [3–8]. The hollow fiber membrane contactor is not only applied for CO_2 removal, but also applied to remove SO_2. Ogundiran et al. [9] studied SO_2 capture in flue gas by porous hydrophobic hollow fibers and found that it was a more promising technology than conventional scrubbers used in desulfurization. Park et al. [10] studied the effects of operation parameters on SO_2 removal by PVDF hollow fiber membranes and found that it is one of the most competitive alternatives in the future. There is still SO_2 that exists in the flue gas after desulfurization tower. The influence of SO_2 on CO_2 capture gained more attention recently. Zhong [11] studied the effect

of SO_2 concentration on MEA, MEA/MDEA, MEDA/PZ, and DEA/AMP. The tolerance of SO_2 was found to be as follows: MEA > DEA/AMP > MEDA/PZ > MEA/MDEA. Uyanga and Idem [12] studied the degradation of MEA caused by SO_2 in a semibatch reactor. The results show that SO_2 accelerates the rate of MEA degradation and established a dynamic model. Supap et al. [13] studied the kinetics of SO^{2-} and O^{2-} induced degradation of aqueous MEA during CO_2 capture. The results show that an increase in temperature and concentration of MEA, O_2, and SO_2 causes a higher degradation rate of MEA. Gao et al. [14] studied the effect of SO_2 on the CO_2 capture process in a pilot plant. The results show that SO_2 causes amine oxidative degradation, which is beneficial to remove SO_2 induced heat stable salts using appropriate methods. Bonenfant et al. [15] studied the absorption of CO_2 and SO_2 mixtures with the absorbent of aqueous 2-(2-aminoethylamino)ethanol (AEE) solution and its blends with N-methyldiethanolamine (MDEA) and triethanolamine (TEA) to estimate the influence of SO_2. The results show that SO_2 decreases the CO_2 absorption rate. The addition of 5 and 10 wt.% of MDEA and TEA does not influence the CO_2 absorption rate in AEE. TEA decreases the absorption capacity of AEE. Yang et al. [16] studied the influence of SO_2 on the CO_2 capture in an absorption-desorption experimental setup using MEA as the absorbent. The results show that there were sharp decreases in CO_2 removal efficiency and mass transfer rate of CO_2 after the initial several days of operation; more progress is needed in high-efficiency and stable absorbents.

According to the present research situation, SO_2 causes the degradation of alcohol amine absorbent, resulting in the decrease of CO_2 removal efficiency. The influence of SO_2 on CO_2 absorption by alcohol amine absorbent deserves attention. It is necessary to research the optimization of CO_2 absorption characteristic under the influence of SO_2. Research on appropriate absorbent and parameter range which can inhibit the influence of SO_2 is needed. MEA, MDEA, DEA, and other amine solutions [11–16] are selected as absorbent of CO_2 capture by many researchers. The disadvantage of MEA is the high energy consumption in the CO_2 desorption. The tolerance ability to SO_2 of MEA is better than that of MDEA [11]. Studies on EDA as an absorbent used in CO_2 capture are relatively fewer. In the study of Shunxiang [18], the performance of the absorbents used in CO_2 absorption is as follows: PZ > EDA > MEA > DEA. Considering that CO_2 removal efficiency of EDA is higher than of MEA, the tolerance ability to SO_2 of MEA is high and the activation ability of PZ is good, and EDA, EDA + MEA, and EDA + MEA + PZ are selected as absorbents of CO_2 capture in this paper. This paper researches the performance of these absorbents under the influence of SO_2 in order to study the appropriate absorbent composition ratio and specific operating parameters to optimize CO_2 absorption under the influence of SO_2. The results of this study are an important reference for the industrial application of CO_2 absorption by hollow fiber membrane contactor.

2. Materials and Methods

2.1. Reaction Mechanism. SO_2 diffuses from gas phase to gas-liquid interface firstly and then diffuses from gas-liquid interface to liquid phase and dissolves in liquid. The reaction between SO_2 and amine solution can be assumed as a combination of the physical dissolution of SO_2 in water and the chemical absorption of amine solution. SO_2 in water generates SO_3^{2-} firstly [11, 19]:

$$SO_2 + H_2O \longleftrightarrow H^+ + HSO_3^- \quad (1)$$

$$HSO_3^- \longleftrightarrow H^+ + SO_3^{2-} \quad (2)$$

The solubility of SO_2 increased by the addition of amine solution, and the amine reacted with the hydrogen ion from the water and formed a compound of strong heat stability:

$$RR'NH + SO_2 + H_2O \longleftrightarrow RR'NH_2^+ + HSO_3^- \quad (3)$$

$$\text{With oxygen: } 2HSO_3^- + O_2 = 2HSO_4^- \quad (4)$$

The compound generated in formula (3) is stable and cannot be regenerated by heating, which results in degradation and depletion of the amine solution. In addition to this, it will cause solution foaming and decrease CO_2 removal efficiency in the system in the long run.

For MEA, the reaction between CO_2 and MEA is as follows [20–22]:

$$CO_2 + 2RNH_2 \longrightarrow RNH^+CO_2^- + RNH_3^+ \quad (5)$$

The reaction between SO_2 and MEA is as follows [19]:

$$SO_2 + 2RNH_2 + H_2O \longrightarrow 2RNH_3^+ + SO_3^{2-} \quad (6)$$

where R is $HOCH_2CH_2$.

2.2. Materials. The solutions of EDA (ethylenediamine), EDA + MEA (monoethanolamine), and EDA + MEA + PZ (piperazine) are selected as absorbents for CO_2 absorption in this experiment. The concentration of absorbent is 500 mol/m^3, and the mole ratio of the component in hybrid absorbent is EDA : MEA = 0.6 : 0.4 and EDA : MEA : PZ = 0.4 : 0.4 : 0.2.

The pp (polypropylene) hollow fiber membrane contactor of KH-MF-4040N-PP is produced by Hangzhou Kaihong Membrane Technology Co., Ltd., and the specification and parameters are shown in Table 1. The membrane is designed by internal pressure and stretch forming. The inlet and outlet of the gas and liquid are arranged on the side and the end, respectively. The maximum pressure designed is 0.3 MPa, applicable to the pH of 1~14, at 15~40°C.

2.3. Experimental Procedures. The system is shown in Figure 1. The flue gas is simulated by mixed gas of CO_2, SO_2, and N_2. The flue gas is introduced into fiber membrane contactor from compressed gas cylinders. The absorbent is introduced into the contactor by a pump. The gas flows in the tube side and the absorbent flows in the shell side. There are regulating valves at the outlet of the simulative flue gas

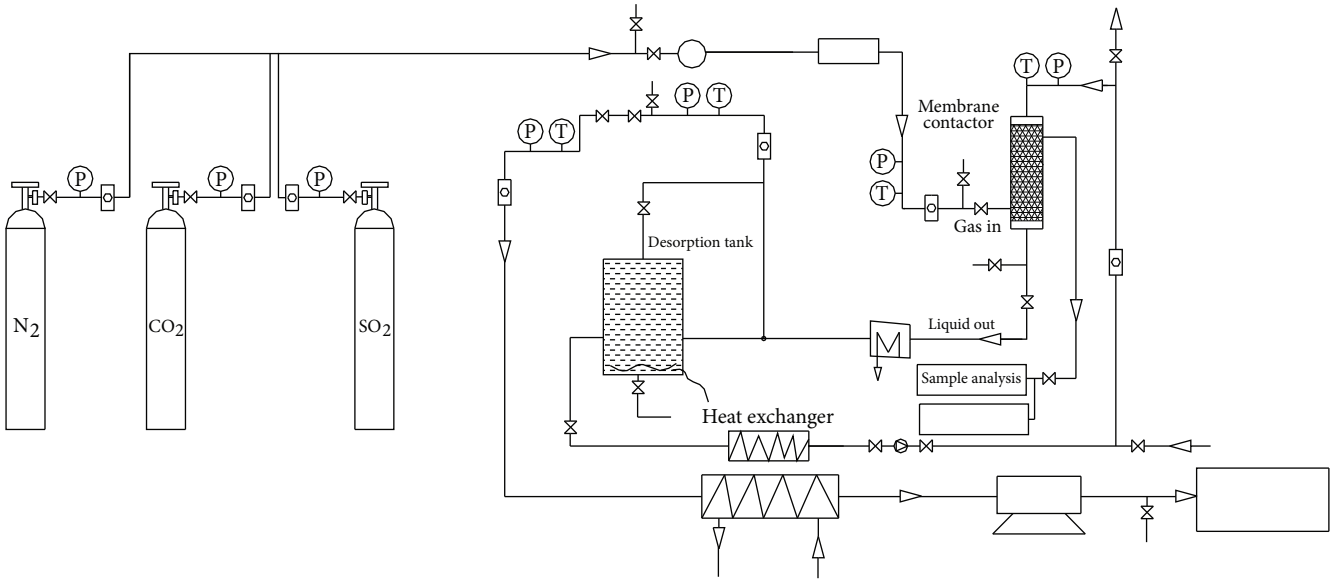

Figure 1: Flow chart of the experiment using the flue gas.

Table 1: Specifications and parameters of PP hollow fiber membrane contactor.

Physical	Unit	Value	Parameter
Liquid flux	L/h	800–1000	U
Outer diameter of module	mm	94	D_{out}
Inner diameter of module	mm	90	D_{in}
Module length	mm	1125	L_m
Fiber length	mm	920	L
Membrane pore diameter	μm	0.1–0.2	d_p
Inner diameter of fiber	mm	0.3	d_{in}
Outer diameter of fiber	mm	0.4	d_{out}
Module area	m^2	8~12	S
Number of fibers		7000	n
Tortuosity factor		2	τ
Fiber porosity	%	45	ε
Packing density	%	13.8	(1-Φ)

and absorbent pump which can control the flow rate of gas and absorbent. The absorbent reacts with CO_2 and becomes a rich liquid and is then introduced into the absorbent tank by a pump. The desorption tank desorbs CO_2 by heating the rich liquid. This is one cycle of absorption and desorption. The desorption tank is designed by electric heating. There are sample portions to analyze the gas component by a gas analyzer (ECOM-J2KN, German RBR Company) and gas chromatograph (GC7900, Shanghai Tianmei Scientific Instruments Co., Ltd.). Values are obtained when the reaction is stable for 5 min, and then an average value of three times is obtained, each time interval of 30 s.

The experimental conditions and parameters are shown in Table 2. Gas flow rate is 4 m^3/h, and absorbent flow rate is 0.7 m^3/h. Volume fraction of CO_2 in gas is 14 vol.%.

Table 2: Parameters of operating conditions.

Parameter	Unit	Physical	Value
T_g	K	Gas temperature	288
T_l	K	Absorbent temperature	288
U_g	m^3/h	Gas flow rate	4
U_l	m^3/h	Absorbent flow rate	0.7
C	mol/m^3	Absorbent concentration	500
φ_{CO_2}	vol.%	Volume fraction of CO_2 in gas	14
P	MP	Operating pressure	0.1

3. Results and Discussion

The CO_2 removal efficiency is the parameter that reflects the CO_2 removal performance; it can be calculated by [23]

$$\eta = \frac{Q_{in} \times \varphi_{in} - Q_{out} \times \varphi_{out}}{Q_{in} \times \varphi_{in}} \times 100, \quad (7)$$

where η is the CO_2 removal efficiency, Q_{in} is the gas flow rate of inlet, Q_{out} is the gas flow rate of outlet, and φ_{in} and φ_{out} are the volume fraction of CO_2 at inlet and outlet, respectively.

The mass transfer rate reflects the performance of mass transfer. It can be calculated by [23]

$$J_{CO_2} = \frac{(Q_{in} \times \varphi_{in} - Q_{out} \times \varphi_{out}) \times 273.15 \times 1000}{22.4 \times T_g \times S}, \quad (8)$$

where J_{CO_2} is the mass transfer rate, T_g is gas temperature, and S is the total area of the membrane.

3.1. Influence of SO_2 Concentration on CO_2 Absorption. In order to emphasize the influence of SO_2 concentration, the concentration of SO_2 is amplified from 500 ppm to 2000 ppm in this research. The influences of SO_2 concentration on CO_2

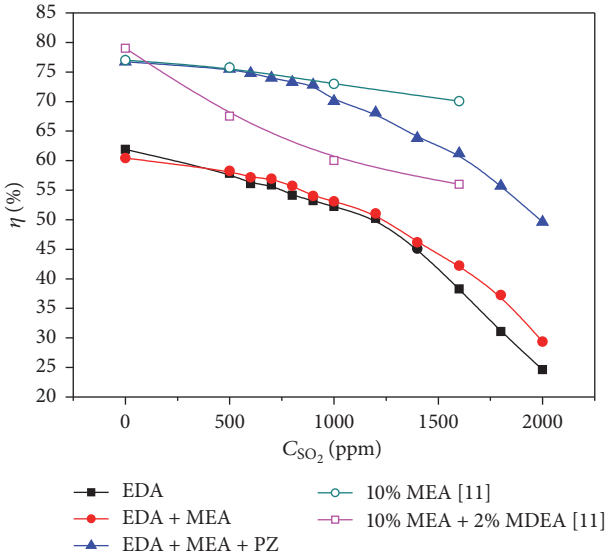

Figure 2: Influence of SO_2 concentration on the CO_2 removal efficiency (U_g = 4 m^3/h, U_l = 0.7 m^3/h, and T = 288 K).

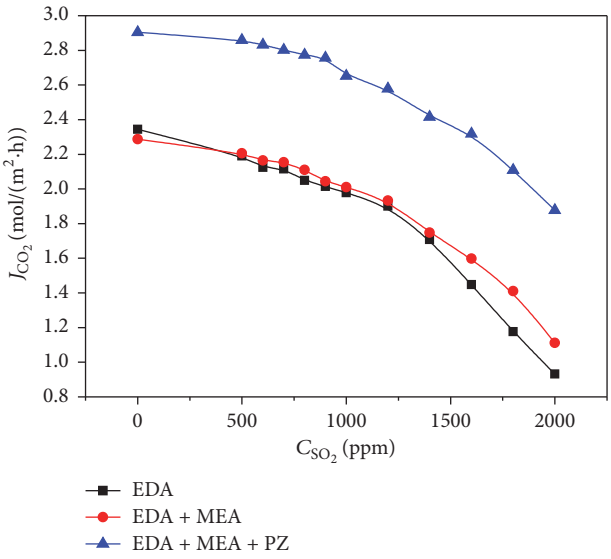

Figure 3: Influence of SO_2concentration on the CO_2mass transfer rate (U_g = 4 m^3/h, U_l = 0.7 m^3/h, and T = 288 K).

removal efficiency and mass transfer rate are shown in Figures 2 and 3. The CO_2 removal efficiency and mass transfer rate of the three absorbents decrease with the increasing of SO_2 concentration. The solubility of SO_2 is much higher than of CO_2. The pH value of SO_2 aqueous solution is smaller than the pH value of CO_2 equilibrium solution. The reaction between SO_2 and amine absorbent can be considered as instantaneous [11]. The reaction rates and opportunities for SO_2 and absorbent are much higher than those of CO_2 and absorbent, which leads to the decrease of CO_2 removal efficiency.

The CO_2 removal efficiency of three absorbents decreased suddenly after 1000 ppm SO_2. The effective components keep constant when the absorbent concentration is fixed. When SO_2 concentration increased to a certain value, the effective components of absorbent are consumed largely by SO_2, which leads to the sudden decrease of CO_2 removal efficiency. The CO_2 removal efficiency of EDA decreases by 4.05% with 500 ppm SO_2 and decreases by 37.3% with 2000 ppm SO_2. It can be considered that the influence of SO_2 on CO_2 removal efficiency with EDA is not significant when the SO_2 concentration is under 500 ppm. Because of the low concentration of SO_2, even with the faster reaction rate of SO_2, there is still a chance for CO_2 to react with the absorbent. The concentration gradient of the gas and the liquid vapor interface increases with increasing SO_2 concentration, which improves the mass transfer dynamics. This is favorable for SO_2 molecules to diffuse to the surface and the interior of the absorption solution and speed up the reaction of SO_2 with EDA. Therefore, the absorption of CO_2 reduced greatly with the increasing of SO_2 concentration. The influence of SO_2 on CO_2 removal efficiency is more significant with the increase of SO_2 concentration. The SO_2 concentration in the outlet of flue gas is always zero, which indicates that SO_2 is absorbed by the absorbent completely, and the reaction rate of SO_2 and the absorbent is significantly higher than that of CO_2 and the absorbent.

The CO_2 removal efficiency of EDA + MEA decreases by 2.1% with 500 ppm SO_2, the efficiency is 53.1% with 1000 ppm SO_2, and the efficiency decreases to 29.3% with 2000 ppm SO_2. Comparing the results of EDA + MEA (0.6 : 0.4) and EDA, the CO_2 removal efficiency and mass transfer rate of EDA are higher than those of EDA + MEA without the addition of SO_2. With the increasing of SO_2 concentration, the CO_2 removal efficiency and mass transfer rate of EDA + MEA (0.6 : 0.4) are higher than those of EDA. The CO_2 absorption capacity of EDA is better than that of MEA [18]; therefore, the CO_2 removal efficiency and mass transfer rate of EDA are higher than those of EDA + MEA (0.6 : 0.4) without the influence of SO_2. The active ingredient increases after the addition of MEA, which promotes the tolerance ability of the absorbent to SO_2. The CO_2 removal efficiency and mass transfer rate reduction of EDA + MEA (0.6 : 0.4) are smaller than those of EDA; therefore, the tolerance ability of EDA + MEA (0.6 : 0.4) to SO_2 is better than that of EDA.

Zhong [11] researched the influence of SO_2 concentration on CO_2 absorption with the absorbent of 10% MEA and 10% MEA + 2% MDEA (liquid flow rate 18 L/h, temperature 40°C; flue gas flow rate 1800 L/h, temperature 15°C; SO_2 concentration is 500–1500 ppm). The results are shown in Figure 2. The results indicate that the CO_2 removal efficiency decreases with the increase of SO_2 concentration, and the influence of SO_2 is not significant till the SO_2 concentration becomes greater than 500 ppm, which agrees well with the results in this paper. The CO_2 removal efficiency of 10% MEA + 2% MDEA is higher than that of 10% MEA when SO_2 concentration is under 117 ppm, and the decrease extent of CO_2 removal efficiency in 10% MEA + 2% MDEA is more than that in 10% MEA with the increase of SO_2 concentration. The CO_2 removal efficiency of 10% MEA is higher than that of 10% MEA + 2% MDEA with 200 ppm SO_2. This indicates that the reaction between 10% MEA + 2% MDEA and SO_2

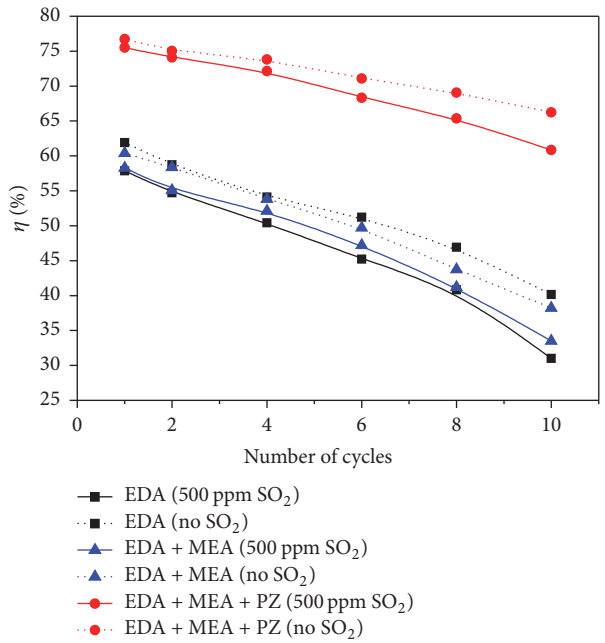

Figure 4: Influence of cycle absorption and desorption on the CO_2 removal efficiency (U_g = 4 m^3/h, U_l = 0.7 m^3/h, and T = 288 K).

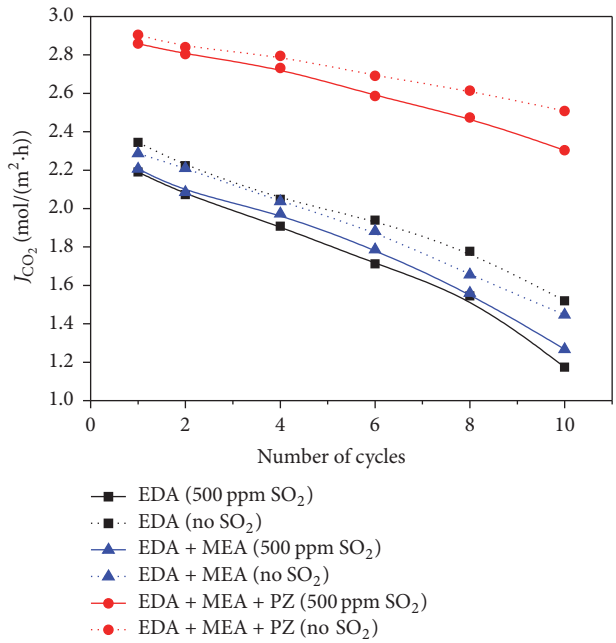

Figure 5: Influence of cycle absorption and desorption on the CO_2 mass transfer rate (U_g = 4 m^3/h, U_l = 0.7 m^3/h, and T = 288 K).

is more rapid and intense, so the decrease extent of CO_2 removal efficiency with the absorbent of 10% MEA + 2% MDEA is more significant than of 10% MEA. Because of the poor absorptive capacity and slow absorption rate of MDEA, MDEA is not suitable for CO_2 absorption with the influence of SO_2. The tolerance ability of 10% MEA + 2% MDEA to SO_2 is lower than that of 10% MEA.

Comparing the results of EDA and 10% MEA, the CO_2 removal efficiency of 10% MEA is higher than of EDA without SO_2, and the decrease extent is smaller than EDA with the increase of SO_2 concentration. So, the tolerance ability to SO_2 of 10% MEA is greater than 500 mol/m^3 EDA. After adding of MEA, the CO_2 removal efficiency of EDA + MEA (0.6 : 0.4) is higher than of EDA with the increase of SO_2 concentration. So, the hybrid absorbent of EDA + MEA (0.6 : 0.4) is appropriate for removal of CO_2 in the flue gas containing SO_2.

The absorbent of EDA + MEA + PZ is the most efficient in the three absorbents. The CO_2 removal efficiency of EDA + MEA + PZ decreases by 1.2% with 500 ppm SO_2, decreases by 3.4% with 800 ppm SO_2, and decreases by 27.1% with 2000 ppm SO_2. The CO_2 removal efficiency reduction of EDA + MEA + PZ is not significant until 1000 ppm SO_2. Because of the activity of PZ, the influence of SO_2 on CO_2 absorption with EDA + MEA + PZ is not significant under the condition of low SO_2 concentration in a short time. And the tolerance ability of EDA + MEA + PZ to SO_2 is greater than that of EDA and EDA + MEA. The influence of SO_2 is getting more significant when the PZ active effect is gradually consumed. Therefore, the CO_2 removal efficiency decreases significantly with 2000 ppm SO_2.

The results of the three absorbents indicate that the influence of SO_2 on CO_2 is not significant with low SO_2 concentration in the short run performance; the hybrid absorbent with high absorptive capacity component and high tolerance ability to SO_2 can inhibit the influence of SO_2 on CO_2 absorption effectively.

3.2. Cycle Absorption and Desorption Characteristic of Absorbent. According to the previous research, the influence of SO_2 on CO_2 absorption is not significant in the low concentration of SO_2. The absorption experiment is conducted in a short time, and the cycle absorption and desorption of the absorbent are not considered. It is necessary to study the cycle absorption and desorption of the absorbent. Based on the influence of SO_2 concentration on CO_2 removal efficiency, the influence is not significant when the SO_2 concentration is below 500 ppm of the three absorbents. In order to study the influence of SO_2 on CO_2 absorption in low SO_2 concentration, the SO_2 concentration of 500 ppm is selected in this experiment.

The results are shown in Figures 4 and 5. The absorbent from absorption to desorption is one cycle. The CO_2 removal efficiency and mass transfer rate decrease with the increase of cycle number. The CO_2 removal efficiency of EDA decreases by 26.85% with SO_2 and decreases by 21.8% without SO_2; the CO_2 removal efficiency of EDA + MEA decreases by 24.7% with SO_2 and decreases by 22.1% without SO_2; the CO_2 removal efficiency of EDA + MEA + PZ decreases by 14.6% with the influence of SO_2.

Desorption of the absorbent by heating the rich liquid results in absorbent degradation. SO_2 reacts with the absorbent and generates stable salts, which cannot be regenerated by heating. The existence of SO_2 accelerates the degradation of most amine solutions. Strazisar et al. [24] studied the effect of SO_2 on the degradation of MEA. The

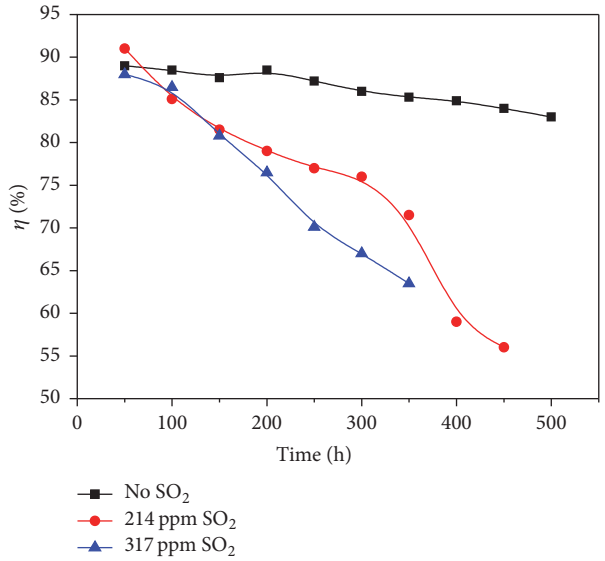

FIGURE 6: The influence of circulating time on the CO_2 removal efficiency [17] (U_g = 86 Nm^3/h, U_l = 0.6 m^3/h, and T = 319 K).

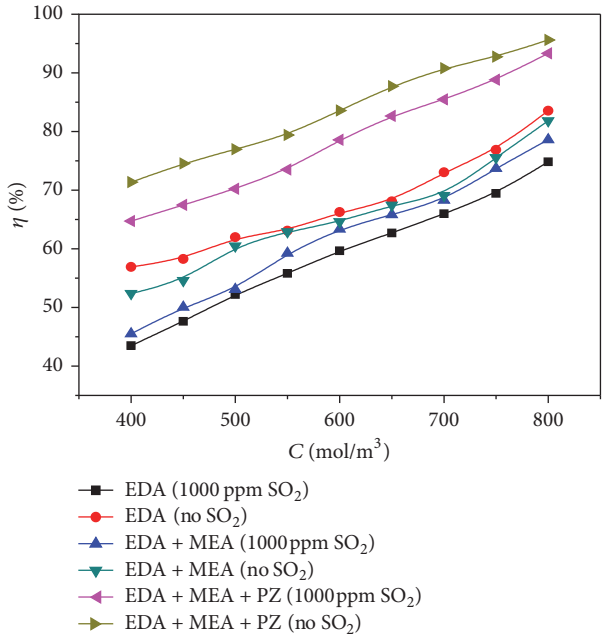

FIGURE 7: Influence of SO_2 on the CO_2 removal efficiency in different concentrations of absorbent (U_g = 4 m^3/h, U_l = 0.7 m^3/h, and T = 288 K).

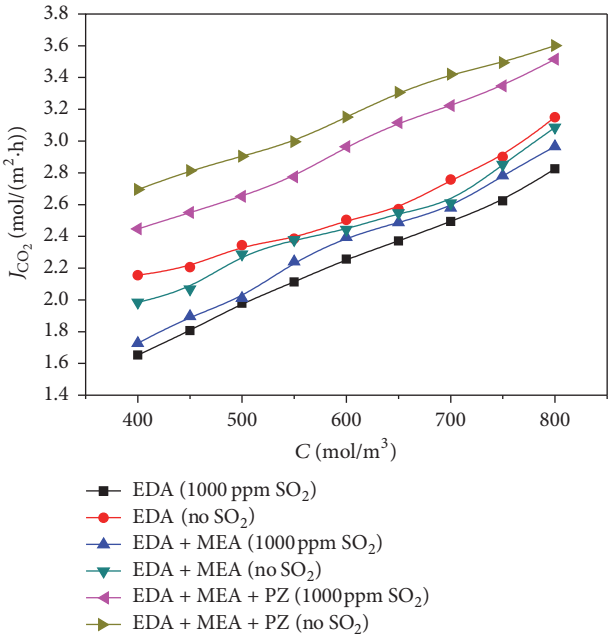

FIGURE 8: Influence of SO_2 on the CO_2 mass transfer rate in different concentrations of absorbent (U_g = 4 m^3/h, U_l = 0.7 m^3/h, and T = 288 K).

results show that SO_2 accelerates the degradation rate of MEA, which is significant in higher concentration of SO_2. Therefore, the CO_2 removal efficiency and mass transfer rate decrease significantly with the increasing cycle of absorption and desorption.

Gao et al. [17] studied the influence of SO_2 on the absorption character of absorbent in the following campaign: no SO_2, 214 ppm SO_2, and 317 ppm SO_2, respectively. The result is shown in Figure 6. The CO_2 removal efficiency decreases gradually with increasing circulating time. And the decrease extent of CO_2 removal efficiency increases with SO_2 concentration. The absorbent degradation and heat stable salts formation are the main reasons for the significant influence of SO_2. The trend of Figure 4 in this experiment agreed with the trend of Figure 6.

The study in this section indicated that there is a significant influence of SO_2 on CO_2 absorption even in low SO_2 concentration in the long run performance. The order of tolerance ability to SO_2 is EDA + MEA + PZ (0.4 : 0.4 : 0.2) > EDA + MEA (0.6 : 0.4) > EDA. The CO_2 removal efficiency of EDA + MEA + PZ (0.4 : 0.4 : 0.2) decreased to 60% after ten absorption and desorption cycles. Therefore, it is necessary to study the appropriate parameter range in the operation to inhibit the influence of SO_2.

3.3. The Influence of Absorbent Concentration on CO_2 Absorption. The concentration of absorbent is one of the most important parameters of CO_2 absorption in operation. The influence of absorbent concentration on CO_2 removal efficiency is studied in this section for confirming the appropriate concentration of the absorbent which can inhibit the influence of SO_2.

The CO_2 removal efficiency of the three absorbents decreased suddenly after 1000 ppm SO_2 in the study of influence of SO_2 concentration. Therefore, the experiment is conducted under the condition of 1000 ppm SO_2. The concentration of the absorbent is from 400 mol/m^3 to 800 mol/m^3. The CO_2 removal efficiency and mass transfer rate increase with the increasing absorbent concentration which is shown in Figures 7 and 8. Comparing the result of 1000 ppm SO_2 with that of no SO_2, the CO_2

removal efficiency of 400 mol/m^3 EDA, 600 mol/m^3 EDA, and 650 mol/m^3 EDA decreases by 13.27%, 6.5%, and 5.3%, respectively. The decreasing extent of CO_2 removal efficiency and mass transfer rate of absorbent reduce with the increasing absorbent concentration.

A certain amount of absorbent is needed when the concentration of SO_2 keeps constant in flue gas. There are more active ingredients in the absorbent to improve the CO_2 absorption with the increase of absorbent concentration. Therefore, increasing absorbent concentration can inhibit the influence of SO_2 on CO_2 absorption. The cost and the energy consumption increase with the increasing absorbent concentration. Hence, there is an appropriate concentration of absorbent which can inhibit the influence of SO_2 on CO_2 absorption with low cost and low energy consumption. The CO_2 removal efficiency of 800 mol/m^3 EDA, 750 mol/m^3 EDA + MEA, and 650 mol/m^3 EDA + MEA + PZ is 75%, 74%, and 83%, respectively, with 1000 ppm SO_2. Continuing to increase the absorbent concentration, the increment of CO_2 removal efficiency will reduce because the absorbent viscosity and the mass transfer resistance increase with the increasing absorbent concentration. Furthermore, continuing to increase the absorbent concentration will increase investment and operating costs. Considering the above factors, under the condition of 1000 ppm SO_2, the appropriate concentrations of EDA, EDA + MEA, and EDA + MEA + PZ are 800 mol/m^3, 750 mol/m^3, and 650 mol/m^3, respectively.

3.4. Influence of the Liquid-Gas Flow Rate Ratio on CO_2 Absorption. The flow rates of absorbent and gas are important parameters which can affect the CO_2 absorption significantly. It is necessary to study the appropriate ratio of liquid-gas flow rate for inhibiting the influence of SO_2.

With the increasing ratio of liquid-gas flow rate under the condition of 1000 ppm SO_2, the CO_2 absorption characteristic of EDA, EDA + MEA, and EDA + MEA + PZ is shown in Figures 9 and 10. The CO_2 removal efficiency and mass transfer rate rise with the increasing ratio of liquid-gas flow rate. With the addition of SO_2, the CO_2 removal efficiency of EDA decreases by 7.9%, 6.28%, and 5.26%, respectively, when the ratio of liquid-gas flow rate is 0.1, 0.15, and 0.25 individually. The CO_2 removal efficiency difference between the case with SO_2 and that without SO_2 decreases with the increasing ratio of liquid-gas flow rate. The experimental results of EDA + MEA and EDA + MEA + PZ are similar to that of EDA. Therefore, the influence of SO_2 on CO_2 absorption decreases with the increasing ratio of liquid-gas flow rate. Lv et al. [25] studied the simultaneous removal of CO_2 and SO_2 in a polypropylene hollow fiber membrane contactor using MEA. The CO_2 removal efficiency of MEA with 1600 ppm increased with the liquid flow rate. The experimental result in this section of this paper agrees with the result of Lv et al.

With a certain concentration of SO_2, the reaction of absorbent with CO_2 increases gradually with the increasing ratio of liquid-gas flow rate. The mass transfer rate increases with the ratio of liquid-gas flow rate under a certain gas condition. Because of the increment of concentration gradients,

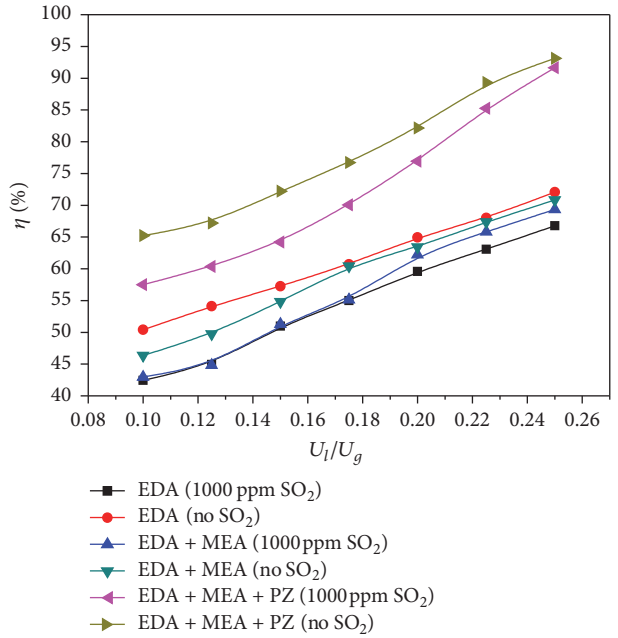

Figure 9: Influence of SO_2 on the CO_2 mass transfer rate in different liquid-gas flow rate ratios (T = 288 K).

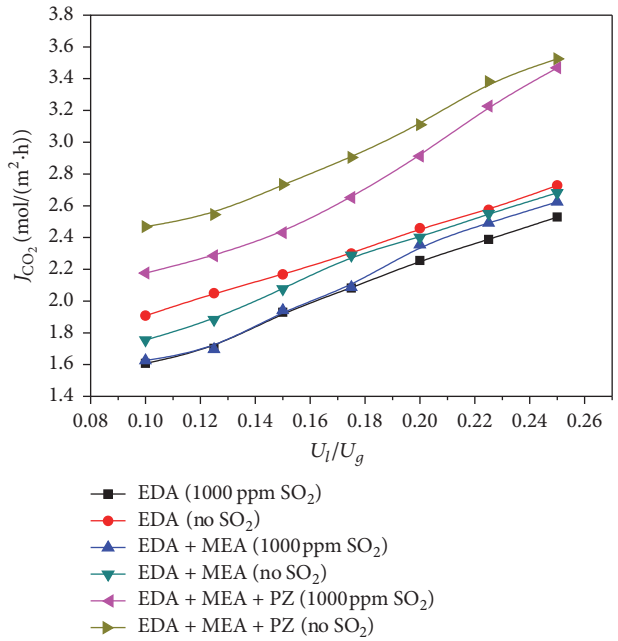

Figure 10: Influence of SO_2 on the CO_2 mass transfer rate in different liquid-gas flow rate ratios (T = 288 K).

the mass transfer and the reaction of absorbent and CO_2 are improved. The increase of absorbent flow rate accelerates the membrane wetting and wear, which result in a mass transfer resistance increase. Therefore, the increments of CO_2 removal efficiency and mass transfer rate reduce with the increasing ratio of liquid-gas flow rate. Meanwhile, the consumption of absorbent and pump increases with the increasing liquid-gas flow rate ratio, which raises the operation cost. In the

liquid-gas flow rate ratio of 0.2–0.25, the lowest CO_2 removal efficiencies of EDA, EDA + MEA, and EDA + MEA + PZ are 60%, 63%, and 77%, respectively; the highest CO_2 removal efficiencies of EDA, EDA + MEA, and EDA + MEA + PZ are 67%, 70%, and 92%, respectively. In order to inhibit the influence of SO_2 on CO_2 absorption and maintain high CO_2 removal efficiency and low operating cost, under the condition of 1000 ppm SO_2, the appropriate liquid-gas flow rate ratio of EDA, EDA + MEA, and EDA + MEA + PZ is from 0.2 to 0.25.

4. Conclusions

There is a significant influence of SO_2 on CO_2 absorption in the long run performance, which affects the industrial application prospects of this technology. It is necessary to study the SO_2 influence characteristic on CO_2 absorption and the measure to optimize the CO_2 absorption under the influence of SO_2.

This paper studied the optimization of CO_2 absorption characteristic under the influence of SO_2 with the absorbent of EDA, EDA + MEA, and EDA + MEA + PZ by hollow fiber membrane contactor. The SO_2 concentration, cycle absorption and desorption characteristic of absorbent, absorbent concentration, and ratio of liquid-gas flow rate are analyzed to evaluate the influence of SO_2 on CO_2 absorption characteristic. The reaction rate and absorption performance of SO_2 with amine solution are much greater than those of CO_2 with amine solution, resulting in decreases of CO_2 removal efficiency and mass transfer rate in different extent with the absorbent of EDA, EDA + MEA, and EDA + MEA + PZ. The CO_2 removal efficiency and mass transfer rate decrease with the increasing SO_2 concentration and absorption and desorption cycle of absorbent.

This paper proposes appropriate absorbent composition ratio and operation parameters range which can inhibit the influence of SO_2 on CO_2 absorption and optimize the CO_2 absorption under the influence of SO_2. Depending on the results in this research, hybrid absorbent with activator agent, appropriate absorbent concentration, and ratio of liquid-gas flow rate can inhibit the influence of SO_2 on CO_2 absorption effectively. EDA + MEA + PZ (0.4 : 0.4 : 0.2) has the best tolerance ability to SO_2 among the three absorbents. Under the condition of 1000 ppm SO_2 in flue gas, the appropriate absorbent concentrations of EDA, EDA + MEA, and EDA + MEA + PZ are 800 mol/m^3, 750 mol/m^3, and 650 mol/m^3, respectively, and the appropriate ratio of liquid-gas flow rate is in the range from 0.2 to 0.25.

Nomenclature

C: Concentration (mol·m^{-3})
d: Average pore diameter (μm)
J_{CO_2}: CO_2 mass transfer rate (mol·m^{-2}·h^{-1})
L: Length (m)
n: Number of fibers
S: Contact area of fiber (m^2)
t: Time (s)
T: Temperature (K)
U: Velocity (m^3·h^{-1})
V: Instantaneous velocity of gas at a point of module (m·s^{-1}).

Greek Letters

η: CO_2 removal efficiency (%)
ε: Porosity of fiber membrane (%)
φ: Volume fraction of CO_2 in gas (vol.%)
τ: Tortuosity factor of fiber membrane
(1-Φ): Packing density of fiber membrane.

Subscripts

g: Gas
l: Liquid
in: Inlet
out: Outlet.

Abbreviations

EDA: Ethylenediamine
PZ: Piperazine
MEA: Monoethanol
PP: Polypropylene.

Competing Interests

The authors declare no competing interests regarding the publication of this paper.

Acknowledgments

This research is supported by the Science and Technology Project of Chongqing Municipal Education Commission (KJ1502503) and the Fundamental Research Funds for the Central Universities (no. CDJZR14145501).

References

[1] J. G. J. Olivier, G. Janssens-Maenhout, M. Muntean, and J. A. H. W. Peters, *Trends in Global CO_2 Emissions: 2014 Report*, PBL Netherlands Environmental Assessment Agency, The Hague, The Netherlands, 2014.

[2] V. Y. Dindore, *Gas Purification Using Membrane Gas Absorption Processes*, University of Twente, 2003.

[3] H.-K. Lee, H.-D. Jo, W.-K. Choi, H.-H. Park, C.-W. Lim, and Y.-T. Lee, "Absorption of SO_2 in hollow fiber membrane contactors using various aqueous absorbents," *Desalination*, vol. 200, no. 1–3, pp. 604–605, 2006.

[4] R. Faiz and M. Al-Marzouqi, "Mathematical modeling for the simultaneous absorption of CO_2 and H_2S using MEA in hollow fiber membrane contactors," *Journal of Membrane Science*, vol. 342, no. 1-2, pp. 269–278, 2009.

[5] W. Wammers, "A flexible process for acid gas removal from natural gas," in *73rdGPA Annu Groc Gas Process Handbook*, vol. 75, no. 4, p. 105, 1996.

[6] P. Luis, A. Garea, and A. Irabien, "Zero solvent emission process for sulfur dioxide recovery using a membrane contactor and ionic liquids," *Journal of Membrane Science*, vol. 330, no. 1-2, pp. 80–89, 2009.

[7] P. Luis, A. Garea, and A. Irabien, "Environmental and economic evaluation of SO_2 recovery in a ceramic hollow fibre membrane contactor," *Chemical Engineering and Processing: Process Intensification*, vol. 52, pp. 151–154, 2012.

[8] U. Carbide, "New Cansolv technology from Union Carbide uses thermally regenerable organic amine salt to remove sulfur dioxide from flue gas," *Chemical & Engineering News*, vol. 69, no. 46, p. 7, 1991.

[9] O. S. Ogundiran, S. Varanasi, and S. E. LeBlanc, "A novel gas desulfurization process using hollow fiber membranes," in *Proceedings of the Air Pollution Control Association Annual Meeting*, Cleveland, Ohio, USA, 1998.

[10] H. H. Park, B. R. Deshwal, I. W. Kim, and H. K. Lee, "Absorption of SO_2 from flue gas using PVDF hollow fiber membranes in a gas–liquid contactor," *Journal of Membrane Science*, vol. 319, no. 1-2, pp. 29–37, 2008.

[11] W. Zhong, *Study on CO_2 Chemical Absorption Technology*, ZheJiang University, 2008.

[12] I. J. Uyanga and R. O. Idem, "Studies of SO_2- and O_2-induced degradation of aqueous MEA during CO_2 capture from power plant flue gas streams," *Industrial and Engineering Chemistry Research*, vol. 46, no. 8, pp. 2558–2566, 2007.

[13] T. Supap, R. Idem, P. Tontiwachwuthikul, and C. Saiwan, "Kinetics of sulfur dioxide- and oxygen-induced degradation of aqueous monoethanolamine solution during CO_2 absorption from power plant flue gas streams," *International Journal of Greenhouse Gas Control*, vol. 3, no. 2, pp. 133–142, 2009.

[14] J. Gao, S. Wang, S. Zhou, B. Zhao, C. Chen, and X. Xu, "Experimental study on the influence of SO_2 on the CO_2 capture process," *Proceedings of The Chinese Society of Electrical Engineering*, vol. 31, no. 5, pp. 52–57, 2011.

[15] D. Bonenfant, M. Mimeault, and R. Hausler, "Estimation of the CO_2 absorption capacities in aqueous 2-(2-aminoethylamino)ethanol and its blends with MDEA and TEA in the presence of SO_2," *Industrial & Engineering Chemistry Research*, vol. 46, no. 26, pp. 8968–8971, 2007.

[16] J. Yang, X. Yu, J. Yan, S.-T. Tu, and E. Dahlquist, "Effects of SO_2 on CO_2 capture using a hollow fiber membrane contactor," *Applied Energy*, vol. 112, pp. 755–764, 2013.

[17] J. Gao, S. Wang, B. Zhao, G. Qi, and C. Chen, "Pilot-scale experimental study on the CO_2 capture process with existing of SO_2: degradation, reaction rate, and mass transfer," *Energy & Fuels*, vol. 25, no. 12, pp. 5802–5809, 2011.

[18] J. Shunxiang, *Numerical and Experimental Study on Absorption of Carbon Dioxide from Flue Gas in the Hollow Fiber Membrane Contactor*, Chongqing University, 2014.

[19] H. Hikita, S. Asai, and T. Tsuji, "Absorption of sulfur dioxide into aqueous sodium hydroxide and sodium sulfite solutions," *AIChE Journal*, vol. 23, no. 4, pp. 538–544, 1977.

[20] M. Caplow, "Kinetics of carbamate formation and breakdown," *Journal of the American Chemical Society*, vol. 90, no. 24, pp. 6795–6803, 1968.

[21] E. F. Da Silva and H. F. Svendsen, "Ab initio study of the reaction of carbamate formation from CO_2 and alkanolamines," *Industrial & Engineering Chemistry Research*, vol. 43, no. 13, pp. 3413–3418, 2004.

[22] S.-W. Park, D.-W. Park, K.-J. Oh, and S.-S. Kim, "Simultaneous absorption of carbon dioxide and sulfur dioxide into aqueous 2-amino-2-methy-1-propanol," *Separation Science and Technology*, vol. 44, no. 3, pp. 543–568, 2009.

[23] Z. Zhang, Y. Yan, L. Zhang, and S. Ju, "Numerical simulation and analysis of CO_2 removal in a polypropylene hollow fiber membrane contactor," *International Journal of Chemical Engineering*, vol. 2014, Article ID 256840, 7 pages, 2014.

[24] B. R. Strazisar, R. R. Anderson, and C. M. White, "Degradation pathways for monoethanolamine in a CO_2 capture facility," *Energy and Fuels*, vol. 17, no. 4, pp. 1034–1039, 2003.

[25] Y. Lv, X. Yu, S.-T. Tu, J. Yan, and E. Dahlquist, "Experimental studies on simultaneous removal of CO_2 and SO_2 in a polypropylene hollow fiber membrane contactor," *Applied Energy*, vol. 97, pp. 283–288, 2012.