# Separation and Fixation of Carbon Dioxide Using Polymeric Membrane Contactor

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***ABSTRACT:*** Polypropylene hollow fiber membrane (PPHFM) contactor, with aqueous solution absorbent such as sodium hydroxide (NaOH), monoethanolamine (MEA) and diethanolamine (DEA), was designed and used to separate and fix $CO_2$ from $CO_2/N_2$ gas mixtures. The factors that influence the separation properties of $CO_2/N_2$ were investigated. It was found that the $CO_2$ removal efficiency is the best by using MEA solution as absorbent. The overall mass transfer coefficient (*K*) increases with the increase of liquid flow, gas flow and the concentration of the absorbent; however, it decreases with the carbon dioxide concentration in the gas mixture and the temperature of the absorbent solution. Preliminary results showed that carbon dioxide can be fixed efficiently into sodium carbonate and/or sodium bicarbonate with NaOH as the absorbent in the membrane contactor. Pure carbon dioxide, on the other hand, can be produced when MEA or DEA was used as the absorbent.

## INTRODUCTION

Membrane separation of gases has emerged into an important unit operations technique offering specific advantages over more conventional separation procedures (e.g. cryogenic distillation and adsorption). One can envisage that these technologies will also make great contribution to the growth of new research area, such as carbon dioxide capture from flue gas. However, even through there are a large number of potential applications for gas separation with polymer membranes, only relatively few of them have become applied in practice. The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible. However, it was found that simple structural modifications, which lead to increases in polymer permeability usually, cause losses in permselectivity and vice versa. This so-called ″trade-off″

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relationship is well described in the literature. It is thus possible to find polymers that exhibit high selectivity and low permeability and vice versa, in addition to that combine low selectivity with low permeability. There do not appear to be any polymers that show the desired trend to large values for both permeability and selectivity. Therefore, new membrane materials and technologies should be exploited to accommodate new applications, such as the simultaneous separation and capture of carbon dioxide from flue gas.

## TECHNOLOGY

Membrane contactors are devices that achieve gas/liquid or liquid/liquid mass transfer without dispersed one phase within another. As schematically represented in Figure 1, they are accomplished by passing the fluid on opposite side of a microporous membrane or a composite membrane (e.g. microporous membrane coated with PDMS rubber). The porous membrane acts as a non-selective barrier between both phases. Separation is determined by the reaction of one component in the gas mixture with the absorbent in the liquid.

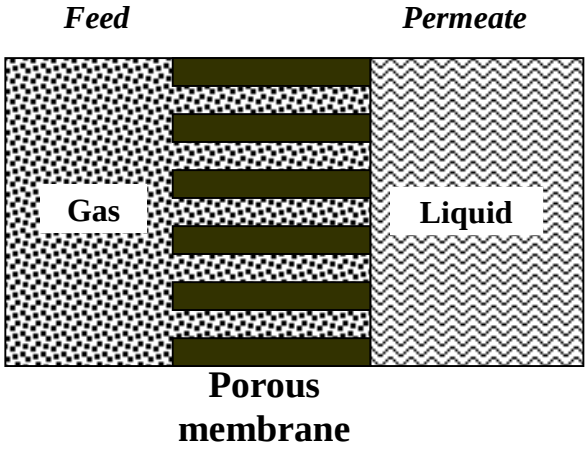


**Figure 1**. Schematic representation of membrane contactor for gas separation

This approach offers a number of important advantages over conventional dispersed phase contactor for gas sorption, such as large contact area per unit volume (as much as 300 to 1000 $m^{-1}$), no flooding and foaming phenomena, high removal efficiency, larger treatment capacity, low energy consumption and easy scale-up. Comparing with gas separation by asymmetric or composite membranes, the main advantages of membrane contactor include low resistance (in turn, low energy consumption), suitable for high gas flux separation and flexible applicability with absorbent variation. A simple comparison between these two membrane technologies is listed in Table 1.

**Table 1.** Comparison between membrane contactor and asymmetric membrane for gas separation

| | Membrane Contactor | Asymmetric Membrane |
|---|---|---|
| Separation Mechanism | Selective reaction | Solution and diffusion |
| Drive force | Low pressure | High pressure |
| Resistance | Low | High |
| Gas flux | 4000 | 1 |
| Mass transfer coefficient | $10^{-3}$ | $>10^{-5}$ |
| Flexible applicability | Depend on absorbent | Depend on membrane structure |

The potential applications of gas-liquid membrane contactor for the separation of $CO_2$ from gas mixtures were explored by several groups[1-3]. In this paper, polypropylene hollow fiber membrane contactor was designed and used to separate and fix $CO_2$ from a simulative flue gas mixture ($CO_2/N_2$). The operation conditions that influence on separation properties were studied.

The equipment employed in this study consists of a gas flow section, absorbent circulation, flowmeter, pump and analyzing system using gas chromatography (GC). A schematic diagram of the experimental apparatus is shown in Figure 2. The area of the membrane in the membrane module for this equipment is $0.8m^2$. The microporous polypropylene hollow fiber membranes were prepared with melt-extruded/cold-stretched (MECS) method in our lab. The inner and outer diameters of this hollow fiber were 350μm and 450μm, respectively, with porosity of 50%, an average pore diameter of 0.070μm and a $N_2$ permeation flux of $3.7 \times 10^{-2}$ $cm^3(STP)/cm^2.s.cmHg$. The absorbents were aqueous solutions of sodium hydroxide (NaOH), monoethanolamine (MEA) and diethanolamine (DEA) respectively. Gas mixtures of $CO_2/N_2$ were introduced into the inside of the hollow fibers at different flow rate and concentration. The operation pressure difference between liquid phase and gas phase was lower than the pore penetration pressure of the liquids. Experiments were conducted with counter current operation with varying flow rates of each fluid. All data were obtained under steady state conditions. Gas

chromatography was used to determine the concentration of $CO_2$ in gas phase, while the absorbent phase was analyzed by a standard titration method.

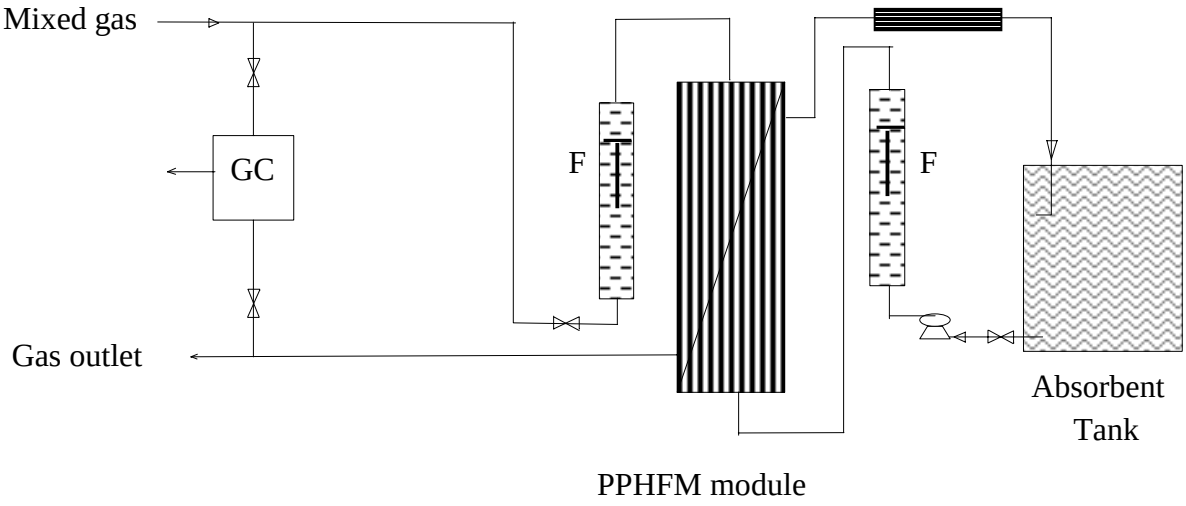


**Figure 2**. Schematic diagram of PPHFM contactor for $CO_2$ separation

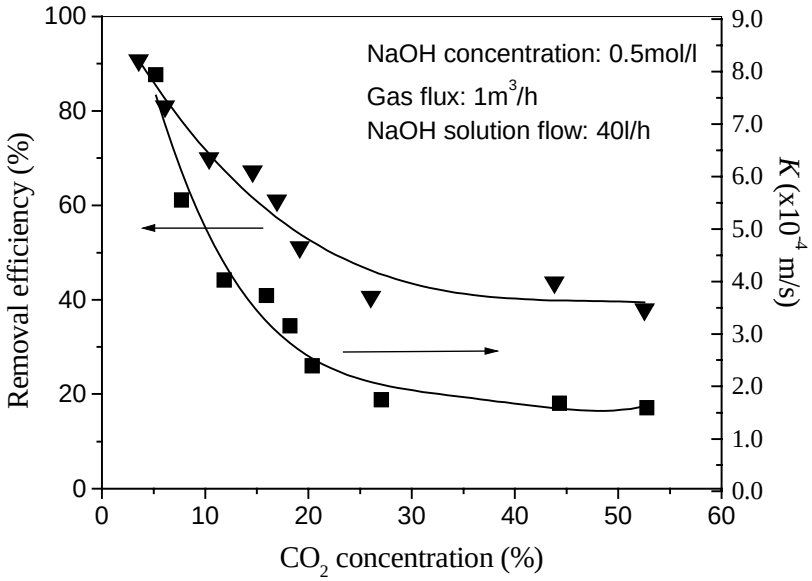


**Figure 3** Influence of $CO_2$ concentration in the gas mixtures on the removal efficiency and mass transfer coefficient

## RESULTS AND DISCUSSION

The influences of $CO_2$ concentration in the gas mixture on K, removal efficiency and mass transport are presented in Figure 3 and Figure 4. Both the removal efficiency and the mass transfer coefficient decrease with the increase of $CO_2$ concentration in the gas mixture. On the other hand, the mass transport increases from 0.045mol/$m^2$.s to 0.28 mol/$m^2$.s with the $CO_2$

concentration raised from 3% to 52%. The decrease in K and removal efficiency may be due to the quick exhaustion of NaOH in the absorbent solution. Increasing the NaOH concentration and/or its flow can weaken even eliminate these behaviors.

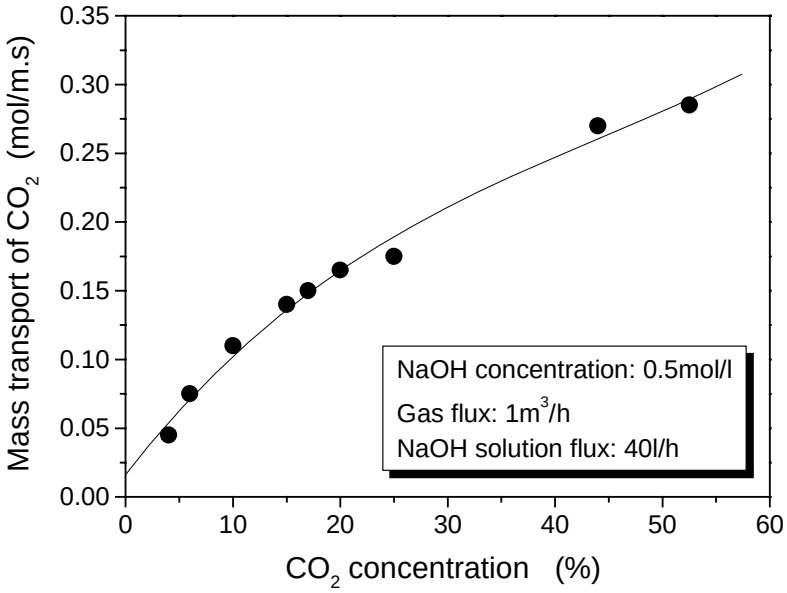


**Figure 4** Relationship between the mass transport and the concentration of $CO_2$

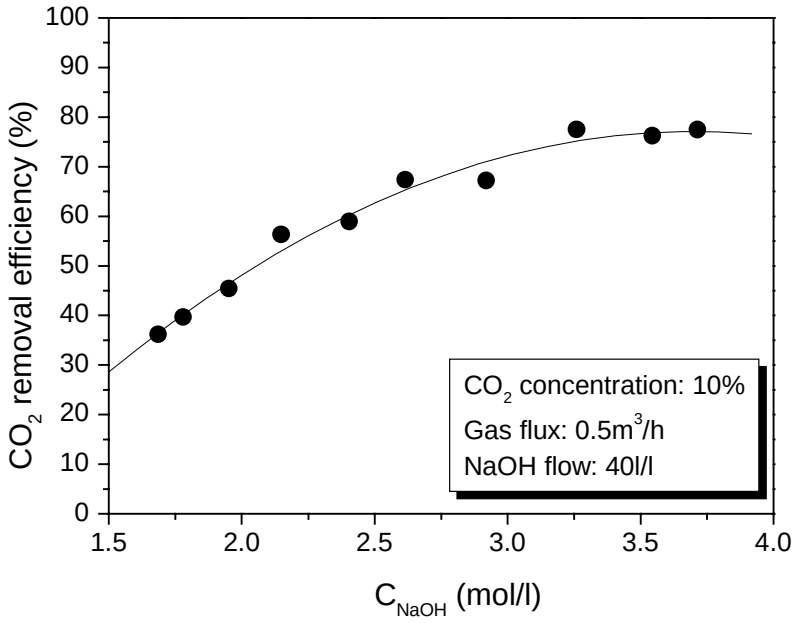


**Figure 5**. Effect of NaOH concentration on the CO2 removal efficiency

Effects of the NaOH concentration on the removal efficiency, mass transfer coefficient and mass transport of carbon dioxide were studied. The results are shown in Figure 5 and 6 respectively. It was found that the $CO_2$ removal efficiency, the mass transfer coefficient ($K$) and the mass transport across the membrane increase almost linearly with the increase of NaOH concentration from 1.5 to 3.0mol/l, and then followed by a weak decrease of the slopes of three values. These phenomena could be ascribed to a kinetic limitation of the reaction because of the large amount of $CO_2$ consumed when NaOH concentration is higher than 3.0mol/l.

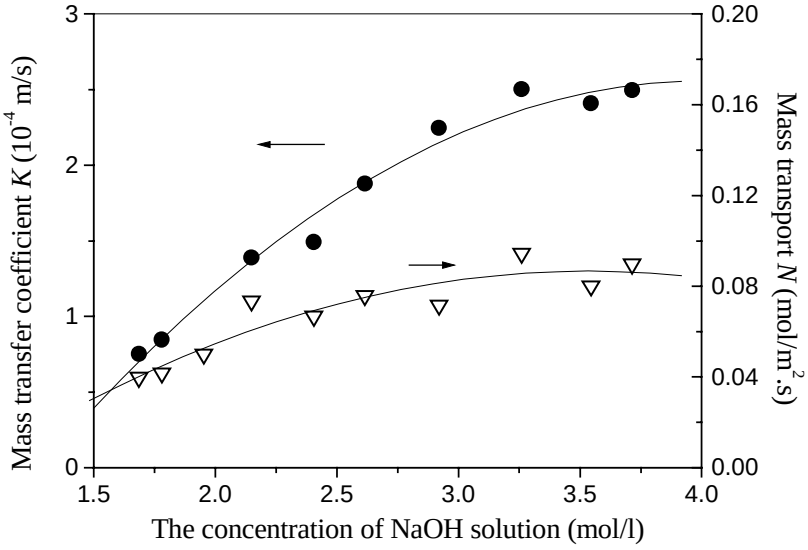


**Figure 6** Effects of NaOH concentration on $K$ and $N$

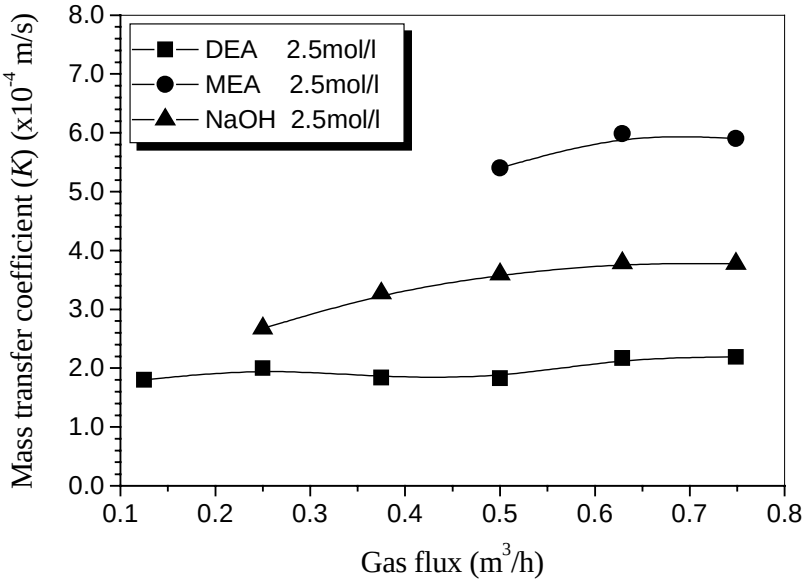


**Figure 7** Effect of gas flux on the mass transfer coefficient with different absorbent
Flux of the absorbent solution: 160l/h, Concentration of $CO_2$: 20%

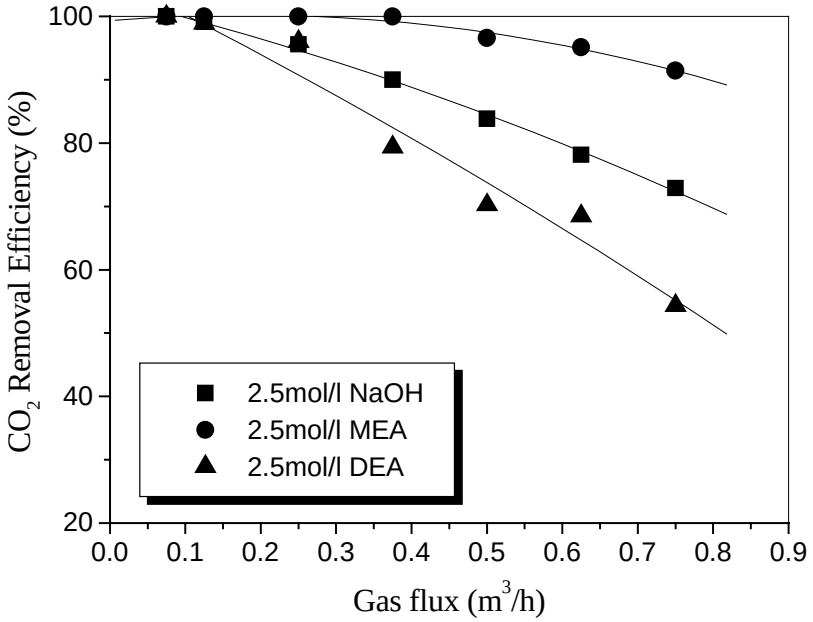


**Figure 8** Effect of gas flux on the $CO_2$ removal efficiency at absorbent solution flow of 160l/h and $CO_2$ concentration of 20%

Three aqueous solutions, NaOH, monoethanolamine (MEA) and diethanolamine (DEA) were compared in our work. The results can be seen from Figure 7 to Figure 10 respectively. The overall reactions between these absorbents with CO2 can be written as follows:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

$$CO_2 + 2HOCH_2CH_2NH_2 \longleftrightarrow HOCH_2CH_2NHCOO^- + HOCH_2CH_2NH_2^+$$

$$CO_2 + 2(HOCH_2CH_2)_2NH \longleftrightarrow (HOCH_2CH_2)_2NCOO^- + (HOCH_2CH_2)_2NH^+$$

Therefore, NaOH can be used to separate and fix $CO_2$ from gas mixtures simultaneously while the two-amine absorbents can be circularly applied to separate $CO_2$ from gas mixtures and to produce pure CO2 for other applications.

Figure 7 illustrates the relationship between the mass transfer coefficient and the gas flux passing through the membrane module. It is interesting that relatively slight effects of gas flux on the mass transfer coefficient were observed. These mean that, although the *K* value varied from $2.0 \times 10^{-4}$m/s for DEA to $6.0 \times 10^{-4}$m/s for MEA, the three absorbent solutions are effective for the removal of carbon dioxide from the gas mixture at this condition. Compared the removal efficiency, Figure 8 shows that it decreases as follows: MEA > NaOH >DEA.

MED is the best absorbent for removal CO2 in our membrane contactor.

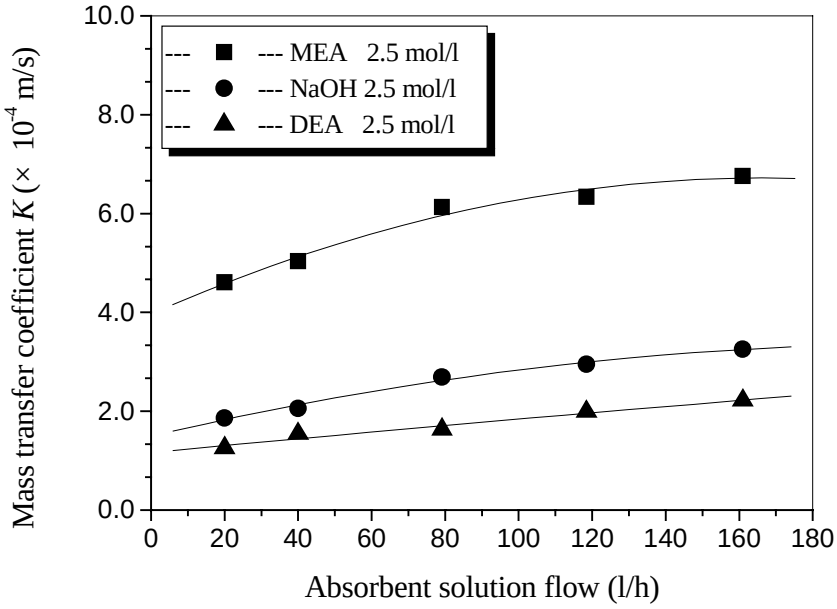


**Figure 9** Effect of liquid flow on the mass transfer coefficient

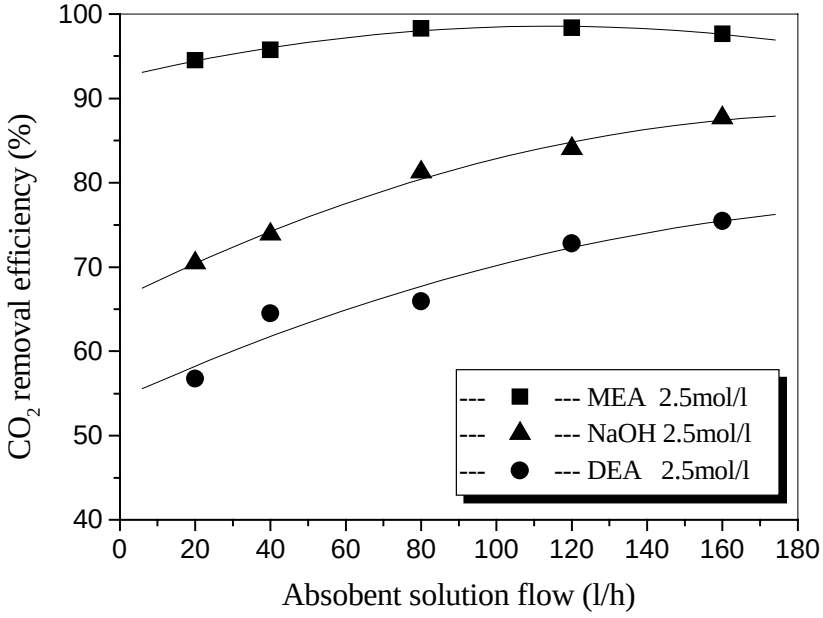


**Figure 10** Effect of liquid flow on the $CO_2$ removal efficiency

Figure 9 and Figure 10 reveal that increasing the flow of the absorbent solutions increase both the mass transfer coefficient and the removal efficiency of carbon dioxide. The overall resistance to mass transfer in this membrane contactor is determined by the resistance in the gas phase and the liquid phase as well as in the membrane pores. The resistance contributed by the

liquid phase may be eliminated with the increase of liquid flow. As a result, the K and the removal efficiency increase slightly with the liquid flow.

## CONCLUSIONS AND FUTURE ACTIVITIES

Our preliminary results demonstrate that polypropylene hollow fiber membrane contactor can be effectively used to separate and fix CO2 from gas mixtures. The separation performance of this membrane technology can be adjusted flexibly by changing the kinds, concentration and flow of the absorbent solutions. Future works will be focused on the mathematical model, scale-up and the separation properties for practical flue gases.

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