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Sun-Hwa Yeon[a]; Bongkuk Sea[a]; You-In Park[a]; Ki-Sub Lee[a]; Kew-Ho Lee[a]
[a] Membranes and Separation Research Center, Korea Research Institute of Chemical Technology, Taejon, South Korea

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Absorption of Carbon Dioxide Characterized by Using the Absorbent Composed of Piperazine and Triethanolamine

**Sun-Hwa Yeon, Bongkuk Sea, You-In Park,
Ki-Sub Lee, and Kew-Ho Lee***

Membranes and Separation Research Center, Korea Research
Institute of Chemical Technology, Taejon, South Korea

ABSTRACT

This work studies the CO_2 absorption of alkanolamine, piperazine, and TEA (triethanolamine), and the chemical reaction kinetics of CO_2 by using the mixed solution of piperazine and TEA in polyvinylidine-fluoride hollow fiber membrane contactor-stripper hybrid process. Absorption was studied from 303K to 382K in the mixed solution of piperazine 0.26 M, 0.64 M, and TEA 0.38 M, 1.13 M, 2.26 M. Also, absorption rates were measured as a function of CO_2 partial pressure in the mixed solutions. The increase of the initial absorbent concentration and CO_2 partial pressure showed a high absorption rate of CO_2. Our

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*Correspondence: Kew-Ho Lee, Membranes and Separation Research Center, Korea Research Institute of Chemical Technology, Taejon 305-600, South Korea; Fax: +82-42-861-4151; E-mail: khlee@krict.re.kr.

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experiment revealed that the absorption capacity of the mixed absorbent of TEA and piperazine with CO_2 was mostly governed by the piperazine concentration. The TEA is a tertiary amine with low CO_2 absorption capacity, but it helps the hollow fiber membrane keep the non-wetting condition in the fiber's pores because of the high viscosity of TEA. Therefore, the addition of piperazine to TEA, which has too low absorption capacity with CO_2, makes it possible to obtain a high CO_2 removal efficiency. Finally, the kinetic data on the reaction of piperazine and CO_2 were investigated, and the activation energy was calculated through the Arrhenius expression.

Key Words: Carbon dioxide absorption; Piperazine; Triethanolamine; PVDF hollow fiber; Membrane contactor.

INTRODUCTION

As the use of energy has been steadily increasing with the industrial development and the advance of culture, the environmental problems have grown exponentially. Carbon dioxide has been proven to be responsible for 80% of greenhouse gases, contributing to the increase of the earth's surface temperature. And it is reported that half of the CO_2 emission is produced by industries and power plants using fossil fuels.[1] Therefore, the development of a separation process is urgently needed to remove and to recover the CO_2 from the places generating CO_2 gas.

The gas absorption process for removing the CO_2 can be carried out in many reactors, such as bubble columns, packed towers, venturi scrubber, sieve trays, etc. The commercial process widely known for CO_2 separation is the packed column system, but new technology is required for this because of disadvantages of the packed column system, such as flooding, channeling, large-scale equipment, etc. The microporous hollow fiber membrane module made from polymeric material is a new type of gas absorber, [2,3] which has the advantage of a large interfacial area, independent gas–liquid phase control, no flooding, and no channeling among others.

The absorbent for removal of the CO_2 mainly uses an alkanolamine group because of its high reaction rate. Various alkanolamines have been proposed in the literature, such as monoethanolamine (MEA), N-methyldiethanolamine (MDEA), diglycolamine (DGA), di-2-propanolamine (DIPA), and 2-amino-2-methyl-l-propanol (AMP).[4–7] Aqueous MEA is widely used for removing CO_2 from natural gas streams and refinery process streams. A number of investigators have studied the solubility[8–11] and reaction kinetics[12–16] of CO_2 in aqueous MEA. Also piperazine is a kind of second alkanolamine, and it is known that piperazine has a higher reaction than MEA because of two characteristics: its cyclic and diamine nature.[17] Piperazine have also been investigated as a promoter for methyl diethanolamine.[18–21] These solvents have been used successfully for high-capacity CO_2 removal in ammonia plants. The tertiary alkanolamine such as triethanolamine (TEA) has an absorption rate lower than the first and second alkanolamine in its reaction with CO_2, but it has the merit of a small energy consumption, because TEA does not react directly with CO_2.[22]

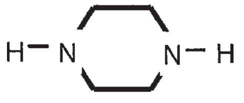
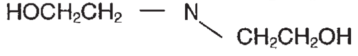
The mass transfer resistance of gas, membrane, and liquid phase limits the CO_2 absorption rate in the membrane contactor module. Although the interfacial area of the membrane is greater than conventional absorbers, the increase of its additional resistance can cause a decrease in the mass transfer capacity of the membrane, because of the resistance of the membrane itself.[23] Therefore, selection of the absorbent to minimize the membrane resistance plays an important part in the gas absorption process by using a polymeric membrane contactor.

In the present study, we experimentally investigated the CO_2 absorption rate on piperazine and TEA, respectively, in a porous hollow fiber membrane contactor system. Moreover, we adjusted the mixed solution of piperazine and TEA to the membrane contactor for CO_2 separation and estimated the effects on the CO_2 absorption rate and the stability of membrane. Finally, we attempted to summarize the available kinetic data for piperazine and CO_2.

Kinetic Theory

The theory of mass transfer with chemical reaction will be useful in analyzing the experimental results. Table 1 shows the molecular structures of the piperazine and TEA compounds reacting with CO_2. As shown in Figs. 1 and 2, piperazine expresses carbamate formation, and TEA shows hydratation reaction.[22] In this paper we deal only with piperazine reaction, because TEA has a very low reaction with CO_2. In the reaction of piperazine and CO_2, the rate of

Table 1. Chemical structure of piperazine and triethanolamine.

Material	Chemical structure
Piperazine	
Triethanolamine	 $HOCH_2CH_2-N(CH_2CH_2OH)_2$

$$P_{CO2}(v) \leftrightarrow CO_2(l)$$

$$CO_2(l) + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^-(l) + H_2O \leftrightarrow CO_3^{-2} + H_3O^+$$

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$

$$\underbrace{PZH^+}_{\text{Protonated Piperazine}} + H_2O \leftrightarrow PZ + H_3O^+$$

$$PZ + CO_2 + H_2O \leftrightarrow \underbrace{PZCOO^-}_{\text{Piperazine Carbamate}} + H_3O^+$$

$$H_2O + \underbrace{H^+PZCOO^-}_{\text{Protonated Piperazine Carbamate}} \leftrightarrow H_3O^+ + PZCOO^-$$

$$PZCOO^- + CO_2 + H_2O \leftrightarrow \underbrace{{}^-OOCPZCOO^-}_{\text{Piperazine Dicarbamate}} + H_3O^+$$

Figure 1. Reactions of piperazine and CO_2.

disappearance of CO_2 depends on temperature and composition. The most significant simplification arises from the pseduo-first-order assumption for the reaction kinetics. This assumption means the concentration of amine is uniform across the cross section of the liquid boundary layer. We can obtain the second-order reaction expression of CO_2 with an amine into a first-order expression.[22] Therefore, it can be written as the product of second-order reaction rate constant k_2 and a function of the concentrations of piperazine $[PZ]$ and CO_2 $[CO_2]$ as Eq. (1).

$$\begin{aligned} R_{CO_2} &= k_2[PZ]\{[CO_2]-[CO_2]^*\} \\ &= k_1\{[CO_2]-[CO_2]^*\} \end{aligned} \tag{1}$$

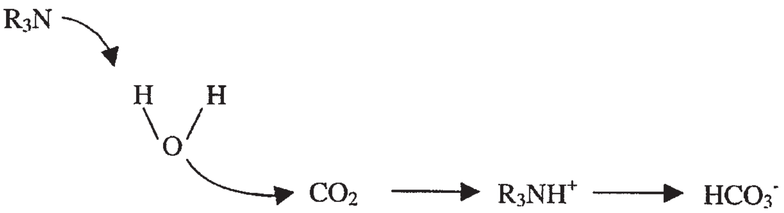


Figure 2. Reaction of triethanolamine and CO_2.

where $[CO_2]^*$ is the equilibrium concentration of carbon dioxide, and k_1 is the first-order reaction rate constant.

A pseudo-first-order expression for the flux(N) by using the surface renewal theory[13] is expressed by Eq. (2). Furthermore, in most experiments conducted, we assume that the equilibrium partial pressure will approach zero, because the solution loading is low:

$$N_{CO_2} = k_l^o \sqrt{1 + \frac{k_1 D_{CO_2}}{k_l^{o^2}}} \frac{(P^I co_2 - P^* co_2)}{H_{CO_2}} \tag{2}$$

Because the number 1 under the square root of Eq. (2) will have no effect at the high enhancement factors in this work. Eq. (2) can be simplified as follows

$$N_{CO_2} = \sqrt{\frac{k_2[PZ]D_{CO_2}}{H_{CO_2}}} P^I_{CO_2} \tag{3}$$

The diffusion coefficient (D) of CO_2 in water was calculated with the correlation of Versteeg and van Swaaij.[5]

$$D^O_{CO_2}(cm^2/s) = 0.024 \exp\{-2122/T(K)\} \tag{4}$$

Pacheco[22] correlated the Henry's Law constant for CO_2 in pure water measured by Versteeg and van Swaaij and reported by Al-Ghawas, Hagewiesche, Ruiz-Ibanez, and Sandall:[5]

$$H^O_{CO_2}(atm\ cm^2/mol) = 1.7107\text{E} + 07 \exp\{-1886.1/T(K)\} \tag{5}$$

EXPERIMENTAL

Materials

Piperazine and TEA were purchased from Aldrich Chemicals (Milwaukee, WI). Polyvinylidinefluoride (PVDF) hollow fiber membrane was supported from Membranes and Separation Research Center (KRICT, South Korea). Ultrapure deionized water was used. All chemicals were used without any further purification.

Absorption Test

The experimental setup for CO_2 removal and recovery was shown in Fig. 3, and this setup is composed of a hybrid process in which a membrane contactor and a thermal stripping column coexist. In the case of the absorber, the gas containing 10 ~ 40% of CO_2 (balance N_2) was passed upstream in the tube side of the membrane module, and the absorbent was supplied downstream in the shell side. The absorbents used in this system are piperazine 2 ~ 10 wt%, TEA 5 ~ 15 wt%, and the mixed solution of piperazine and TEA. The gas flow rate was changed at the range of 100 ~ 700 cm^3/min, and the liquid flow rate was changed at the range of 12 ~ 60 cm^3/min. The solution was reused after the CO_2 dissolved in the solution was totally stripped in the desorption tower connected with the reboiler. The heating band was tied

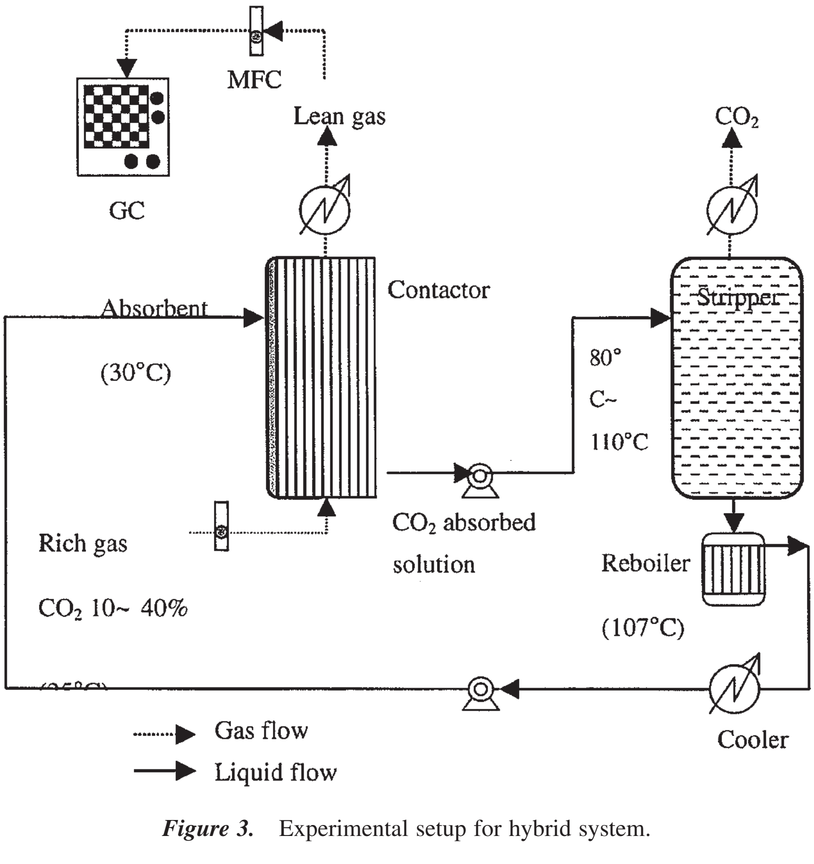


Figure 3. Experimental setup for hybrid system.

at the inlet of the desorption tower into which the high temperature absorbent flowed to increase the desorption efficiency. At the top of the tower, the condenser was installed to minimize the evaporation of steam. In the membrane module, the pressure difference of the gas phase and the liquid phase was kept in the range of 2–4 psig by a needle valve to form the stable gas–liquid interface. The gases coming from the absorption and desorption module were analyzed by TCD-GC(GC-14B; Shimadzu).

The membrane contactor used as CO_2 absorbers in this study is the PVDF hollow fibers. Also to compare the performances of absorbers, the packed column was used as another absorber. Table 2 shows the properties of each absorber. The polymeric hollow fiber materials are basically hydrophobic. However, this surface nature may be changed according to the physical properties of the fiber, such as pore size, surface tension, and contact angle against the absorbent used. Details of the hollow fiber have been reported previously.[23–25]

To separate CO_2 dissolved in the absorbent and to reuse the absorbent, the desorption module was equipped nearby the absorption module. The desorption tower was made of glass, and the vacuum surface was coated with silver, which helped prevent heat emission.

RESULTS AND DISCUSSION

CO_2 Removal Efficiency and Absorption Rate

Figure 4 presents the CO_2 removal efficiency and the absorption rate per module volume when the PVDF hollow fiber membrane contactor was used as the absorption module. The TEA 5 wt%, piperazine 5 wt%, and the mixed solution of piperazine 5 wt% + TEA 5 wt% were used as the absorbents of

Table 2. Dimensions of packed column and PVDF hollow fiber.

	Packed column	PVDF
Diameter	0.027 m	0.02 m
Length	0.2 m	0.23 m
Surface area/module vol.	710 m^2/m^3	1391.4 m^2/m^3
Module volume	114.45 cm^3	72.2 cm^3
PVDF fiber	I.D.	830 μm
	O.D.	1070 μm
	Pore size	0.03 μm
	Packing density	0.4
	Number of fibers	130

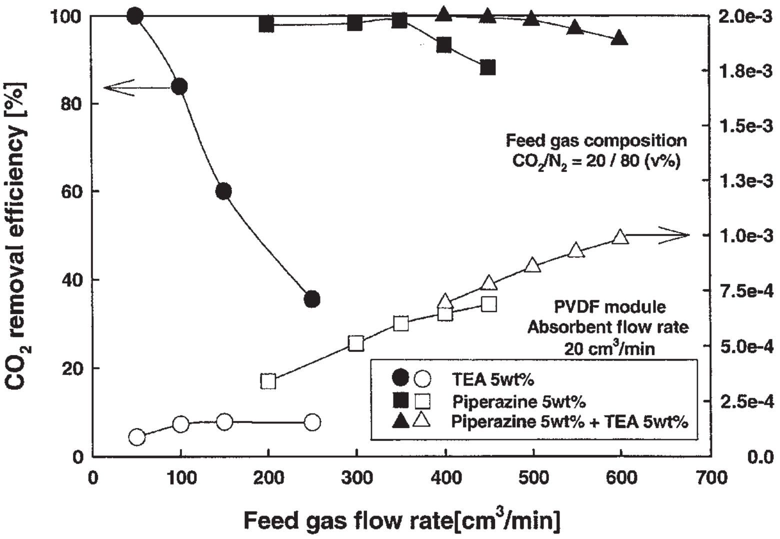


Figure 4. CO_2 removal efficiency and CO_2 flux of various absorbents in PVDF hollow fiber membrane contactor, adsorption module 30°C, and stripper 80°C.

this hybrid system. The absorbent flow rate is fixed to 20 cm^3/min. The feed gas flow rate in the region of CO_2 removal efficiency of about 95% showed the highest amount, 550–600 cm^3/min, for the mixed solution and the lowest amount, 50–100 cm^3/min, for the TEA 5 wt%. Thus, the CO_2 absorption rate of the mixed absorbent of piperazine and TEA was 8 times higher than that of the TEA alone. As mentioned above, these results are caused by the difference of the reaction mechanism between piperazine and TEA. The prime reaction mechanism between the aqueous piperazine and CO_2 is the carbamate formation, but tertiary alkanolamines do not react directly with CO_2 according to Fig. 1 because they lack the free protons.[22]

The polymeric hollow fiber as the contactor has a disadvantage, showing the wetting phenomena according to the affinity of membrane material and a kind of absorbent. To get a high absorption rate, it is absolutely necessary to minimize the membrane resistance by penetration of the liquid into pores. Figure 5 shows the nonwetting time of PZ 5 wt% + TEA 15 wt% and PZ 5 wt% in the PVDF hollow fiber membrane contactor hybrid system. When the mixed absorbent of PZ 5 wt% and TEA 5 wt% was used, the initial CO_2 removal efficiency was kept for about 3000 min, but in the case of absorbent PZ 5 wt%, after about 200 min of the nonwetting time, the removal efficiency was observed to be rapidly decreasing. The difference in nonwetting times

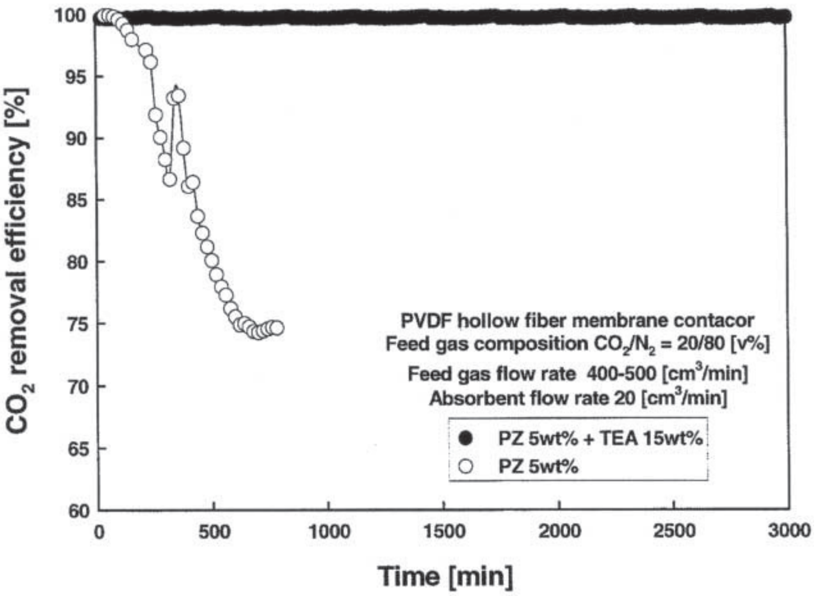


Figure 5. Nonwetting time of PVDF hollow fiber membrane contactor for absorbents of PZ 5 wt% + TEA 15 wt% and PZ 5 wt%, absorption module 30°C, and stripper 80°C.

between the two absorbents was explained by the membrane's wetting phenomena. It is the phenomena in which the absorbent easily penetrates into the gas phase of the fiber's tube side and induces the decrease in CO_2 removal efficiency attributed to the increase of membrane resistance. Although tertiary alkanolamine, TEA, has a low reactivity on CO_2, its high viscosity prevents the liquid phase from passing into the gas phase.[26] Therefore, the addition of TEA 5 wt% into piperazine 5 wt% contributes to a long stable operating time in the membrane contactor process.

Figures 6–8 show the comparisons of the CO_2 removal performances between PVDF membrane and packed column process. Figure 6 indicates the CO_2 removal efficiency of PVDF membrane and packed column according to the various absorbent concentrations. The feed gas flow rate satisfying CO_2 removal efficiency of about 95% was $400\,cm^3/min$ in the piperazine 5 wt% solution and $600\,cm^3/min$ in the mixed solution of piperazine 5 wt% + TEA 5 wt% of the PVDF membrane. The mixed absorbent showed a disposal amount of feed gas flow rate greater than piperazine absorbent in the 95% removal efficiency. We observed that the addition of TEA in the piperazine solution improves the absorption capacity of PVDF membrane, because

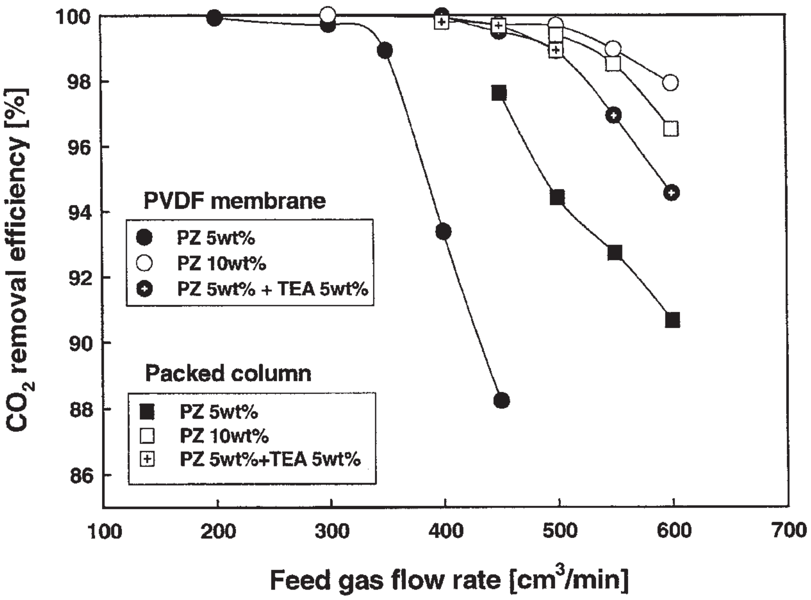


Figure 6. CO_2 removal efficiency according to concentrations of piperazine and TEA in PVDF hollow fiber membrane contactor and packed column, absorption module 30°C, and stripper 80°C.

the membrane resistance becomes low because of the formation of the stable gas–liquid interface in the pore of the membrane.[23] In the packed column system, the piperazine 5 wt% and mixed solution of TEA 5 wt% + piperazine piperazine 5 wt% showed a similar disposal amount of feed gas flow rate, 450–500 cm^3/min at the removal efficiency of about 95%. Therefore, the above results enable us to predict that the addition of TEA into piperazine solution does not function as an important factor in the packed column system.

Figure 7 presents the CO_2 absorption rate per module volume to compare the removal performances on the various absorbents of the PVDF hollow fiber membrane contactor and the packed column. The PVDF hollow fiber membrane was 1.5 times higher than the packed column in the CO_2 absorption rate per module volume under the same conditions. When we compare the dimension of PVDF membrane and packed column of Table 1, the aforementioned result is attributed to the fact that the surface area per unit volume of the PVDF membrane is 1.5–2 times higher than the packed column.

Figure 8 shows the CO_2 flux between two modules. The CO_2 flux of the PVDF hollow fiber membrane is 1.5 times lower than the packed column because of the large surface area of the membrane module.

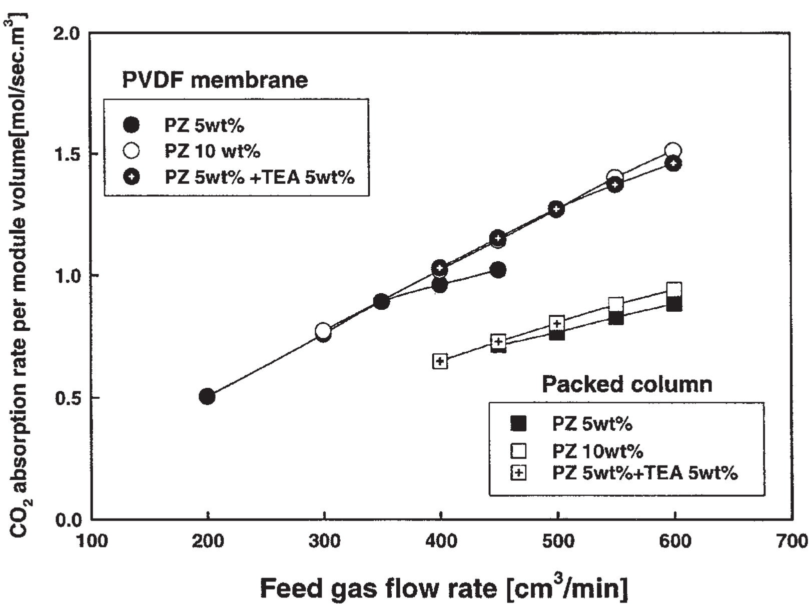


Figure 7. CO_2 absorption rate per module volume according to concentrations of piperazine and TEA in PVDF hollow fiber membrane contactor and packed column, absorption module 30°C, and stripper 80°C.

Energy Consumption of Stripping Module

Figure 9 shows the energy consumption in the stripping module when the piperazine and TEA are used as absorbents. In the packed column system, the steady-state time appeared through these figures when the temperature of the reboiler connected in the stripping system was changed from 90°C to 109°C.

Figure 9a indicates the removal efficiency of a 20-min interval in the absorber when the temperature of the stripping system is kept to 109°C and 90°C, respectively, in the case of piperazine 2 wt%. When the temperature of the stipping system is 109°C, the CO_2 removal efficiency of about 95% is kept under the stable steady-state condition for a long time, and at 90°C, the CO_2 removal efficiency decreases rapidly to about 30% after the stable efficiency for about 100 min. It is presumed that the decrease of the CO_2 removal efficiency in the absorber is attributed to the decrease in CO_2 stripping efficiency by insufficient thermal stripping energy. It was discovered that the absorbent piperazine alone has the advantage of obtaining the high removal efficiency but that the energy consumption is high, because the high heat of over 109°C is needed to strip the CO_2 dissolved in the used absorbent in the stripping system.

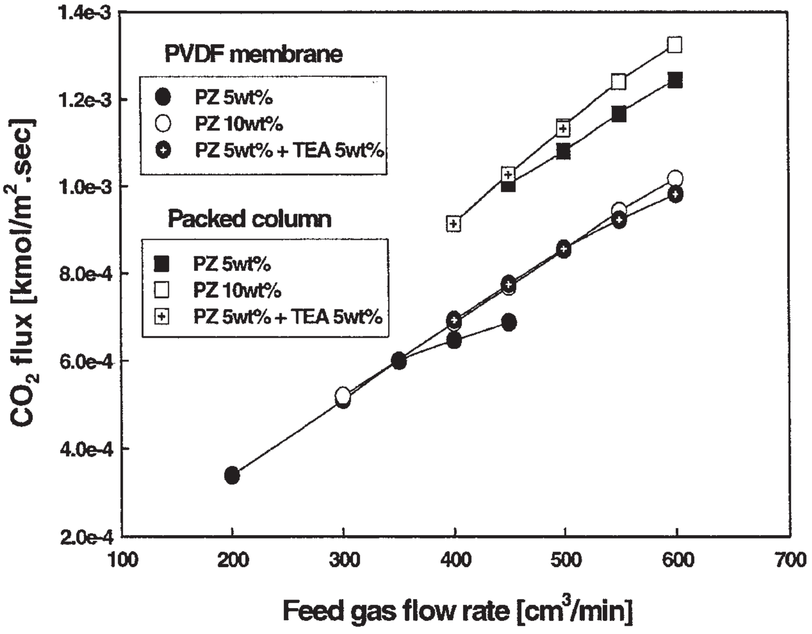


Figure 8. CO_2 fluxes according to concentrations of piperazine and TEA in PVDF hollow fiber membrane contactor and packed column, absorption module 30°C, and stripper 80°C.

Figure 9b shows the removal efficiency of a 20-min interval in the case of TEA 5 wt%. Although the temperatures of the stripping system are changed to 109°C, 100°C, and 90°C, the decrease of the CO_2 removal efficiency did not appear as time went by. Thus, it was observed that the absorbent of TEA 5 wt% needs a lower CO_2 stripping energy than piperazine 5 wt% in keeping the removal efficiency over 95% because TEA 5 wt% is capable keeping the steady-state condition for a long time in spite of the reboiler temperature of 90°C. However, the use of TEA alone as the absorbent is not suitable in this system, because the aqueous TEA has a lower reactivity with CO_2 than the aqueous piperazine.

Figure 9c shows removal efficiency of a 20-min interval when the mixed absorbent of TEA 5 wt% and piperazine 5 wt% was used. This removal efficiency showed a decrease of less than only 5% from the initial efficiency for about 500 min when the temperature of the reboiler was 90°C. Therefore, we expected the mixed absorbent to consume a CO_2 stripping energy lower than piperazine absorbent. Also, with respect to the CO_2 removal efficiency,

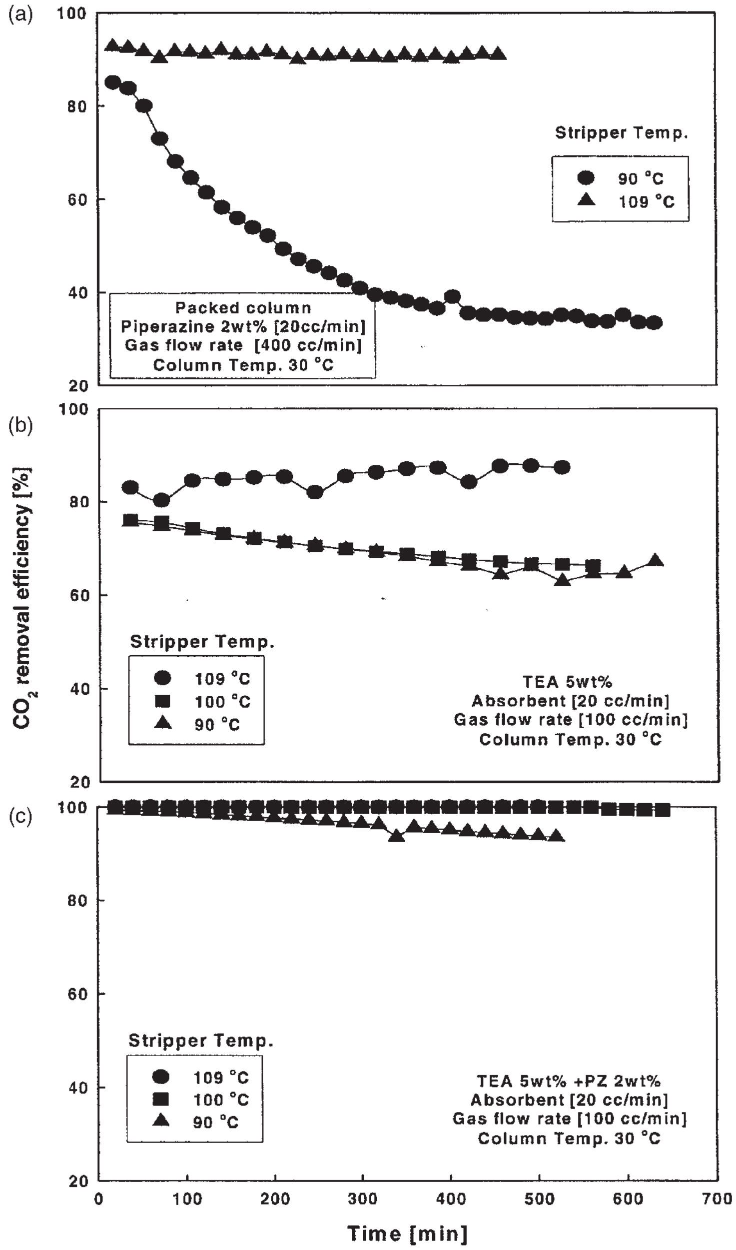


Figure 9. CO_2 removal efficiency according to time of piperazine 2 wt% (a), TEA 5 wt% (b) and TEA 5 wt% + PZ 2 wt% (c) in packed column.

this mixed absorbent showed efficiency similar to that of the piperazine absorbent. Therefore, the mixed absorbent in this membrane contactor stripping system has proved to be a very suitable absorbent, satisfying both the high efficiency and the stable operation required.

Reaction of Absorbent Piperazine

Figure 10 shows the relation of CO_2 absorption flux according to CO_2 partial pressure and the various concentrations on the mixed absorbent of TEA and piperazine in the PVDF membrane contactor system. The CO_2 absorption flux increases with the increasing concentration of piperazine in the mixed solution. On the other hand, the effect on the various concentrations of TEA in the mixed solution was not clearly observable. As stated earlier, since the aqueous TEA has a low reactivity with CO_2, the piperazine component in the mixed absorbent plays an important role in the reaction with CO_2. It was also observed that the higher the CO_2 partial pressure in the mixed feed gas, the greater the CO_2 flux in the same mixed absorbent concentrations.

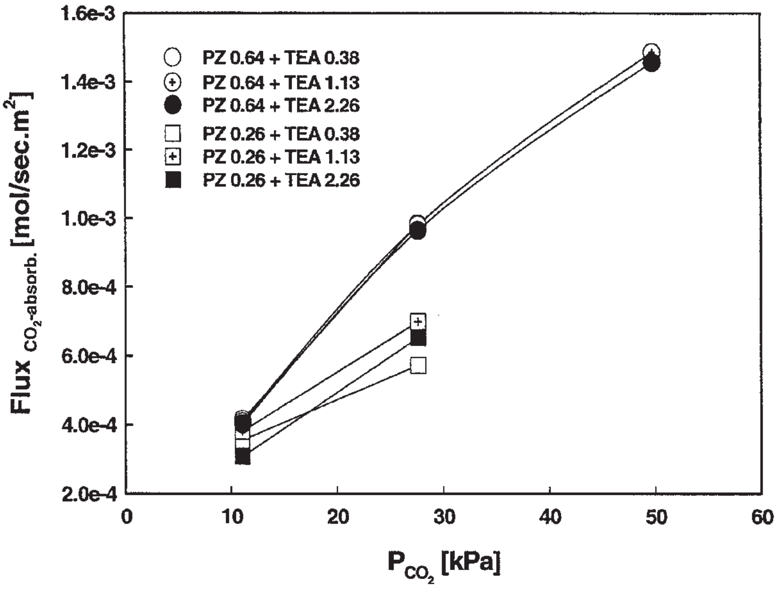


Figure 10. CO_2 fluxes on CO_2 partial pressure in the case of the mixed solutions in PVDF hollow fiber membrane contactor, absorption module 30°C, and stripper 80°C.

Figure 11 shows the apparent reaction rate constant k_l (k_{app}) of CO_2 on the concentrations of the various mixed absorbents calculated from Eq. (1) in the PVDF membrane contactor. As shown in Fig. 11, the increment of the piperazine concentration caused an increase in the value of k_{app} under the condition of constant TEA concentration, while the change of the TEA concentration did not affect the value of k_{app} under the condition of constant piperazine concentration. The results shown in Figs. 10 and 11 made it possible for us to predict that the reaction of the mixed absorbent with CO_2 is mainly achieved by the piperazine out of the various mixed absorbents present.

If we suppose that the reaction with CO_2 is only related to piperazine owing to the low reactivity with TEA, we can obtain the second-order reaction rate constant k_2 as shown in Fig. 12. From Eq. (3), we can see that a plot of the flux vs. interfacial partial pressure will yield a straight line. Figure 12 shows the results of partial pressures and two amine concentrations (0.26 and 0.63 M). The second-order rate constant was extracted by taking the best-fit straight line of each series represented in Fig. 12.

To investigate the dependence of the reaction temperature and the CO_2 partial pressure in the reaction of piperazine and CO_2, the CO_2 flux was obtained in the packed column system as shown in Fig. 13. We can note that the CO_2 flux increases as the operating temperature increases. From

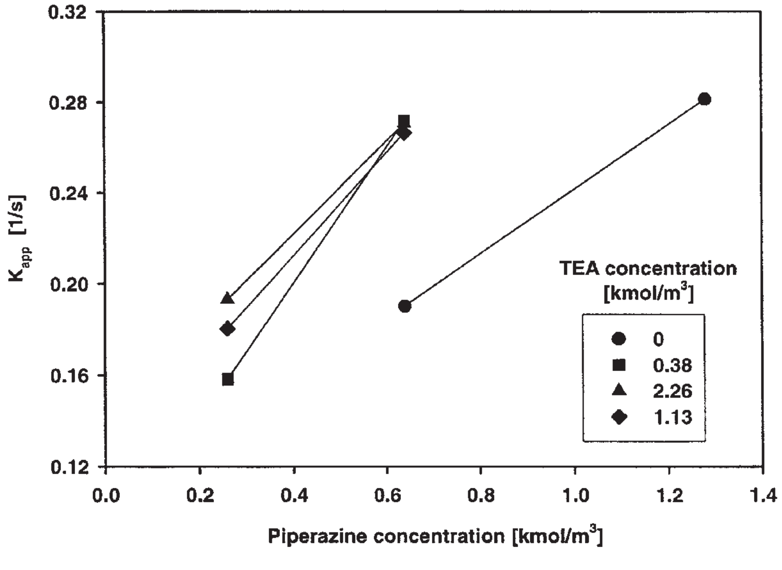


Figure 11. Apparent reaction rate constants on the mixed solutions in PVDF hollow fiber membrane contactor.

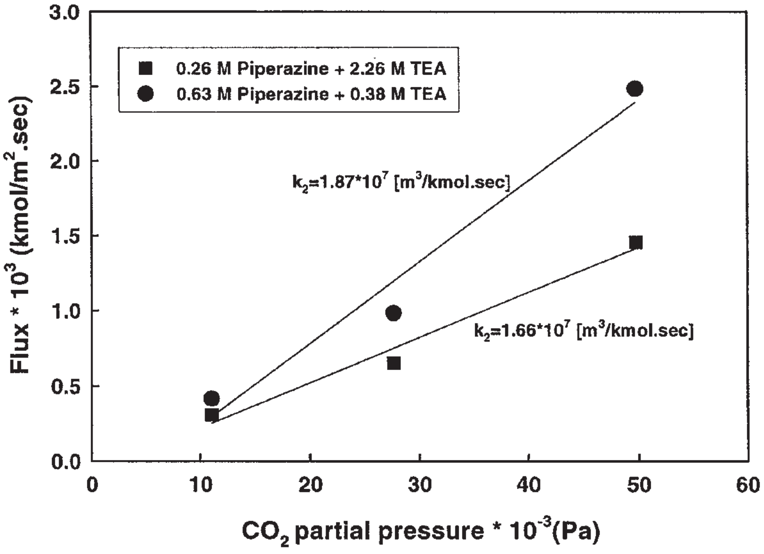


Figure 12. Straight line fit for rate of CO_2 absorption into aqueous piperazine solution, absorption module 30°C, and stripper 80°C.

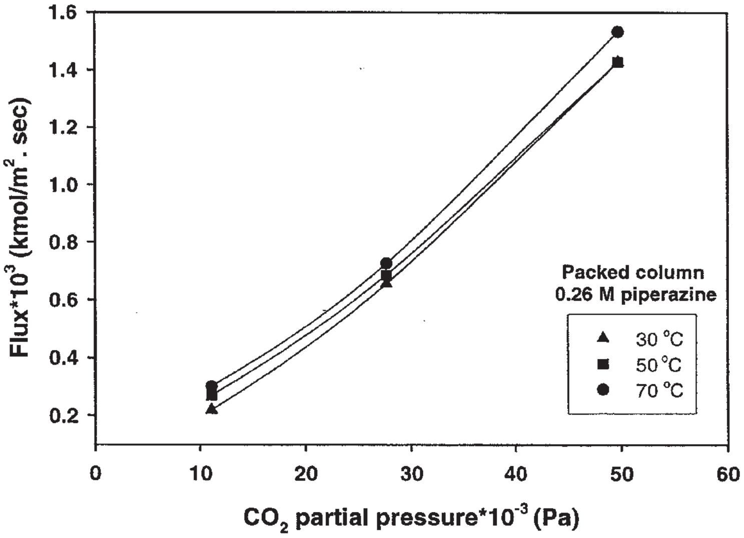


Figure 13. CO_2 fluxes on CO_2 partial pressure and operating temperature in the case of the 0.26 M piperazine in packed column system, stripper 80°C.

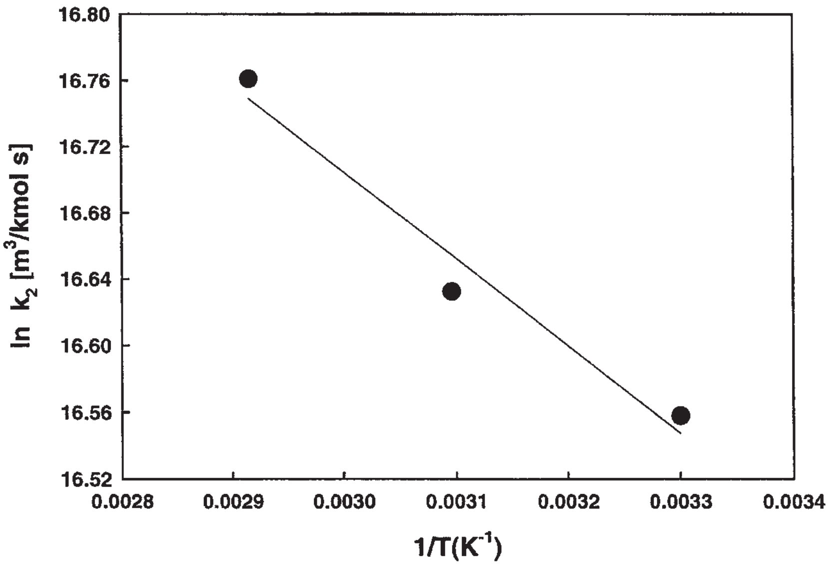


Figure 14. Second-order reaction rate constant of piperazine and CO_2.

Eq. (3), we can estimate the second-order reaction constant, k_2. Temperature dependence of the rate constant is shown in Fig. 14 as an Arrhenius plot. An Arrhenius expression can be expressed as

$$k_2 = k_{25^\circ\mathrm{C}} \exp\left[-\frac{\Delta H_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \tag{6}$$

where $k_{25^\circ\mathrm{C}} = 5.37\mathrm{E}4\ \mathrm{m}^3/\mathrm{kmol}$, $R = 8.314\,\mathrm{KJ/kmol\ K}$. Consequently, the activation energy, ΔH_a obtained from the second-order rate constants of Fig. 9 was 18,073.8 kJ/kmol.

CONCLUSIONS

The gas absorption process for removing CO_2 can be carried out in a PVDF hollow fiber membrane contactor system. The experiment on the removal and recovery of CO_2 was conducted in a hybrid process of a membrane contactor and a thermal stripping column. Absorbents used in this process were piperazine and TEA. The gas containing $10 \sim 40\%$ of CO_2 (balance N_2) was passed upstream in the tube side of the membrane module, and the absorbent was supplied downstream in the shell side. The

CO_2 absorption capacity on these two absorbents estimated through the membrane contactor process and piperazine shows an absorption rate much higher than tertiary alkanolamine, TEA. But the piperazine absorbent has two main disadvantages: 1) the short nonwetting time owing to the increasing membrane resistance caused by the penetration of liquid phase into membrane pores, and 2) the large stripping energy consumption in the continuous operating system due to strong combination with CO_2. To overcome these disadvantages, the TEA solution is introduced to the piperazine solution. The experimental results proved that this mixed solution of piperazine and TEA is suitable as an absorbent for CO_2 gas separation through the membrane contactor process. All the data obtained from the PVDF hollow fiber membrane contactor were compared with the data obtained from the packed column process, and the hollow fiber membrane turned out to be 1.8 times higher than the packed column in CO_2 absorption rate per module volume. Finally, the kinetic data on the reaction of piperazine and CO_2 was investigated, and the activation energy calculated from Arrhenius plot was 18,073.8 kJ/kmol.

NOMENCLATURE

D_{CO_2}	diffusion coefficient of CO_2, m^2/sec
H_a	activation energy in Arrhenius expression, kJ/kmol
H_{CO_2}	Henry's law constant of CO_2, $m^3\,Pa/kmol$
k_1	pseudo-first-order rate constant, $m^3\,Pa/kmol$
k_2	second-order rate constant, $m^3\,Pa/kmol$
K_{app}	apparent reaction rate constant, 1/sec
k_L^o	liquid film mass transfer coefficient, m/sec
$k_{25^\circ C}$	reaction rate constant in 25°C
N_{CO_2}	flux of CO_2, $kmol/m^2\,sec$
$P_{CO_2}^I$	interfacial partial pressure of CO_2, Pa
$P_{CO_2}^*$	equilibrium partial pressure of CO_2, Pa
R_{CO_2}	CO_2 rate of reaction, $kmol/m^3\,sec$
R	gas constant, kJ/mol K

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