

A comparative study on the carbon dioxide capture power between 30 wt% 2-amino-2-methyl-1-propanol and 30 wt% methyldiethanol amine aqueous solutions

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Abstract—A comparative study has been performed to compare the 30 wt% of 2-amino-2-methyl-1-propanol (AMP) aqueous solution and 30 wt% of methyldiethanol amine (MDEA) aqueous solution to capture carbon dioxide contained in the flue gas stream. The equilibrium constants for each electrolyte reactions have been used to estimate the carbon dioxide absorption process. Henry's constants for each binary pairs between solute gases and solvent have been used to estimate solubility of the gas components.

Key words: Carbon Dioxide Capture, Electrolytes, 2-Amino-2-methyl-1-propanol, Methyldiethanol Amine

INTRODUCTION

Carbon dioxide coming out from the combustion of fossil fuel has been known as a greenhouse gas that is mainly responsible for global warming. According to the Kyoto protocol [1], it is obvious that Korea has to decrease 5.2% of greenhouse gas emission from 1990 levels from the year of 2013. Table 1 shows the list of the greenhouse gases and their greenhouse potential [1]. According to Table 1, although the greenhouse potential of carbon dioxide is lowest among the gases, its effects on global warming are huge due to its great amount of emissions into the atmosphere.

Up to now, several methods have been developed to reduce CO₂ emission [2-4]. Among them, one of the most efficient ways of capturing CO₂ coming out from the flue gas outlet stream is to use an absorber and regenerator process scheme by using an absorbing solvent such as aqueous amine solution [5-11], aqueous ammonia solvent [12], nearly pure methanol solvent [13] or AMP aqueous solvent [14,15]. Fig. 1 presents a typical process flow diagram for a CO₂ capture process using aqueous amine solution [16]. In Fig. 1, a flue gas stream, which contains CO₂, is introduced into the bottom of the absorber column where it is contacted counter-currently with aqueous amine solution flowing down from the top of the column. CO₂ in the flue gas is selectively absorbed into the amine solution, where the rich amine leaving the bottom of the absorber. In the re-

generator, the CO₂ is stripped from the rich amine solution by direct steam reboiling. Water is condensed at the overhead condenser and used to be refluxed the column. CO₂ that is vented from the reflux drum is saturated with water [17].

Carbon dioxide capture process by the use of aqueous amine solution has many advantages over other capturing processes using nonaqueous solvents. Fig. 2 shows a schematic flow diagram of CO₂ capture process using the nearly pure methanol as a solvent [13]. According to Fig. 2, the CO₂ capture process with methanol solvent needs a methanol-water separation column in addition to an absorber and regenerator. Furthermore, methanol solvent supply temperature should be sufficiently low to -20 °C, which cannot be cooled down enough with cooling water and its scheme needs additional refrigeration cycle illustrated in Fig. 3. Fig. 4 shows another process scheme to capture CO₂ using aqueous ammonia solution [12]. According to Fig. 4, the CO₂ capture process with aqueous ammonia solvent needs an additional ammonia capture column as well as a refrigeration cycle due to the high volatility of ammonia. On the other hand, the CO₂ capture process with AMP aqueous solution is exactly the same as the process using aqueous amine solution as a solvent. Since this process is using the same process scheme as shown in Fig. 1, the process is superior to the other processes that are using a methanol solvent or aqueous ammonia solution in the aspects of the initial investment cost and the utility cost such as steam consumption and the refrigeration cost.

In this study, process simulation was performed for the CO₂ capture process that is uses 30 wt% AMP aqueous solution as a solvent. In addition, the optimum feed stage was determined to minimize the heat duty of the reboiler in regenerator. To compare the CO₂ capture ability and energy consumption of the process between 30 wt% of the AMP aqueous solution and 30 wt% MDEA aqueous solution, the solvent to feed ratio versus the CO₂ absorption ratio was compared.

THEORY

Electrolyte equilibrium reactions between AMP, MDEA, carbon

Table 1. List of greenhouse gases and greenhouse potentials [21]

Component	Greenhouse potential
CO ₂	1
CH ₄	21
N ₂ O	310
HFCs	1,300
PFCs	7,000
SF ₆	23,000

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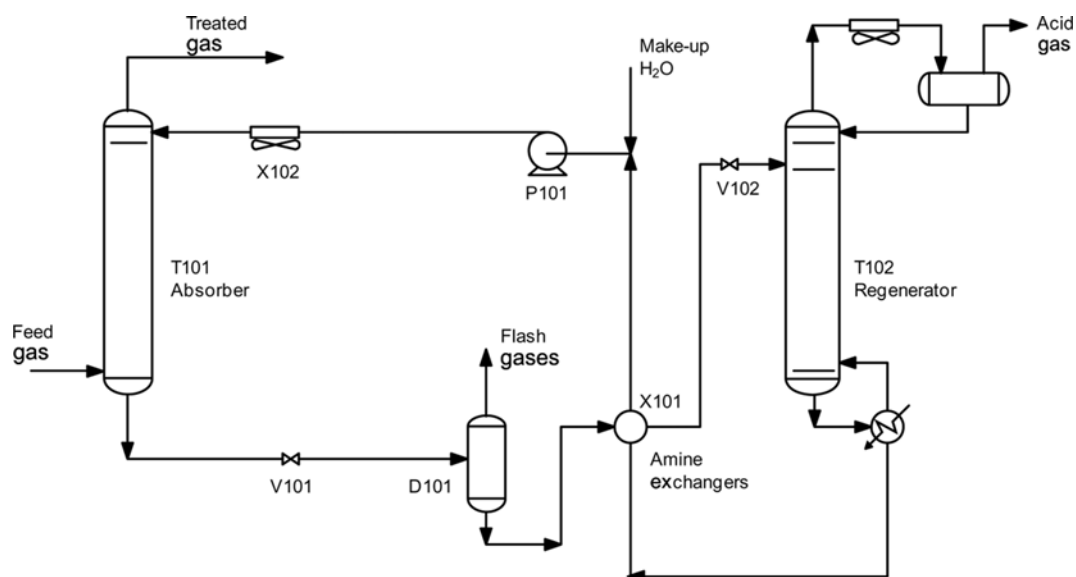


Fig. 1. Schematic diagram for an absorber-regenerator to capture CO₂ using aqueous amine solution.

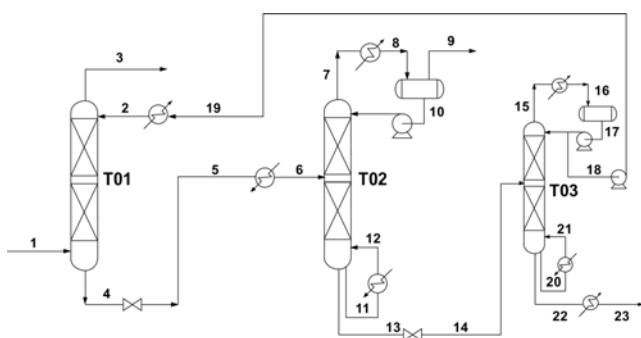


Fig. 2. Schematic diagram for a CO₂ capture process using a methanol solvent.

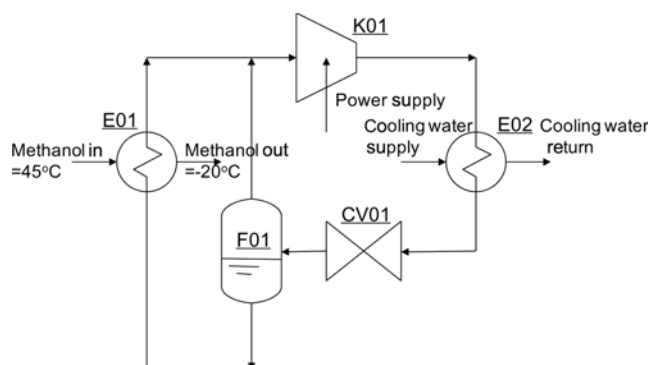


Fig. 3. Schematic diagram for a refrigeration cycle to cool down the methanol solvent using propylene refrigerant.

dioxide and water can be expressed in Eqs. (1) through (5) [18-20].

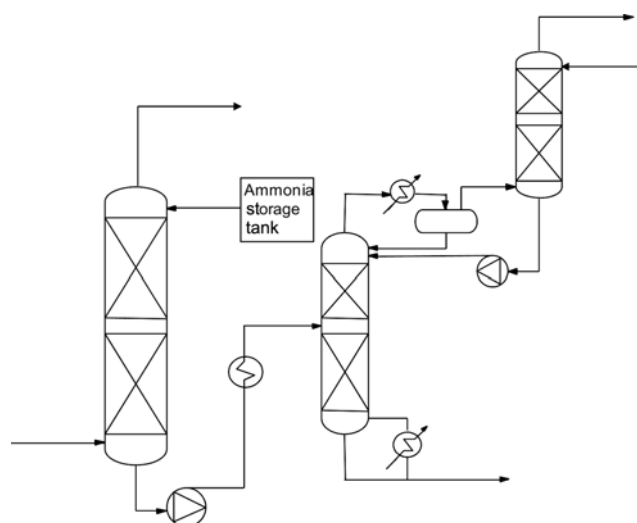


Fig. 4. Schematic diagram for a CO₂ capture process using an aqueous ammonia solution as a solvent.



The K_i 's in Eqs. (1) through (5) are electrolyte reaction equilibrium constants. These are expressed in temperature dependent form as shown in Eq. (6).

$$\ln K_i=A_i+B_i/T+C_i\ln T \quad (6)$$

In Eq. (6), A_i , B_i and C_i are the coefficients of temperature dependent terms in each reaction equilibrium constants and these values of the coefficients are listed in Table 2.

Constituents contained in the flue gas are N₂, O₂ and CO₂. The solubilities of CO₂, N₂ and O₂ in water can be expressed with Henry's law. According to Henry's law, the solubilities of non-condensable supercritical gases in water are proportional to pressure and inversely

proportional to temperature. Therefore, the Henry constant can be expressed in Eq. (7) as a function of temperature and pressure.

Table 2. Coefficients in equilibrium constants for each electrolyte equilibrium reactions [22]

	A_i	B_i	C_i
K_1	132.89888	-13,445.9	-22.4773
K_2	231.465439	-12,092.1	-36.7816
K_3	216.050446	-12,431.7	-35.4819
K_4	-9.4165	-4,234.98	0.0000
K_5	-3.68672	-6,754.686	0.0000

Table 3. Coefficients in Henry's law constant for each solute-solvent pairs [22]

	$C_{1,i}$	$C_{2,i}$	$C_{3,i}$	$C_{4,i}$
O_2 -H ₂ O	155.5533	-7,442.2900	-20.2359	1.7186×10^{-6}
N_2 -H ₂ O	158.2643	-7,260.1400	-20.7005	1.4409×10^{-6}
CO_2 -H ₂ O	154.9498	-8,498.7200	-20.0841	7.3032×10^{-6}

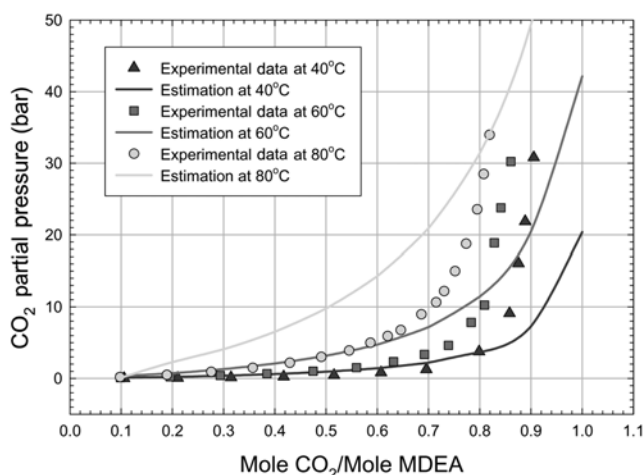


Fig. 5. Experimental CO₂ absorption equilibrium and its prediction at 40 °C, 60 °C and 80 °C, respectively [23].

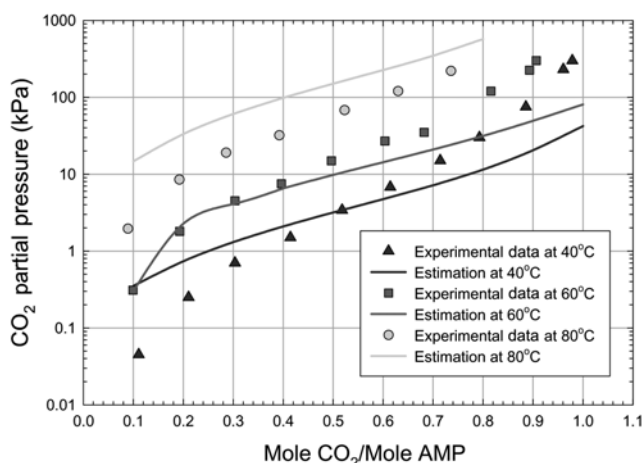


Fig. 6. Experimental CO₂ absorption equilibrium and its prediction at 40 °C, 60 °C and 80 °C, respectively [24].

$$\ln H_i = C_{1i} + C_{2i}/T + C_{3i} \ln T + C_{4i} P \quad (7)$$

The solubilities of CO₂, N₂ and O₂ in water can be estimated by using Eq. (7), and the coefficients of temperature and pressure dependent terms are summarized in Table 3.

In Fig. 5 and Fig. 6, the estimated result of the model equation applied in this study was compared with the experimental data of absorption equilibrium for CO₂ with 30 wt% MDEA aqueous solution and 30 wt% AMP aqueous solution at several isotherms. According to Fig. 5, the partial pressure of CO₂ at gas phase increases as CO₂ loading (CO₂ moles/MDEA moles) increases. From this it could be known the CO₂ loading value for acquiring the desired degree of CO₂ absorption. Furthermore, it could be known that the partial pressure of CO₂ for the same CO₂ loading increases as the absorption equilibrium temperature increases. These trends are also similar in AMP aqueous solution as shown in Fig. 6.

PROCESS SIMULATION

1. Absorber Simulation

CO₂ absorption capability in solvent can be determined by the following variables.

1. Solvent feed temperature to the absorber
2. Absorber operating pressure
3. Solvent circulation rate
4. Solvent concentration
5. Type of solvent
6. Absorber column height

Since the solubility of non-condensable supercritical gases in liquid solvent increases as temperature decreases and pressure increases by Henry's law, absorption ability of CO₂ by solvent increases at the lower temperatures and higher pressures.

In this study, the operation pressure of the absorption column was set to 1.1 bar of near atmospheric pressure, and the supply temperature of the absorption agent was set to 45 °C, which is possible with water as cooling medium. Moreover, the concentration of absorption agent was set to the 30 wt% aqueous solution for AMP and MDEA. Since the theoretical number of the stages was set to 5, variables for the CO₂ absorption capability are the molar circulation flow rate of solvent to the molar flow rate of flue gas. The temperature, pressure, composition and flow rate of flue gas that are used in this study are listed in Table 4. Fig. 7 shows the molar flow ratio of solvent to the molar flow rate of flue gas versus the CO₂ absorption ratio expressed in percent in the absorber column between 30 wt% MDEA aqueous solution and 30 wt% AMP aqueous solution. Ac-

Table 4. Flue gas conditions

Component	mol%
H ₂ O	9.80
CO ₂	8.34
O ₂	5.10
N ₂	76.76
Total (mol%)	100.00
Temperature (°C)	80.0
Pressure (bar)	1.50
Flow (Nm ³ /h)	350.0

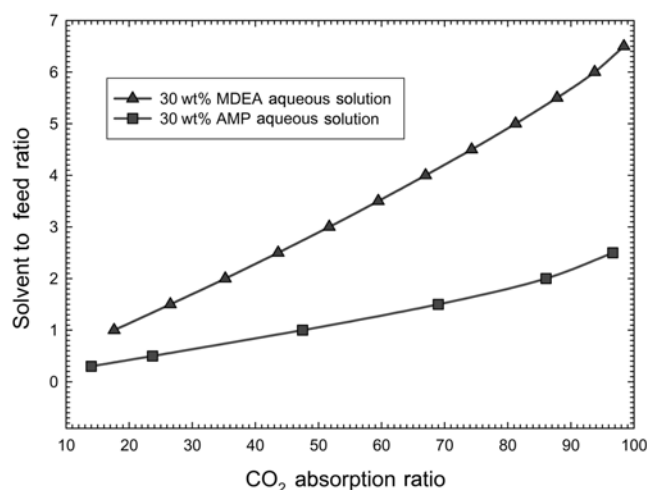


Fig. 7. A comparison of CO₂ absorption power between 30 wt% of MDEA aqueous solution and 30 wt% of AMP aqueous solution.

cording to Fig. 7, solvent to feed (S/F) ratio using 30 wt% AMP aqueous solution is lower than the 30 wt% MDEA aqueous solution for the all range of the CO₂ absorption ratio. This means the CO₂ capture ability as a solvent of 30 wt% AMP aqueous solution is superior to the 30 wt% MDEA aqueous solution.

2. Regenerator Simulation

Rich solvent stream coming out from the bottom of the absorption column is supplied to the middle section of the regenerator after exchanging heat with the lean solvent stream obtained as a regenerator bottom product. CO₂ is vented to be recovered as a top vapor stream from the regenerator. The lean solvent stream as a bottom product of the regenerator exchanges heat with the rich solvent stream coming out from the bottom of the absorber, and is recycled to the top of absorption column after cooling down to 45 °C by cooling water. Fig. 8 shows the flow sheet of CO₂ capture process with AMP

Table 5. Operating conditions of the absorber

Item	Value
Theoretical tray number	5
Flue gas feed location	Bottom
Lean solvent feed location	Top
Lean solvent feed temperature (°C)	45.0
Top pressure (bar)	1.1
Column pressure drop (bar)	0.1

Table 6. Operating conditions of the regenerator

Item	Value
Theoretical tray number	12
Rich solvent feed location	Middle
Overhead reflux drum temperature (°C)	Top
Overhead reflux drum pressure (bar)	45.0
Condenser pressure drop (bar)	0.1
Column pressure drop (bar)	0.2
Cooling water supply temperature (°C)	32
Cooling water return temperature (°C)	40
Steam temperature (°C)	130

and MDEA aqueous solution using Aspen Plus release 2006.5. According to Fig. 8, same amount of water content that is removed with CO₂ at top gas streams of stripper in stream 7 are supplemented at stream 11. Operating conditions of the stripper are summarized in Table 6. The theoretical number of stripper stages was assumed as 12, the same as the typical amine recovery column. The operating pressure of the overhead reflux drum was set to 1.1 bar as near atmospheric pressure, and pressure drop of condenser and column was assumed as 0.1 bar and 0.2 bar respectively. Operating temperature of the overhead reflux drum was set to 45 °C that is able to be cooled with water. Supply temperature of cooling water was

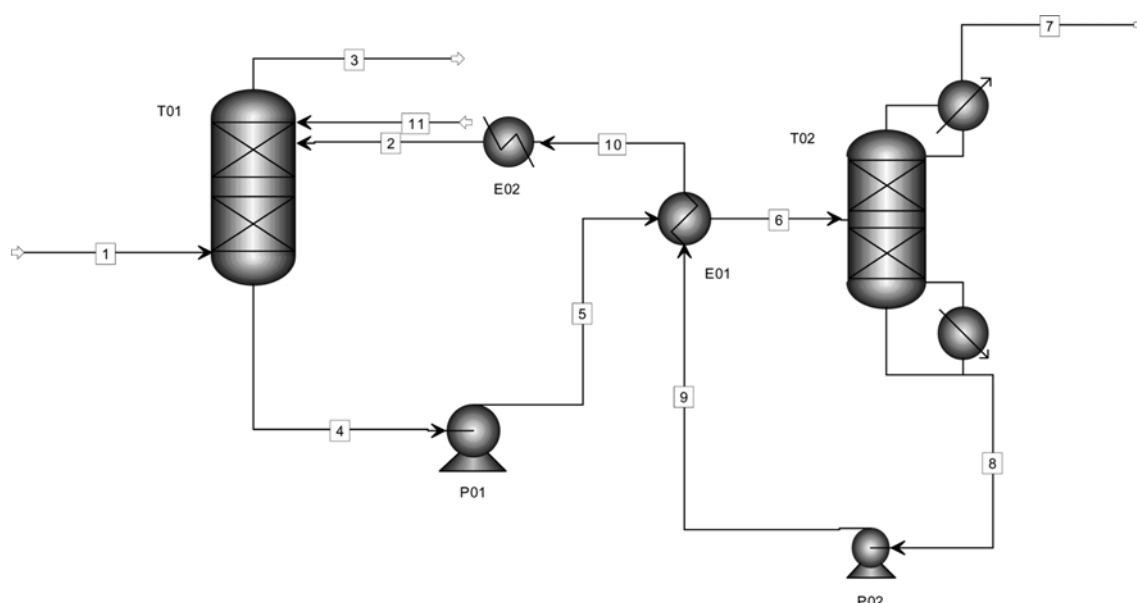


Fig. 8. Process flow sheet drawing for CO₂ capture process using aspen plus.

set to 32 °C and recovery temperature was 40 °C. The supply temperature to the reboiler was set to 130 °C. Feed stage of the lean solvent was determined at mid-stage by optimization to minimize the reboiler heat duty.

RESULTS AND DISCUSSION

The heat and mass balances for the CO₂ capture process with 30 wt% AMP aqueous solution in this study are summarized in Table 7. According to the mass balance, the degree of CO₂ removal was 95% and recycle ratio of solvent for the feed gas was 2.364 on molar base. Since the recycle ratio of the solvent as mole ratio for feed

gas in case of the degree of CO₂ absorption is 5.895 for the case of using 30 wt% MDEA aqueous solution as shown in Fig. 7, the AMP aqueous solution is superior to MDEA aqueous solution in the CO₂ capture ability by its lower recycle ratio of 40.1% of MDEA aqueous solution. Table 8 summarizes the simulation results to each solvent. According to Table 8, S/F ratio is 2.364 for case 1 and 5.895 for case 2 for the same condition in which the degree of CO₂ absorption is 95%. Heat duty of condenser in stripper is −343,037 kJ/h for case 1 and −1,780,890 kJ/h for case 2. In addition, the consumption of cooling water is 10.24 ton/h for case 1 and 45.46 ton/h for case 2, where case 2 consumed 4.44 times more cooling water than case 1. The heat duty of reboiler in stripper was determined

Table 7. Heat and material balance around CO₂ capture process using 30 wt% AMP aqueous solution as a solvent

	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	80	45	62.65	59.44	59.64	84.16	45.00	109.06	109.24	86.16
Press (Bar)	1.5	3.5	1.1	1.2	3.5	3.5	1.1	1.3	3.5	3.5
Mole flow (kmol/hr)	17.90	40.52	18.12	40.70	40.70	40.70	1.51	40.52	40.52	40.52
Mass flow (kg/hr)	562.69	973.53	529.24	1036.09	1036.09	1036.09	62.56	973.53	973.53	973.53
Vol. flow (m ³ /hr)	350	1.00	459.28	1.01	1.01	1.04	36.17	1.05	1.05	1.03
Enthalpy (10 ⁶ kcal/hr)	−0.23471	−2.7892	−0.20057	−2.93699	−2.9368	−2.91696	−0.13326	−2.73497	−2.73479	−2.75463
Mole flow (kmol/hr)										
H ₂ O	1.754678	37.06492	3.432373	35.86302	35.86304	35.86948	0.133521	37.06571	37.06572	37.06519
CO ₂	1.493267	8.25E-07	0.074658	0.001114	0.001131	0.007588	1.33758	0.000296	0.000301	4.37E-05
N ₂	0.913149	0	0.913138	1.12E-05	1.12E-05	1.12E-05	1.12E-05	4.63E-17	0	0
O ₂	13.74379	1.95E-07	13.70342	0.040365	0.040365	0.040365	0.040365	2.00E-07	2.00E-07	1.95E-07
AMP	0	3.226725	0.000487	1.494716	1.496704	1.711155	1.01E-34	3.280806	3.280919	3.262392
AMP ⁺	0	0.147247	0	1.879256	1.877267	1.662817	0	0.093166	0.093053	0.11158
H ₃ O ⁺	0	2.51E-11	0	1.42E-09	1.43E-09	4.19E-09	0	7.58E-10	7.65E-10	2.42E-10
HCO ₃ [−]	0	0.015967	0	0.955843	0.957797	1.159349	0	0.068965	0.069067	0.051326
OH [−]	0	0.001152	0	0.000108	0.000109	0.000122	0	0.000664	0.000662	0.000929
CO ₃ ^{−−}	0	0.065064	0	0.461652	0.459681	0.251673	0	0.011768	0.011662	0.029663
Mole Frac.										
H ₂ O	0.098	0.914707	0.189382	0.88124	0.88124	0.881259	0.088338	0.91472	0.91472	0.914713
CO ₂	0.0834	2.04E-08	0.004119	2.74E-05	2.78E-05	0.000186	0.884949	7.31E-06	7.42E-06	1.08E-06
N ₂	0.051	0	0.050383	2.76E-07	2.76E-07	2.76E-07	7.43E-06	1.14E-18	0	0
O ₂	0.7676	4.82E-09	0.756089	0.000992	0.000992	0.000992	0.026706	4.94E-09	4.94E-09	4.82E-09
AMP	0	0.079631	2.69E-05	0.036729	0.036778	0.04204	6.65E-35	0.080965	0.080968	0.080511
AMP ⁺	0	0.003634	0	0.046178	0.046129	0.040853	0	0.002299	0.002296	0.002754
H ₃ O ⁺	0	6.20E-13	0	3.49E-11	3.52E-11	1.03E-10	0	1.87E-11	1.89E-11	5.97E-12
HCO ₃ [−]	0	0.000394	0	0.023487	0.023535	0.028483	0	0.001702	0.001704	0.001267
OH [−]	0	2.84E-05	0	2.67E-06	2.67E-06	2.99E-06	0	1.64E-05	1.63E-05	2.29E-05
CO ₃ ^{−−}	0	0.001606	0	0.011344	0.011295	0.006183	0	0.00029	0.000288	0.000732

Table 8. Computer modeling results comparison

Item	Case 1 (30 wt% AMP solution)	Case 2 (30 wt% MDEA solution)
S/F Ratio	2.364	5.895
Regenerator condenser duty (kJ/h)	−343,037	−1,780,890
Regenerator reboiler duty (kJ/h)	547,026	2,428,452
Cooling water consumption (Ton/h)	10.24	45.46
Steam consumption (kg/h)	261	1,159
E01 duty (kJ/h)	83,066	238,007
E02 duty (kJ/h)	−144,745	−344,619

by optimization of feed stage in both case; the heat duty of reboiler was 547,026 kJ/h for case 1 and 2,428,452 kJ/h for case 2, where the case 2 is 4.44 times much more than case 1. The steam consumption was 261 kg/h for case 1 and 1,159 kg/h for case 2. On the other hand, E01 heat exchanger could be regarded as heat recovery process since it does not need extra utility. Case 1 recovered 83,066 kJ/h and case 2 recovered 238,007 kJ/h. From this result, case 2 seems to give superior result than case 1. However, case 2 needed a bigger heat exchanger than case 1, which means initial equipment cost is high and is not economic. In addition, heat duty of E01 heat exchanger that is using lean solvent cooler is -144.745 kJ/h for case 1 and -344,619 kJ/h for case 2, where case 1 is smaller than case 2.

CONCLUSIONS

Computational simulations have been completed for the CO₂ capture process by use of reaction equilibrium model among the water, AMP, MDEA and CO₂ components using Aspen Plus general purpose chemical process simulator, and the proper selection of the thermodynamic model to model the CO₂ capture process was proposed. The performance of CO₂ capture was compared between the 30 wt% AMP aqueous solution and 30 wt% MDEA aqueous solution. As a result of the simulation, we found that AMP aqueous solution is a superior solvent to MDEA aqueous solution.

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NOMENCLATURE

A	: coefficients in Eq. (6)
B	: coefficients in Eq. (6)
C	: coefficients in Eq. (6)
C ₁	: coefficients in Henry's law constant in Eq. (7)
C ₂	: coefficients in Henry's law constant in Eq. (7)
C ₃	: coefficients in Henry's law constant in Eq. (7)
C ₄	: coefficients in Henry's law constant in Eq. (7)
H	: Henry constant in Eq. (7)
K	: electrolyte reaction equilibrium constants in Eq. (1)-(6)
P	: pressure [kPa]
T	: absolute temperature [K]

Subscripts

i : component i

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