

A comparative study of carbon dioxide capture capabilities between methanol solvent and aqueous monoethanol amine solution

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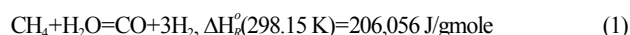
Abstract—Simulations have been performed to compare the performance of CO₂ capture power between 98.5 wt% methanol solvent and 30 wt% MEA aqueous solution. A general purpose chemical process simulator, PRO/II with PROVISION release 8.3 was used for the modeling of CO₂ capture process. For the simulation of CO₂ capture process using methanol as a solvent, NRTL liquid activity coefficient model was used for the estimation of the liquid phase non-idealities, Peng-Robinson equation of state model was selected for the prediction of vapor phase non-idealities, and Henry's law option was chosen for the prediction of the solubilities of light gases in methanol and water solvents. Amine special thermodynamic package built-in PRO/II with PROVISION release 8.3 was used for the modeling of CO₂ capture process using MEA aqueous solution. We could conclude that the 30 wt% of MEA aqueous solution showed better performance than the 98.5 wt% methanol solvent in CO₂ capture capability. Through this study, we tried to compare the differences between the two processes from the aspects of capital and operating costs using a commercial process simulator. This will guide the optimal process design in the carbon dioxide capture process.

Key words: CO₂ Capture Process, Simulation, Modeling, Thermodynamic Model

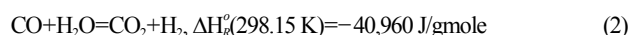
INTRODUCTION

Carbon dioxide, which comes from the various chemical processes, is mainly responsible for the global warming and it should be removed before being emitted to the atmosphere. Until recently, several methods have been developed to reduce CO₂ emission [1-3]. Among them, one of the most efficient ways of capturing CO₂ from the flue gas outlet stream is to use an absorber and a regenerator scheme by using a solution such as an aqueous amine solution [4-9], an aqueous ammonia solution [10], nearly pure methanol solvent [11] or 2-amino-2-methyl-1-propanol (AMP) aqueous solution [12-14].

Methane reforming is the reaction of methane with water vapor to form carbon monoxide and hydrogen as shown in Eq. (1).



The standard heat of reaction in Eq. (1) is 206,056 J/gmole and its positive value means the reforming reaction is highly endothermic. CO obtained from the reforming reaction reacts with water vapor to give CO₂ and H₂ as shown in Eq. (2).



The shift reaction in Eq. (2) is exothermic.

Table 1 shows the conditions of the exit stream of the reactor after the reforming and shift reaction. Due to its greenhouse effect, it is necessary to remove CO₂ before it is emitted to the atmosphere, and the CO₂ capture process modeling by using solution was con-

Table 1. The reaction effluent stream entering to the absorber

Component	Flow rate
H ₂	36.30
CO	33.62
CH ₄	0.18
CO ₂	26.57
H ₂ O	16.84
Total flow (kmol/h)	113.51
Temperature (°C)	118
Pressure (kPa)	6,000

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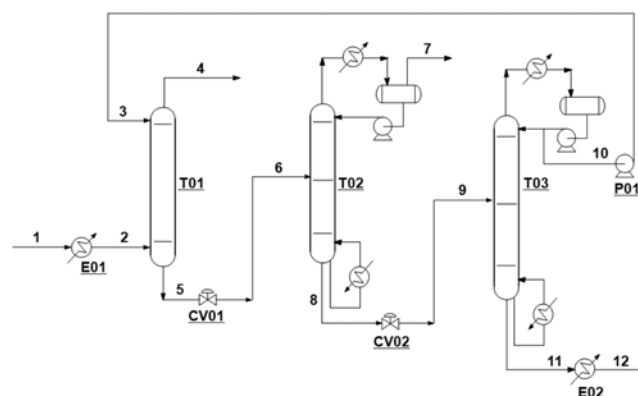


Fig. 1. A schematic diagram for the CO₂ capture process using methanol as a solvent.

sidered in this study. We evaluated the CO₂ capture capability for both 98.5 wt% of methanol solvent and 30 wt% of monoethanol amine (MEA) aqueous solution.

Fig. 1 shows a typical CO₂ capture process configuration using methanol as a physical solution. Inlet gas stream containing CO₂ is cooled down to 45 °C by a heat exchanger, E01, before it enters the CO₂ absorption column, T01, and then enters the bottom of the absorber which is operating at 6,000 kPa. A methanol solution enters the top of the absorber to contact with the acid gas stream counter-currently. The flow rate of an aqueous methanol solution is manipulated to absorb 95% CO₂ contained in the feed gas stream. The CO₂-removed sweet gas is emitted to the atmosphere at the top of the absorber. The rich solvent at the bottom of the absorber enters the middle stage of CO₂ stripper, T02, after pressure is reduced by pressure-reducing valve. The operating pressure of the CO₂ stripper is 4,000 kPa. CO₂ is removed as a top vapor stream in the stripper and the slightly diluted methanol solution is withdrawn as a bottom stream of the stripper. The bottom stream of the stripper goes into the methanol-water separation column, T03, which is operating at atmospheric pressure. A 98.5 wt% of methanol solution stream is separated as a top product of the methanol-water separation column and is refluxed to the top of the absorber after being pressurized by pumping. Water stream containing methanol under 500 ppm is obtained as a bottom product and is sent to the wastewater treatment facilities.

Fig. 2 shows a typical process configuration for the CO₂ capture process using a 30 wt% of MEA aqueous solution. The primary difference in a process configuration between Figs. 1 and 2 is that the methanol-water separation column is not necessary for the configuration in Fig. 2. In Fig. 2, the feed mixture is cooled to 45 °C by a heat exchanger before it enters the absorber. The 30 wt% MEA aqueous solution enters the top of the absorber to dissolve CO₂ selectively by a counter-current contact with the feed gas stream. In this case, the flow rate of a 30 wt% MEA aqueous solution is manipulated to absorb 95% of CO₂ in the feed gas. The operating pressure of the absorber is 6,000 kPa, which is relatively high pressure. The rich solvent withdrawn as a bottom stream of the absorber enters the stripper after reducing the pressure. CO₂ is removed selectively as a top vapor stream and the lean solvent at the bottom of stripper

is recycled to the top of the absorber after being cooled to 45 °C. In this study, utility consumption, the flow rate of the absorption solutions and the initial investment costs were compared for the two process configurations, respectively.

THERMODYNAMIC THEORY

Two-model approach was applied to predict the liquid phase non-idealities for methanol and water mixture and to estimate the vapor phase non-idealities due to the high operating pressure of the absorber. Basic principle for the two-model approach is shown in Eq. (3).

$$\hat{\phi}_i y_i P = \gamma_i x_i P_i^{\text{vap}} \quad (3)$$

Fugacity coefficient for a component 'i' in a mixture was introduced to estimate the vapor phase non-idealities. On the other hand, activity coefficient was introduced for the liquid phase non-idealities prediction. We can re-write the above Eq. (3) to estimate the solubilities of light gases like H₂, CO, CO₂ and CH₄ in methanol and water solvents by introducing Henry constants in Eq. (4).

$$\hat{\phi}_i y_i P = \gamma_i x_i H_i(T, P) \quad (4)$$

The activity coefficient of a component 'i' in the liquid phase can be estimated by NRTL liquid activity coefficient model suggested by Renon and Prausnitz as in Eq. (5) [15]. We used PRO/II with PROVISION releases 8.3, which is a general-purpose commercial process simulator supplied by Invensys [16].

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right] \quad (5)$$

The τ_{ij} and G_{ij} in Eq. (5) are the regressed optimum binary interaction parameters to minimize deviations from each experimental data and they can be expressed by Eq. (6) and (7).

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (6)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (7)$$

In these equations, temperature T is an absolute temperature and there are five interaction parameters of a_{ij} , a_{ji} , b_{ij} , b_{ji} and α_{ij} including temperature dependent terms for each binary pairs. The NRTL activity coefficient model was used for non-ideality of water-methanol solution in liquid phase. The methanol-water binary interaction parameters of NRTL liquid activity coefficient model for experimental gas-liquid phase equilibrium data are listed in Table 2. The objective function for the estimation of experimental vapor-liquid phase equilibrium data was determined to minimize the deviation

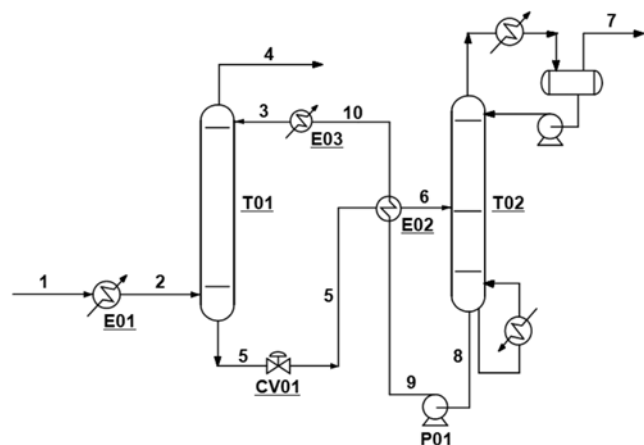


Fig. 2. A schematic diagram for the CO₂ capture process by using a 30 wt% MEA aqueous solution.

Table 2. The NRTL binary interaction parameters for methanol and water (Embedded in the PRO/II with PROVISION release 8.3)

Component 'i'	Component 'j'	a_{ij} a_{ji}	b_{ij} b_{ji}	α_{ij}
Methanol	Water	0.736107 0.511068	-360.692 199.854	0.2442

of boiling-point temperature and gas-phase composition with experimental data at the given temperature-composition vapor-liquid phase-equilibrium data at constant pressure. Pattern search algorithm suggested by Nelder and Mead was used for the optimization [17]. The objective functions are shown in Eqs. (8) and (9):

$$\text{Objective 1} = \left[\sum_{j=1}^N \left(\frac{T_j^{\text{exp}} - T_j^{\text{cal}}}{T_j^{\text{cal}}} \right)^2 + \sum_{j=1}^N \left(\frac{y_j^{\text{exp}} - y_j^{\text{cal}}}{y_j^{\text{cal}}} \right)^2 \right] / N \quad (8)$$

$$\text{Objective 2} = \left[\sum_{j=1}^N \left(\frac{x_j^{\text{I,exp}} - x_j^{\text{I,cal}}}{x_j^{\text{I,cal}}} \right)^2 + \sum_{j=1}^N \left(\frac{x_j^{\text{II,exp}} - x_j^{\text{II,cal}}}{x_j^{\text{II,cal}}} \right)^2 \right] / N \quad (9)$$

The fugacity coefficients of arbitrary component 'i' in gas phase mixture as in Eq. (3) can be written as in Eq. (10):

$$\ln \hat{\phi}_i = -\ln Z - \int_{\infty}^V \left[\left(\frac{\partial(nZ)}{\partial n_i} \right)_{T, V, n_{j \neq i}} - 1 \right] \frac{dV}{V} \quad (10)$$

Peng-Robinson equation of state as shown in Eq. (11) is applied to Eq. (10):

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) - v(v-b)} \quad (11)$$

Both sides of Eq. (11) can be multiplied by v/RT to apply to Eq. (10) as shown in Eq. (12):

$$Z = \frac{v}{v-b} - \frac{av/RT}{v(v+b) - v(v-b)} \quad (12)$$

Parameters a and b are energy and size parameters which are the functions of critical temperature and pressure as in Eqs. (13) and (14):

$$a = 0.45723 \frac{R^2 T_c^2}{P_c} \quad (13)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (14)$$

If they are applied to mixture, the energy and size parameters can be rewritten as in Eqs. (15) and (16):

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \quad (15)$$

$$b_{\text{mix}} = \sum_i x_i b_i \quad (16)$$

In Eq. (15), a_{ij} is energy parameter between 'i' and 'j' and can be written as in Eq. (17):

Table 3. The binary interaction parameters in energy parameter for the Peng-Robinson equation of state (Embedded in the PRO/II with PROVISION release 8.3)

Component 'i'	Component 'j'	k_{ij}
H ₂	CO	0.0900
H ₂	CO ₂	-0.1622
H ₂	CH ₄	0.0160
H ₂	N ₂	-0.0300
CO	CO ₂	-0.0300
CO	CH ₄	0.0300
CO	N ₂	0.1200
CO ₂	CH ₄	0.0919
CO ₂	N ₂	-0.0170
CH ₄	N ₂	0.0350

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (17)$$

In Eq. (17), k_{ij} is binary interaction parameter between components 'i' and 'j' to estimate non-ideal phase behavior among H₂, CO, CO₂ and CH₄ which are main components in gas phase. Its values are shown in Table 3.

Since components H₂, CO, CO₂ and CH₄ are light gases, Henry's law will be used to estimate the solubility of these components with respect to methanol and water as shown in Eq. (18):

$$\ln H_i(T, P) = C_1 + C_2/T + C_3 \ln T + C_4 P \quad (18)$$

Table 4 shows the coefficients of Henry's constant for the light gases CO, CO₂, H₂, CH₄ and N₂ with respect to water and methanol solvent.

THE SIMULATION OF CO₂ CAPTURE PROCESS

1. The CO₂ Capture Process by Using Methanol as a Solution

The role of column, T01, in Fig. 1, is to absorb CO₂ component selectively contained in the feed gas stream by methanol as a solution. The absorbing performance of solvent for CO₂ capture can be determined by several factors as listed below.

- The operation pressure of the absorber
- The number of theoretical stages of the absorber
- The circulation rate of the solution
- The supply temperature of the solution
- The concentration of the solution

Table 4. The parameters of the Henry's law (temperature in K, pressure in kPa) (Embedded in the PRO/II with PROVISION release 8.3)

Solute	Solvent	C ₁	C ₂	C ₃	C ₄
CO	H ₂ O	166.6723	-7,847.1602	-21.899	9.8692E-7
CO	CH ₃ OH	8.8170	1,144.4000	0.000	0.0000
CO ₂	H ₂ O	154.9483	-8,498.7197	-20.084	7.3032E-6
CO ₂	CH ₃ OH	217.0283	-10,620.0000	-30.136	0.0000
H ₂	H ₂ O	116.4133	-4,881.3198	-14.788	3.5529E-6
H ₂	CH ₃ OH	15.5643	271.3300	-0.549	0.0000
CH ₄	H ₂ O	169.8923	-8,132.2300	-22.356	1.4409E-6
CH ₄	CH ₃ OH	-63.1517	2,617.0000	11.520	0.0000

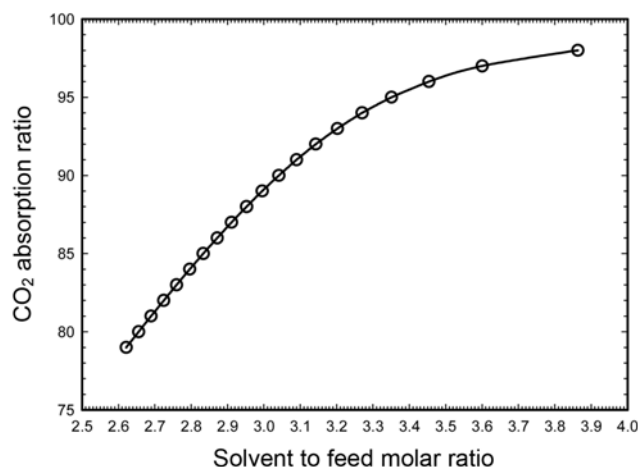


Fig. 3. A relation between CO₂ absorption ratio versus solvent to feed molar ratio.

The operation pressure of the absorber was fixed to 6,000 kPa and the number of theoretical stages was assumed to 10 stages. The supply temperature of the solution was set to 45 °C. The concentration of a methanol in the solution was set to 98.5 wt%, and the flow rate of the solution was determined to absorb 95% of CO₂. According to Fig. 3, when the molar flow rate ratio of solution to feed is 3.35, CO₂ absorption is 95%.

The operating pressure of the CO₂ stripper was fixed at 3,000 kPa, and the number of theoretical stages was set to 12 stages including overhead condenser and bottom reboiler. The temperature of the overhead reflux drum was set to 45 °C, which is the temperature cooled by cooling water. The CO₂ content in the lean solvent stream was fixed to 1,000 ppm by mole. The operation pressure of the methanol-water separation column was atmospheric pressure, the methanol purity at the top of the column was fixed to 98.5 wt% and the methanol content as an impurity at the bottom of the column was 500 ppm mole. Fig. 4 shows the relation between reflux ratio and

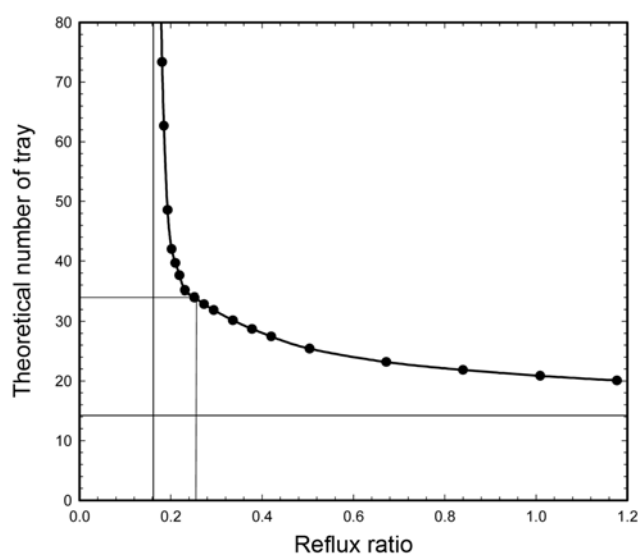


Fig. 4. The relation of the number of theoretical stage with respect to reflux ratio in the methanol-water separation column.

Table 5. The simulation result of the CO₂ capture process by using methanol solution

Column name	T01 (CO ₂ Absorber)
- Solvent to feed ratio	3.35
- CO ₂ absorption ratio	95%
- Methanol concentration	98.5 wt%
- Theoretical number of stage	10
Column name	T02 (CO ₂ Stripper)
- Condenser duty	-1.2961×10^6 kJ/hr
- Reboiler duty	7.0711×10^6 kJ/hr
- CO ₂ capture ratio for feed stream	95%
- Theoretical number of stage	12
Column name	T03 (Methanol Separation Column)
- Condenser duty	-16.8487×10^6 kJ/hr
- Reboiler duty	11.1037×10^6 kJ/hr
- Methanol purity at column top	98.5 wt%
- Methanol content at column bottom	500 ppm mol
- Theoretical number of stage	34

the number of theoretical stages for the methanol-water separation column. Fig. 4 shows that the reflux ratio is inversely proportional to the theoretical number of stages. Judging from Fig. 4, the optimal theoretical stages are located around the stages number.

Table 5 shows the simulation results for the CO₂ capture process by using a 98.5 wt% methanol solution. To absorb 95% CO₂ of the feed at the absorber, the flow rate ratio of solvent to feed was 3.35. The heat duty of the condenser at the CO₂ stripper was -1.2961×10^6 kJ/hr and the heat duty of reboiler was 7.0711×10^6 kJ/hr. The most part of absorbed CO₂ at the absorber is removed at the stripper as a top vapor stream. To maintain the purity level of methanol solution with 98.5 wt%, a methanol-water separation column is necessary. Since the heat duties of condenser and reboiler in the separator are -16.8487 kJ/hr and 11.1037×10^6 kJ/hr, the utility cost is much higher than for the stripper. Furthermore, the number of theoretical stages of the separator is 34 stages, which demand much higher initial invest cost than the stripper of 12 stages.

2. The CO₂ Capture Process by Using a 30 wt% MEA Aqueous Solution

In Fig. 2, a simulation was performed for the absorption process

Table 6. The simulation result of the CO₂ capture process by using 30 wt% MEA solution

Column name	T01 (CO ₂ Absorber)
- Solvent to feed ratio	2.83
- CO ₂ absorption ratio	95%
- MEA concentration	30.0 wt%
- Theoretical number of stage	10
Column name	T02 (CO ₂ Stripper)
- Condenser duty	-6.5839×10^6 kJ/hr
- Reboiler duty	8.9486×10^6 kJ/hr
- CO ₂ capture ratio for feed stream	93.7%
- Theoretical number of stage	12

which absorbs 95% CO₂ of feed by CO₂ capture process with 30 wt% MEA solution. The process has two column arrangements of absorber and stripper. The simulation result for the CO₂ capture process by using 30 wt% MEA solution are summarized in Table 6. The flow rate ratio of solvent to feed is 2.83 to absorb 95% CO₂ at the stripper, which is lower than the case of the methanol solution. This means the MEA solution is superior to the methanol solution as a CO₂ capture solution.

CONCLUSION

Comparative studies have been performed to absorb CO₂ from the product of the reforming reaction in the three-column arrangement by using 98.5 wt% methanol solution and in the two-column arrangement by using 30 wt% MEA solution. The thermodynamic models for the CO₂ capture process by using the methanol solution were the NRTL liquid activity coefficient model for the non-ideality of the liquid phase between water and methanol, the Peng-Robinson equation of state for the non-ideality of gas phase and the Henry's law for the estimation of solubilities of light gases such as H₂, CO, CO₂ with respect to water and methanol solution. The thermodynamic model for the CO₂ capture process by MEA solution was Amine special package.

In this study, we could conclude as:

First, the ratios of solvent to feed (S/F ratio) which can compare the performance of CO₂ capture solvent were 3.35 for the methanol solution and 2.83 for the MEA solution; this means MEA solution is superior to the methanol solution.

Secondly, the total heat duty of the reboiler for 95% CO₂ capture was 18.1748×10⁶ kJ/hr for methanol solution and the heat duty of reboiler at the stripper was 8.9486×10⁶ kJ/hr, which is half of the case of methanol solution.

Finally, since the case of the methanol solution needs total three columns and the MEA solution case needs only two columns, this means the MEA solution is superior to the methanol solution from the viewpoint of initial investment cost.

ACKNOWLEDGEMENT

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NOMENCLATURE

T : absolute temperature [K]
 P : pressure [kPa]
 ΔH_R^0 : the standard heat of reaction [J/gmole]

$\hat{\phi}_i^v$: the fugacity coefficient of component i in a mixture
 γ_i : the activity coefficient of component i in a solution
 H_i : Henry constant of component i
 x_j, x_k : liquid mole fraction of component j and k
 $a_{ij}, a_{ji}, b_{ij}, b_{ji}$ and α_{ij} : binary interaction parameters in NRTL model
 Z : compressibility factor
 a : energy parameter
 b : size parameter
 T_c, P_c : critical temperature and critical pressure
 C_1, C_2, C_3 and C_4 : the coefficients in Henry's constant

Subscripts

i : component i

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