Simulation for Absorption of Acid Gas into Piperazine Promoted Methyl Diethanolamine Solution Using Sieve Tray Column

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Abstract. The removal of CO₂ and H₂S gas is a crucial process in the sweetening of natural gas. One of the processes for taking these gases is reactive absorption using piperazine (PZ) promoted methyl diethanolamine (MDEA) solution. The absorption process is carried out in the sieve tray column to avoid liquids distribution problems in large diameter columns. No research discusses the acid gas absorption process simulation in the MDEA-PZ system using a sieve tray column. Therefore, this research simulates the acid gas absorption process in the MDEA-PZ system using a sieve tray column with a rate based modeling approach. The development of the rate-based model is based on the Film model's theory. The effect of the reaction on the mass transfer coefficient is expressed by the enhancement factor. The diffusion interaction of the components in the mixture is expressed by the Stefan-Maxwell equation. The research’s main objective is to observe the effect of lean amine temperature and absorber pressure on the percentage removal of CO₂ and H₂S. The simulation prediction results showed the highest percentage of CO₂ and H₂S removal when the lean amine temperature was 60°C and the absorber pressure was 35 atm.

1. Introduction

In recent years, there has been increasing interest in developing carbon dioxide (CO₂) and hydrogen sulfide (H₂S) removal technologies due to their impact on global warming and climate change, mainly due to CO₂ emissions [1]. Besides, CO₂ and H₂S are abundant in natural gas exploration. Natural gas is an alternative resource that has high CO₂ and H₂S content, so it requires a separate process before further processing. As impurities, CO₂ and H₂S can become corrosive in the presence of water and cause damage to gas pipelines.

There are many CO₂ and H₂S removal processes including adsorption, absorption, cryogenic, microbes and algae, membrane technology [2]. The absorption method is the most widely used and most effective method. In the absorption process, absorbents that function as solvents for CO₂ and H₂S are needed. The selection of the most effective absorbent takes into account many factors, both in terms of selectivity, effectiveness, conditions, and optimal operating costs. Several absorbents are commonly used including methyl ethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA). Of the three absorbents, MDEA has good selectivity in removing CO₂ and H₂S, has a good capacity, and has a very low vapor pressure. For this reason, MDEA is the most widely used solvent in gas treating [3]. However, MDEA has the lowest reaction rate when compared to MEA and DEA. Therefore we need an additional promoter (piperazine) to speed up the reaction.
rate.

Modeling and simulation for absorption CO₂ and H₂S are needed to assist in planning the absorber unit on an industrial scale in detail which includes mass transfer, energy requirements, and operating conditions so that optimal conditions are achieved. Several studies have been conducted regarding the modeling and simulation of absorption in MDEA solutions. Among them is Borhani, et al [4] who explains the use of a rate-based model in reactive absorption between CO₂ and H₂S with MDEA solution in a packed column, Falahat, et al [5] which uses the RATEFRAC module of Aspen Plus for modeling acid gas in MDEA solution.

2. Method

The research was carried out theoretically by developing a mathematical model of the absorption process of acid gas using piperazine promoted MDEA solution with a natural gas feed. The system studied is a sieve tray column absorber which is used in the petroleum and natural gas industries [6][7][8].

2.1. Data of Reaction Kinetics

The reaction system that occurs between CO₂-H₂S-MDEA-PZ is as follows:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + \text{MDEA} & \rightleftharpoons \text{MDEAH}^+ + \text{HCO}_3^- \\
\text{H}_2\text{S} + \text{MDEA} & \rightleftharpoons \text{MDEAH}^+ + \text{HS}^- \\
\text{CO}_2 + \text{PZ} + \text{H}_2\text{O} & \rightleftharpoons \text{PZH}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- + \text{OH}^- & \rightleftharpoons \text{H}_2\text{O} + \text{CO}_3^{2-} \\
\text{H}_2\text{O} + \text{MDEA} & \rightleftharpoons \text{MDEAH}^+ + \text{OH}^- \\
\text{PZ} + \text{H}^+ & \rightleftharpoons \text{PZH}^+ \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- 
\end{align*}
\]

2.2. Data of Reaction Equilibrium

The equilibrium constant data for the reaction of CO₂ and H₂S with MDEA-PZ solutions are as follow:

\[
\begin{align*}
K_1 = \frac{k_{\text{CO}_2}}{k_{\text{MDEA}}} \quad [6] \\
K_2 = \frac{k_{\text{H}_2\text{S}}}{k_{\text{MDEA}}} \quad [6] \\
\ln K_4 K_7 = 220,067 - \frac{12431.7}{T} - 35,4819 \ln T \quad [7] \\
\ln K_5 = 6,018 - \frac{4794.1}{T} - 1,6744 \ln T \\
K_6 = 11,91 - \frac{4351}{T} \quad [8] \\
\log_{10} K_7 = 185,52 - \frac{11988}{T} + 0,061656T \quad [7]
\end{align*}
\]

For the absorber system, the equation for the reaction speed coefficient for CO₂ gas to MDEA solution, using experimental results according to the general model, is estimated by the Arrhenius
While the reaction rate coefficient for $\text{H}_2\text{S}$ gas to MDEA solution is as follows:

$$k_{\text{H}_2\text{S}} = 10k_{\text{MDEA}}$$  \hfill (16)

### 2.3. Data of Component Solubility

The gas solubility data in MDEA-PZ solution is obtained from Henry's law:

$$P_A^* = \frac{\text{HeC}_A^*}{C}$$  \hfill (17)

By considering the resistance on the liquid and gas side, to get the $\text{CO}_2$ concentration at the interface can be obtained from the following equation:

$$C_{Ai} = \frac{k_{G} y_A P + E_k L C_A^0}{E_k + k_{G} \text{He}}$$  \hfill (18)

Where the Henry constant data in pure water ($\text{He}^0$) at temperature $T$ of each gas component can be obtained using the following equation:

$$\text{He}_T^0 = \text{He}_{298}^0 \exp \left( -\frac{d \ln \text{He}^0}{d(\frac{1}{T})} \left( \frac{1}{T} - \frac{1}{298} \right) \right)$$  \hfill (19)

$$\log \frac{\text{He}}{\text{He}^0} = h_1 I_1 + h_2 I_2$$  \hfill (20)

The Henry constant value for pure water at $T = 298$ K for each gas component can be seen in Table 1.

| Component | $\text{He}_{298}^0$ (mol/cm$^3$atm) | $-\text{dln kH}/d (1/T)$(K) |
|-----------|----------------------------------|-----------------------------|
| $\text{CO}_2$ | 3,6x10$^{-3}$ | 2200 |
| $\text{H}_2\text{S}$ | 1x10$^{4}$ | 2000 |
| $\text{N}_2$ | 6,1x10$^{-7}$ | 1300 |
| $\text{CH}_4$ | 1,4x10$^{-6}$ | 1600 |
| $\text{C}_2\text{H}_6$ | 1,9x10$^{-6}$ | 2300 |
| $\text{C}_3\text{H}_8$ | 1,5x10$^{-6}$ | 2700 |
| $\text{C}_4\text{H}_{10}$ | 1,2x10$^{-6}$ | 3100 |
| $\text{C}_5\text{H}_{12}$ | 1,1x10$^{-6}$ | 3500 |
| $\text{C}_6\text{H}_{14}$ | 1x10$^{-6}$ | 4000 |

Whereas $h_1$ and $h_2$ are constants which are the sum of the $h$ values of positive ion and negative ion
species and gas species.

\[ h = h^* + h^* + h_G \]  \hspace{1cm} (21)

\[ h^* (\text{MDEAH}^+) = 0.041 \text{ dm}^3/\text{mol} \]
\[ h^* (\text{CO}_3^{2-}) = 0.021 \text{ dm}^3/\text{mol} \]
\[ h_G (\text{HCO}_3^-) = 0.021 \text{ dm}^3/\text{mol} \]

For the temperature-dependent \( h_G \) constant \((T)\) it can be calculated using the equation:

\[ h_G = h_{G,0} + h_T (T-298,15) \]  \hspace{1cm} (22)

\( h_G \) and \( h_T \) values for each component can be seen in Table 2.

**Table 2.** Value of \( h_G \) and \( h_T \) for each component [10]

| Component | \( h_{G,0} \) (mol/cm\(^3\) at) | \( h_T \) (mol/cm\(^3\) at) |
|-----------|-------------------------------|-----------------------------|
| CO\(_2\)  | -17.2                         | -0.338                      |
| H\(_2\)S  | -33.3                         | -0.299                      |
| N\(_2\)   | -1                            | -0.605                      |
| CH\(_4\)  | 2.2                           | -0.524                      |
| C\(_2\)H\(_6\) | 12                         | -0.601                      |
| C\(_3\)H\(_8\) | 24                         | -0.702                      |
| C\(_4\)H\(_10\) | 29.7                  | -0.815                      |
| C\(_5\)H\(_12\) | 33.5                     | -0.922                      |
| C\(_6\)H\(_14\) | 37.1                     | -0.971                      |

2.4. Data of Heat and Mass Transfer

The estimated coefficient of gas and liquid diffusion by (Taylor and Khrisna, 1993) [11]:

\[ D_{AB} = \frac{7 \times 10^{-8} \times 0.5 (\Phi B M) x T}{\mu_B \times V_A^{-0.6}} \]

\hspace{1cm} (23)

While the diffusivity of MDEA in solution is as follows:

\[ D_{\text{MDEA,L,} \muL}^{0.6} = (D_{\text{MDEA,H}_2\text{O,} \mu\text{H}_2\text{O}})^{0.6} \]  \hspace{1cm} (24)

The development of a mathematical model is carried out by making a mass balance on the tray column using a film model and the enhancement factor approach. The flux \((N_{i,z})\) of the dissolved gas \(i\) is obtained from the following equation:

\[ N_i = \frac{V_{in} Y_{i, in} - V_{in} Y_{i, out}}{a} = k_{G,i} (P_{i, blk} - P_{i, int}) = k_{L,i} E_i (C_{i, in} - C_{i, bulk}) \]  \hspace{1cm} (25)

Where \( k_{G,i} \) dan \( k_{L,i} \) are the coefficient of dissolved gas \(i\) in mass transfer for the gas and liquid phases. Whereas \( a \) is the area of the interface and \( E_i \) is the enhancement factor of dissolved gas \(i\). \( k_G \) in this study uses the equation:
Where:
\[ a_t = \frac{4}{d} \]  
(27)

In this study \( k_L \) uses an empirical equation proposed by Calderbank (1959), which is used for mass transfer of liquid and gas in a tray.

\[ k_L = 8.5 \times 10^{-5} \left( \frac{x}{\rho d^3} \right)^{\frac{1}{3}} \left( \frac{D_{AB}}{\mu} \right)^{\frac{1}{2}} \]  
(28)

According to Danckwertz [12], the specific interfacial area (a) on the tray is calculated using the following equation:

\[ a = 0.38 \left( \frac{\mu}{\mu_t} \right)^{0.775} \left( \frac{\mu \rho}{n d \mu} \right)^{0.125} \left( \frac{g \rho}{d \sigma} \right)^{\frac{1}{3}} \]  
(29)

3. Results and Discussion

From the simulation results of the absorption of acid gas into piperazine promoted methyl diethanolamine solution in the sieve tray column, several factors can influence the results of CO\(_2\) and H\(_2\)S removal, including lean amine temperature and absorber pressure.

The simulation for the effect of lean amine temperature on the percentage removal of CO\(_2\) and H\(_2\)S can be seen in Figure 1. The simulation was carried out with a piperazine concentration of 3%, a lean amine flow rate of 45.4 m\(^3\)/hour, and an absorber pressure of 30 atm.
Based on Figure 1. At lean amine temperature variations of 30 °C to 60 °C, there was an increase in the percentage removal of CO$_2$ of 5,372% from 57.923% to 63.295% and percentage removal of H$_2$S of 0.885% from 97.29% to 98.175%. This is because the increase in lean amine temperature can cause an increase in the rate of reaction so that the amount of CO$_2$ gas that reacts with the solvent increases and results in an increase in the percentage removal of CO$_2$ and H$_2$S [13].

However, temperature lean amine also affects the solubility of the gas. If the lean amine temperature increases, it will cause the solubility of the gas in the solution to decrease. This is because at high temperatures the gas molecules move faster so that it is easy to leave the solvent. Figure 1 shows that the effect of the reaction rate is greater than the effect of gas solubility on the percentage removal. Besides, an increase in temperature can cause an increase in the diffusivity constant of the gas. If the diffusivity constant of the gas increases, the mass transfer rate on the liquid side is easier so that it can increase the absorption rate.

Besides lean amine temperature, absorber pressure also affects the percentage removal of CO$_2$ and H$_2$S.

The effect of absorber pressure on the percentage removal of CO$_2$ and H$_2$S can be seen in Figure 2. The simulations were carried out when the piperazine concentration was 3%; lean amine temperature 312.15 K; lean amine flow rate 45.4 m$^3$/hour. At absorber pressure variations of 20 atm to 35 atm, there was an increase in the percentage removal of CO$_2$ of 23.956% from 42.594% to 66.55% and percentage removal of H$_2$S of 7.492% from 91.284% to 98.776%. This is because the increase in absorber pressure will cause the solubility of the gas in the solution to be greater. The greater the solubility of the gas will increase the diffusivity value so that the gas is forced to enter the solution. This is consistent with the literature which states that increased pressure will increase the separation efficiency in this type of tray column type [14].

4. Conclusions
Based on the results of the above discussion, it can be concluded that the increase in lean amine temperature and absorber pressure is directly proportional to the increase in the percent removal of CO$_2$ and H$_2$S. From the simulation results, the highest percent removal of CO$_2$ and H$_2$S was obtained when the lean amine temperature was 60 °C and the absorber pressure was 35 atm.

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