Modeling and simulation of CO₂ gas desorption process in promoted MDEA solution using packed column

A Ariani, A Chalim* and H Hardjono
Chemical Engineering Department, Politeknik Negeri Malang, Indonesia

*ariani.chalim@gmail.com

Abstract. Carbon dioxide (CO₂) gas at atmospheric pressure will tend to freeze, because of low temperature (-78°C), this results in frequent blockages in the piping section. In the process of synthesis of ammonia in the industry in the presence of a catalyst, CO₂ gas will be toxic because it can cover the active-side of the catalyst. The process of CO₂ gas absorption that is often used is reactive absorption using promoted solvent. The most commonly used solvent is a tertiary amine alkanol solution, one of which is a solution of Methylidethanolamin (MDEA) using a piperazine catalyst. The output solution from the absorption of CO₂ gas is processed by desorption to regenerate the solvent. CO₂ gas desorption process is needed to save the use of solvents and catalysts. The purpose of this research is to do modeling and simulation on the process of desorption of CO₂ gas from a promote MDEA solution using a packed column. Modeling assisted software media with a rate-based model approach using numerical equations with the completion of Ordinary Differential Equation (ODE) - 45. The data obtained was simulated and validated by comparing experimental data. The research parameters are the temperature of the input solution desorber, type and concentration of catalyst. Increasing the temperature of the solution and the concentration of the catalyst will increase the percent removal of CO₂. This is caused by the effect of the temperature of the solution on the value of the reaction rate constant, and the type of catalyst influences the catalyst reactivity level of CO₂ gas. The results of simulation data validation with experimental data show the average deviation of 22.05%, 14.24% and 7.85%.

1. Introduction
Carbon dioxide (CO₂) gas can disrupt processes in the chemical industry because CO₂ gas binds to the air in the form of corrosive acid gas in the piping system. In the Liquified Natural Gas (LNG) industry, CO₂ gas must be removed because at very low temperatures (-78°C, 1 atm) CO₂ will freeze and can clog the piping system and damage the tubing of the main heat exchanger. In the fertilizer industry, CO₂ gas is a byproduct of the process of making ammonia, where CO₂ gas is toxic to the catalyst which can cover the active site of the catalyst. This can inhibit the performance of the catalyst in the ammonia synthesis process [1,2].

The separation process using the absorption method is always integrated with the desorption process because it requires regeneration of the absorbent solvent which is called the desorption process. The process of absorption and desorption is a unitary system. CO₂ gas is absorbed by the solvent in the countercurrent absorber to produce a CO₂-rich solution then goes to the desorber. Before entering the desorber, the solution exchanges heat with a lean solution of CO₂ that comes out of the stripper to the absorber. CO₂ gas is removed from the rich solvent in the desorber column. The
desorption process takes place in three parts, namely in the desorber inlet, the packed column and the reboiler. Optimal conditions in the desorber are very important because the energy demand in the process is 80% of the operational costs in the absorption-desorption system [3].

Energy requirements in the desorption process require industry to optimize operating conditions in order to maximize desorption efficiency. Therefore, modeling and simulating the CO\textsubscript{2} desorption process in a promoted MDEA solution is needed to plan and know the details of the operation of the system. This requires some thermodynamic data and equations including mass and heat transfer, energy requirements according to operating conditions in order to achieve optimal conditions. Rochelle [4] has conducted research on the desorption process using several types of solvents, the best results are using MDEA solution with piperazine promoter. And also in 2009 modeling and simulation of CO\textsubscript{2} gas desorption from potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) solution promoted by piperazine (PZ) using a rate-based modeling approach [3].

In this research, modeling and simulation of CO\textsubscript{2} gas from methyl diethanolamine (MDEA) promoted by diethanolamine (DEA), Glycine (Gly) and Piperazine (PZ) was carried out using a rate-based modeling approach. Making mathematical models in this desorption process using Matlab with the temperature of the desorber entering solution is 353.15K, 358.15K and 363.15K; the promoter concentration is 3% by volume, 4% by volume and 5% by volume and the types of promoters are DEA, Gly and PZ. The CO\textsubscript{2} gas desorption from MDEA was 20% by volume with the addition of a promoter according to variables using a packed column. Then perform mathematical model validation by comparing the results of the calculation of prediction equation against the experimental data and theoretically study the effect of various process variables such as the inlet rich solution temperature, desorber column pressure, and inlet steam temperature on desorption efficiency.

2. Steam desorption
The feed of a stream of mixed solutions is heated and contacted with steam in a packed tower. Steam is injected through the bottom of the tower to provide heat of a vapor stream. Solution without CO\textsubscript{2} content exits through the bottom of the tower. The mixed solution is introduced through the top of the tower and steam containing organic matter exits through the top of the tower.

![Figure 1. Schematic diagram of desorption process.](image)

3. Reaction kinetic
The reaction mechanism of CO\textsubscript{2} gas desorption from MDEA solution using the PZ promoter is as follows [5-8].

\[
R_3NH^+ + HCO_3^- \overset{k_{26}}{\rightleftharpoons} CO_2 + R_3N + H_2O
\] (1)
\[ HCO_3^- \xrightleftharpoons{k_{21}} CO_2 + OH^- \] (2)

For the CO₂ (MDEA-PZ-H₂O) system the values of \( k_{21} \) and \( k_{26} \) can be estimated using the Arhenius equation, so that the following correlation is obtained. This correlation is in accordance with the experimental results carried out by Bishnoi dan Rochelle [1].

\[
k_{21} = 1.75 \times 10^4 \exp \left( \frac{-8.75 \times 10^4}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right)
\] (3)

\[
k_{26} = 1.55 \times 10^4 \exp \left( \frac{-8.75 \times 10^4}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right)
\] (4)

Based on research by Pawlak, et al. [5] regarding the study of the absorption kinetics of CO₂ gas in activated MDEA solution, the results show that basically the overall reaction between CO₂ and MDEA is as follows.

\[ CO_2 + R_3N + H_2O \xrightleftharpoons{k_{21}} R_3NH^+ + HCO_3^- \] (5)

So for the kinetics of CO₂ gas desorption in MDEA solution, the overall reaction is as follows.

\[ R_3NH^+ + HCO_3^- \xrightleftharpoons{k_{26}} CO_2 + H_2O + R_3N \] (6)

In an activated MDEA solution, the model of the stripping rate can be described as two parallel rapid pseudo-first-order reversible reactions and the overall reaction rate of CO₂ is.

\[
r = \left( k_a C_{am} + k_p C_p \right) \left( C_{CO_2,eq} - C_{CO_2} \right)
\] (7)

Where \( C_{am} \) and \( C_p \) are the concentrations of amine and piperazine. While the Arhenius plot value for \( k_p \) is given in the following equation.

\[
k_p = 2.98 \times 10^{11} \exp \left( -6424 / T \right)
\] (8)

### 4. Mathematical model

Rochelle, et.al [3] developed a mathematical model for CO₂ gas desorption in a PZ promoted K₂CO₃ solution in a packed column. The mathematical model was adopted and used in the CO₂ gas desorption process in a PZ promoted MDEA. Mass balance in each segment :

\[
\left( L_{ij-1} + V_{ij+1} \times y_{ij+1} \right) = L_{ij} + \left( V_{ij} \times y_{ij} \right)
\] (9)

Assuming the evaporation of amines is neglected, where \( L_{ij-1} = L_{ij} ; i = amine, j = segment \)

Total pressure on each segment :

\[
P_{CO_2,i} + P_{H_2O,i} = P_T ; \quad P_{CO_2} + P_{H_2O} = P_T
\] (10)

CO₂ which transfer in the liquid phase :

\[
N_{CO_2} = k'_g \times 1000 \times \left( P_{CO_2}^* - P_{CO_2,i} \right)
\] (11)

CO₂ which transfer in the gas phase :

\[
N_{CO_2} = k_g \times 1000 \left( P_{CO_2,i} - P_{CO_2} \right) + \left[ N_{CO_2} + N_{H_2O} \right] \frac{P_{CO_2,i} - P_{CO_2}}{P_T \ln \left( P_{CO_2,i}/P_{CO_2} \right)}
\] (12)

### 5. Methods

The research was carried out theoretically by developing a mathematical model of the CO₂ gas desorption process from a PZ promoted MDEA solution on an industrial-scale packed column. The research steps can be seen schematically in Figure 2.
Figure 2. Schematic diagram of the research steps.

5.1 Development of mathematical model
The development of a mathematical model is calculating by making a differential mass balance assuming an isothermal system. Differential mass balance:

\[ 0 = LC_A - L(C_A + dC_A) - \bar{R}A_adz + rlAdz \]  
\[ 0 = -L \frac{dC_A}{dz} - \bar{R}Aa + rlA \]  
\[ \bar{R}AaA = rlA \text{ (assuming no dissolved gases)} \]

The numerical solution used in this study is to use the orthogonal collocation method. This process produces a series of simultaneous algebraic equations. The equation is then solved by the Newton Raphson method:

\[ \% \text{ Efficiency} = \left[ 1 - \frac{C_{A_{\text{in}}}}{C_{A_{\text{out}}}} \right] \times 100\% \]

Simultaneous solving of mathematical models of differential equations is made in the Matlab program, based on the Ordinary Differential Equation (ODE) – 45 method. With this method, the gas composition exiting the column is iterated until the inlet gas composition meets the predetermined conditions and convergence can be achieved.

Validation is done by comparing the predicted simulation data with the real data from the equipment design.

6. Results and discussion
The CO₂ gas desorption simulation program has been created using Matlab with the formulation of a differential mass balance involving four main parameters, consist of reaction kinetics, reaction equilibrium, gas solubility data, and mass – heat transfer. The system is created using several assumptions, as follows:

- Steady-state system
- Adiabatic operation
- Evaporation of solvent is negligible
- Pressure across columns is constant
The reaction in the liquid phase and component transferred at the interface are only CO$_2$ and H$_2$O.

Validation of the simulation model that has been created using experimental data from the desorber column with the same system. Comparison of simulation data with experimental data after parameter fitting can be seen in Figure 3.

Validation is done by comparing the removal of each promoter with the same input variable, namely the temperature of the rich solution.

![Figure 3](image1.png)

**Figure 3.** Comparison of simulation data with experimental data on each promoter based on the temperature of the rich solution to CO$_2$ removal

Figure 3 shows the comparison of simulation data, namely lines and experimental data in the form of solid markers. Each promoter is marked with a different marker for PZ (▲), Glycine (♦) and DEA (■).

The determination of the CO$_2$ removal value is based on the CO$_2$ gas content in the liquid. In a system with DEA, Glycine and PZ promoters, the error is 22.05%, 14.24% and 7.85%, respectively. However, the reduction in error of each promoter can be due to the use of empirical correlation to estimate the thermodynamic properties and component displacements and the parameters associated with mass transfer that have been shown to be suitable [9].

6.1. Molar flow distribution of HCO$_3^-$, MDEAH $^+$, MDEA, H$_2$O and CO$_2$ to column height

![Figure 4](image2.png)

**Figure 4.** Distribution curves of molar flow liquid and molar distribution of gas phase to column height.

Figure 4 (a) Distribution of molar flow liquid HCO$_3^-$, MDEAH $^+$ and MDEA. (b) The molar distribution of H$_2$O and CO$_2$ gas flow to column height, rich solution rate (20% MDEA 5% DEA) 0.6 L / min, pressure 2 atm.
Based on the desorption reaction above, MDEA's molar flow in the liquid phase will gradually decrease from 0.1038 kmol / m²s to 0.0102 kmol / m²s starting from the bottom towards the top of the column and is called lean solution (solution with low CO₂ content).

Figure 4 (b) shows that as the desorption process progresses, the molar flow of CO₂ increases in contrast to H₂O which decreases from the bottom to the top of the column. This shows that high column affects the desorption process [10].

7. Conclusions

Based on the results of the simulation model, it can be concluded as follows:

- A mathematical model for the process of desorption of CO₂ gas from MDEA solution with promoters in the form of Piperazine (PZ), Glycine (Gly) and Diethanolamine (DEA) in a lab-scale packed column equipped with a condenser and a reboiler can be carried out.
- Validation of the mathematical model for the process of desorption of CO₂ gas from MDEA solution with promoters in the form of PZ, Gly and DEA in the packing column has been carried out from experimental data with the same system obtained an error of 22.05%, 14.24% and 7.85%.
- Several operating variables have been studied theoretically for their effect on column performance and it is stated that the model used can be accepted as a real process, although the accuracy still has errors.

Modeling and simulating the stripping process integrated with the absorption process to evaluate the overall performance of the CO₂ removal unit.

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