Modeling and Simulation of CO₂ Absorption into
Promoted Aqueous Potassium Carbonate Solution in
Industrial Scale Packed Column

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Abstract

Carbon dioxide gas is a harmful impurity which is corrosive and it can damage the utilities and the piping system in industries. Chemical absorption is the most economical separation method which is widely applied in chemical industries for CO₂ removal process. Hot potassium carbonate (K₂CO₃) is the most effective solvent that has been used extensively, especially for the CO₂ separation process from gas synthesis and natural gas. This paper aims to develop mathematical model for investigating the CO₂ absorption into promoted hot K₂CO₃ solution in industrial scale packed column in an ammonia plant. The CO₂ was removed from the gas stream by counter-current absorption in two stages column. To represent the gas-liquid system, a rigorous mathematical model based on the two-film theory was considered. The model consists of differential mass and heat balance and considers the interactions between mass-transfer and chemical kinetics using enhancement factor concept. Gas solubility, mass and heat transfer coefficients, reaction kinetics and equilibrium were estimated using correlations from literatures. The model was validated using plant data and was used to compute temperature and concentration profiles in the absorber. The variation of CO₂ recovery with respect to changes in some operating variables was evaluated. The effect of various kinds of promoters added into K₂CO₃ solution on the CO₂ recovery was also investigated. The simulation results agree well with the plant data. The results of the simulation prediction, for the absorber pressure of 33 atm with a lean flow rate of 32,0867 kg/h, temperature of 343 K, and semi lean flow rate of 2,514,122 kg/h, temperature of 385 K, showed %CO₂ removal of 95.55%, while that of plant data is 96.8%. © 2015 BCREC UNDIP. All rights reserved

Keywords: Reactive Absorption; packed column; industrial scale; carbon dioxide; promoter; multicomponents


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1. Introduction

Carbon dioxide (CO₂) needs to be separated from gas stream, especially in Petrochemical, oil, and natural gas industries, because CO₂ is an acid gas and corrosive which can damage the plant utility and the piping system. CO₂ can decrease the heating value of natural gas. In liquefied natural gas (LNG) refinery, CO₂ gas has to be removed because CO₂ will freeze at very low temperature so that can block the piping system and also can damage the tube in
the main heat exchanger. Instead of that, CO$_2$ is a byproduct of the ammonia industry. CO$_2$ is a poison to the ammonia synthesis catalyst [1], therefore CO$_2$ must be separated from the gas stream before heading to the ammonia synthesis unit.

A number of separation technologies could be employed for CO$_2$ capture. These include adsorption, physical absorption, chemical absorption, cryogenic separation and membranes [2,3]. Chemical absorption is the most practical and effective technique and is widely used in chemical and petrochemical industry [4,5]. Chemical absorption involves the reaction of CO$_2$ with a chemical solvent to form a weakly bonded intermediate compound which may be regenerated with the application of heat producing the original solvent and a CO$_2$ stream [6]. The selectivity of this form of separation is relatively high. In addition, a relatively pure CO$_2$ stream could be produced. These factors make chemical absorption well suited for CO$_2$ capture for industrial applications.

The biggest cost factor for CO$_2$ capture is the energy consumption for solvent regeneration, which can attain 49% of the total cost of CO$_2$ capture [7]. Another factor is the capacity of the solvent that can determine the amount of CO$_2$ absorbed per unit of solvent. Many solvents are used in the gas processing, but alkanolamine and “hot” K$_2$CO$_3$ solvents are the most effective solvents that can be used [8]. The advantage of alkanolamine is the rapid absorption rate and high solvent capacity. While the disadvantage of alkanolamine, mainly in primary and secondary groups, is the formation of a stable carbamate compounds and it requires high energy for regeneration. Moreover, it cannot separate the mercaptan compounds, the loss of a large vapor causes a high vapor pressure, degraded at overheating (>100 °C), and occur further reaction which produce by-products that cannot be degraded [9].

Potassium carbonate (K$_2$CO$_3$) aqueous solution has been used extensively, especially for the separation of CO$_2$ from gas synthesis and natural gas. Because it has a high stability, low cost, and energy consumption for solvent regeneration is low, but the reaction rate is slow compared to alkanolamine [10-12]. The addition of promoter in the K$_2$CO$_3$ aqueous solution can increase the CO$_2$ absorption process. Potassium carbonate solution with alkanolamine as a promoter show an effective way to improve the overall performance of solvents, especially at primary and secondary groups of alkanolamine [1, 13-17].

In industries, the process of CO$_2$ absorption occurs at high pressure. Several components beside CO$_2$ can be absorbed and interaction between the components can be occurred in the gas film and liquid film that affect the mass transfer process and chemical reactions. Reactive absorption involves various components of the gas mixtures and liquid mixtures that represent multicomponent system. The properties of mass transfer in the multicomponent system are more complex than the binary mass transfer. Furthermore, it is an industrial practice to use two stages column each with different diameter to meet certain hydrodynamic characteristic requirement. Most of previous models assume only one component which moves through the interface or single component absorption and use one stage column [1, 18-20].

The objective of this study is to develop a mathematical model of CO$_2$ absorption in industrial scale packed column, consisting of two stages, with different diameter of each, using promoted K$_2$CO$_3$ aqueous solution by considering the absorption of carrying gases and the multicomponent diffusion model was devised. To simplify the model, the concentration of species was defined based on the influent molal flow rate.

2. Theoretical Background

2.1. Reactions Kinetic and Absorption Rate

The following elementary reactions take place when CO$_2$ is absorbed in potassium carbonate and bicarbonate solution [11, 21]:

\[
\begin{align*}
\text{CO}_2 + \text{OH}^- & \leftrightarrow \text{HCO}_3^- \\
\text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^- + \text{H}^+ \\
\text{HCO}_3^- & \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \\
\text{H}_2\text{O} & \leftrightarrow \text{OH}^- + \text{H}^+ 
\end{align*}
\]

Reactions (2)-(4) are assumed always in equilibrium condition. The overall stoichiometric reaction can be represented in the following reaction,

\[
\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^-
\]

Reactions (2)-(4) are assumed always in equilibrium condition. The equilibrium constant of these reactions are available in the literature [22] and are expressed as follows:
Then,

\[ K_2 = \frac{C_{\text{HCO}_3^-} - C_{\text{H}^+}}{C_{\text{CO}_2^e}} = \exp\left(-\frac{12092.1}{T} - 36.7816 \ln T + 231.4\right) \]  

(7)

\[ K_3 = \frac{C_{\text{CO}_2^e} - C_{\text{H}^+}}{C_{\text{HC}_3O_5^-}} = \] 

\[ \exp\left(-\frac{124331.7}{T} - 35.4819 \ln T + 216.067\right) \]  

(8)

\[ K_4 = K_W = \frac{C_{\text{H}^+} C_{\text{DH}^-}}{C_{\text{HCO}_3^-}} = ] 

\[ \exp\left(-\frac{124445.9}{T} - 22.4773 \ln T + 132.932\right) \]  

(9)

From equations (7)-(9), the concentration of \( \text{OH}^- \) ion and equilibrium concentration of \( \text{CO}_2 \) in liquid phase can be obtained as follow:

\[ C_{\text{CO}_2^e} = \frac{K_3 C_{\text{HCO}_3^-}}{K_2 C_{\text{CO}_2^e}} \]  

(10)

\[ C_{\text{OH}^-} = \frac{K_W C_{\text{HCO}_3^-}}{K_2 C_{\text{CO}_2^e}} \]  

(11)

Reaction (1) is the rate controlling step for \( \text{CO}_2 \) absorption in hot \( \text{K}_2\text{CO}_3 \) solution. When the forward reaction is pseudo first order and reverse reaction rate is constant then the reaction rate can be expressed as follows [1, 11, 23]:

\[ \dot{n}_{\text{OH}} = k_{1,\text{OH}} \left( C_{\text{CO}_2^e} - C_{\text{CO}_2^2,\text{a}} \right), \quad k_{1,\text{OH}} = k_{\text{DH}} C_{\text{OH}} \]  

(12)

In Equation (12), is second order reaction rate constant of the forward reaction and is obtained from the following correlation [24]:

\[ k_{\text{OH}} = 2.53 \times 10^{11} e^{-\frac{4311}{T}} \]  

(13)

It is industrial practice to add promoter to the carbonate-bicarbonate solution to increase the reaction rate. The reaction between several types of promoters with \( \text{CO}_2 \) is given as follows. Reaction of \( \text{CO}_2 \) with primary and secondary amine follows zwitterion mechanism with the formation of zwitterion intermediate which react with any base, \( \text{B} \) to form carbamate and or bicarbonate. Reaction of \( \text{CO}_2 \) with monoethanolamine (MEA) [25, 26]:

\[ \text{CO}_2 + \text{RNH}_2 \leftrightarrow \text{RNH}_2^+ \text{COO}^- \]  

(14)

\[ \text{RNH}_2^+ \text{COO}^- + \text{B} \leftrightarrow \text{RNHCOO}^- + \text{BH}^+ \]  

(15)

\[ \text{RNHCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{RNH}_2^+ + \text{HCO}_3^- \]  

(16)

\[ K = \frac{C_{\text{RNH}_2^+ C_{\text{HC}_3O_5^-}}}{C_{\text{RNHCOO}^-}} = \exp\left(-3.4 - \frac{5851}{T}\right) \]

Reaction of \( \text{CO}_2 \) with diethanolamine (DEA) [14, 27, 28]:

\[ \text{CO}_2 + R_2\text{NH} \leftrightarrow R_2\text{N}^+ \text{HCOO}^- \]  

(17)

\[ R_2\text{NH}_2^+ \leftrightarrow R_2\text{NH} + \text{H}^+ \]

\[ K = \frac{C_{R_2\text{NH} C_{\text{H}^+}}}{C_{R_2\text{NH}_2^+}} \]

\[ \exp\left(-\frac{3071.15}{T} + 6.776904 \ln T - 48.7594\right) \]

\[ R_2\text{N}^+\text{HCOO}^- + \text{OH}^- \leftrightarrow R_2\text{NH} + \text{HCO}_3^- \]  

(18)

\[ K = \frac{C_{R_2\text{NH} C_{\text{HCO}_3^-}}}{C_{R_2\text{NHCOO}^- C_{\text{OH}^-}}} = \] 

\[ \exp\left(-\frac{17067.2}{T} - 66.8007 \ln T + 439.709\right) \]

Reaction of \( \text{CO}_2 \) with Arginine [29]:

\[ \text{CO}_2 + \text{H}_2\text{N} - \text{CHR}' - \text{COO}^- K' \leftrightarrow \text{COO}^+ \text{H}_2\text{N} \]
\[ -\text{CHR}' - \text{COO}^- K^+ \]  
(19)

\[ -\text{COO}^+ H_2 N - \text{CHR}' - \text{COO}^- K^+ + B \rightarrow -\text{COOH} N \]
\[ -\text{CHR}' - \text{COO}^- K^+ + BH^+ \]  
(20)

Reaction of CO\textsubscript{2} with boric acid can be described through the following mechanism [30]:

\[ B(OH)_3 \cdot H_2 O \leftrightarrow B(OH)_\bar{4}^- + H^+ \]  
(21)

\[ B(OH)_4^- + \text{CO}_2 \leftrightarrow B(OH)_4 \text{CO}_2^- \]  
(22)

\[ B(OH)_4 \text{CO}_2^- + H_2 O \leftrightarrow B(OH)_3 \cdot H_2 O + H\text{CO}_3^- \]  
(23)

Reactions (14), (17), (19) and (22) are the controlling step for the reaction between CO\textsubscript{2} with promoter MEA, DEA, Arginine and Boric acid respectively. When the forward reaction is pseudo first order and reverse reaction rate is constant then the reaction rate can be expressed as follows:

\[ r_{\text{cat}} = k_{\text{cat}} (C_{\text{CO}_2} - C_{\text{CO}_2,e}) \]  
(24)

where \( k_{\text{cat}} \) is second order reaction rate constant of the forward reaction and is obtained from Table 1.

If the operating condition of absorption process is in fast reaction regime, then, the absorption rate can be obtained from the following equation:

\[ N_{\text{CO}_2} a = E k_{\text{LCO}_2} a (C_{\text{CO}_2} - C_{\text{CO}_2,e}) \]  
(25)

where the enhancement factor (\( E \)) is obtained from Equation (26).

\[ E = H_a \]  
(26)

In Equation (26), \( H_a \) is Hatta number which can be obtained from equation (27) and \( k_{i} \) is overall pseudo first order reaction rate constant defined as Equation (28):

\[ H_a^2 = \frac{D_k}{D_{\text{LCO}_2}} \]  
(27)

\[ k_1 = k_{\text{OH}} C_{\text{OH}} + k_{\text{cat}} C_{\text{cat}} \]  
(28)

Fast pseudo first order reaction assumption is valid under the following condition:

\[ 3 < H_a < 0.5 E_{\infty} \]  
(29)

where \( E_{\infty} \) is enhancement factor for instantaneous reaction which can be obtained using film theory described in Equation (30):

\[ E_{\infty} = 1 + \frac{D_{\text{CO}_2} C_{\text{CO}_2}}{D_{\text{CO}_2} C_{\text{CO}_2}} \]  
(30)

### 2.2. Gas Solubilities

The solubility of gases in promoted carbonate solutions were estimated using modified Henry law with empirical model of Schumpe which describes the solubility of gases in mixed electrolytes solutions considering salting out effects:

\[ \log \left( \frac{H_{\text{e,jw}}}{H_{\text{e,j}}(T)} \right) = \sum (h_i + h_G) c_{i,L} \]  
(31)

where \( h_i \) is the ion-specific parameter (m\textsuperscript{3}/kmole), \( h_G \) is the gas-specific parameter (m\textsuperscript{3}/kmole) and \( c_{i,L} \) is the concentration of ion \( i \) (kmole/m\textsuperscript{3}). The Henry constant of gas-water system (can be obtained from Equation (32)):

\[ H_{\text{e,jw}}(T) = H_{\text{e,jw}}(298 K) \exp \left( \frac{-d \ln k_{\text{e}}}{d(1/T)} \left( \frac{1}{T} - \frac{1}{298} \right) \right) \]  
(32)

The value of \( H_{\text{e,jw}} \) (298 K) and \( -d \ln k_{\text{e}}/d(1/T) \) are shown in Table 2 [31]. Gas-specific parameter was extended from Equation (31) to wider temperature range using Weissenberger and Schumpe method [30] and expressed in Equation (33).

**Table 1. Second order reaction rate constant of various promoters**

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>( k_{\text{cat}} ) [m\textsuperscript{3}/kmole\textsuperscript{1}.s\textsuperscript{-1}]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MEA</td>
<td>( k_{\text{MEA}} = 4.24 \times 10^9 \text{e}^{-3925/T} )</td>
<td>[24]</td>
</tr>
<tr>
<td>2</td>
<td>DEA</td>
<td>( k_{\text{DEA}} = 5.65 \times 10^{11} \text{e}^{-5284.4/T} )</td>
<td>[19]</td>
</tr>
<tr>
<td>3</td>
<td>Boric Acid</td>
<td>( k_{\text{boric}} = 5.5 \times 10^{11} \text{e}^{-6927/T} )</td>
<td>[30]</td>
</tr>
<tr>
<td>4</td>
<td>Arginine</td>
<td>( k_{\text{Arg}} = 2.58 \times 10^{16} \text{e}^{-8645/T} )</td>
<td>[29]</td>
</tr>
</tbody>
</table>

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In equation (33), \( h_T \) is the temperature correction (m\(^3\)/kmole.K). The values of \( h_T \), \( h_i \), \( h_{G0} \), and \( h_T \) can be seen in Table 3 [32] and Table 4 [32, 33]. Equations (32) and (33) are substituted into Equation (31) to obtain the value of \( H_{e,j} \).

### 2.3. Mass and Heat Transfer Coefficient

Gas side mass transfer coefficient is obtained from the empirical correlation by Onda et al. [34] shown in Equation (34) where constant \( A \) equal to 2 for packing diameter less than 0.012 m and equal to 5.23 for packing diameter greater than 0.012 m.

\[
k_G = \frac{A}{RT} \left( R_{stg} \right)^{0.7} \left( S_{ctg} \right)^{1/3} (\alpha \ d_p)^{-2.0} (\alpha \ D_{kg})
\]

(34)

Reynold and Schmidt number are defined as, respectively:

\[
R_{eL} = \frac{L}{\alpha \ u_L} \quad \text{and} \quad S_{cl} = \frac{\mu_i}{\rho L \ D_{kl}}
\]

Liquid side mass transfer coefficient is obtained from the empirical correlation by Taylor and Krishna [35] shown in Equation (35):

\[
k_{Lk} = 0.0051 \left( \frac{R_{stL}}{R_{stL}^2 + S_{cl}^{1.05}} \right)^{-0.55} \left( \frac{\alpha \ d_p}{\rho u_L} \right)^{0.4} \left( \frac{D_{kl}}{\rho u_L} \right)^{1/3}
\]

(35)

The liquid Reynold and Schmidt number are defined as, respectively:

\[
R_{eL} = \frac{L}{\mu_L} \quad \text{and} \quad S_{cl} = \frac{\mu_i}{\rho L \ D_{kl}}
\]

Gas-liquid interfacial area per unit volume of packed column, \( a \), is obtained from packing specific area from the correlation provided by Onda et al. [34].

\[
\frac{a}{S} = 1 - \exp \left[ -1.45 \left( \frac{R_{stL}}{R_{stL}^2 + S_{cl}^{1.05}} \right)^{0.55} (R_{etL})^{-3.55} (W_{et})^{0.3} \right]
\]

(36)

In Equation (36), Froude and Weber number are defined as, respectively:

\[
F_{eL} = \frac{a \ L^2}{\rho L \ d_p \ g} \quad \text{and} \quad W_{eL} = \frac{L^2}{\rho L \ a_p \ g}
\]

Diffusion coefficient of species in gas phases was determined from binary diffusion coefficient using Maxwell-Stevan equation as follows:

\[
1 \frac{1}{D_{im}} = \sum \left( \frac{1}{D_{ij}} \right) (x_j N_i - x_i N_j)
\]

(37)

where the binary diffusion coefficient was obtained from correlation by Fuller et al. [36] recommended by Taylor and Krishna [35], Reid et al. [37], and also Daubert and Danner [38].

### Table 2. The values of \( H_{e,jw} \) (298 K) and \(-d \ln k_{ui} / d(1/T)\) for various gases [31]

<table>
<thead>
<tr>
<th>Component</th>
<th>( 1/H_{e,jw} ) ( (\text{kmole/m}^3\text{.Pa}) )</th>
<th>(-d \ln k_{ui} / d(1/T) ) ( \text{(K)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>3600</td>
<td>2200</td>
</tr>
<tr>
<td>CO</td>
<td>99</td>
<td>1300</td>
</tr>
<tr>
<td>H2</td>
<td>78</td>
<td>500</td>
</tr>
<tr>
<td>N2</td>
<td>61</td>
<td>1300</td>
</tr>
<tr>
<td>CH4</td>
<td>140</td>
<td>1600</td>
</tr>
<tr>
<td>Ar</td>
<td>140</td>
<td>1500</td>
</tr>
</tbody>
</table>

### Table 3. The value of gas parameters [32, 33]

<table>
<thead>
<tr>
<th>Component</th>
<th>( h_{G0} ) ( (\text{m}^3/\text{kmole}) )</th>
<th>( h_T ) ( (\text{m}^3/\text{kmole.K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>-1.72 \times 10^{-3}</td>
<td>-3.38 \times 10^{-7}</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H2</td>
<td>-2.18 \times 10^{-3}</td>
<td>-2.99 \times 10^{-7}</td>
</tr>
<tr>
<td>N2</td>
<td>-1 \times 10^{-6}</td>
<td>-6.05 \times 10^{-7}</td>
</tr>
<tr>
<td>CH4</td>
<td>2.2 \times 10^{-6}</td>
<td>-5.24 \times 10^{-7}</td>
</tr>
<tr>
<td>Ar</td>
<td>5.7 \times 10^{-6}</td>
<td>-4.85 \times 10^{-7}</td>
</tr>
</tbody>
</table>

### Table 4. The value of ion specific parameter [32, 33]

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>( h_i ) ( (\text{m}^3/\text{kmole}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K+</td>
<td>HCO(_3^-)</td>
<td>0.0922</td>
</tr>
<tr>
<td>MEAH(^+)</td>
<td>CO(_2^-)</td>
<td>0.0550</td>
</tr>
<tr>
<td>DEAH(^+)</td>
<td>Arg(^-)</td>
<td>0.0470</td>
</tr>
<tr>
<td>OH</td>
<td>MEACOO(^-)</td>
<td>0.0610</td>
</tr>
<tr>
<td>DEACOO(^-)</td>
<td>0.0540</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEACOO(^-)</td>
<td>0.0430</td>
</tr>
</tbody>
</table>
Due to dilute solution condition, diffusion coefficient of species in liquid phase was assumed binary with respect to water and determined using Wilke and Chang Equation [23]:

\[
D_{ij,G} = \frac{1 \times 10^{-7} T^{1.76} \left( \frac{1}{M_i} - \frac{1}{M_j} \right)}{P \left( \nu_i^{1/3} + \nu_j^{1/3} \right)^2}
\]

Heat transfer coefficient in gas phase was determined from mass transfer coefficient in gas phase using Chilton-Colburn analogy, while the heat transfer resistance in liquid phase was neglected.

3. Method

3.1 Mathematical Model

This study was conducted with the theoretical approach (simulation) by developing mathematical model for heat and mass transfer phenomena accompanied by chemical reaction in CO\textsubscript{2} removal process at non-isothermal condition using promoted K\textsubscript{2}CO\textsubscript{3} aqueous solution. The model is based on the following assumptions: steady state and adiabatic operations, plug-flow pattern for gas and liquid, neglected amount of solvent evaporation and constant pressure throughout the column. Thereaction in the liquid phase is fast enough for a substantial amount of the gas absorbed to react in the liquid film, rather than to be transferred unreacted to the bulk. Mathematical model development was conducted by constructing differential mass balances in the packed column. Figure 1 shows schematic diagram of packed bed absorption column showing an infinitesimal element for mass and energy balances.

Figure 1. Schematic diagram of packed bed absorption column showing an infinitesimal element for mass and energy balances
packed bed absorption column showing an infinitesimal element for mass and energy balances. Microscopic or differential mass and energy balance was constructed based on System I, while macroscopic balance to correlate several process variables in packed column was constructed through System II (see Figure 1).

Differential Mass Balances:

**System I**

\[
N_{\text{CO}_2} A \, dz = r_{\text{CO}_2} \phi_c A \, dz
\]

\[ \text{CO}_2 : \]  

\[ -L_i n dX_{\text{CO}_2} - \nu r_{\text{CO}_2} \phi L A \, dz = 0 \]

\[ \text{K}_2\text{CO}_3 : \]  

\[ \frac{dX_{\text{CO}_3^2}}{dz} = -\frac{\nu N_{\text{CO}_2} a A}{L_{in}} \]

(40)

(41)

(42)

(43)

When \( N_{\text{CO}_2} \) was substituted from Equation (25), then the following equation was obtained after some rearrangements:

\[ \frac{dX_{\text{CO}_2}}{d\zeta} = \frac{-\nu E k_{\text{LCO}_2} a C (x_{\text{CO}_2}^* - x_{\text{CO}_2}^0)}{L_{in}} Z_T A \]

\[ \text{where } \zeta = Z / Z_T \] and \( x_{\text{CO}_2}^0 = \text{CO}_2 / C \)

(44)

(45)

(46)

where \( N_i a \) was obtained from \( N_i a = k_{\text{LCO}_2} (C_i^* - C_i) \), and Equation (46) can be rearranged as follows:

\[ \frac{dX_k}{dz} = \frac{N_i a A}{L_{in}} \]

(47)

The concentration of bicarbonate ion was determined using stoichiometry as follows:

\[ X_{\text{HCO}_3^2} - X_{\text{HCO}_3^2,\text{in}} = 2 \left[ X_{\text{CO}_2^2,\text{in}} - X_{\text{CO}_2^2} \right] \]

(48)

The concentration of other species (expressed as mole ratio) in liquid phase was determined using equilibrium and electro neutrality constrain. Molar concentration of various species in liquid phase was determined from \( C_i = \chi_i C \), where mole-fraction, \( \chi_i \), was determined from mole ratio as follows:

\[ x_i = \frac{Y_i}{\sum X_k} \]

(49)

and molar density, \( C \), was calculated from liquid mass density as \( C = \rho / M \), where \( M \) is molecular weight of liquid mixture, \( M = \sum M_i \chi_i \), and \( \rho \) is its density which was obtained by regression fitting of data from literature [39] as follows:

\[ \rho_l = \rho_{l,293} + 17816.45 \left( \frac{1}{T} - \frac{1}{293} \right) \]

(50)

(51)

The presence of catalyst in the liquid phase does not affect significantly liquid density.

The concentration of \( \text{CO}_2 \) and carrying gases in the gas phase can be obtained by performing a mass balance over System II:

\[ \text{CO}_2 : \]  

\[ k \text{ (carrying gases):} \]  

\[ \text{CO}_2 \text{ concentration on the interface } (C_{\text{CO}_2}^*) : \]  

\[ C_{\text{CO}_2}^* = \frac{k_{G\text{CO}_2} y_{\text{CO}_2} \rho + E \, k_{L\text{CO}_2} C_{\text{CO}_2}^*}{E \, k_{L\text{CO}_2} + k_{G,C} H_C} \]

(52)

(53)

(54)

Concentration of other gases on the interface (\( C_k^* \)):

\[ C_k^* = \frac{k_{G,k} y_{\text{CO}_2} + k_{L,k} C_k}{k_{L,k} + k_{G,k} H_C} \]

(55)

Differential heat balance on the gas side is given in Equation (56):

\[ \frac{dT_G}{dz} = -\frac{h_G a}{C_p G} (T_G - T_L) \]

(56)

while liquid temperature was calculated from energy balance for System II:

\[ T_l = T_{L,\text{in}} + \frac{G C_p G}{C_{pl}} \left[ C_p (T_G - T_{G,\text{in}}) \right] \]

(57)
3.2. Numerical Solution

Equations (44) and (47) were solved numerically using orthogonal collocation method with 6 internal collocation points, thus:

\[
\frac{\Delta H_{mw}}{L \cdot C_{pl}} \left[ Y_{CO_2, \text{in}} - Y_{CO_2} \right]
\]

(57)

where \( N_0 \) was defined as:

\[
N_0 = \frac{h_{\ell} a \cdot Z_T}{C_{pl} \cdot G}
\]

(62)

The solution of nonlinear algebraic equation obtained from orthogonal collocation method was conducted by successive approximation method. Thus, % CO\(_2\) removal can be calculated by following equation:

\[
\% \text{Removal} = 1 - \frac{Y_{\ell, \text{out}}}{Y_{\ell, \text{in}}}
\]

(63)

4. Results and Discussion

This study was carried out by constructing a simulation program for CO\(_2\) gas absorption process with reversible reaction at non-isothermal condition. The system studied was packed column in a large-scale ammonia plant to remove CO\(_2\) from the process gas stream containing 18.47% CO\(_2\), 59.88% H\(_2\), 20.82% N\(_2\), 0.32% CH\(_4\), 0.25% CO and 0.25% mole Argon with flow rate of 204020 kg/h. The CO\(_2\) is removed from the gas stream by counter-current absorption in two stages column, lower part with diameter of 3.89 m and upper part with diameter of 2.365 m. The lower part column is filled with 7 cm IMPT packing to the height of 18.29 m, while the upper part is filled with 5 cm IMPT packing to the height of 15.85 m. Lean solution, containing 21.22 % K\(_2\)CO\(_3\) and 5.60 % KHCO\(_3\), was fed into the top of upper part column while semi lean solution containing 18.12 % K\(_2\)CO\(_3\) and 9.76 % KHCO\(_3\) was fed into the top of lower part column. To enhance the absorption rate, an amine promoter, DEA, was added into the carbonate-bicarbonate solution. It can be seen from Table 5 that for the same operating condition the predicted percent CO\(_2\) removal is 95.5465 compared to 96.8 % in the ammonia plant.

### Table 5. Comparison between simulation result and ammonia plant data

<table>
<thead>
<tr>
<th>Variable comparison</th>
<th>Simulation</th>
<th>Ammonia plant data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of gas (kg/h)</td>
<td>204020</td>
<td>204020</td>
</tr>
<tr>
<td>Flow rate of lean solution (kg/h)</td>
<td>320867</td>
<td>320867</td>
</tr>
<tr>
<td>Flow rate of semi lean solution (kg/h)</td>
<td>2514122</td>
<td>2514122</td>
</tr>
<tr>
<td>Temperature of gas (K)</td>
<td>362</td>
<td>362</td>
</tr>
<tr>
<td>Temperature of lean solution (K)</td>
<td>343</td>
<td>343</td>
</tr>
<tr>
<td>Temperature of semi lean solution (K)</td>
<td>385</td>
<td>385</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Promoter</td>
<td>DEA</td>
<td>DEA</td>
</tr>
<tr>
<td>CO(_2) removal (%)</td>
<td>95.3465</td>
<td>96.8</td>
</tr>
</tbody>
</table>

4.1. Concentration Distribution in Packed Column

Predicted concentration distribution of dissolved gases, K\(_2\)CO\(_3\) and KHCO\(_3\) in liquid phase in packed column can be seen in Figures 2-4. Figure 2 shows that the concentration of CO\(_2\) gas in the liquid increases because it is absorbed by K\(_2\)CO\(_3\) aqueous solution from 0 (no CO\(_2\) in K\(_2\)CO\(_3\) solution) to 1.98x10\(^{-1}\) kmole/m\(^3\), beside that the composition of other gas such as CH\(_4\), CO, H\(_2\), N\(_2\) and Ar increase. Axial position 0 is the position at the bottom of top packing while the axial position 1 is the position at the top. The liquid effluent from the top packing
mixed with the semi lean solution is the influ-
ent of the bottom packing. In this packing the
concentration of dissolved gases in liquid phase
increases down the column. This phenomenon
is shown in Figure 3. The liquid effluent from
the bottom packing contains $5.9588 \times 10^{-5}$
k mole/m$^3$ CO, $4.1834 \times 10^{-2}$ kmole/m$^3$ H$_2$,
$6.9029 \times 10^{-3}$ kmole/m$^3$ N$_2$, $1.7063 \times 10^{-4}$ kmole/m$^3$
CH$_4$, and $1.2599 \times 10^{-4}$ kmole/m$^3$ argon. It shows
that not only CO$_2$ gas are dissolved in K$_2$CO$_3$
solution, but also other gases, such as: CO, H$_2$,
N$_2$, CH$_4$ and Ar, are also dissolved in K$_2$CO$_3$
solution in significant amount to affect the purity
of recovered CO$_2$ in stripping column. Increas-
ing pressure will increase the concentration of
these gases in liquid solution.

The predicted concentration distribution of
K$_2$CO$_3$ and KHCO$_3$ are shown in Figure 4 both
for top packing and bottom packing. From Fig-
ure 4, it can be seen that the K$_2$CO$_3$ concentra-
tion decreases as liquid moves down the col-

Figure 2. Concentration distribution of dis-
solved gases in Top Packing

Figure 3. Concentration distribution of dis-
solved gases in lower section of the column

Figure 4. Concentration distribution of
K$_2$CO$_3$ and KHCO$_3$ in: a) column upper sec-
tion, and b) column lower section
umn, where the initial concentration of K₂CO₃ is 29.986 kmole/m³ and the outlet K₂CO₃ concentration is 6.959 kmole/m³. It is because the K₂CO₃ solution reacts with CO₂ gas in a packed column forming KHCO₃. Thus, KHCO₃ concentration increases from 14.393 to 53.853 kmole/m³ as the liquid stream flows from the top to the bottom of the column.

4.2. Temperature Distribution

The predicted liquid temperature distribution in packed column is shown in Figure 5. At the upper section of the column, the liquid temperature increases around 29 K due to the exothermic nature of the reactive absorption process, while at the lower part section the liquid temperature increase around 4 K.

4.3. The Effect of Absorbent Flow Rate on %CO₂ Removal

The effect of absorbent flow rate on % CO₂ removal from simulation result is shown in Figure 6 under the operation conditions of 30% K₂CO₃ solution and DEA concentration of 3%. From Figure 6, it can be seen that the increase of the absorbent flow rate (lean solution and semi lean solution) give significant effect on the increase of %CO₂ removal. It indicates that the liquid side resistance has a considerable effect on the process of CO₂ absorption in K₂CO₃ aqueous solution. Although in this simulation the mass transfer resistance of gas side is also counted. The increase of absorbent flow rate will increase the turbulence and driving force and shorten life time of liquid film [40], consequently the mass transfer coefficient increases so that CO₂ absorption increases. The liquid side mass transfer coefficient is proportional to liquid flow rate to the power of 2/3 [35].

Figure 5. Liquid temperature distribution: (a) column upper section, and (b) column lower section

Figure 6. (a) The effect of lean solution flow rate on %CO₂ removal for semi lean solution flow rate = 2514122 kg/h; (b) The effect of semi lean solution flow rate on %CO₂ removal for lean solution flow rate = 320867 kg/h. Gas flow rate = 204020 kg/h, pressure = 33 atm, temperature of inlet lean solution= 343 K, temperature of inlet semi lean solution = 385 K, and temperature of inlet gas = 362 K

Figure 7. (a) The effect of lean solution temperature on %CO₂ removal for semi lean solution temperature of 385 K; (b) The effect of semi lean solution temperature on %CO₂ removal for lean solution temperature of 343 K
4.4. The Effect of Temperature on %CO₂ Removal

The effect of temperature (lean solution and semi lean solution) on %CO₂ removal can be seen in Figure 7. Figure 7 represents that the temperature gives a considerable effect in %CO₂ removal, indicating that the process of absorption of CO₂ into promoted K₂CO₃ solution is sensitive to temperature change. A higher temperature resulting in a higher reaction rate constant according to the Arrhenius equation, a higher diffusivity and a lower gas solubility. From Figure 7a, it indicates that at temperature less than 343 K reaction rate and diffusivity factor are more important than the gas solubility factor, therefore CO₂ removal efficiency increases with increasing lean solution temperature. Cullinane and Rochelle [41] also reported the same results for this temperature range. However, at temperature more than 343 K the solubility factor is more important than reaction rate and diffusivity factors that the CO₂ removal efficiency decreases with further increasing lean solution temperature. The highest CO₂ removal efficiency is 97.3599 % at lean solution temperature of 343 K. Thus, the increase of absorption rate depends on the relative effect of temperature on the reaction rate constants, diffusivity and solubility of gas absorbed. Hence, it is beneficial for a reactive absorption, to increase temperature to some extent for higher CO₂ removal efficiency. Figure 7b indicates that CO₂ removal efficiency decreases with increasing semi lean solution above 360 K.

4.5. The Effect of Absorber Pressure and Promoter Types on %CO₂ Removal

The effect of absorber pressure on %CO₂ removal from simulation result can be seen in Figure 8. Figure 8 shows that CO₂ removal efficiency increases with increasing operation pressure of the absorption column. This is due to the higher pressure will increase gas solubility and therefore the absorption rate. Figure 8 shows that increasing pressure from 25 atm to 33 atm will increase the CO₂ removal efficiency for various promoters. At pressure of 25 atm, the CO₂ removal efficiency for promoter arginine, DEA, MEA, and boric acid are 94.1554%; 90.7901%; 88.2275%; and 78.5847%, respectively. Meanwhile, at pressure of 33 atm the CO₂ removal efficiency are 97.2671%; 95.5465%; 94.0046%; and 86.6837%, respectively. These show that Arginine gives the highest CO₂ removal efficiency. The reason for this is that Arginine contains a primary amine group which have fast reaction rate with carbon dioxide [29].

6. Conclusions

In this study, a mathematical model has been developed for investigating the CO₂ absorption into promoted hot potassium carbonate (K₂CO₃) solution in industrial scale packed column consisting of two sections, lower section with diameter larger than upper section. The model was based on two-film theory incorporating reaction-diffusion interaction through enhancement factor concept. Heat effect due to exothermic chemical reaction and the absorption of carrying gases such as H₂, N₂, CO, CH₄ and Argon were taken into account in the model. In this case the multi-component diffusion model was devised. The model was used to simulate CO₂ removal from synthesis gas at packed absorber column in an ammonia plant using hot K₂CO₃ solution promoted by DEA. The result of the simulation prediction for the absorber pressure of 33 atm with a lean flow rate of 320,867 kg/h, temperature of 343 K and semi lean flow rate of 2,514,122 kg/h, temperature of 385 K showed %CO₂ removal of 95.55%, while the plant data showed 96.8% CO₂ removal. This result shows that the accuracy of our prediction model is high with 1.29% error compared with plant data. The effect of various process variables such as flow rate of lean solution and semi lean solution, temperature, and pressure of the absorber on CO₂ removal efficiency was investigated. The effect of various kinds of promoters (such as Arginine, DEA, DE...
MEA and Boric Acid) added into K₂CO₃ solution on the CO₂ recovery was also investigated.

Nomenclatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sectional area of the column, m²</td>
</tr>
<tr>
<td>a</td>
<td>Gas-liquid interfacial area per unit volume of packed column, m².m⁻³</td>
</tr>
<tr>
<td>a_p</td>
<td>Specific area of packing, m².m⁻³</td>
</tr>
<tr>
<td>C</td>
<td>Molar density, kmole.m⁻³</td>
</tr>
<tr>
<td>C_{CO₂}</td>
<td>CO₂ concentration at interface, kmole.m⁻³</td>
</tr>
<tr>
<td>C_{CO₂, e}</td>
<td>Equilibrium concentration of CO₂ in liquid phase, kmole.m⁻³</td>
</tr>
<tr>
<td>C_i</td>
<td>Molar concentration of component i, kmole.m⁻³</td>
</tr>
<tr>
<td>C_{i,L}</td>
<td>Concentration of ion i, kmole.m⁻³</td>
</tr>
<tr>
<td>C_{k}</td>
<td>Molar concentration of component k at interface, kmole.m⁻³</td>
</tr>
<tr>
<td>C_{k}^*</td>
<td>Molar concentration of component k in the bulk liquid phase, kmole.m⁻³</td>
</tr>
<tr>
<td>C_{G}</td>
<td>Heat capacity of gas, Joule.kg⁻¹.K⁻¹</td>
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<tr>
<td>C_{L}</td>
<td>Heat capacity of liquid, Joule.kg⁻¹.K⁻¹</td>
</tr>
<tr>
<td>D</td>
<td>Diffusivity, m².s⁻¹</td>
</tr>
<tr>
<td>d_p</td>
<td>Packing diameter, m</td>
</tr>
<tr>
<td>E</td>
<td>Enhancement factor</td>
</tr>
<tr>
<td>E_e</td>
<td>Enhancement factor for instantaneous reaction</td>
</tr>
<tr>
<td>F_{i,L}</td>
<td>Froude number</td>
</tr>
<tr>
<td>G</td>
<td>Mass velocity of gas, kg.m⁻².s⁻¹</td>
</tr>
<tr>
<td>g</td>
<td>Gravity acceleration, m.s⁻²</td>
</tr>
<tr>
<td>H_a</td>
<td>Hatta number as defined by Equation (27)</td>
</tr>
<tr>
<td>H_{CO₂}</td>
<td>Henry constant of CO₂ in aqueous electrolyte solution system, Pa.m³.kmole⁻¹</td>
</tr>
<tr>
<td>H_{e,j}</td>
<td>Henry constant of gas-aqueous electrolyte solution system, Pa.m³.kmole⁻¹</td>
</tr>
<tr>
<td>H_{e,jw}</td>
<td>Henry constant of gas-water system, Pa.m³.kmole⁻¹</td>
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<td>H_{jm}</td>
<td>Quadrature weight</td>
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<tr>
<td>H_{T,k}</td>
<td>Height of transfer unit for component k</td>
</tr>
<tr>
<td>h_G</td>
<td>Gas-specific parameter, m³.kmole⁻¹</td>
</tr>
<tr>
<td>h_{G,0}</td>
<td>Gas-specific parameter at 298.15 K, m³.kmole⁻¹</td>
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<tr>
<td>h_i</td>
<td>Ion-specific parameter, m⁰.kmole⁻¹</td>
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<td>h_i*</td>
<td>Cation-specific parameter, m⁰.kmole⁻¹</td>
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<tr>
<td>h_r</td>
<td>Anion-specific parameter, m³.kmole⁻¹</td>
</tr>
<tr>
<td>h_T</td>
<td>Temperature correction, m³.kmole⁻¹.K⁻¹</td>
</tr>
<tr>
<td>K</td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>k_{cat}</td>
<td>Second order reaction rate constant of the forward reaction with catalyst, m³.kmole⁻¹.s⁻¹</td>
</tr>
<tr>
<td>k_G</td>
<td>Mass transfer coefficient of gas side, kmole.m⁻².s⁻¹</td>
</tr>
<tr>
<td>k_H</td>
<td>The reverse of Henry Constant, kmole.m⁻³.Pa⁻¹</td>
</tr>
<tr>
<td>k_L</td>
<td>Mass transfer coefficient of liquid side, kmole.m⁻².s⁻¹</td>
</tr>
<tr>
<td>k_{OH}</td>
<td>Second order reaction rate constant of the forward reaction with OH⁻, m³.kmole⁻¹.s⁻¹</td>
</tr>
<tr>
<td>k_i</td>
<td>Overall pseudo first order reaction rate constant, s⁻¹</td>
</tr>
<tr>
<td>L</td>
<td>Mass velocity of liquid, kg.m⁻².s⁻¹</td>
</tr>
<tr>
<td>L_{in}</td>
<td>Inlet molar flow rate of liquid, kmole.s⁻¹</td>
</tr>
<tr>
<td>M_i</td>
<td>Molecular weight of component i, kg.kmole⁻¹</td>
</tr>
<tr>
<td>N_{CO₂}</td>
<td>Molar flux (absorption flux) of CO₂, kmole.m⁻².s⁻¹</td>
</tr>
<tr>
<td>N_{G}</td>
<td>Dimensionless quantity defined in Equation (62)</td>
</tr>
<tr>
<td>N_i</td>
<td>Molar flux of component i, kmole.m⁻².s⁻¹</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant in Joule.kmole⁻¹.K⁻¹</td>
</tr>
<tr>
<td>R_{G}</td>
<td>Reynold number of gas</td>
</tr>
<tr>
<td>R_{L}</td>
<td>Reynold number of liquid</td>
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<tr>
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<td>Reaction rate of CO₂ with catalyst, kmole.m⁻³.s⁻¹</td>
</tr>
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<td>Reaction rate of CO₂, kmole.m⁻³.s⁻¹</td>
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<tr>
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<td>Reaction rate of CO₂ with OH⁻, kmole.m⁻³.s⁻¹</td>
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<td>S_G</td>
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<td>S_{L}</td>
<td>Schmidt number of liquid</td>
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<tr>
<td>T</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>T_{G}</td>
<td>Temperature of gas stream, K</td>
</tr>
<tr>
<td>T_{L,m}</td>
<td>Temperature of gas in collocation points in packed column, K</td>
</tr>
<tr>
<td>T_{L}</td>
<td>Temperature of liquid stream, K</td>
</tr>
<tr>
<td>T_{L,m}</td>
<td>Temperature of liquid in collocation points in packed column, K</td>
</tr>
<tr>
<td>v</td>
<td>Stoichiometric coefficient of K₂CO₃</td>
</tr>
<tr>
<td>w_i</td>
<td>Molar volume of component i, m³.kmole⁻¹</td>
</tr>
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<td>W_{L}</td>
<td>Weber number</td>
</tr>
<tr>
<td>w_{i}</td>
<td>Mass fraction of component i</td>
</tr>
</tbody>
</table>

\[ x_{CO₂}^* \] : Mole fraction of CO₂ at interface

\[ x_{CO₂}^e \] : Equilibrium mole fraction of CO₂ in liquid phase

\[ x_{k}^* \] : Mole fraction of component k at interface

\[ x_{h,m} \] : Mole fraction of component k at interface in collocation points m in packed column

\[ x_{k}^{o} \] : Mole fraction of component k in the bulk liquid phase

\[ x_{h,m}^{o} \] : Mole fraction of component k in the bulk liquid phase in collocation points m in packed column
x_i : Mole fraction of component i in liquid phase
X_i : Molar ratio of component i (mole component i per mole inlet liquid)
y_i : Mole fraction of component i in gas phase
Y_i : Molar ratio of component i (mole component i per mole inlet gas)
z : Axial position in packed column, m
Z_r : Height of packing, m

Greek letters
\( \Delta H_s \) : Heat reaction, Joule.kmole\(^{-1} \)
\( \zeta \) : Dimensionless axial position in packed column
\( \mu \) : Viscosity, Pa.s
\( \rho \) : Density, kg.m\(^{-3} \)
\( \sigma_c \) : Critical surface tension, N/m
\( \sigma_l \) : Surface tension of liquid, N/m
\( \phi \) : Association factor for solvent (\( \phi = 2.6 \) for water)
\( \phi_l \) : Liquid hold up in packed column

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References


