Modeling of CO₂-MEA absorption system in the packed column using Sulzer DX structured packing

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Abstract. The accurate design of a packed column is largely dependent upon the accurate calculation of the effective mass transfer area (aₑ) of a packing. The experimental and the modelling study for the packed column with CO₂-Monoethanolamine (MEA) system has been reported by employing Sulzer DX packing. The model validation results revealed that the modification in the available simple aₑ correlations is necessary to attain the reliable results using Sulzer DX packing. Recently, a new simple aₑ correlation suitable for Sulzer DX packing with MEA-CO₂ system has been reported. Therefore, in the present study, the rate-based model is developed using the newly developed aₑ correlation for the packed absorption column with Sulzer DX structured packing for CO₂-MEA system. The model has been successfully validated with the experimental data. Overall results depict good accuracy (AAD < 15%) of predicted CO₂ concentration profiles due to the reliable aₑ calculations. However, the relative accuracy is low at high liquid flowrates (> 8 m³/m²h) due to the design limitations of the aₑ correlation. Therefore, in this study, the adopted aₑ mass transfer correlation is found suitable for the reliable modelling of the packed absorption column with Sulzer DX packing.

1. Introduction
Carbon dioxide (CO₂) being a greenhouse gas is a major cause of global warming. Therefore, the industrial flue gases are treated to remove CO₂ before releasing to the environment [1]. There are several techniques available for the separation of CO₂ from the flue gases such as membrane separation, chemical absorption, and adsorption. However, chemical absorption using amine solvents is the most commercially implemented technique [2, 3]. In order to separate a solute gas from the flue gas mixture by using a liquid solvent, it is necessary to provide intimate contact between gas and liquid phases. This is possible in different types of equipment such as tray columns, bubble columns and packed columns. Packed columns have gained much importance relative to other separating columns for the advantages of low pressure drop, higher efficiency, and controlling sensitivities [4, 5].

Several types of packings are available in terms of the geometry and materials. These packings are divided into three principle types: dumped, stacked, and structured packing. Mass transfer operations depend upon the properties of the absorbent and the type of packing used [4, 6]. The liquid and gas side mass transfer coefficients are dependent upon the type of packing material used. Furthermore, the effective mass transfer interfacial area of the packing is not similar to the geometric surface area of packing materials. This is because of packing wettability limitations. Therefore, the accurate calculation of the effective mass transfer area of a packing is necessary for the accurate column designs [6, 7]. Among the different packings, structured packings have gained attention in the
chemical process industry in the last three decades. The is because of their advanced hydraulic behaviors, of low pressure drops, high throughputs and efficiency [8]. Therefore, the extensive demand of structured packings needs reliable models for the estimation of mass transfer behavior. There are number of models published based on various experimental and theoretical studies. They have different limitations in terms of packing types, solvent properties and hydrodynamic conditions [8-10].

De Montigny et al. [11] performed the CO$_2$ absorption study using aqueous monoethanolamine (MEA) solution in a packed column with Sulzer DX structured packing (of high surface 900 m$^2$/m$^3$). The mathematical model for the packed column is also proposed in which the effective mass transfer area is calculated using Onda et al. [12] and Henriques de Brito et al. [13] correlations. However, it is reported that the mentioned correlations have underpredicted the effective area value ($a_e$). Therefore, in their study, the Henriques correlation has been modified by fitting with their packed column experimental data for the reliable results. Morteza Afkhamipour et al. [14] have performed comprehensive modelling study by evaluating several $a_e$ models including simple and complex models for random (pall rings and IMTP 40) and structured packings (Sulzer DX) using CO$_2$ absorption in aqueous MEA, MDEA and AMP solutions. It is reported that the simple $a_e$ correlations such as of Henriques de Brito et al. [13] has not given good results for Sulzer DX packing system. Recently, Gao et al. [15] have performed experimental study to investigate the hydrodynamics of Sulzer DX structured packing and also proposed simple $a_e$ correlation suitable for Sulzer DX packing. This correlation has not been evaluated before using any rate-based modelling study for packed absorption column with Sulzer DX packing and CO$_2$-MEA system.

In the present study, the rate-based model is developed using the Pandya modelling approach for the packed absorption column with Sulzer DX structured packing for CO$_2$-MEA system [17]. The effective mass transfer area of the packing has been calculated using the correlation proposed by Gao et al. [15] The model has been validated with the experimental data taken from the study of De Montigny et al. [11].

2. Model development

Pandya proposed the first steady state adiabatic rate-based model and later several modelling studies are reported on its basis [17-18]. In this study, a system consists of five components including, CO$_2$ gas (A), carrier gas (B), reactant (R) and a non-volatile product (P).

2.1. Chemical reaction scheme

The chemical absorption of CO$_2$ in aqueous monoethanolamine (MEA) solution is caused by the number of chemical reactions. However, at low CO$_2$ loadings (<0.5 mol/mol) the CO$_2$ absorption can conveniently be described by only considering the carbamate formation reaction (which is the case in this study) as represented in equation (1) [5,16,18].

\[
CO_2 + 2RNH_2 \rightarrow RNHCOO^- + RNH_3^+ 
\]  

(1)

2.2. Main model assumptions

The model is described using two film theory based on Pandya’s approach and main assumptions are described below [17]:

1. The chemical reaction is fast enough to be completed within the liquid film, while is liquid bulk is considered in equilibrium.
2. The interfacial mass and heat transfer surface area is assumed to be same.
3. The axial dispersion is not ignored.
4. Packed column is assumed to be in adiabatic state.
5. Solvent evaporation is not accounted.
The differential mass and energy balance for the CO\textsubscript{2} absorption system are expressed in Equations (2-4) based on Pandya model [17]. Where, \(G_B\) is the molar gas flow rate, \(L\) is the molar liquid flow rate, \(\alpha_e\) is the effective mass transfer area, \(K_g\) is gas side mass transfer coefficient, \(Y_A\) and \(Y_{A_i}\) are CO\textsubscript{2} mole fraction per unit inert gas (B), at bulk and gas-liquid interface, \(h_g\) is heat transfer coefficient, and \(C_{pi}\) represents molar heat capacity of respective components.

\[
\frac{dY_A}{dx} = \frac{a_e k_g (Y_A-P-Y_{A_i}P)}{G_B} \tag{2}
\]

\[
\frac{dT_B}{dx} = \frac{h_g \alpha_e (T_B-T_L)}{G_B (Y_A C_{PA}+C_{PB})} \tag{3}
\]

\[
\frac{dT_L}{dx} = \frac{G_B (C_{PB}+Y_{A_i} C_{PA}) \frac{dT_B}{dx} + G_B (C_{PA} (T_B-T_L)+\Delta H_R) \frac{dY_A}{dx}}{L C_{PL}} \tag{4}
\]

The interfacial concentration of CO\textsubscript{2} is calculated using the following expression (5). Where, \(C_{le}\) is the equilibrium concentration of CO\textsubscript{2} gas in the liquid bulk phase which is negligible due to CO\textsubscript{2}-MEA fast reaction. Further, \(E\) is the enhancement factor which is calculated using the Wellek et al. [19] model shown in equation (6). The mass transfer coefficients \((K_g, K_l)\) are calculated using the model of Rocha et al. [10, 20] shown in Equations (7-8) for further details. The effective mass transfer area is calculated using the correlation of Gao et al. [15] as shown in equation (9). The chemical and thermophysical properties used in the model development are described in Table 1.

\[
Y_A P = \frac{Y_{A_i} P + \frac{E h g C_{le}}{k_g}}{1 + \left(\frac{1}{E h g C_{le}}\right)^{1.85}} \tag{5}
\]

\[
E = 1 + \frac{1}{\left(\left[\frac{1}{E h g C_{le}}\right]^{1.85} + \left[\frac{1}{E h g C_{le}}\right]^{1.85}\right)^{0.35}} \tag{6}
\]

\[
k_g = 2 \frac{0.9 D_{A1} U_{le}}{a S} \tag{7}
\]

\[
\frac{k_g S}{D_{A, g}} = 0.054 \left(\frac{(U_{ge}+U_{le}) P_{ge} S}{\mu_g}\right)^{0.8} \left(\frac{\mu_g}{D_{A, g} \rho_g}\right)^{0.33} \tag{8}
\]

\[
\alpha_e = 921 \left(\frac{W_{fr} F_{g}}{R_{Ble}}\right)^{0.2} \left(\frac{\mu_g}{\rho_L}\right) \tag{9}
\]

| Table 1. Chemical and thermophysical properties |
|-----------------------------------------------|
| Property                     | Functional dependency | References |
|-------------------------------|-----------------------|------------|
| Liquid density               | \(T, x_{MEA}\)        | [21]       |
| Liquid viscosity             | \(T, x_{MEA}\)        | [22]       |
| Henry Constant               | \(T, x_{MEA}\)        | [23]       |
| Rate constant                | \(T\)                 | [24]       |
| Liquid surface tension       | \(T, x_A\)            | [25]       |
| Binary gas diffusivity       | \(P, T, y_i\)         | [26]       |
The differential Equations (2-4) are solved to simulate the profiles of CO₂ concentration along the height of a packed column. Initially, only the gas and solvent compositions are known at the bottom and top of the column respectively. This is a two-point boundary value problem, which can be solved numerically using the shooting method. For this purpose, the programming script has been written in MATLAB to resolve the differential Equations simultaneously. The calculations are initiated from the top segment of the packed column and continued until the bottom composition of gas is attained.

3. Results and discussion
The model presented in the preceding section has been validated with the experimental data runs taken from the work of De Montigny et al. [11]. Figure 1 (a-d) depicts the comparison of experimental and simulated data for the runs referred as dx-2, dx-3, dx-4 and dx-7.

![Figure 1. Comparison of experimental (square) and simulation data (solid line): (a) dx2 (b) dx3 (c) dx4 (d) dx7](image)

It can be observed that generally, there is a good agreement between experimental and simulated data throughout the column for all the runs. The best agreement between experimental and simulated data is in the case of dx2 in Figure 1(a). However, this agreement is seemed to be reduced in the case of dx3 and dx7 and it is most prominent in the case of dx4. This is because the effective mass transfer area (a_e) correlation used in this study has been built in the range of liquid flow rate 3.09-8.77 m³/m² h and dx3 and dx7 are at the edge of this range. Moreover, dx4 has been operated above this flow rate range (10.6 m³/m² h). As mentioned earlier that De Montigny et al. have earlier validated their model on the presented data [11]. They have used the Onda et al. [12] and Henriques de Brito et al. [13] correlations for the calculation of effective interfacial area (a_e). It has been reported in their study that these correlations have underpredicted the a_e value. Therefore, they optimized the parameters of Henriques de Brito et al correlation for the reliable results [13]. However, in the present study, the
calculations of $a_e$ are found reliable because the used correlation has been particularly designed for Sulzer DX packing and CO$_2$-MEA system.

Figure 2 shows the simulated effective mass transfer area over the column height for each of the experimental run. It can be observed that the $a_e$ value is almost constant over the column and slightly varies at the end of the column. The maximum value of $a_e$ is observed in case of dx7 run while minimum $a_e$ is found for dx2 run. This is because of the difference in the liquid flow rates which is highest as 10.84 m$^3$/m$^2$h and minimum as 6.7 m$^3$/m$^2$h respectively for dx7 and dx2 runs. With increasing $a_e$ the mass transfer efficiency of a packed column increases for CO$_2$ capture.

![Figure 2. Effective mass transfer area ($a_e$)](image)

4. Conclusion
In this study, the rate-based model has been developed for the packed absorption column with Sulzer DX structured packing for CO$_2$-MEA system. The effective mass transfer area ($a_e$) has been calculated using the Gao et al. correlation. The model has been successfully validated with the experimental data. Overall results depict good accuracy (AAD < 15%) of predicted CO$_2$ concentration profiles due to the reliable $a_e$ calculations. However, the relative accuracy is low at high liquid flowrates (> 8 m$^3$/m$^2$h) due to the design limitations of the $a_e$ correlation. Therefore, in this study, the adopted $a_e$ mass transfer correlation is found suitable for the reliable modelling of the packed absorption column with Sulzer DX packing.

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