

NUMERICAL SIMULATION OF AMINE BASED ABSORPTION PROCESSES FOR CARBON DIOXIDE CAPTURE IN CCS PROJECTS

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Abstract.

Absorption is a process where the components of a gaseous stream are separated through the use of a liquid solvent. The process may be simply physical or being followed by a chemical reaction. In industry, one of the most important absorption processes is the removal of carbon dioxide (CO₂), by using an aqueous solution of monoethanolamine (MEA), from flue gases exhausted by fossil-fuel-fired power plants, the pharmaceutical industry, the petroleum industry, and so on. The design of chemical absorption processes is more complex than for physical absorption. On top of that, the projects carried out by large companies are truly black-boxes and the companies avoid the dissemination of their technological solutions. In addition, there is almost nothing published in Brazil about this subject. In this work, we present a simple model that simulates the absorption of CO₂ by a MEA based aqueous solution. The model involves the equations for the conservation of mass, momentum, and energy, and may predict the general behavior of the absorption process. Results for the simulation of the absorption of CO₂ in a countercurrent liquid film contactor showed a good agreement with experimental data, thereby suggesting the utility of the basic model, even with some adaptations, in predicting the performance of the chemical absorption of CO₂ for other reactor geometries.

Keywords: Absorption, Gas-liquid contactor, Modeling, CO₂ separation, Monoethanolamine.

1. INTRODUCTION

Gas absorption using liquid absorbents is one of the common mass-transfer operations widely used in industry for separating some components (such as useful, toxic, or environmentally unfavorable species) from gas mixtures before feeding them to subsequent in-plant operations or releasing them to the atmosphere. Separating carbon dioxide (CO₂) from the flue gases in fossil-fuel-fired power plants, pharmaceutical industry, petroleum industry, etc., a potential measure to mitigate the human-originated greenhouse effect, requires the use of a gas-liquid contact device that efficiently removes CO₂ from a flue-gas flow at an enormously high rate without imposing on the flow such a substantial pressure loss as to necessitate the addition of a flue-gas compression process. Thus for treating huge amount of low-pressure (not much higher than atmospheric pressure) gases of no further use, it is critically important to devise gas-liquid contactors that allow effective gas absorption without pressurizing the gases to balance the hydrodynamic pressure losses inside the contactors. Packed columns have been widely used in industries for separation and purification processes involving gas and liquid contact (such as distillation and absorption) due to its high efficiency and high capacity but are not well suited for processing huge amounts of industrial waste gases due to inevitable insufficient contact-area-to-volume ratios and large gas-side pressure losses during operation. Thus from all the available designs, continuous film contactors for processing flue gases or other industrial waste gases are considered to be more advantageous. These are vertical columns where liquid flows downward wetting the wall while the gas flow counter currently contacting the liquid.

Various technologies have been developed for CO₂ removal from gas streams. These include absorption by chemical and physical solvents, cryogenic separation and membrane separation. Gas absorption by chemical solvents such as aqueous solution of alkanolamine is one of the most popular and effective methods compared to other methods. Absorption of gas using alkanolamines has been practiced in industry for over half a century; however, it is only recently that substantial progress has been made in developing a fundamental understanding of these seemingly simple processes. A number of mathematical models for falling film reactors have been proposed by Kanksha, A., et al. (2007), Dabir, B., et al. (1996) and Nielsen, P., et al. (1983), in the field of absorption; however limited attempts have been to include realistic fluid mechanics to model the liquid film flow. Several researchers such as Migita, H., et al. (2005), Mandal, B.P., et al. (2001), and Bosch, H., et al. (1989), have illustrated the mass transfer studies. The present work is to develop a mathematical model that can predict the non-isothermal absorption using observational knowledge of configurations and motion of the film. An empirical correlation for the dimensionless mass transfer coefficients, (Sh_G) in falling film reactor at low Reynolds numbers is determined based on the experimental investigations, which was used directly in the modeling equations. Experimental results were utilized in estimating gas-absorption performance in a continuous film contactor.

2. CO₂ ABSORPTION EXPERIMENTS

2.1. Apparatus and procedure

The schematic diagram of the experimental setup is shown in Fig. 1. The setup consists of three major sections: (1) the main part of the unit or the reactor section consisting of jacketed tubular falling liquid film column, (2) the liquid flow section consisting of the trough and peristaltic pump and (3) gas collection section consisting of gas sampler and a gas-chromatograph for identifying the gaseous components. The reactor was made of glass (inner diameter 0.014m, length 1m) and cooling water was circulated through the jacket. The liquid was fed by peristaltic pump into the trough (holding capacity ~0.12mL) of the liquid flow section from where it was made to flow down ward wetting the walls of the reactor. Feed gas (a mixture of CO₂ and N₂) was introduced from the bottom of the reactor and flows upward in the main reaction section counter current to the liquid phase.

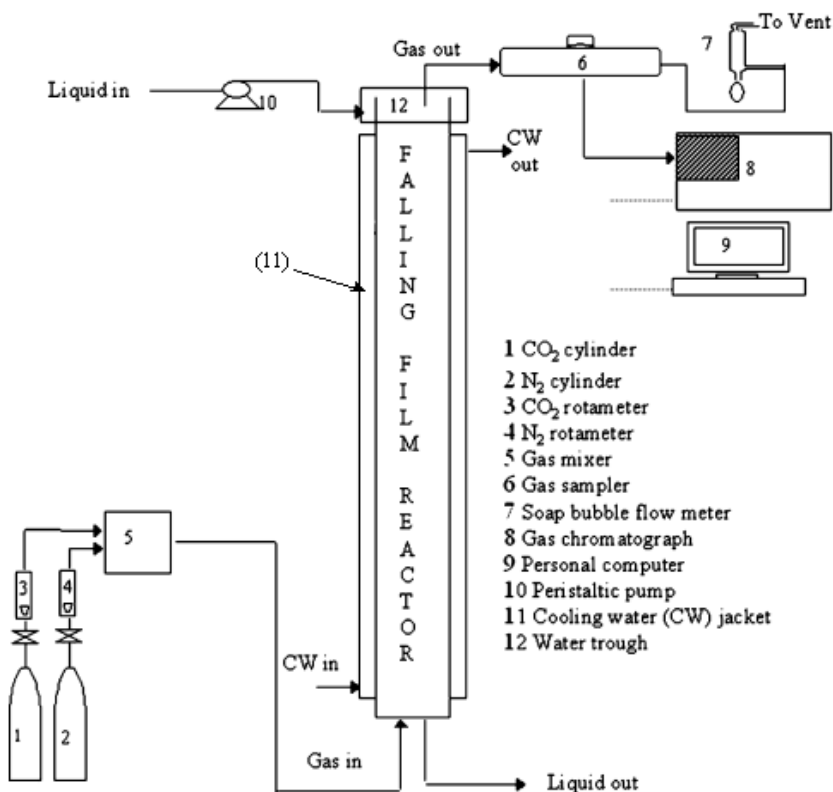


Figure. 1. Experimental setup.

Source: Kanksha, A., Pant, K.K. and Srivastava, V.K., 2007

3. MODELING OF CHEMICAL GAS-ABSORPTION

A numerical model has been developed for predicting the absorption of any species initially mixed in a gas phase by a chemically reactive liquid flowing down a reactor wall. It has been modified according to the CO₂-MEA system with CO₂ as gas species and MEA as liquid for better comparison and for validating with the experimental results described in the preceding section.

3.1. Basic assumptions

The basic assumptions considered for the CO₂ absorption by MEA solution in a falling film flow are listed below:

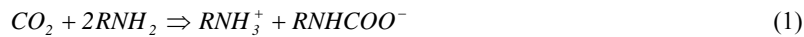
1. The physical properties of the liquid are held constant over the entire gas-liquid contact section irrespective of the special variation in the concentration of the liquid due to its absorption of CO₂.
2. The film thickness is small compared to the column diameter.
3. The liquid film is symmetric with respect to the reactor axis.

4. The CO₂ solubility in the liquid reactant and in the reaction products is in accordance with the Henry's law.
5. The liquid reactant is assumed to be non-volatile at working temperatures.

The flow is formulated as two-dimensional, and a Cartesian coordinate system is used instead of cylindrical coordinates, thus simplifying the model.

3.2. Model description

The overall reaction occurring in the liquid phase may be expressed as.



Where R indicates HCOH₂CH₂. This overall reaction is second order, i.e., first order with respect to CO₂ and MEA separately Henstock, W.H. and Hanratty, T.J., (1976)., and thus the reaction rate *r*, being defined as the molar rate of loss of CO₂ per unit volume, is expressed in terms of a reaction rate constant *k* and molar concentrations of CO₂ and MEA, C_A and C_B, as follows:

$$r = kC_A C_B \quad (2)$$

Where *k* can be calculated, using the empirical correlation given by Henstock, W.H. and Hanratty, T.J., (1976).

The modeling includes all the three transfer processes i.e., mass, momentum and heat to study the coupled effect of temperature and concentration on the rate of absorption. The developed equations include both ordinary differential equations (ODE's) and partial differential equations (PDE's) of non-linear nature. The flow model is described in Figure 2.

The coupled partial differential equations representing the mass and heat balances for reaction.



can be written as follows.

3.2.1. Liquid phase

i) Momentum balance.

The governing differential equation describing the momentum balance is given as:

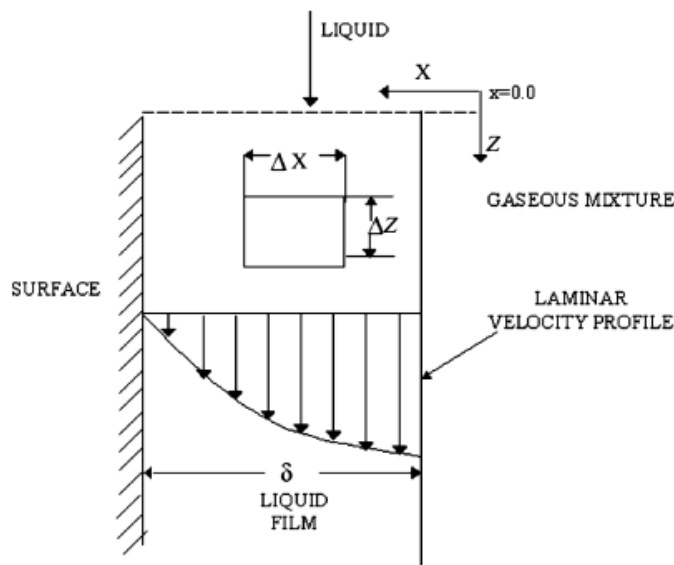


Figure. 2. Flow model of the film reactor

Source: Kanksha, A., Pant, K.K. and Srivastava, V.K., 2007

$$\rho g_z + \frac{\partial \tau_{xz}}{\partial x} = 0 \quad (4)$$

Applying the following boundary conditions gives velocity distribution as given by Eq. (7), where Boundary conditions.

Interface,

$$x = 0, \rightarrow \tau_{xz} = \tau_i = \tau_G \quad (5)$$

Wall,

$$x = \delta, \rightarrow w_L = 0 \quad (6)$$

Velocity distribution.

$$w = \frac{\rho g \delta^2}{2\mu} \left[1 - \left(\frac{x}{\delta} \right)^2 \right] - \frac{\tau_G \delta}{\mu} \left[1 - \frac{x}{\delta} \right] \quad (7)$$

Film thickness, δ is calculated from the volumetric rate of liquid obtained by the integration of the velocity distribution (Eq. (7)) and is given as.

$$\Gamma = \pi d \left[\frac{\rho g}{3\mu} \delta^3 - \frac{\tau_G}{2\mu} \delta^2 \right] \quad (8)$$

where:

$$\tau_G = f \rho_G w_G^2 \quad (9)$$

The friction factor, f was evaluated using relations proposed by Henstock, W.H. and Hanratty, T.J., (1976), which accounts for the irregularities at the surface of the liquid layer and is given by:

$$\frac{f}{2} = \left\{ \begin{array}{l} \frac{\delta}{Re_G} \dots\dots\dots Re_G < 2000 \\ \frac{Re_G^{0,33}}{3050} \dots\dots\dots 2000 < Re_G < 4000 \\ \frac{0,04}{Re_G^{0,25}} \dots\dots\dots Re_G > 4000 \end{array} \right\} \quad (10)$$

ii) Mass balance.

For component A

$$w \frac{\partial C_A}{\partial z} = \frac{\partial}{\partial x} \left(D_A \frac{\partial C_A}{\partial x} \right) - k C_A C_B \quad (11)$$

For component B:

$$w \frac{\partial C_B}{\partial z} = \frac{\partial}{\partial x} \left(D_B \frac{\partial C_B}{\partial x} \right) - k_b C_A C_B \quad (12)$$

iii) Heat balance

$$w \frac{\partial T}{\partial z} = \frac{\partial}{\partial x} \left[\alpha \frac{\partial T}{\partial x} \right] + \left(\frac{\Delta H_R}{\rho C_p} \right) k C_A C_B \quad (13)$$

Boundary equations:

For $x = \delta$ at the wall

$$x = \delta \rightarrow w_L = 0$$

$$\frac{\partial C_A}{\partial x} = 0, \quad \frac{\partial C_B}{\partial x} = 0$$

$$-k_\lambda \frac{\partial T}{\partial x} = U(T_{x=0} - T_R) \quad (14)$$

For $x = 0$ at the interface

$$x = 0$$

$$\frac{\partial C_B}{\partial x} = 0$$

$$k_G(C_{AG} - C_A H_O) = -D_A \frac{\partial C_A}{\partial x} \quad (15)$$

$$h_G(T - T_G) - k_\lambda \frac{\partial T}{\partial x} = (-\Delta H_S) \left[D_A \frac{\partial C_A}{\partial x} \right] \quad (16)$$

At. $z=0$,

$$z = 0$$

$$C_A = 0 \quad C_B = C_B^O \quad T = T_O$$

3.2.2. Gas phase

i) Mass balance.

Assuming a steady, unidirectional plug flow of a CO_2/N_2 gas mixture inside the test column, we can write the conservation of CO_2 in the differential control volume.

$$\frac{d(\omega_G C_{AG})}{dz} = \frac{a_c k_G a \tilde{\rho}_G A_{sup}}{P_m} (C_{AG} - C_A H_O) \quad (17)$$

Where ω_G is molar flow rate of gas per unit wetted perimeter, C_{AG} is the mixed mean concentration of CO_2 in the gas mixture, $\tilde{\rho}_G$ is molar densities of the gas mixture, k_G is mass transfer coefficient, a is surface area per unit volume, C_A is the CO_2 concentration in the gas mixture that would be in equilibrium with the mixed-mean concentration of CO_2 physically dissolved in the MEA solution, a_c is correction factor for the interfacial area, a is the

gas-liquid interfacial area per unit volume, A_{sup} is surface area, p_m is per wetted perimeter, H_o is Henry's constant and z is the vertical distance measured downward from the top end of the gas-liquid contact section of the column.

ii) Heat balance.

$$\frac{d(\omega_G C_G T_G)}{dz} = h_G (T_{x=0} - T_G) \quad (18)$$

Where h_G is heat transfer coefficient in gas phase and C_G is molar heat capacity.

For evaluating the effectiveness of CO₂ transfer, rate of absorption (mass based), R_A defined as.

$$R_A = Q_G (C_{in} - C_{out}) \quad (19)$$

Where Q_G is volumetric flow rate of gas, C denotes the mass of CO₂ transferred from a unit volume of the gaseous mixture, and subscripts "in" and "out" indicate the gas mixture sampled before and after the gas flowing up the test column.

4. RESULTS

4.1. Physical and chemical properties

The physical and chemical properties used in the numerical simulations with the model are presented in Table 1, below. They correspond to the same situation as that of the experiment which was described earlier.

Table 1. Physical and chemical properties of CO₂-MEA system, temperature 298K and a total pressure of 101.32 kPa

Composite Properties	
Density, ρ_L (kg/m ³) ⁽¹⁾	1010
Viscosity, μ_L (kg/ms) ⁽¹⁾	2.41×10^{-3}
Thermal conductivity, k_L (W/mK) ⁽¹⁾	0.4837
Surface tension (N/m) ⁽¹⁾	55.1×10^{-3}
Liquid diffusivity of CO ₂ , D_A (m ² /s) ⁽¹⁾	1.42×10^{-9}
MEA diffusivity D_B (m ² /s) ⁽¹⁾	1.10×10^{-9}
Diffusivity of CO ₂ in gas, D_G (m ² /s) ⁽¹⁾	1.67×10^{-5}
Density of gas mixture, ρ_G (kg/m ³) ⁽¹⁾	1.248
Viscosity of gas mixture, μ_G (kg/ms) ⁽¹⁾	1.72×10^{-5}
Henry constant, H_o (kmol/m ³ kPa) ⁽¹⁾	0.316×10^{-3}
Heat of reaction (kJ/kmol) ⁽¹⁾	65,000
Heat of solution (kJ/kmol) ⁽¹⁾	19,500

⁽¹⁾: Kanksha, A., Pant, K.K. and Srivastava, V.K., (2007)

4.2. Numerical results

Results for the numerical simulations using different gas velocities and different liquid velocities are summarized in Figure 3 and Figure 4, below.

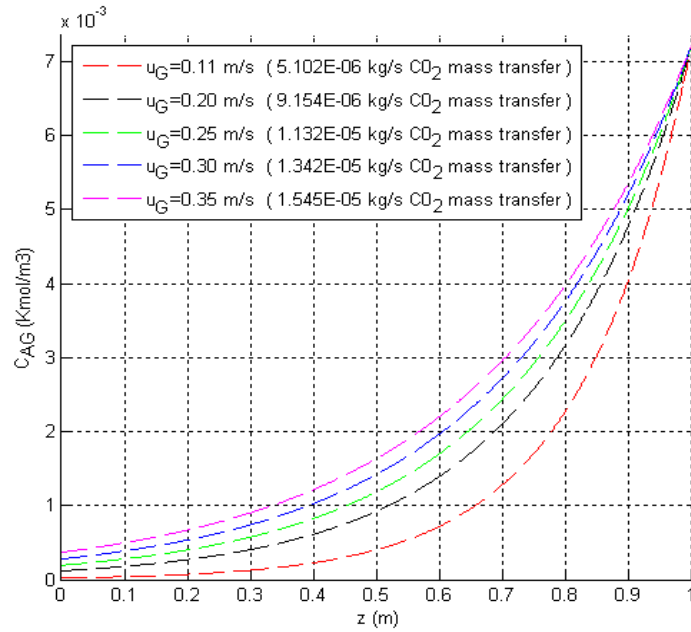


Figure 3. Effect of CO₂ concentration along the column, $u_L = 0.0412$ m/s, MEA concentration = 30wt.%

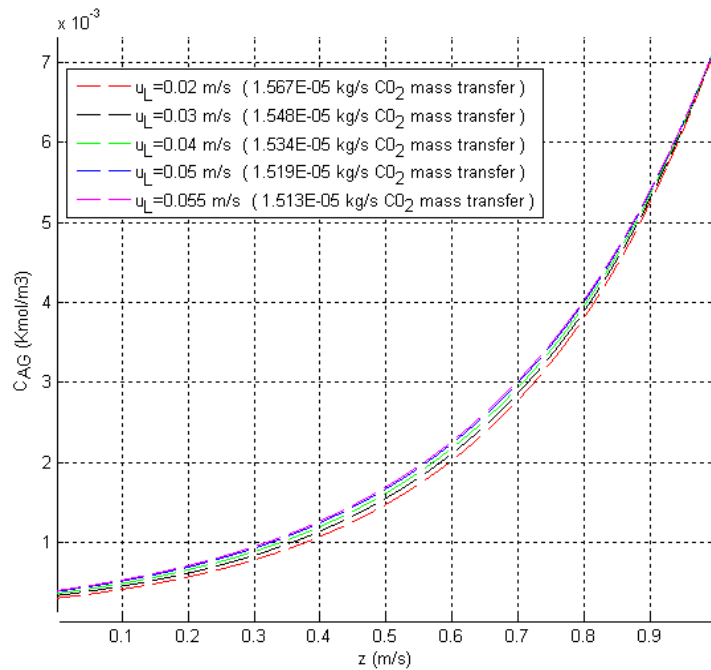


Figure 4. Effect of CO₂ concentration along the column, $u_G = 0.3236$ m/s, MEA concentration = 30wt.%

The mathematical relations were incorporated into an iterative Solution procedure to elucidate the CO₂ absorption changes with respect to the fall distance of the MEA solution.

The complexity of the model can be seen from the counter current flow direction of the two phases resulting into two iterative loops, whereas all the mathematical models reported are for co-current flow thus simplifying the numerical procedure. These coupled PDE's were solved using backward implicit finite difference numerical scheme and for ODE's implicit trapezoidal scheme was used to solve the gas-phase heat and mass transport equations. The tridiagonal matrix obtained from the discretization of highly coupled partial differential equation was solved using a subroutine TDMA.

The results show the variation of CO₂ concentration in the gas region, in Figure 3 curves show the fall down CO₂ concentration along the column for different gas velocities and keeping constant liquid absorbent velocity, note that with increase gas velocity also increase mass transfer of CO₂ but the concentration decrease. In Figure 4 the results are presented for a varying liquid velocity and keeping constant gas velocity, fall down CO₂ concentration between the curves is not very pronounced with respect to Figure 3 and mass transfer is almost constant.

4.3. Model Validation

Results for the numerical simulations comparison of predicted R_A whit corresponding experimental data and simulated by Kanksha, A., Pant, K.K. and Srivastava, V.K., 2007, were summarized in Figure 5 and Figure 6, below.

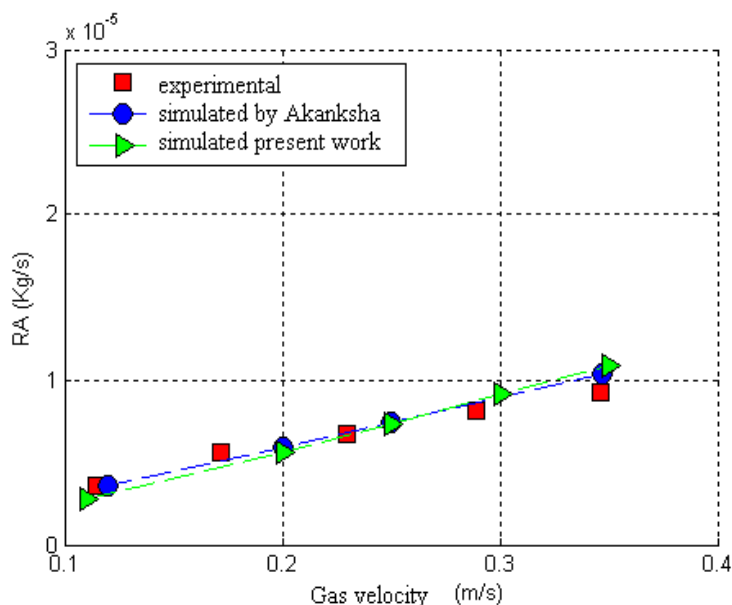


Figure 5. Comparison of predicted R_A whit corresponding experimental data and simulated by Akanksha (effect of changing gas flow rate).

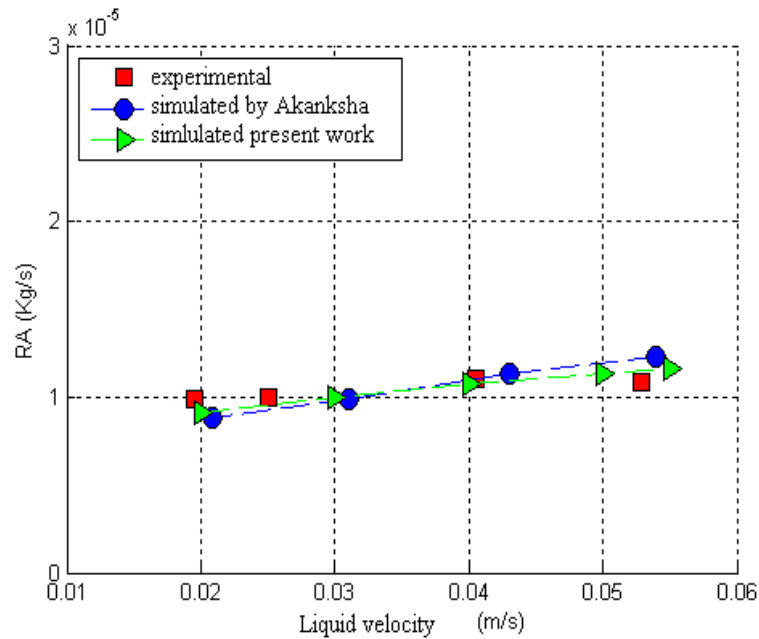


Figure 6. Comparison of predicted R_A whit corresponding experimental data and simulated by Akanksha (effect of changing liquid flow rate).

5. CONCLUSION

CO_2 absorption by monoethanolamine MEA in a continuous film contactor has been numerically simulated. The proposed numerical scheme was based on the solution of the momentum, mass and energy conservation equations, with the objective of predicting the gas-absorption performance for different adjustments of the operational parameters such as the reactants (gas and liquid) concentration, the flow rate of the absorbent, and the flow rate of the gas mixture. The gas-phase mass transfer process occurred in the laminar regime according to the gas and liquid-phase Reynolds numbers. Reasonably good agreement was obtained between model predictions and the corresponding available experimental data. The results support the validity of the physical hypothesis assumed in the construction of the model. This demonstrates that a simple geometry may produce high efficiency absorption of CO_2 in comparison with conventional columns (packed-bed).

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