Determination effects of process parameters on CO_2 reactive absorption system by mathematical modeling

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Abstract: A steady state model for CO_2- reactive absorption system was developed based on principle of mass transfer and chemical reaction. The pseudo-first order model is assumed and reversibility of chemical reaction was also neglected. The continuity model equation in term of material balance with chemical reaction across an elemental stage K on CO_2 was developed. The model consists of system of linear simultaneous equations, and the equations representing the composition of CO_2 in both liquid and gas phases were solved. The simulation studies were performed to investigate the effect of changing various process variables such as number of plate, gas flow rate, and CO_2 composition in the feed vapor.

Keywords: Carbon dioxide, Reactive Absorption Column, Process Variables, Modeling

1. Introduction

Carbon dioxide has been identified as one of the major causes of greenhouse effect which results to global warming. It is produced in significant amount from various industrial processes, including fossil fuel firing electric power generation, steel production, chemical and petrochemical manufacturing, coal gasification, etc. As a mean of mitigating the global warming, removal of CO_2 from industrial flue gas is considered important (Park *et al*, 2004). The method of removing CO_2 gas mixture include absorption (physical or chemical), cryogenic separation, membrane separation, adsorption and so on. Among these methods, CO_2 absorption by amine aqueous solution has been considered as the most efficient way and various research activities were conducted by this method and most commercial processes for the bulk removal of CO_2 from gaseous streams involved the use of amines (Mimura *et al,* 1998; Sartori *et al*, 1983; Paiton *et al*, 1996).

Methyldiethanolamine (MDEA) is a tertiary amine used extensively as solvent for removing CO_2 and H_2S from process gases [Astarita *et al*, 1983]. The addition of a primary or secondary amine to a tertiary amine has found widespread application in the absorption and removal of carbon dioxide from process gases. The success of these solvents is due to the high rate of reaction of primary or secondary amine with CO_2 combined with the low heat of reaction of tertiary amine (Bishnoi *et al*, 2000). The equilibrium solubility of CO_2 in aqueous MDEA solutions has been experimentally studied by several researchers (Jou, Mather & Otto, 1982, 1984; Jou, Caroll, Mather & Otto, 1993; Bhair, 1984; Ho and Eguren, 1988; Austgen, Rochelle & Chen, 1991).

Many researchers had also recognized the importance of using a fundamental rate-based approach for modeling the heat and mass transfer processes present in separation systems (Pacheco *et al*, 1998; Darton 1992).

Tomcej *et al*, [1987] implemented an efficiency model based on the solution of the differential mass balance on a tray of a given contactor. In the application to the removal of CO_2 using alkanolamines were made to estimate the enhancement factor.

Pacheco et al [1998] had also developed a general framework to model the transport processes that take place during reactive absorption. The work was aimed at developing a better understanding of the rate processes present in reactive absorption systems. This present study is aimed at studying the effects of operating parameters on column performance and how its size depend on the feed concentration (mole fraction) of carbon dioxide in the process gases.

2. Mathematical Model

In order to develop a model able to represent chemical absorption of carbon dioxide in process gases, the following assumptions are made:

(1) Gas and liquid flow rates in each of the plate are equal i.e.

$$G_1 = G_2 = -------- G_N = G_F$$

$$L_1 = L_2 = --------- L_N = L_F$$

(2) Every stage is in equilibrium stage or perfect stage.i.e. $y_k = Mx_k \ \forall k$.

(3) The absorption process is assumed to be steady state and counter-current.

(4) There is negligible heat effect in the column, thus the column operates with constant temperature.

(5) Liquid holdup is uniform throughout the column.

(6) The absorbent is of dilute concentration.

(7) A pseudo-first order model is assumed and the reversibility of the chemical reaction is neglected (Tomcej et al, 1987).

2.1. Kinetics of Reaction

In the absorption process model, the stoichiometry equation of reaction between trace component (CO_2) and absorbent [Aqueous amine (MDEA)] is written as:

$$CO_2 + H_2O + MDEA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MDEAH^+ + HCO_3^- \quad (1)$$
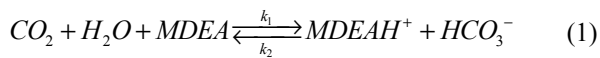
The rate of reaction of CO_2 with MDEA is represented as:

$$R_{MDEA} = k_1 C_{CO_2} C_{MDEA} - k_2 C_{MDEAH^+} C_{HCO^-} \quad (2)$$

$$k_1 (m^3/kmol.s) = 2.576x10^9 \exp(-6027/T) \text{ (Pacheco et al,}$$
1998)   (3)

2.2. The Material Balance

Considering an elemental volume K in a reactive absorption column
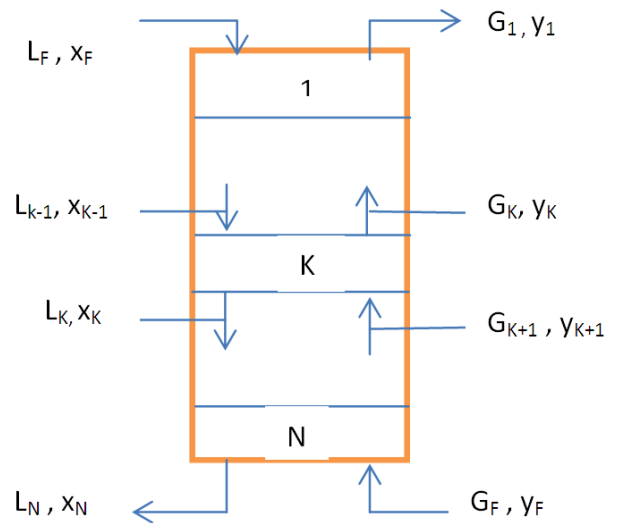
The mathematical model is based on the continuity equation:

Rate of material in – Rate of material out + Rate of material generated by reaction + Rate of Accumulation

Subject to those aforementioned assumptions and continuity equation

Material balance across the K on CO_2 stage,

$$L_{k-1}x_{k-1} + G_{k+1}y_{k+1} = L_k x_k + G_k y_k + K_R x_k h_L \quad (4)$$

All the terms are expressed in kmol/CO_2 per hour.

The liquid holdup per tray (h_L) is approximated by using correlation found by Miyahara and Takahashi (1979 & 1992).

$$h_L = 1.53x10^{-4}/d_p^{1.2} + 1.42x10^{-5}\varepsilon^{0.66}\left(\frac{\mu_L}{\mu_{H_2O}}\right)^{0.75} d_p^{-1.2} + 4.11x10^1 \left(\frac{z}{d_p}\right)^{-0.35} C_a^{0.8} M^{-0.16} F_{r_G} \quad (5)$$

Every stage is an equilibrium stage or perfect stage

$$y_k = mx_k \ \forall k \quad (6)$$

Put equation (6) into equation (4), we obtained

$$mG_F x_{k+1} - (L_F + mG_F + k_R h_L)x_k + L_F x_{k-1} = 0 \quad (7)$$

Equation (7) above can be written as follows:

$$\gamma x_{k+1} + \beta x_k + \alpha_{k-1} = 0 \quad (8)$$

Where:

$$\gamma = mG_F \quad (9)$$

$$\beta = -(L_F + mG_F + k_R h_L) \quad (10)$$

$$\alpha = L_F \quad (11)$$

Equation (8) is a second order linear, constant coefficient difference equation. Since it is second order, two boundary conditions are required for a specific solution. Here they are:

$$x_0 = x_F \quad (12)$$

$$y_{N+1} = mx_{N+1} = y_F \Rightarrow x_{N+1} = \frac{y_F}{m} \quad (13)$$

Equation (8) has an analytical solution; however, it can be expanded as follows:

$$k = 1: \gamma x_2 + \beta x_1 + \alpha x_F = 0 \qquad (14)$$

$$k = 2: \gamma x_3 + \beta x_2 + \alpha x_1 = 0 \qquad (15)$$

$$k = 3: \gamma x_4 + \beta x_3 + \alpha x_2 = 0 \qquad (16)$$

$$k = N-1: \gamma x_N + \beta x_{N-1} + \alpha x_{N-2} = 0 \qquad (17)$$

$$k = N: \gamma x_{N+1} + \beta x_N + \alpha x_{N-1} = 0 \qquad (18)$$

This is the system of linear equations;

$$Ax = b \qquad (19)$$

In the n-unknowns x where

$$A = \begin{pmatrix} \beta & \gamma & 0 & 0 & \text{---------} & 0 & 0 & 0 \\ \alpha & \beta & \gamma & 0 & \text{--------} & 0 & 0 & 0 \\ 0 & \alpha & \beta & \gamma & \text{--------} & 0 & 0 & 0 \\ - & & & & & - & - & - \\ - & & & & & - & - & - \\ - & & & & & - & - & - \\ - & & & & & & & \\ 0 & 0 & 0 & 0 & \text{--------} & \alpha & \beta & \gamma \\ 0 & 0 & 0 & 0 & \text{--------} & 0 & \alpha & \beta \end{pmatrix}$$

$$b = \begin{pmatrix} -\alpha x_F \\ 0 \\ 0 \\ 0 \\ - \\ - \\ - \\ 0 \\ \dfrac{-\gamma y_F}{m} \end{pmatrix}$$

This is $N*N$ tri-diagonal matrix.

Computing the degree of absorption η_a attainable by the column, mathematical expression written below is employed:

$$0 \leq \eta_a \triangleq \frac{y_{FEED} - y_{EXIT}}{y_{FEED}} \leq 1 \qquad (20)$$

3. Method of Numerical Solution

The method adopted for the solution of system of linear simultaneous equations, which resulted to tri-diagonal matrix for the model of chemical absorption of carbon dioxide (CO_2) in methyldiethanolamine solution is the Gaussian elimination method. A mathematical algorithm to solve these systems of linear simultaneous equations was developed and implemented into program using Microsoft Excel. The parameters reported by Pacheco et al; 1998, Muhammad et al; 2008 and literature were used for simulation in this study, which are given below.

3.1. CO2- Reactive Absorption System

The used parameters in simulating the developed model are summarized in Tab 1, 2 & 3.

Table 1: *Used parameters in simulation of CO_2-Reactive Absorption System.*

Parameter	Reactive Solvent	Feed Vapor
MDEA	50 wt%	-
H_2S	0.005 kmolH2S/kmol MDEA	0.6mol %
CO_2	0.005 KmolCO2/kmol MDEA	15,16.3*& 17.2*mol %
H_2O	Balance	Saturated
CH_4	-	84.05 mol%.
Flow rate (kmol/h)	2700	3200, 4920*& 5200*
Temperature (^{0}C)	32	32
Pressure (atm)	20	20

Source: Pacheco *et al*, 1998.

Table 2: *Characteristics of the Packed Column*

Characteristics	Corresponding Parameter
Column diameter (d)	1.68m
Column height (h) and Parking height (z)	8.0m and 0.533/segment respectively
Number of Plate (N)	4*, 5* & 6
Type of contactor	Pall rings, 0.0381m (d_p)
Surface Tension of packing (dyne/cm)	75.0
Void fraction (ε) of the packing	0.95

Source: Pacheco *et al*, 1998.

Table 3: *Physical properties of the MDEA and Feed Vapor*

Property	MDEA (Absorbent)	Feed Vapor
Density (ρ) (kg/m3)	1041	0.4246
Dynamic Viscosity(μ) (mPa.s)	6.14	-
Surface Tension (η) (mN/m)	47.56	0.03689
Molecular Mass (M)	119.16	20.315
Superficial Velocity (u) (m/s)	0.387	1.1*

Source: Muhammad *et al*, 2008 & literature.

4. Simulation Results and Discussion

Reactive absorption of CO_2 in an absorption column was studied and a model equation which described the mass transfer and chemical reaction processes in the column was developed based on continuity equation.

In the modeling process, various assumptions had to be made in order to simplify the model equation. A pseudo-first order model was assumed and the reversibility of the chemical reaction was as well neglected. A material balance equation was obtained which result into system of linear equations, which describe the concentration (mole fraction) of CO_2 in both gas and liquid phases.

The first step taken in the solution of these systems of linear equation was the determination of the initial and boundary conditions of the system. The final equations obtained were then solved using Excel software. The results of the analytical solution of the model are presented in Tables 4 to 8.

Since no experimental studies were carried out, the input data used for the model simulation were obtained from Pacheco *et al*, (1998); Muhammad *et al*, (2008) work and literature, however few parameters were assumed and changed to suit the purpose of this work. The simulation of the model gives concentrations (mole fractions) of CO_2 in liquid phase and corresponding mole fractions of CO_2 in gas phase were determined for different operating conditions. The degree of adsorption was also obtained using equation (20).

Table 4: *Compositions of CO_2 in Liquid and Gas Phases at* $G_F = 3200\,kmol/hr$ $L_F = 2700\,kmol/hr$, $y_F = 15mol\%$, $m = 1.215$ *and* $N = 4$

Composition of CO_2 in Liquid phase (x)	Composition of CO_2 in Gas Phase (y)
$5.52 * 10^{-5}$	$6.70 * 10^{-5}$
$1.11 * 10^{-6}$	$1.34 * 10^{-6}$
$3.12 * 10^{-5}$	$3.79 * 10^{-5}$
$1.96 * 10^{-3}$	$2.38 * 10^{-3}$

Table 5: *Composition of CO_2 in Liquid and Gas Phase at* $G_F = 3200\,kmol/hr$ $L_F = 2700\,kmol/hr$, $y_F = 15mol\%$, $m = 1.215$ *and* $N = 5$

Composition of CO_2 in Liquid Phase (x)	Composition of CO_2 in Gas Phase (y)
$5.52 * 10^{-5}$	$6.71 * 10^{-5}$
$6.17 * 10^{-7}$	$7.50 * 10^{-7}$
$5.02 * 10^{-7}$	$6.10 * 10^{-7}$
$3.12 * 10^{-5}$	$3.80 * 10^{-5}$
$1.96 * 10^{-3}$	$2.38 * 10^{-3}$

Table 6: *Composition of CO_2 in Liquid and Gas Phases at* $G_F = 3200\,kmol/hr$ $L_F = 2700\,kmol/hr$ $y_F = 15mol\%$ $m = 1.215$ *and* $N = 6$.

Composition of CO_2 in Liquid Phase (x)	Composition of CO_2 in Gas Phase (y)
$5.52 * 10^{-5}$	$6.70 * 10^{-5}$
$6.09 * 10^{-7}$	$7.40 * 10^{-7}$
$1.46 * 10^{-8}$	$1.77 * 10^{-8}$
$4.95 * 10^{-7}$	$6.02 * 10^{-7}$
$3.12 * 10^{-5}$	$3.79 * 10^{-5}$
$1.96 * 10^{-3}$	$2.38 * 10^{-3}$

4.1. Effect of Number of Plate on the Absorption Process

Table 4, 5 and 6 show the effect of number of plate on reactive absorption of CO_2 at constant gas flow rate, liquid flow rate, CO_2 concentration (mole fraction) in feed vapor and equilibrium slope. Three different numbers of plates (N), which are 4, 5 and 6, were considered, it was observed that the concentration of CO_2 in the exit gas stream was constant. The degree of absorption was then determined using equation 20 and was obtained to be 98.4%. This phenomenon is due to the fact that gas and liquid flow rate are large, which result in a low value of x (mole fraction of CO_2 in liquid phase) for the liquid leaving at the bottom.

Table 7: *Composition of CO_2 in Liquid and Gas Phases at* $G_F = 4920\,kmol/hr$ $L_F = 2700\,kmol/hr$ $y_F = 16.3mol\%$ $m = 1.215$ *and* $N = 5$

Composition of CO_2 in Liquid Phase (x)	Composition of CO_2 in Gas Phase (y)
$5.47*10^{-5}$	$6.65*10^{-5}$
$6.45*10^{-7}$	$7.84*10^{-7}$
$1.91*10^{-6}$	$2.32*10^{-6}$
$7.87*10^{-5}$	$9.56*10^{-5}$
$3.25*10^{-3}$	$3.95*10^{-3}$

Table 8: *Composition of CO_2 in Liquid and Gas Phases at* $G_F = 5200\,kmol/hr$ $L_F = 2700\,kmol/hr$ $y_F = 17.2mol\%$ $m = 1.215$ *and* $N = 5$

Composition of CO_2 in Liquid Phase (x)	Composition of CO_2 in Gas Phase (y)
$5.36*10^{-5}$	$6.51*10^{-5}$
$6.30*10^{-7}$	$7.66*10^{-7}$
$2.24*10^{-6}$	$2.72*10^{-6}$
$8.90*10^{-4}$	$1.08*10^{-4}$
$3.55*10^{-3}$	$4.31*10^{-3}$

4.2. Effect of Gas Flow Rate and Mole Fraction of CO_2 on Absorption Process

Tables 5, 7 and 8 show the effect of gas flow rate and mole fraction of the trace component (CO_2) on absorption process, it was observed that at different values of gas flow rate (3200, 4920 and 5200 kmol/hr) and corresponding

values of inlet mole fraction of CO_2 (15, 16.3 and 17.2 mol%) respectively holding other parameters constant, the degree of absorption decreases. When 3200kmol/hr of gas flow rate and mole fraction of 15mol% were considered, the degree of absorption was obtained to be 98.4%, at 4920kmol/hr and 16.3mol%, it was 97.8% and also, it was 97.5% at gas flow rate and mole fraction of 5200kmol/hr and 17.2mol% respectively. This phenomenon was due to the fact that liquid flow rate remained unchanged when gas flow rate and mole fraction of trace component (CO_2) increased. This problem could be solved to some extent by increasing the liquid flow rate or recirculating the liquid over the tower.

5. Conclusion

In this present study, a mathematical model able to represent both mass transfer and chemical reaction processes at a given operating conditions for the reactive absorption of CO_2 in an absorption tower was developed and solved analytically by Matrix method via Excel. Parametric study carried out on the model shown that the concentration of CO_2 in the exit gas stream was constant using different numbers of plate; this was due to large values of gas and liquid flow rates, which result in a low value of mole fraction of CO_2 in liquid phase. Also, the degree of absorption decreases as gas flow rate and trace component's composition increases holding other parameters constant.

Notation

G   gas flow rate, kmol/hr.
L   liquid flow rate, kmol/hr
y   mole fraction (composition) of CO_2 in gas phase.
x   mole fraction (composition) of CO_2 in liquid phase.
R_{MDEA} rate of reaction of methyldiethanolamine, mol/m^{3}s
C   concentration of specie, mol/m^3
T   temperature, K
h_L liquid hold up per tray, kmol.m^3/m^3
m   equilibrium slope
N   number of plate
d   column diameter, m
h   column height, m
P   pressure, atm
z   parking height, m

$$M = \frac{g\mu_L^4}{\rho_L\sigma_L^3}$$, Morton number of liquid

$$C_a = \frac{\mu_L U_L}{\sigma_L}$$, Capillary number of liquid

$$F_{RG} = \frac{U_G^2}{gd}$$, Froude number of gas

U_L superficial velocity of liquid, m/s

U_G superficial velocity of gas, m/s

g   acceleration due to gravity, m/s^2

Greek Letter

ε void fraction of the parking
ρ density, kg/m^3
μ viscosity, Ns/m^2
η surface tension, mN/m
η_a degree of Absorption
$\alpha = L_F$ liquid flow rate, kmol/hr.
$\beta = -(L_F + mG_F + k_R h_L)$, kmol/hr.
$\gamma = G_F$, gas flow rate, kmol/hr.

Subscript

a   absorption
F   feed
N   number of plate
G   gas
L   liquid
K   stage
P   parking
R   reaction
0   initial values

Superscript

*(Asterisk)   assumed Value

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