Modelling of High Pressure, High Concentration Carbon Dioxide Capture in Absorption Column

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Keywords: Mass transfer, countercurrent packed column, CO₂ absorption, high pressure.

Abstract. With the depletion of low carbon dioxide (CO₂) content natural gas reserves, there is a pressing need to explore the vastly undeveloped high CO₂ content natural gas reserves and reduce the release of greenhouse gas CO₂ into environment. Our previous investigation on the absorption performance of CO₂ at high concentration level of 50% from mixture of CO₂-natural gas stream for 20wt% monoethanolamine (MEA) solution in countercurrent packed column indicated efficient removal at high pressure condition. In this present work, a combination mass transfer, chemical reaction of MEA as well as mass conservation equation was developed to model the removal behavior of the high pressure, high concentration CO₂ capture along the absorption column. The model developed in this study had satisfactorily represented the mass transfer behavior for high pressure and high CO₂ concentration gas removal along the absorption column.

Introduction

Natural gas is known to be the cleanest and most hydrogen-rich of all the hydrocarbon energy sources with high energy conversion efficiencies for power generation [1]. However, the existing low carbon dioxide (CO₂) natural gas reserves are depleting fast. In order to support the continuous increasing demand for energy worldwide [2], there is an urgent need to explore the vastly undeveloped natural gas reserves with high CO₂ content up to 80% [3]. Absorption of CO₂ for natural gas purification has been in place in the industry for decades [4]. Research on CO₂ capture from flue gas is also being conducted rigorously worldwide in effort to reduce the catastrophic global warming effect [3]. Nevertheless, the existing system/research mainly focused on low CO₂ concentration up to 20% [5]. Hence, in order to move forward with the implementation of purification process for high CO₂ content natural gas, it is of utmost importance to have an understanding of the mass transfer performance under continuous flow process at high CO₂ content and high pressure condition.

Our previous investigation on the absorption performance of CO₂ at high concentration level of 50% from mixture of CO₂-natural gas stream at high pressure condition for 20wt% monoethanolamine (MEA) aqueous solution in countercurrent packed column indicated efficient removal at higher pressure [6]. In order to simulate and predict the CO₂ removal behavior in counter current absorption column, several models with constant gas flow rate assumption had been previously developed by other researchers [7, 8]. However, in the case of high concentration CO₂ capture conducted in our work, the reduction of the total flow rate of vapor was significant along the column. As such, this current work aims to develop a model applicable for high pressure and high concentration CO₂ capture along the absorption column. A combination of mass transfer, chemical reaction of MEA as well as mass conservation equation model was utilized to develop and elucidate the transport of the conserved mass along the column with the significant reduction of total gas flow rate along the column from high concentration of CO₂ at inlet point to low concentration of CO₂ at gas outlet. The predicted trend of absorption performance at high pressure and high concentration of CO₂ using the developed model was then compared with the actual experimental results for model validation.

Theory and background

Model. A CO₂ absorption model for the countercurrent packed column was developed based on the mass conservation of liquid and gas (vapor) phases. Several assumptions were made for the model, including : (i) Gas conservation was in steady-state, (ii) pressure drop was not significant along the column, (iii) the density and flow rate of the liquid was constant and (iv) the temperature was constant along the column.

Along the absorption column, the amount of the initially high CO₂ concentration in gas stream that was absorbed in liquid/solvent reduced the flow rate of the total gas volume along the column at constant pressure. Hence, a model which considers the significant reduction of the total gas flow rate needs to be developed to predict the performance of the high pressure and high CO₂ concentration absorption column. The correlation of axial velocity with the CO₂ absorption rate can be obtained by mass conservation equation. One dimensional total mole conservation of the CO₂ gas phase in steady state can be expressed in Eq. 1:

$$x_v \frac{d(Cu_v)}{dz} = x_v \frac{Cd(u_v)}{dz} = -N_{CO_2} \quad (1)$$

where, C is the total mole concentration of gas phase, N_{CO_2} is the source term in one unit space meter cube representing the CO₂ mole absorption rate ($\text{kg mole s}^{-1} \text{ m}^{-3}$), x_v is the gas volume fraction in space column and u_v is the gas phase velocity in the z direction (along the column height). For constant total pressure and high concentration CO₂, the correlation of gas flow rate with the CO₂ mole transfer with distance is expressed as in Eq. 2:

$$x_v \frac{d(C_{CO_2})}{dz} = -\frac{N_{CO_2}}{u_v} (1 - y_{CO_2}) \quad (2)$$

where, y_{CO_2} is the CO₂ mole fraction in gas phase and C_{CO_2} is the mole concentration in gas phase (kg mole m^{-3}). Equation 2 includes the factor $(1 - y_{CO_2})$, as the pressure was assumed to be constant, which is different from the other model with the constant flow rate assumption [7]. N_{CO_2} in one unit space meter cube is functioned by the overall coefficients and partial pressure of CO₂, as expressed in Eq. 3:

$$N_{CO_2} = K_G a_{\text{eff}} (p_{CO_2} - p_{e,CO_2}) \quad (3)$$

where, K_G is the overall mass transfer coefficient ($\text{kgmol m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$), a_{eff} is the effective surface area of liquid and gas phase in one unit space meter cube (m^2), p_{CO_2} is the CO₂ partial pressure (kPa) and p_{e,CO_2} is the CO₂ partial pressure in equilibrium condition (kPa). The overall mass transfer coefficient that considered MEA enhancement can be obtained based on liquid and gas phase mass transfer coefficient, as expressed in Eq. 4:

$$\frac{1}{K_G} = \frac{(1-y_{CO_2})}{k_g} + \frac{H_{CO_2}}{k_l^o E} \quad (4)$$

where, k_g is the gas mass transfer coefficient ($\text{kgmol m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$), k_l^o is the liquid mass transfer coefficient, E is the enhancement factor, H_{CO_2} is Henry's constant ($\text{kPa kgmol}^{-1} \text{ m}^3$). $\frac{1}{(1-y_{CO_2})}$ was introduced in the gas mass transfer coefficient by assuming that methane (CH₄) was not absorbed by the solvent. The enhancement factor of MEA solvent can be determined using the approximate solutions provided by Pintola et al (1993) [9], as expressed in Eq. 5:

$$E = 1 + \frac{1}{\left[\left(\frac{1}{E_{\infty}-1} \right)^{1.35} + \left(\frac{1}{E_1-1} \right)^{1.35} \right]^{\frac{1}{1.35}}} \quad (5)$$

where,

$$E_{\infty} = 1 + \frac{C_{MEA} D_{MEA}}{b D_{CO_2} C_{CO_2i}}, \quad E_1 = \frac{\sqrt{M}}{\tanh \sqrt{M}}, \quad M^2 = \frac{D_{CO_2} k_2 C_{MEA}}{k_l^2 \rho^2}$$

C_{MEA} is the MEA concentration in solvent, C_{CO_2i} is the CO_2 mole concentration ($kg \text{ mole m}^{-3}$) in liquid and vapor interface, k_2 is the rate constant of overall MEA and CO_2 reaction given by Hikita et al (1977) [10], b is the stoichiometric factor of MEA reaction and D_{MEA} and D_{CO_2} are the diffusivity of MEA and CO_2 in liquid ($m^2 \text{ s}^{-1}$). The gas mass transfer coefficients were calculated using the correlation function of Onda et al (1968) [11], which is expressed in Eq. 6:

$$k_g = C_1 \frac{a_v D_v}{RT} \left(\frac{G}{a_v \mu_v} \right)^{0.7} \left(\frac{\mu_v}{\rho_v D_v} \right)^{0.33} (a_v dp)^{-2} \quad (6)$$

where, C_1 is the corrected factor, D_v is diffusivity of vapor ($m^2 \text{ s}^{-1}$), μ_v is gas viscosity ($kg \text{ m}^{-1} \text{ s}^{-1}$), a_v is dry packing area per unit volume (m^{-1}), ρ_v is mass density of gas ($kg \text{ m}^{-3}$), and dp is nominal diameter of a piece of packing (m). Meanwhile, the liquid mass transfer coefficient is validated by fitting the experimental results with the simulated results. For liquid phase, the unsteady state one dimensional conservation of liquid flow was introduced to predict the variation of CO_2 and MEA concentration in liquid, as stated in Eq. 7:

$$\frac{d(C_{CO_2}^l)}{dt} + \frac{u_l d(C_{CO_2}^l)}{dz} = \frac{N_{CO_2}}{1-x_v} \quad (7)$$

where, u_l is the liquid phase velocity ($m \text{ s}^{-1}$) in the z direction (along the column height) and $C_{CO_2}^l$ is the mole concentration of CO_2 in liquid phase ($kg \text{ mole m}^{-3}$). Meanwhile, the mole concentration of MEA in liquid phase ($kg \text{ mole m}^{-3}$) can be calculated using Equation 8.

$$C_{MEA}^l = C_{MEA}^l - b C_{CO_2}^l \quad (8)$$

Numerical method. The CO_2 absorption model was executed using Matlab code. In the numerical model, the countercurrent absorption column was divided into an infinite cell with a distance Δz from the bottom to the top of the column as shown in Fig. 1 (a). The mass conservation equation of each cell was solved from the bottom to the top of the column. The vapor mass conservation was assumed to be in the steady state. The iteration time calculations were performed until the liquid steady state solution was achieved. The increasing of the CO_2 concentration for liquid phase with an iteration time can be calculated through the mass transfer rate from the gas steady state conservation equation. The liquid mass transfer coefficient was assumed to be constant under different pressure.

Experiment Methodology

Materials. Monoethanolamine (MEA) (99%) used in this study were purchased from Acros Organics. Distilled water was used to prepare the aqueous solvent for this work. CO_2 (99.9%) used in this experiment was purchased from Air Product Malaysia while natural gas with 97% of CH_4 and 2% of CO_2 was supplied by Petronas Dagangan Bhd.

Methodology for absorption experiment. The experiments were performed using a pilot scale experimental set up as shown in Fig. 1 (b). The absorption column inner diameter (ID) was 0.145 m with column height of 1.769 m. The packing used in this study was structured packing FLEXIPAC 1Y by Koch-Glitsch. There was a distance of 0.5 m between the packing and liquid distributor.

The absorption performance experiment was started by introducing a gas mixture from gas supply system to the bottom of the absorption column. The concentration of CO_2 in CO_2 and natural gas feed gas mixture was adjusted through mass flow controller. A back pressure regulator in the system would maintain the pressure of column at the desired level. Liquid feed at 1 Litre/min was then

pumped to the top of the column from a 200-litre feed tank to create counter-current contact between gas and liquid. The absorption process was operated until steady state condition was achieved.

The CO_2 concentration in the feed gas and treated gas from the start of experiment until it reached steady state was measured using CO_2 infrared (IR) gas analyzer model ZR4Y25 (Fuji Electric Instruments).

Fig. 1: a) Schematic of the countercurrent absorption column with an infinite cell for mass conservation equation. b) Schematic diagram of experimental setup.

Results & Discussions

Fig. 2 shows the comparison between the simulated results and experimental results of CO_2 removal along the absorption column at 10 bar and 30 bar. The higher pressure condition produced a better efficiency of the mass transfer of CO_2 from gas to the solvent. Fresh solvent was introduced at the top of the column and the simulated results for MEA concentration indicated that at a fixed MEA total mole flow rate, shorter absorption column would be required when the pressure condition was higher.

Fig. 2: The comparison between the simulated results and experimental results of 10 bar operating pressure (a) and 30 bar operating pressure (b).

Fig 3 shows that the maximum overall mass transfer rate is allocated at top of the column of 10 bar and middle of column of 30 bar. The results indicated that higher pressure condition enhanced the efficiency of the mass transfer of CO_2 from gas to the solvent. This was due to the increased physical absorption with higher gas pressure as the physical solubility of CO_2 into the solvent was significantly affected by the gas pressure. The simulated results based on the developed model were found to be in good agreement with the experimental results.

Fig. 3: The simulated overall mass transfer, K_g and mole source term in one unit volume, N_{CO_2} of 10 bar operating pressure (a) and 30 bar operating pressure (b).

Conclusion

As a conclusion, the inclusion of the unsteady state liquid mass conservation equation into the model development was crucial in order to elucidate the transport and the absorption of MEA along the column for high CO_2 concentration in feed gas and operating at high pressure absorption column. Since the total gas flow rate was correlated with the total CO_2 transfer flowing through a certain column distance, the effect of the reduction of total gas flow rate along the column is essential to be implemented for the case of high concentration of CO_2 at inlet point to low concentration of CO_2 at gas outlet. Based on the modelling results, the increased CO_2 loading in MEA solution at the bottom of column significantly reduced the CO_2 absorption at the region. High pressure condition is also found to enhance the efficiency of the mass transfer of CO_2 from gas to the solvent.

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