Simulation Comparison Between Equilibrium and Rate-Based Approach for CO₂ Removal Via Promoted K₂CO₃ with Glycine.

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Abstract. The main limitation of rate-based approach in Aspen Plus is the unavailability of the method under dynamic analysis. Hence, to support the development of the integrated process of natural gas treatment at a higher scale, a comprehensive equilibrium and rate-based simulations of CO₂ removal via potassium carbonate promoted with glycine (PCGly) is conducted. The purpose of this study is to observe the efficiency of the equilibrium-based model to represent the CO₂ removal system before the dynamic simulation can be developed. The validation is conducted based on published experimental data and the result shows that at steady state, the equilibrium-based method is able to predict the CO₂ removal as satisfactorily as the rate-based approach. The error deviation between both methods is 2.11 % and through this study, it is shown that the equilibrium-based method is able to simulate the CO₂-PGly system efficiently. Thus, this would enable further investigation of the CO₂-PGly system under dynamic simulation using the equilibrium-based method.

Nomenclature

A	Effective interfacial area (m²)	y	Vapor mol fraction (mol/mol)
a	Gas liquid interface (m²)	z	Column height (m)
a_w	Wetted area (m²)		
C_p	Heat capacity (kJ/kg⁰C)		
D	Diffusion coefficient (m²/s)	*Abbreviations*	
G	Gas flowrate (m/s)		
h_g/h_L	Heat of reaction (kJ)	AMP	2-amino-2methyl-1-propanol
i	Component species	Gly	Glycine
j	Column stage (m)	PZ	Piperazine
k_L/k_G	Mass transfer coefficient in liquid/gas	PC	Potassium carbonate
L	Liquid flowrate (m/s)		
N	Molar flux (mol/m².s)		
P	Pressure (bar)	*Greek letter*	
Q	Energy (kJ/h)	μ	Viscosity (kg/m.s))
T	Temperature (⁰C)	ρ	Density (kg/m³)
x	Liquid mol fraction (mol/mol)		

1 Introduction

The impact of the world's growing population and the need to fulfil high energy demand from industry have alerted the gas industry players to further explore on alternative potential energy source. The abundance of natural gas resources that often associated with stranded gas fields due to high CO₂ content must be carefully evaluated to ensure the trade-off between quality and cost can be optimized. Natural gas reserves in commercial operations throughout the world include variable amounts of CO₂ ranging from CO₂ free to as high as 90% CO₂ content [1]. Thus, special attention to remove these impurities must be conducted to adhere to pipeline specification, enhance the calorific value of

natural gas, corrosion minimization and further overcome related process bottleneck.

Potassium carbonate also has long been used for CO₂ capture for various kinds of processes and offered better advantages such as low toxicity, a low tendency of degradation, less energy requirement, high solubility in carbonate/bicarbonate system and reasonable solvent cost [2]. Nevertheless, the utilization of this solvent suffers a very low reaction rate that consequently causes a slow mass transfer at the liquid phase. Hence, various promoters have been introduced to overcome this limitation and a few criteria have been listed as guidance to choose which promoter is suitable to be used effectively with potassium carbonate. This includes a level of

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toxicity, the enhancement of rate absorption and solvent cost [3].

Among the many promoters in the market, glycine has shown good potential and meets most of the conditions that are appropriate for implementation with potassium carbonate [3-5]. Glycine is categorized under amino acid promoter and it has attracted a lot of interests as it has the same functional group as amine, however at the advantage of having lower resistance to oxidative degradation, non-volatile and less toxicity [4]. To fully understand and observe the true performance of promoted K_2CO_3 with glycine, a continuous performance in the dynamic simulation of the acid gas removal unit must be conducted. Thus, a steady state simulation must first be established. There are two methods available to simulate such systems, which are equilibrium based or rate based approach.

The equilibrium based model assumes that liquid and vapor phases reach equilibrium at theoretical stages and perfect mixing occurs at each stage [6]. The rate of absorption and desorption in reactive distillation is determined by two main mechanisms, mass transfer and chemical reaction. These assumptions are combined with mass and energy balance equations to determine the concentration and temperature along the packed column. This approach is more suitable for a non-reactive system [7].

Another approach to simulate the absorber is the non-equilibrium method, i.e. the so-called rate-based model. In this method, the vapour–liquid equilibrium is assumed to occur at the phase interface between vapor and liquid. The mass transfer between the vapour and liquid phases is modelled based on the two-film theory and the Maxwell- Stefan formulation [7, 8] while others called penetration theory [7]. Nowadays, the rate-based approach is preferred in many simulation platforms due to the higher accuracy and the prediction ability is better than the equilibrium method [8]. There are various aspects are considered under this approach such as enhancement factor, empirical mass transfer correlations and effective interfacial area that specifically designed based on the type of column, hydraulics and transport properties [9, 10] as illustrated in Figure1. However, due to the complexity of this method, not many simulators are able to support this method in a dynamic environment where thousands of mathematical equations need to be simulated simultaneously.
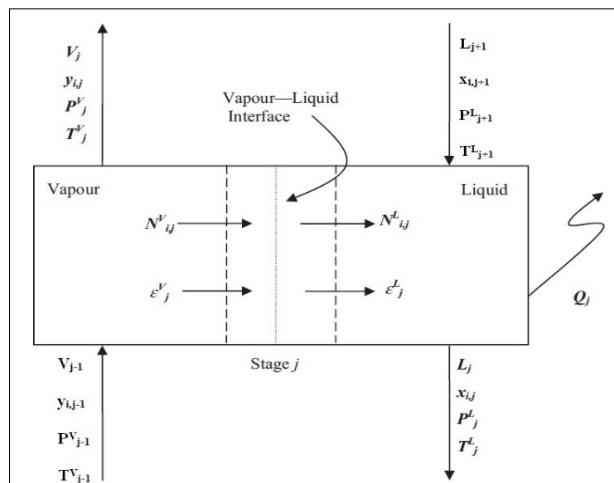
Fig 1 Schematic diagram for rate based method which include vapor and liquid bulk, film and interface [6].

Aspen Plus is a powerful tool that widely used to replicate various kinds of process operation including CO_2 capture. Nevertheless, due to certain limitations, Aspen Plus can only conduct the equilibrium based approach for the dynamic simulation. Hence, this study aims to compare the effectiveness of rate based and equilibrium stage approach at steady sate in predicting the CO_2 removal.

2 Rate Based method

The rate based method is the evolution of equilibrium method stage model that eliminates the necessity of stage efficiency; hence the mathematical equations are separated into two parts, which are gas phase and liquid phase. This method is favourable as it shows the distinction between phases while the convergence is connected through the mass and energy balance that assumed is occurs at the phase interface. The main mathematical equations that governed the rate based method is briefly explained in the following subsection. The details can be found in the [11];

2.1 Mass balance

$$\frac{dG}{dZ} = -(N)_i aA \tag{1}$$

$$\frac{dy_i}{dZ} = \frac{N_i aA(y_i-1) + N_i aA y_i}{G} \tag{2}$$

$$\frac{dG}{dZ} = -(N)_i aA \tag{3}$$

$$\frac{dx_i}{dZ} = \frac{N_i aA(x_i)}{L} \tag{4}$$

2.1 Energy balance

The absorption process that includes chemical reaction will usually produce the heat of reaction, hence this phenomenon will cause the increase of temperature in the column. A simplified energy balance in the liquid and gas phase in presented in the following equation

$$\frac{dT_g}{dZ} = \frac{(N_i+N_{i+1})T}{G} - \frac{(N_i C_{p,i}+N_{i+1}C_{p,i+1})T}{G C_{p,G}} - \frac{h_g a(T_G-T_L)}{G C_{p,G}} \tag{5}$$

$$\frac{dT_L}{dZ} = \frac{(N_i a}{L}T_L - \frac{(N_i C_{p,i}+N_{i+1}C_{p,i+1})T}{L C_{p,L}} - \frac{h_L a(T_G-T_L}{L C_{p,L}} - \frac{(N_i \Delta H_i + N_{i+1}\Delta H_{i+1})a}{L C_{p,L}} \tag{6}$$

2.2 Mass transfer and effective area correlation

Various correlations of mass transfer and effective area are available in the literature. The following equations are the famous Onda correlation that has been well developed and applied in many simulation processes. The detail about the hydraulic correlations that suitable at high operating pressure has been discussed by the author in [12];
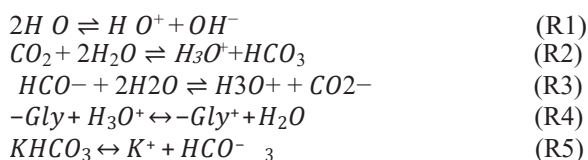
$$k_G = 5.23(a_T D_G)\left(\frac{G_0}{a_w \mu_G}\right)^{0.7}\left(\frac{\mu_G}{D_G \rho_G}\right)^{0.33}\left(a_T d_p\right)^{-2} \tag{7}$$

$$k_L = 0.0051\left(a_T d_p\right)^{0.4}\left(\frac{L_0}{a_w \mu_L}\right)^{0.667}\left(\frac{\mu_L}{D_L \rho_L}\right)^{0.33}\left(\frac{\rho_L}{\mu_L}\right)^{-2} \tag{8}$$

$$a_w = a_T \left(1 - \right.$$
$$\exp \left(1.45 \frac{\sigma_c}{\sigma_L} \right)^{0.75} \left(\frac{L_0}{\mu_L a_T} \right)^{0.1} \left(\frac{a_T L_0^2}{\rho_L^2 g} \right)^{0.05} \left(1.45 \frac{L_0^2}{\rho_L \sigma_L a_T} \right)^{-0.05} \right)$$

(9)

3 Equilibrium method

The equilibrium stage model requires detailed equilibrium reaction and in this study, reactions 1-5 are considered. In this process, the reactions are divided into two main mechanisms which are solvent and promoter reactions. The value of each equilibrium constant is either obtained from literature or from the default provided in Aspen Plus [13]. However, it should be noted that the physical properties of glycine cation are not readily available in the Aspen library. Therefore, the default value of glycine properties is used.

$2H O \rightleftharpoons H O^+ + OH^-$	(R1)
$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3$	(R2)
$HCO^- + 2H2O \rightleftharpoons H3O+ + CO2-$	(R3)
$-Gly + H_3O^+ \leftrightarrow -Gly^+ + H_2O$	(R4)
$KHCO_3 \leftrightarrow K^+ + HCO^-_3$	(R5)

Table 1 Equilibrium constant for the reaction.

Reaction	A	B	C	D
R1	132.9	-13445.9	-22.48	0
R2	231.46	-12092.00	-36.78	0
R3	216.05	-12432.00	-35.48	-0.14
R4	-516.04	20158.62	90.48	-
R5	-274.72	9544.26	41.34	-

4 Experimental data

Both modelling needs to be validated using experimental data. The reliability of any model is questionable without some sort of verification against experimental or bench-scale pilot plant data. Therefore, experimental data from the bench scale mini CHAS pilot plant has been used to validate the simulation models developed using Aspen Plus V10[14]. The bench scale mini CHAS contains a structured typed packing column that is used as absorption medium which capable to be operate up to 100 bar. Structured packing is favorable as it has advantages in providing a lower pressure drop for every single theoretical stage and improved capacity compared to random packing type. Initially, CO_2 and CH_4 is heated in the heat exchanger to avoid liquidation in the tubing. Then, the gas is merged in the static mixer before they are compressed to the bottom of the column. The adjustment of gas feed is controlled by the mass flow controller (MFC) The desired level of pressure is maintained by

regulating the backpressure regulator and in this study, the operating pressure is set at 40 bar. The lean solvent flowrate is transported using high pressure pump to the top of the column. The PC-Gly solvent is prepared with a composition of 15:3 based on weight percentage.

Generally, counter-current mechanism takes place in the absorber column as gas and liquid contacts within the liquid bulk, vapour bulk, films and an interface. Infrared gas analyzer is installed at the top of the column to monitor the CO_2 concentration. The removal of CO_2 is calculated via a simple formulation as shown below. The detail of the absorber for this study is presented in Table 2 while Figure 2 and Figure 3 described the simulation setup and the actual bench scale mini CHAS pilot plant located in Universiti Teknologi PETRONAS.
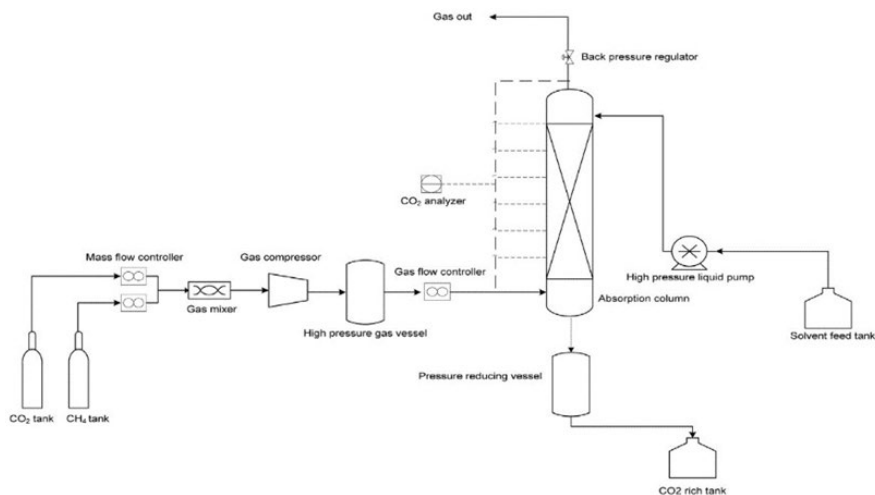
CO_2 removal (%) = (mol $CO_{2\ in}$ - mol $CO_{2\ out}$) /mol $CO2\ in$ (10)

Table 2 Mini CHAS specification

Parameter	Specifications
Material	Sulzer Metal Gauze
Height	2.04 m
Diameter	0.046m
Surface area	500 m^2/m^3
Cross section area	1.67 x 10^{-3} m^2
Void Fraction	0.9
Corrugation inclination angle	60^0
Corrugation side angle	8.9 (mm)

**Fig. 2.** Dynamic bench scale absorption column of mini CHAS

Fig. 3. Schematic diagram of bench scale mini Carbon Hydrogen Absorption System (mini CHAS)

5   Results & Discussion

In this study, the known CO_2-PCGly system is simulated in order to predict the CO2 removal based on the equilibrium and rate based methods. As known, though rate based method offered more advantages in terms of accuracy, the robustness of the equilibrium method can never be neglected. both methods offered different advantages. The equilibrium offered an adjustment of Vaporization efficiency or Murphree efficiency to boost the model accuracy. Number of stages can also be considered as tuning factor for this study and the value is obtained from division of height over HETP (height equivalent to theoretical plate). Hence, the number of stages is kept constant at 7 to reflect the sampling points along the structured column. The efficiency is tuned between 0.1 to 0.9 at stage 7 since the gas inlet located at the bottom of the column.

Figure 4 shows the CO_2 profile based on mole composition using the equilibrium approach for the efficiency tuned between 0.1 to 0.9. As can be observed, stage 7 indicates the bottom of the column and as it moves to stage 1 (top), the mol of CO_2 is reduced significantly. Besides, once the stage efficiency is tuned slowly from 0.9 to 0.1, the removal of CO_2 is improved by a massive reduction of CO_2 mole fraction, and a similar trend is observed for a different stage efficiency. However, the most optimum removal is obtained once the efficiency is tuned at 0.1 and this result is represented by the blue line. The removal obtained from the experimental work is about 75% and the equilibrium method with a tuned Vaporization efficiency managed to replicate the removal up to 74 % once the efficiency is manipulated at 0.1. The efficiency will highly influence the equilibrium constant for the vapor-liquid equilibrium (VLE). Hence, it will amend the volatility of the component calculated by the property model.
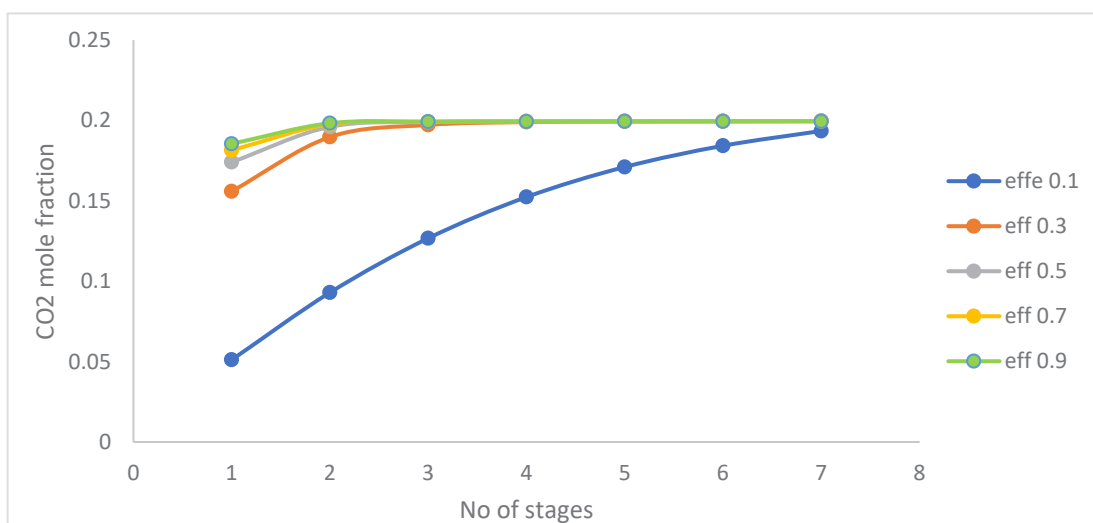
Fig.4. CO_2 profile based on the equilibrium method

Rate based method is contradictory to the equilibrium approach. The stage efficiency will not give any impact on the overall performance but the correct hydraulic data is required for the convergence of the simulation model. Hence, the rate based method offered several types of correlation for mass transfer and heat transfer that will boost simulation accuracy. In this work, several different mass transfer correlations are selected, and the removal is recorded. Based on Figure 5, a similar reduction trend is observed for the mass transfer correlation using Billet 93, Bravo -85. Bravo 92 but slightly different for Hanley Therefore, the focus is given to the three correlations

mentioned and among those three, Bravo-85 produced the highest CO_2 removal which is about 72 %. A good accuracy is obtained using Bravo-85 since this correlation is developed specifically for structured type column. Hence, other aspect such as type of packing, size, packing material will be considered for hydraulic calculation. Looking at the removal obtained using both approaches, the equilibrium method is still worth and capable for the prediction of CO_2 removal as the actual experimental data. Many other tuning factors also can be tuned for rated based approach such as pressure drop, efficiency area and heat transfer to improve the model accuracy .
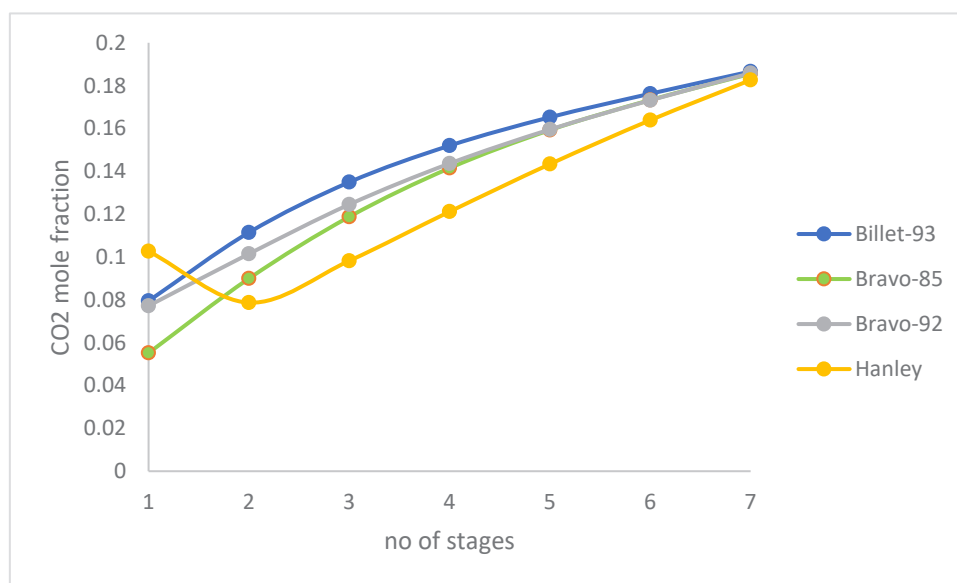

Fig. 5 CO_2 profile rate based method

Conclusion

The simulation of equilibrium and rate based methods for CO_2 removal using promoted potassium carbonate with glycine in this work is based on bench scale mini CHAS pilot plant operated at high pressure. To deduce this study, CO_2 removal via PCGLY can be simulated either using equilibrium or rate-based method, with an error deviation less than 5 %. Hence, this indicates that equilibrium-based model is able to simulate the promoted potassium carbonate with glycine system satisfactorily. This will facilitate further exploration and study in the area of dynamic and control strategies of this solvent in terms of reducing the energy penalty and process efficiency improvements.

Acknowledgement

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