



Assessment of various mass transfer models for CO₂ capture processes by 2-amino-2-methyl-1-propanol.

A. Hemmati^{1*}, A. S. Hemmati², H. Rashidi^{1*}, S. Parandin³

¹ Energy Faculty, Department of Chemical Engineering, Kermanshah University of Technology, Kermanshah, Iran.

² Gachsaran oil and gas production company, Iranian national south oil company, Gachsaran, Iran, 7581873849.

³ Chemical Engineering Faculty, Amirkabir University of Technology, Tehran, Iran

h_rashidi@kut.ac.ir

Abstract

Although there have been various studies on using 2-amino-2-methyl-1-propanol (AMP) as a solvent, none of them have been able to suggest the favorable mass transfer model which accurately predicts CO₂ capture processes' results. In this article, two sets of lab scale data have been used according to Choi et al.'s and Khan et al.'s works [1, 2]. Therefore, the parameters of the kinetics, thermodynamics and hydrodynamics are initially specified with the use of rate-based model, and then in the first validation of the mass transfer models for CO₂ capture process by 2-amino-2-methyl-1-propanol (AMP), the Choi et al.'s experimental data are utilized. To test the reliability of the achieved results in the first validation (and to choose the best correlations for CO₂ capture process by AMP), in the second section of this work Khan et al.'s experimental data have been used. In summary, utilizing correlations of Onda et al., Bravo-Fair (B-F) and Billet-Schultes (B-S) in fourteen different experimental conditions (on the report of Choi et al.'s and Khan et al.'s data), show that Bravo-Fair correlation is more accurate than the two other correlations. After the simulation of Choi et al.'s experimental data and employing mass transfer models, the errors of Onda et al., B-F and B-S are achieved as 10.99, 7.92 and 16.67 % respectively in forecasting CO₂ absorption (%). Considering Khan et al.'s experimental data in 6 different conditions and regarding the three different equations, it is revealed that the mean absolute error (MAE) of Onda et al., B-F and B-S models in forecasting the CO₂ absorption (%) are 9.18, 6.6 and 10.81 % respectively. In the last validation, the accuracy of correlations in predicting absorber loading is investigated according to Khan et al.'s experimental data, which shows that B-F has the highest accuracy compared to two other models. The errors of Onda et al., B-F and B-S models in forecasting rich loading are 14.44, 6.6, and 21.4(%) respectively. Hence, the investigation of the second experimental dataset proves that the B-F is more accurate than the two others models in CO₂ capture process by AMP.

Keywords: Post-combustion CO₂ capture; Rate-based model; AMP; Mass transfer models; Liquid and Gas mass transfer correlations; Effective interfacial area

Introduction

Carbon dioxide is the most destructive green house gas which has irrecoverable effects on climate change [3]. Major generators of CO₂ discharge are energy supplies (47%), industry (30%), transportation (11%) and building sectors (3%) [4]. Therefore, until a permanent solution



is found for the reduction and prohibition of GHGs emission, alternative ways have to be exploited to decrease the harmful effects of this phenomenon; one of these alternatives are post-combustion CO₂ capture [5]. The post-combustion capture technology is the most suitable approach according to the fact that of its easily fitting ability to the existing process units [6]. The most influential and developed method for decreasing the emission of green house gases is employing CO₂ capture processes by chemical solvents especially alkanolamines on condition that flue gas has low pressure [7]. Among alkanolamines, Monoethanolamine is considered the most significant one in CO₂ capture processes, which can be ascribed to its high absorption rate, effortless recovery, and low cost [8]. However, stoichiometry limits the capacity of CO₂ capture to a maximum of 0.5 mole CO₂ per mole amine [9]. The main problems of MEA industrial applications as an absorbent are higher energy demand for solvent regeneration, higher rate of degradation and corrosive nature [10]. To solve these problems, 2-amino-2-methyl-1-propanol (AMP), which is a sterically hindered form of primary amine, can be considered. Some of the qualities of AMP are as follows: considerable CO₂ capture capacity and rate, low solvent recovery energy, high degradation resistance of the solvent, and its minor effect of corrosion on equipment. These characteristics make AMP a favorable option for absorption and desorption processes [11-13]. The absorption process by AMP is explored in this study in agreement with the AMP's capacities for post-combustion CO₂ capture processes, stated in the previous paragraph, and is compared with the industrial benchmark solvents such as MEA. The simulation of industrial CO₂ capture process by AMP is one of the most important steps for the implementation of CO₂ capture units. Thus, in this work the mass transfer models of CO₂ capture by AMP are employed. In previous studies, the validation of CO₂ absorption process by AMP is limited only to absorber column with structured packings [14]. But in this study, the validation of the mass transfer models in CO₂ absorption process by AMP are investigated according to the experimental results of Choi et al. [15, 16] and Khan et al. [2] for the first time. Another parameter that differentiates this study from the previous ones is the low pressure of the absorber and stripper column. Since the flue gas production in the power plant, petrochemical units, refineries, foundries and cement occurs in atmospheric pressure, the cases that have been studied in this work are at low pressure. Finally, it can be said that the aim of this study is to evaluate the mass transfer models for CO₂ capture process by AMP as a solvent in low pressure and in the absorber column with random packings. In this investigation, the models of Onda et al, B-F and B-S are evaluated using the Rate-Base model. The comparison of the simulated and the experimental results are done according to the Khan et al.'s [2] and Choi et al.'s [1] experimental works at the totality of 14 different experimental conditions.

Material and method

Description of experimental CO₂ capture process

The objective of this work is to use the rate-based model to examine the correctness of the mass transfer and effective interfacial area equations in predicting the results of CO₂ capture by AMP. The Aspen Rate-Sep version 8.8 framework, based on the two film theory, has been used as a basis for simulating 14 different experimental conditions for CO₂ absorption by AMP. In this section, first Choi et al.'s and Khan et al.'s experimental setups are explained respectively, then in the second part, the thermodynamic models, physicochemical properties, the kinetic reactions and mass and heat transfer models utilized in this work, are presented. In the experiments done for post-combustion CO₂ capture process by Choi et al., (Figure 1-a), the experimental setup consists of absorption and stripper columns. The absorber and stripper have been made of 316



S.S with an ID of 5.0 cm. The packings that have been used in the columns are 0.635 cm ceramic Raschig ring. The general explanations of CO₂ absorption process by AMP according to Choi et al.'s and Khan et al.'s studies are similar and presented in the following lines. The second validation of mass transfer and effective interfacial area equations is studied according to the Khan et al.'s works (Figure 1-b). The absorber and stripper column's ID is 4 cm and the total height of the absorber and stripper column is 130 cm but the packing height of the column is 84 cm

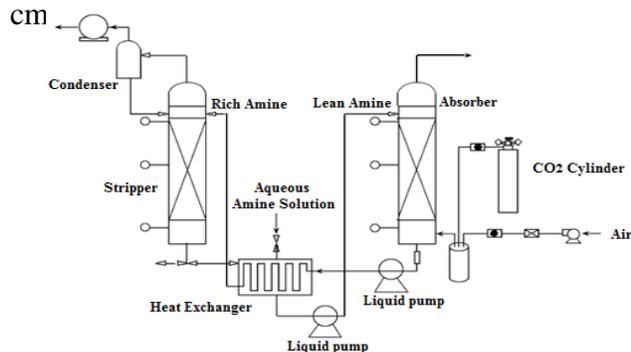


Figure 1-a- Choi et al.'s experimental schematic diagram of the CO₂ absorption [1].

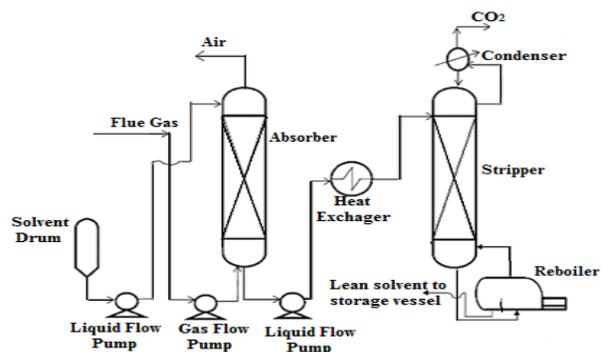


Figure 1-b- Khan et al.'s Experimental schematic diagram of the CO₂ absorption and regeneration [2].

The rate-based model includes the calculations of the reaction rate in the film regions, mass transfer between phases, electrolyte chemistry and hydrodynamics [17]. The mass transfer model used in the present work is based on the two-film theory. Thus, CO₂ is absorbed from the gas phase into the liquid phase. CO₂ absorption process by amines as solvents are described according to the film mass transfer model and the rate base model in previous studies[18].

Rate-Base model parameters

Unlike the equilibrium model, when rate-base model is applied in the simulation of post-combustion CO₂ capture processes, in each stage of absorption and desorption columns, the following parameters are taken into account: kinetic reactions in liquid phase (film area), mass transfer and heat transfer phenomena for each of the gas and liquid phases which leave each stage, effective interfacial area between gas and liquid phases in each stage, many of physical-chemical, hydrodynamic, thermodynamic parameters, and the parameters related to gas and liquid flows in addition to the reactive parameters of gas and liquid phases. The kinetic mechanism of CO₂ capture processes by AMP as well as the parameters considered in the simulation of the capture process by Rate-Base model is elucidated in this section. The rate of CO₂ capture is increased with the use of Amine solvents in the presence of chemical reactions. The bicarbonate and carbonate ions are the only major chemical sinks for CO₂, Carbamate (Reaction 5), is very unstable and effortlessly converts into Amine and Bicarbonate (Reaction6). It is suggested that owing to the instability of the carbamate formed, these promptly undergo hydrolysis to form bicarbonate releasing free amine that again reacts with CO₂ [12]. Reaction 7, which is the general reaction of CO₂-AMP-H₂O system, results from reactions 5 and 6. Conferring to equation (7), one mole of CO₂ is absorbed per mole of amine. Steric effects have an impact on the stability of amine-carbamate formed as a result of amine reacting with CO₂. The reactions of CO₂ absorption process by AMP are introduced in Table 1, equations 1 to 7. The characteristics of the CO₂capture process by AMP using the rate-base model are presented in Table 2.



Table 1- The reactions of CO₂ capture process by AMP in the absorption column.

Reactions	Formation
$2H_2O \leftrightarrow H_3O^+ + OH^-$	(Water Dissociation) (1)
$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$	(Carbonate) (2)
$AMPH^+ + H_2O \leftrightarrow AMP + H_3O^+$	(AMP Protonation) (3)
$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$	(Bicarbonate) (4)
$2AMP + CO_2 \rightarrow AMPCOO^- + AMPH^+$	(Carbamate) (5)
$AMPCOO^- + H_2O \rightarrow AMP + HCO_3^-$	(Amine, Bicarbonate) (6)
$AMP + CO_2 + H_2O \rightarrow AMPH^+ + HCO_3^-$	(Catalyzed hydration) (7)

Table 2- The rate base model parameters which have been employed.

Model approach	Rate-base model approach
Heat transfer coefficient	Chilton and Colburn
Film resistance options	Film for vapor phase and Discrxn for liquid phase
Liquid density	Clarke model
Viscosity	Jones-Dole model
Surface tension	Onsager-Samaras model
Binary diffusivity	Nernst-Hartley model
Thermal conductivity	Riedel model
Thermodynamic properties	Zhang et al.
Thermodynamic model	Electrolyte-NRTL in the liquid and RK equation in the vapor phase
Kinetic reactions	Hikita and Pinsent models

Result and discussion

The characterization of mass transfer models of Onda et al., B-F and B-S are presented in previous Hemmati et al.'s work [18]. Tables 3 and 4 in provide the correlations in gas and liquid phases, respectively. Table 5 present the correlations for the liquid-gas effective interfacial areas in the packed column.

Table 3- Mass transfer coefficients in the liquid phase.

Onda et al.	$k_L = \frac{0.0051}{(a_p d_p)^{-0.4}} \left(\frac{\mu_L g}{\rho_L} \right)^{\frac{1}{3}} \left(\frac{\rho_L u_L}{a_e \mu_L} \right)^{\frac{1}{3}} Sc_L^{-0.5}$ (8)
Billet and Schultes (B-S)	$k_L = C_L \left(\frac{\rho_L g}{\mu_L} \right)^{\frac{1}{6}} \left(\frac{D_L}{d_h} \right)^{0.5} \left(\frac{u_L}{a_p} \right)^{\frac{1}{3}}$ (9)
Bravo-Fair (B-F)	$k_L = 0.0051 (Re_L)^{0.667} Sc_L^{-0.5} (a_p d_p)^{0.4} \left(\frac{\mu g}{\rho} \right)^{0.333}$ (10)

Table 4- Mass transfer coefficients in the vapor phase.

Onda et al.	$k_V = 2 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p < 0.015m$ (11)
	$k_V = 5.23 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p > 0.015m$ (12)
Billet and Schultes (B-S)	$k_G = C_G \frac{a_p^{0.5} D_G}{\sqrt{d_h (\varepsilon - h_L)}} \left(\frac{\rho_G u_G}{a_p \mu_G} \right)^{\frac{3}{4}} Sc_G^{\frac{1}{3}}$ (13)
Bravo-Fair (B-F)	$k_V = 2 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p < 0.015m$ (14)
	$k_V = 5.23 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p > 0.015m$ (15)

Table 5- Effective interfacial areas' equations in the packed column.

	$a_t = a_e A_t h_p$ (16)
Onda et al.	$a_e = a_p \left[1 - \exp \left(-1.45 \left(\frac{\sigma_c}{\sigma} \right)^{0.75} Re_L^{0.1} Fr_L^{-0.05} We_t^{0.2} \right) \right]$ (17)
Billet - Schultes (B-S)	$a_t = a_e A_t h_p \left(\frac{a_e}{a_p} \right) = 1.5 (a_p d_h)^{-0.5} \left(\frac{\rho_L u_L d_h}{\mu_L} \right)^{-0.2} \left(\frac{\rho_L u_L^2 d_h}{\partial_L} \right)^{0.75} \left(\frac{u_L^2}{g d_h} \right)^{-0.45}$ (18)
Bravo-Fair (B-F)	$a_t = a_e A_t h_p \left(\frac{a_e}{a_p} \right) = 19.87 (Ca_L Re_V)^{0.392} \frac{\sigma^{0.5}}{h_p^{0.4}}$ (19)



The prevalent study analyzes the performance of mass transfer and effective interfacial area correlations of Onda et al., B-F and B-S in CO₂ capture by AMP as a solvent. It has investigated two sets of experimental data provided by Choi et al. and Khan et al. [1, 2]. First, Choi et al.'s data and then Khan et al.'s experimental works are studied in 8 and 6 different experimental conditions respectively. Table 6 provides Choi et al.'s experimental conditions, (other parameters such as inlet solvent flow rate, the temperatures of lean solvent and flue gas remain constant).

Table 6- Choi et al.'s experimental conditions for CO₂ absorption by AMP.

Posibilities #1	Solvent flow rate (ml/min)	AMP (wt%)	Gas flow rate (l/min)	CO ₂ inlet concentration (% Vol)
1	110	30	5	12
2	110	30	7.5	12
3	110	30	10	12
4	110	30	12.5	12
5	110	30	15	12
6	110	10	10	12
7	110	20	10	12
8	110	40	10	12

Comparing the results, it is concluded that B-F's error is 7.9 %, which presents the lowest error in predicting CO₂ absorption (%). B-S model with the error of 16.6 % owns the lowest accuracy. Figures 2-a and 2-b demonstrate the comparison between the amounts of CO₂ absorption (%) in 8 different experimental conditions and the average errors of the correlations in forecasting experimental results respectively.

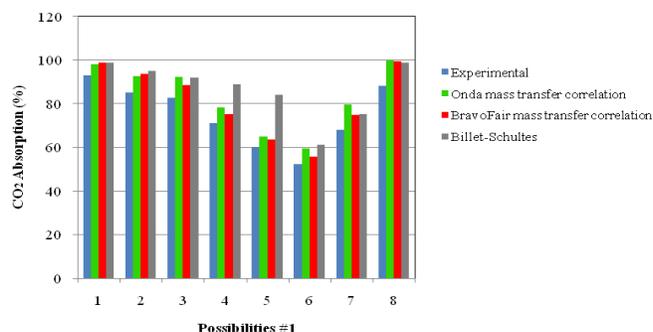


Figure 2-a- Relative errors of the correlations for CO₂ absorption by AMP and according to the Choi et al.'s works.

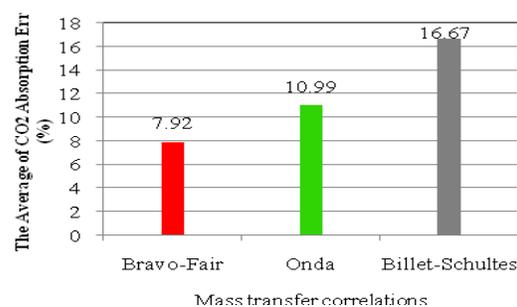


Figure 2-b-The mean absolute error (MAE) of correlations.

To test the reliability of the achieved results, Khan et al.' studies have been utilized in the second validation of the equations which is done to investigate the results of the first validation. For this goal, the 6 different experimental conditions of Khan et al.'s works have been used. These conditions are presented in Table 7. Other parameters such as liquid flow rate, solvent temperature, etc. are kept constant. According to the experimental conditions in Table 7, the validation of the Onda et al., B-F and B-S models is employed for these 6 cases.

Table 7- Khan et al.'s experimental conditions for CO₂ absorption by AMP.

Possibilities #2	Gas flow rate (m ³ /min)	Mole fraction of CO ₂	Solvent concentration (wt %)	Liquid flow rate (m ³ /min)	T (°C)
1	0.006	0.15	30	0.0003	40
2	0.007	0.15	30	0.0003	40
3	0.008	0.15	30	0.0003	40
4	0.005	0.15	10	0.0003	40
5	0.005	0.15	20	0.0003	40
6	0.005	0.15	30	0.0003	40



The comparison of the correlations in proportion to Khan et al.'s and Choi et al.'s works presents that the Bravo-Fair's correlation is the best choice. In other words, Bravo-Fair correlations' mean absolute error (MAE) in forecasting the CO₂ absorption is 6.6 % in proportion to Khan et al.'s works. On the other hand, Onda et al.'s and B-S' models' average errors are 9.18 and 10.81 % respectively. Figure 3-a a comparison between the amounts of CO₂ absorption (%) in 6 different experimental situations, regarding to the Khan et al.'s works, for three different correlations. In Figure 3-b, the MAE of the correlations are presented.

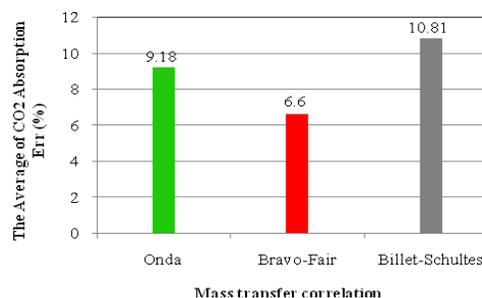
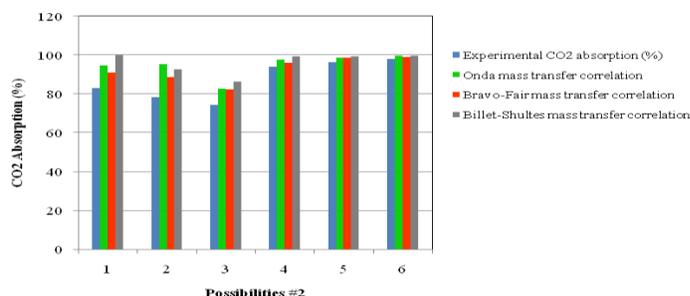


Figure 3-a- Relative errors of three correlations for CO₂ absorption by AMP and according to the Khan et al.'s works.

Figure 3-b- The mean absolute error (MAE) of the correlations.

In the last part of this article, absorber loading, in laboratory situation is compared with the loading gained from mass transfer equations regarding to Khan et al.'s experimental results (Table 7). As it is obvious from Figures 4-a and 4-b, the MAE of B-F model is 6.6%. Onda et al. and B-S models have the average errors of 14.44 and 21.4 % respectively for the same conditions. Therefore, the minimum error belongs to B-F model.

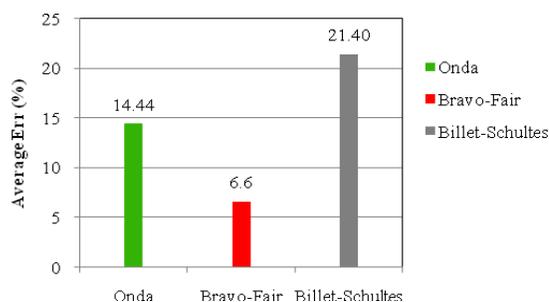
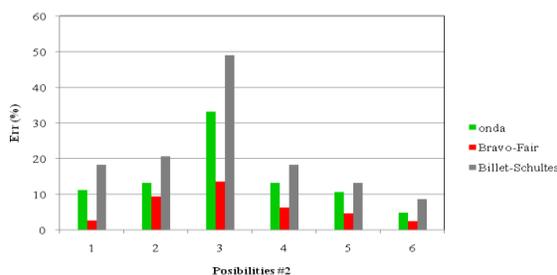


Figure 4-a- Relative error (%) of correlations in predicting rich solvent's loading.

Figure 4-b- The mean absolute error (MAE) of correlations in predicting rich solvent's loading.

The Onda et al. model predicts a wetted area of approximately one half of the total area for the packing used. More area measurements are necessary for a better model. The other reason for Onda et al. model's poor prediction is its incompetence in predicting diffusion calculation. If the main cause of the error is wrong diffusivities, then a constant correction factor is likely to over-predict performance at low loading and to under-predict performance at high loading. This is due to the fact that the diffusivities are unimportant at low loading, whereas they are rate controlling in absorbers that operate at high loading. On the other hand, Choi et al.'s and Khan et al.'s experimental results prove that absorber loading is more than 0.5. Hence, the diffusivities of AMP and reaction products can be significant at this loading. In some cases in the absorber, the mass transfer can be controlled by gas phase resistance. The correlation of Onda et al. for kg is very general, thus it cannot be very accurate for every type of packing and every flow range. However, Bravo-Fair model owns more beneficial prediction compared to other two models.



Although Bravo-Fair used the same expressions as Onda et al. for the mass transfer coefficients, the modified Reynolds number employed in the calculation of liquid phase mass transfer coefficient is hinged on the effective surface area rather than wetted surface area. Consequently, they recommended that a correspondence between liquid holdup and effective transfer area is to be anticipated due to the nature of the hydraulics and geometry of packed beds with gas and liquid in counter flow. For this reason, the trends perceived in liquid holdup behavior at different loading conditions should be applied for effective area. In addition, an added gas kinetic energy effect should be incorporated for the area analysis on account of its influence on film surface rippling, liquid droplet dispersion, and the occurrence of gas bubbling in puddles. According to Bravo-Fair's studies, the product of the liquid's capillary number, and the gas' Reynolds number, appears to give a suitable parameter for representing effective areas.

Conclusion

In this study, the mass transfer models have been inquired into with the aim of introducing the best one used for CO₂ capture process by AMP for the first time. Additionally, two experimental datasets have been employed according to Choi et al.'s and Khan et al.'s works. In the first validation, CO₂ absorption (%) is evaluated in 8 different experimental conditions using Onda et al., B-F and B-S models as stated by Choi et al.'s works. The consequences show that Bravo-Fair correlation is the most accurate model compared to two other correlations. The MAE of Onda et al., B-F and B-S in predicting the CO₂ absorption (%) are 10.99, 7.92 and 16.67 % respectively. To test the reliability of the achieved results in the first validation, Khan et al.'s experimental datasets have been used in the second validation of this work. These evaluations have been done in 6 different experimental conditions. The consequences of Khan et al.'s works regarding mass transfer equations suggest that Bravo-Fair's model has the error of 6.6 % in forecasting CO₂ absorption, which is the lowest, compared to two other ones. The same study has also been carried out about the rich loading and as stated by Khan et al.'s works. Based on the results of rich loading, the MAE of Onda et al., B-F and B-S models are 14.44, 6.6 and 21.4% respectively. As a result, like previous study, this one also shows that Bravo-Fair equation gives more accurate prediction compared to two other ones. With regard to the results described in this work, it is proposed that Bravo-Fair correlation be used as the best model for the simulation of CO₂ capture process by AMP.

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