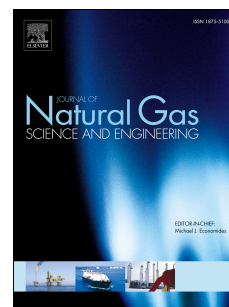


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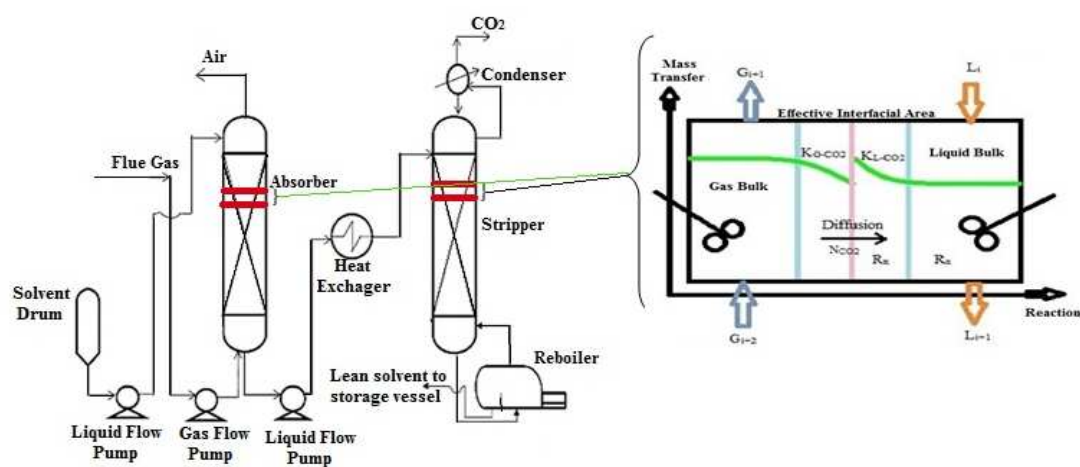
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Assessment of mass transfer correlations used in post-combustion CO₂ capture by piperazine activated 2-amino-2-methyl-1-propanol (a-AMP).

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Abstract

The prevalent solvents used in CO₂ capture processes have such drawbacks as degradability, high energy consumption for solvent regeneration, low absorption capacity, and corrosive nature which have convinced the researchers to suggest a new combination of alkanolamines in place of the commonly-used solvents like MEA. Since Rate-Based model, compared to Equilibrium model, gives more accurate simulations of CO₂ capture processes by amine solvent, it is used in this study. Mass transfer correlations are significant parameters in Rate-Based model, and using them improperly will lead to considerable disagreement between real and simulated results.

In the present work, mass transfer coefficients in CO₂ capture processes are evaluated using an aqueous blend of piperazine activated 2-amino-2-methyl-1-propanol (a-AMP) solution for the first time. It is done according to Khan et al. [1] experimental results in 36 points and for different operational conditions. In the first evaluation, 12 sets of data are achieved following the changes of the operational parameters, gas flow rate and CO₂ partial pressure, while other parameters such as operational absorption temperature, solvent flow rate and solvent blends of AMP+PZ remain constant. The studies indicate that considering the amount of CO₂ absorbed, the Mean Absolute Errors (MAE) of Onda et al., Bravo-Fair, and Billet-Schultes mass transfer coefficients are 12 %, 7.63 %, and 3.2 % respectively in comparison with Khan et al. results. The second evaluation is also done in 12 operational points regarding the variations of PZ concentration and operational absorption temperature. Other parameters remain unchanged in this evaluation, too.

This study demonstrates that Billet-Schultes correlations own higher accuracy compared to the Onda et al. and Bravo-Fair. Mean Absolute Errors (MAE) of Onda et al., Bravo-Fair, and Billet-Schultes are 12.74 %, 8.26 %, and 2.04 % respectively. The third evaluation of this work is of rich solvent loading (absorber loading). Similarly, this evaluation is performed in 12 operational points in regard to the changes of CO₂ partial pressure and the ratio of AMP to PZ, while other operational parameters are kept constant. This evaluation likewise shows that, compared to two other ones, Billet-Schultes correlations have more precision when utilized in CO₂ capture processes by the a-AMP solvent. Mean

Absolute Error (MAE) of Onda et al., Bravo-Fair, and Billet-Schultes in predicting absorber loading and in accordance with experimental data are 24.21 %, 16.44 %, and 6.23 % respectively.

Keywords: Rate-based model, CO₂ absorbed, Absorber loading, Piperazine activated 2-amino-2-methyl-1-propanol (a-AMP), Mass transfer coefficient, Effective interfacial area.

Introduction

According to the statistics provided by Mauna Loa Observatory, CO₂ concentration in July 2019 has been the highest in the earth atmosphere with the amount of 411.77ppm [2]. Figure 1 traces the changes in CO₂ concentrations in Julys of 2000 to 2019.

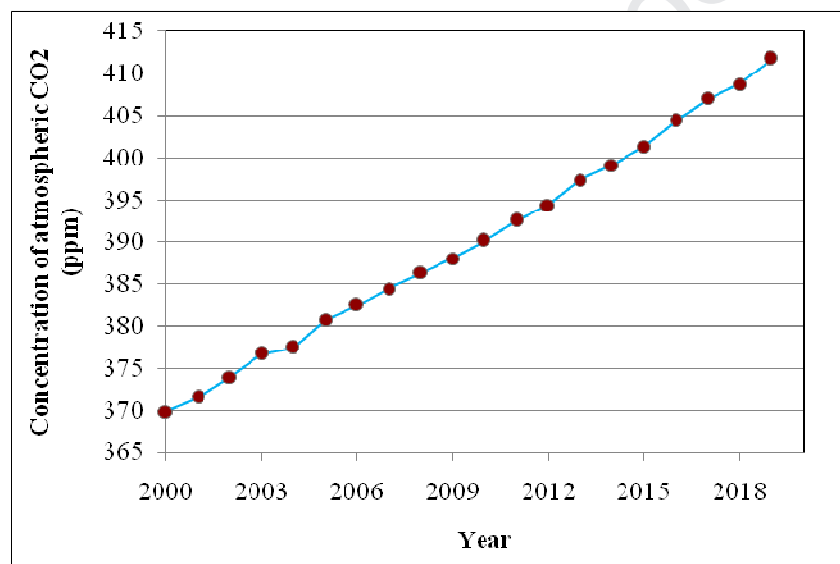


Figure 1- The changes in CO₂ concentration in Julys of 2000 to 2019.

The increase in greenhouse gases emission has caused a lot of concerns regarding global warming's irrecoverable damages. Measurements indicate that 2019 has been the hottest year with the temperature increase of 0.95 degrees centigrade which is attributed to the rise in greenhouse gases especially CO₂ [2]. Global warming has irreversible consequences such as abrupt climate changes, polar ice melting, sea-level rise, drought, extreme cold, flood, sand storms, etc., which will affect the lives of living creatures [3]. The most important processes of converting and utilizing CO₂ are divided into two categories of physical and chemical. As to physical applications, injecting CO₂ in gas and oil wells (in order to enhance gas and oil recovery), dry ice production, and fire extinguishers are the most significant ones. On the other hand, productions of Methanol, Demethylether, urea, dimethyl carbonate, and methane in addition to the Fischer-Tropsch process are some of the major usages of CO₂ in chemical processes [4]. Thus, researchers attempt to prevent this situation from deteriorating by suggesting temporary methods to reduce and control the emissions of greenhouse gases. In order to utilize CO₂ in either physical or chemical processes, it should be absorbed and purified. The physical and chemical processes of CO₂ absorption are increasing continuously. CO₂ chemical absorption by amines is one of the most prevalent CO₂ industrial absorption methods [5]. However, these kinds of

solvents have weak points which will be referred to in the following [6, 7]. Among the post-combustion, pre-combustion and oxy-combustion methods, the most acceptable option is post-combustion CO₂ capture by amine solvents [8, 9]. Amine solvents which are commonly used in post-combustion CO₂ capture processes have such disadvantages as degradability, high energy consumption for solvent regeneration, low absorption capacity and corrosive nature [1, 10].

One of the ways to overcome amine solvents' drawbacks is to use ionic liquids (ILs) solvents [11]. Unfortunately, ILs, which can absorb physically, have high viscosity [7], and their loading capacity is limited compared to chemical solvents such as monoethanolamine [12]. Chemical absorption of CO₂ by ILs can be a good option substituting amine solvents [11-14]. Nonetheless, ILs are not widely used in industrial and semi-industrial scales, which is due to the fact that inexpensive ILs are unavailable [15]. Additionally, the investment costs of CO₂ absorption processes by ILs are higher compared to amine solvents [16]. Another solution is utilizing new chemical solvents or combining them in a way that makes up for each other's downsides and replacing them with prevalent solvents have become the focal point of researchers in recent years [1, 17-19]. Researchers have found ways to improve ILs performance when used with such activators as amine compounds [20, 21]. Studying solvents with unique capabilities are still in progress. Using ILs solvents in CO₂ absorption processes has not been completely rejected yet, and utilizing them in industrial and semi-industrial units are being studied in laboratory and pilot scales [7, 22].

Despite the abundance and diversity of solvents used in CO₂ absorption, few of them have been qualified to be industrialized. However, various studies have been done on determining the optimal conditions of CO₂ absorption in a solvent or a mixture of physical and chemical solvents [23-25]. One of the challenges that industrial CO₂ absorption plants face is using prevalent solvents such as MEA which are highly degradable and need a large amount of energy for solvent regeneration [26]. Among the available solvents, AMP has been the center of expert's interest and activity, for it provides an equilibrium loading capacity twice than that of any primary and secondary amines like as tertiary amines. AMP is known as a strategic option for defeating the problems that prevalent industrial solvents such as MEA have. The capacity of CO₂ absorption by AMP is high and less recovery energy is required in the processes of CO₂ absorption by this solvent. Besides, its thermal degradability and oxidation are low, and equipment corrosion in absorption processes by this solvent is little [27-29].

The main drawback of AMP, which is a sterically hindered form of primary amine, is its low rate of reaction with CO₂ [30]. Therefore, Khan et al. [1] recommend that considering AMP's downsides, piperazine (PZ), as a new cyclic diamine which has advantages such as high kinetic rates, lower corrosion, considerable equilibrium absorption loading capacity, and favorable solvent properties [31] can be introduced as a suitable option to be blended with AMP solvent in capture processes. Therefore, the new absorbent blend represents less corrosion, reasonable thermal stability and thermal degradation rate, higher capacity and efficiency with less regeneration energy consumption [32-34]. Employing blended amines in gas treating will enable us to benefit from the merits of all kinds of amines at the same time, as they can bring about satisfactory absorption performance compared to the benchmark MEA. Due to the above advantages, the blended solvent of AMP+PZ has been considered as promising for absorbing bulk CO₂. Khan et al. [1] used the aqueous blend of AMP+PZ solution for CO₂ capture processes. Seo and Hong [35], Khan et al. [1] and Sun et al. [36] suggest such characteristics as significant CO₂ reactivity with the rate activator PZ, the high equilibrium loading capacity of AMP, and fairly smaller enthalpy heat of AMP that is less solvent regeneration energy for the a-AMP solution. Using a proper approach for precisely simulating CO₂ capture industrial units leads to achieving results that are so close to simulated ones. Since the mass transfer coefficients in Rate-Based model are so influential in the accuracy of simulated results compared to real results, in the present study, mass transfer coefficients, which are given in Rate-Based model, are evaluated for CO₂ capture process by PZ activated AMP (a-AMP) solution for the first time.

The goal of this work is to offer a precise approach to the simulation of CO₂ capture process by AMP+PZ solvent. The Rate-Based model of Aspen Plus v.8.8 has been used in this study, for it is a comprehensive collection of heat and mass transfer coefficients, thermo-physical, and physiochemical properties. Such qualities that Rate-Based model owns enable it to provide accurate results compared to real results. Thus, in the current study, Rate-Based model is used to examine mass transfer coefficients in the capture process of CO₂, existing in flue gas, by the a-AMP solution, which has not done before. The precise explanation of mass transfer correlations which are able to forecast actual results accurately is vital for a correct design. Thus, introducing an exact procedure for using blended solvents such as AMP+PZ in place of benchmark solvents (MEA or AMP) would encourage industry owners to use these new solvents. One of the downsides of the CO₂ capture process by new solvents such as AMP+PZ is that various correlations' validity in the estimation of mass transfer has not been looked into yet. Accordingly, there has been no study regarding the comparison between various mass transfer correlations.

One of the reasons for this is the newness of Rate-Based model and the shortage of process data, either industrial or laboratory, regarding the process of CO₂ absorption by AMP+PZ solvent. consequently, this work is the first study concerning the use of mass transfer correlations in CO₂ absorption process by AMP+PZ solvent. This work aims to cause theoretical viewpoints to approach real results. Hence, the mass transfer coefficients are assessed in 36 points with regard to Khan et al. experimental results. The second novelty of this study is the execution of the absorption process in low pressure. The major sources of greenhouse gases are power plants, petrochemical units, refineries, foundries, and cement plants, which produce flue gas in atmospheric pressure. Therefore, these kinds of capture processes which occur in atmospheric pressure are more efficient concerning viability and cost compared to bulk-removal absorption processes which the pressure of their absorption and desorption columns is high [37]. Hence, in this study, the pressure of CO₂ in the flue gas has been considered low.

Methodology

Experimental setup data

There is no industrial or semi-industrial information in regard to the process of CO₂ absorption by the combination of AMP and PZ as a solvent. Hence, Khan et al. experimental data have been used in the present study to simulate the process of CO₂ absorption by the a-AMP solution. Figure 2 shows the diagram of CO₂ absorption and desorption by AMP+PZ. Experimental setup includes absorption and desorption columns. The flue gases initially enter the absorption column. After passing through 0.75-inch Helipack packing, they come into contact with a-AMP solvent as counter-current streams. Prior to getting into the desorption column, the solvent which exits from the absorption column enters the exchanger to be pre-heated. The exchanger locates between the absorption and desorption columns. Finally, the rich solvent enters the desorption column in which the solvent is regenerated and CO₂ is separated.

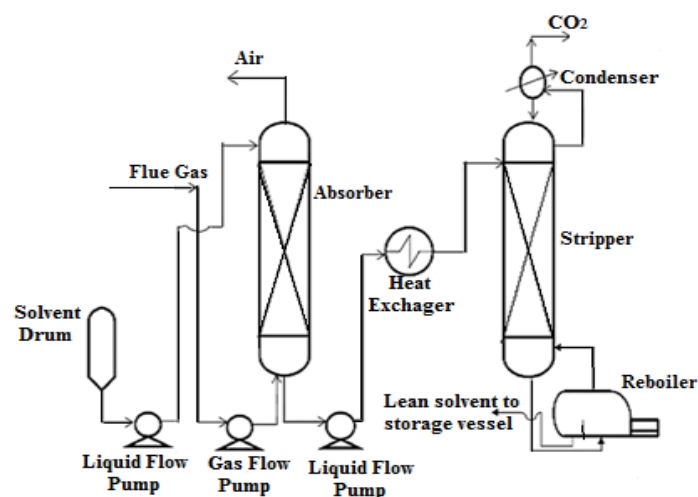


Figure 2- Experimental diagram of CO₂ absorption process.

In order to simulate the absorption and recovery process of flue gas CO₂, comprehensive information of operational conditions especially those of absorption and desorption columns such as the columns' temperature, pressure, diameter, and height as well as their packing's type, material, and size should be available. In addition, the data relating to the reactions, which occur during the absorption process and as a consequence of the contact of the solvent(s) with the flue gas, should be accessible. For the experimental CO₂ absorption process, four amine blends of AMP and PZ are utilized. The total amine concentration is 30 wt %. The concentrations of AMP/PZ (wt/wt) are 28/2, 25/5, 22/8, and 20/10. Table 1 gives the experimental setup of key process parameters.

Table1- process parameters of experimental setup.

Description of operational parameters	
Flue gas source	Generated by firing coal
Flue gas' CO ₂ concentration (Vol %)	10, 12 and 15
Operational absorption temperature (K)	298, 303 and 308
Absorption and stripper columns inner diameter (m)	0.04
Absorption and stripper columns' height (m)	1.3
Absorption and stripper columns' packing height (m)	0.84
Absorber and stripper columns' packings type	Nonreactive metal HELI-PAK
Packing size	0.175 inch
Surface area (m ² /m ³)	1500
Solvent flow rate × 10 ⁻⁴ (m ³ min ⁻¹)	1.5, 2, 2.5 and 3
Gas flow rate × 10 ⁻³ (m ³ min ⁻¹)	5, 6, 7 and 8
solvent blends of AMP/PZ (wt/wt)	28/2, 25/5, 22/8 and 20/10
Total amine concentration (wt %)	30
CO ₂ partial pressure (kpa)	10, 12 and 15
The regeneration temperatures (K)	368, 372, 376, 379 and 383
Operational absorption pressure	Atmospheric
Operational stripper pressure (kPa)	50–55

Rate-Based model description

Mass transfer model

What is significant in this work is the assessment of mass transfer coefficients' precision in predicting the reported experimental conditions, which is due to the fact that this study is the turning point in using an accurate method to simulate and design the units of CO₂ absorption by AMP+PZ solvent. For this reason, Rate-Based model has been employed in the present study in order to simulate CO₂ absorption process. A traditional method for modeling absorption and desorption columns is the Equilibrium model in which, similar to Rate-Based model, the absorption and desorption columns are divided into the specific number of stages, and the gas and liquid phases which leave each stage are in equilibrium[5, 38].

The equilibrium method is not suited to reactive absorption, for it predicts the effect of reactions on heat and mass transfer poorly [39]. Although the Rate-based model employs the mass transfer for a considerably accurate prediction of separation between phases, it takes into account the actual rates of the multi-component mass and heat transfer along with the chemical reactions and hydrodynamics of the system [40, 41].

When Rate-Based model is utilized for simulating post-combustion CO₂ capture process, unlike Equilibrium model, the following parameters are taken into account for each stage of absorption and desorption columns: kinetic reactions in liquid phase (film region), mass and heat transfer for each of the liquid and gas phases leaving each stage, effective interfacial area between gas and liquid phases in each stage, and many other physical-chemical, hydrodynamic, and thermodynamic parameters in addition to the parameters related to gas and liquid streams as well as reactive parameters of gas and liquid phases[39, 42].

Since Rate-Based model has a considerable accuracy, compared to Equilibrium model, which is due to its comprehensive possession of the correlations of mass and heat transfer between gas and liquid as well as at the effective interfacial area of gas and liquid phases [5], it is used in the present study for absorption and desorption columns. Table 2 provides the Rate-Based model's parameters.

Table 2- Rate-Based model's parameters

Parameters	Model
liquid viscosity	Jones-Dole
Liquid hold-up	Billet et al.
liquid surface tension	Onsager-Samaras
Diffusivity	Nernst-Hartley
Liquid density	Clarke model
Thermal conductivity	Riedel
Flooding	Stichlmair et al.
Flow model	Mixed
Resistance model for liquid film	Discrxn
Liquid film discretization	5
Discretization ratio	5
Resistance model for gas phase	Film
Heat transfer coefficient	Chilton and Colburn
Thermodynamic properties	Electrolyte-NRTL for liquid phase and RK for vapor phase

The kind of mass transfer coefficients and the coefficients connected with the effective interfacial area between gas and liquid phases that Rate-Based model considers are highly influential in the precision of experimental or industrial results prediction [43].

The mass transfer model employed by Rate-Based model is based on Two-film theory. In the film model, the mass transfer of gas and liquid phases is divided into two regions i.e. film and bulk regions. According to the film theory of mass transfer model, CO₂ diffuses through the gas film and is absorbed in the liquid phase. All the concentrations are assumed to change only in the film region. As shown in Figure 3, the liquid's film region is subdivided into equal sections, which is called liquid film discretization. The reactions of the absorption process in liquid bulk are in equilibrium. The reactions of the film region will be explained in the following.

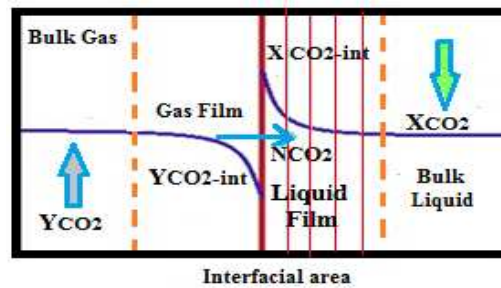
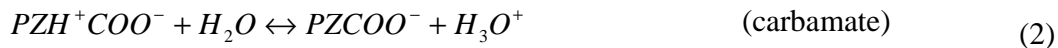


Figure 3- profile of CO₂ absorption regarding to the Rate-Based model.

Reactions mechanism

The reaction's systems of CO₂-H₂O-AMP-PZ in the absorber and stripper are reported according to the kinetic model. The reactions' mechanism are described according to Bishnoi and Rochelle's [44], Dash et al's [45] and Bosch-Versteeg' works [46].

According to the studies, the process of CO₂ absorption by amine blend aqueous solvent occurs in a first-order and fast reactional system [45, 47]. Two sets of reactions occur in the process of CO₂ absorption by a-AMP aqueous solvent: 1- reversible reactions with limited rate, 2- Reversible reactions with the high rate, which only include proton transferring. The following reversible reactions are given in the first set of reactions (1 to 5). The equilibrium reactions' instantaneous are presented in relations 1 to 5. In these reactions, the reactions such as PZ Protonation, the carbamate production, Water dissociation, and AMP protonation are provided.



In order to define the equilibrium reactions, the thermodynamic equilibrium constants of the reactions and their stoichiometric coefficients are used considering the activity of species taking part in the reactions [45].

As mentioned previously, another set of reactions that are influential in the absorption process is reversible reactions with limited rate. The reactive mechanisms of two-step zwitterion [48, 49] and single-step termolecular [50-52] can be employed to justify the process of CO₂ capture by a secondary alkanolamine. Hydration mechanism is used for the reactive system of CO₂-AMP according to Chakraborty et al., and Yih and Shen [28, 53]; zwitterions mechanism is employed for both reactive systems of CO₂-PZ, on the report of Bishnoi and Rochelle [27], and CO₂-AMP-PZ, as stated by Sun et al. [36]. Comparing Khan et al. [47] findings regarding reaction total rate constant, it is concluded that the activation energy which they have suggested for CO₂ absorption by the AMP-PZ solvent is so close to the amounts reported by Bishnoi and Rochelle [54] for CO₂ absorption by PZ and by Saha et al. [29] for CO₂ absorption by AMP.

The reversible reactions 6 to 11 describe CO₂'s mass transfer rate in the absorption process by a-AMP solution. These reactions have limited rates. The kinetic rates' constant of reactions 6 to 11 are presented in Table 3.

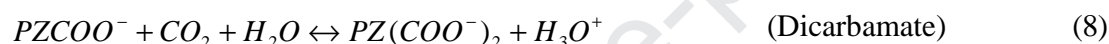


Table 3- Reaction rate coefficients

NO of reactions	Reaction rate constant
6	$K_6 = 10^{(13.635-2895/T)}$
7	$K_7 = \exp(32.52-6433.73/T)$
8	$K_8 = 5.95 \times 10^4 \exp(-3.55 \times 10^4/RT)$
9	$K_9 = \exp(23.69-5176.49/T)$
10	$K_{10} = 3.516 \times 10^4 \exp(-7.2 \times 10^4/RT)$
11	$K_{11} = 1.836 \times 10^4 \exp(-7.6 \times 10^4/RT)$

3. Results and Discussion

The researchers have recommended various mass transfer correlations for gas and liquid phases[39, 55], yet few studies have been done on finding the most efficient coefficients which are able to predict experimental results precisely. This may be attributed to different reactive mechanisms for various solvents, and lack of process information of laboratory set-ups or industrial plants, etc. There has been no method suggested for the usage of these coefficients in the process of CO₂ capture by a-AMP, which is owing to the lack of laboratory and experimental data connected with this process. In the current study and for the first time, all mass transfer coefficients available in Aspen Plus for gas and liquid phases are evaluated. The coefficient which has been listed in Table 4, 5 and 6 are applied to estimate the liquid-side, vapor side and effective interfacial areas in the absorption column, respectively [55].

Table 4- Mass transfer correlations in the liquid phase.

Onda et al.	$k_L = \frac{0.0051}{(a_p d_p)^{-0.4}} \left(\frac{\mu_L g}{\rho_L} \right)^{\frac{1}{3}} \left(\frac{\rho_L u_L}{a_e \mu_L} \right)^{\frac{1}{3}} Sc_L^{-0.5} \quad (12)$	[56]
Billet and Schultes	$k_L = C_L \left(\frac{\rho_L g}{\mu_L} \right)^{\frac{1}{6}} \left(\frac{D_L}{d_h} \right)^{0.5} \left(\frac{u_L}{a_p} \right)^{\frac{1}{3}} \quad (13)$	[57]
Bravo et al.	$k_L = 0.0051 (Re_L)^{0.667} Sc_L^{-0.5} (a_p d_p)^{0.4} \left(\frac{\mu g}{\rho} \right)^{0.333} \quad (14)$	[58]

Table 5- Mass transfer correlations in the vapor phase.

Onda et al.	$k_V = 2 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p < 0.015m \quad (15)$	[56]
	$k_V = 5.23 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p > 0.015m \quad (16)$	
Billet and Schultes	$k_G = C_G \frac{a_p^{0.5} D_G}{\sqrt{d_h (\varepsilon - h_L)}} \left(\frac{\rho_G u_G}{a_p \mu_G} \right)^{\frac{3}{4}} Sc_G^{\frac{1}{3}} \quad (17)$	[57]
Bravo et al.	$k_V = 2 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p < 0.015m \quad (18)$	[58]
	$k_V = 5.23 (Re_V)^{0.7} Sc_V^{0.333} a_p (a_p d_p)^{-2} D_V \text{ if } d_p > 0.015m \quad (19)$	

Table 6-Effective interfacial area correlations in the packed column.

Onda et al.	$a_I = a_e A_t h_p \quad (20)$	[56]
	$a_e = a_p \left[1 - \exp \left(-1.45 \left(\frac{\sigma_c}{\sigma} \right)^{0.75} Re_L^{0.1} Fr_L^{-0.05} We_l^{0.2} \right) \right] \quad (21)$	
Billet - Schultes	$a_I = a_e A_t h_p$ $\left(\frac{a_e}{a_p} \right) = 1.5 (a_p d_h)^{-0.5} \left(\frac{\rho_L u_L d_h}{\mu_L} \right)^{-0.2} \left(\frac{\rho_L u_L^2 d_h}{\partial_L} \right)^{0.75} \left(\frac{u_L^2}{g d_h} \right)^{-0.45} \quad (22)$	[57]
Bravo et al.	$a_I = a_e A_t h_p$ $\left(\frac{a_e}{a_p} \right) = 19.87 (Ca_L Re_v)^{0.392} \frac{\sigma^{0.5}}{h_p^{0.4}} \quad (23)$	[58]

The operational conditions of experiments regarding the process of CO₂ capture by AMP+PZ solvent have previously been outlined. Since the aim of this work is to assess the accuracy of coefficients in predicting Khan et al. results, Onda et al., Bravo-Fair and Billet-Schultes correlations are employed in 36 points with different operational conditions. The changes applied in operational conditions are stated in Tables 7, 8 and 9. These tables provide the experimental results.

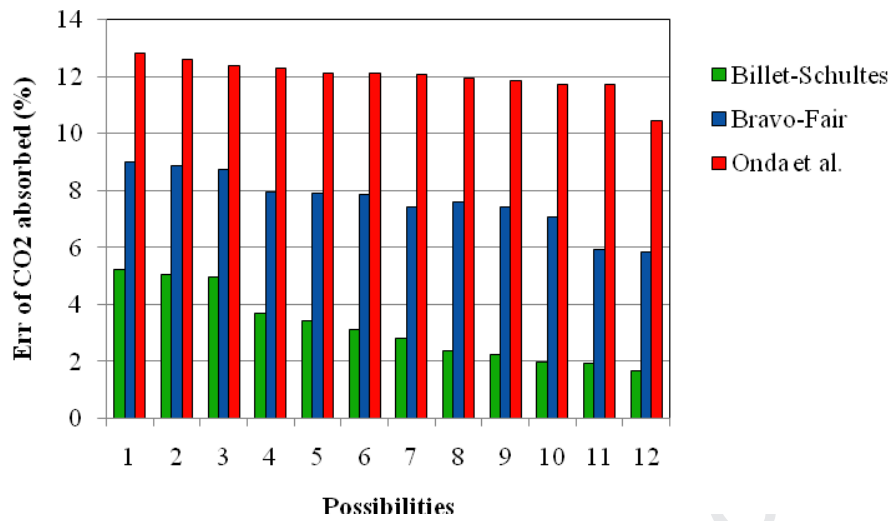
In the first evaluation and as given by Table 7, gas flow rate and CO₂ partial pressure (kPa) vary in 12 operational points, while other parameters such as operational absorption temperature, solvent flow rate, and the solvent blend of AMP+PZ remain unchanged. The decrease in CO₂ partial pressure results in a drop in the amount of CO₂ which has been absorbed physically, and a rise in the chemical absorption through the reaction between CO₂ and AMP+CO₂+H₂O aqueous solvent.

Table 7- Effect of CO₂ partial pressure and gas flow rate on the percentage of CO₂ absorbed.

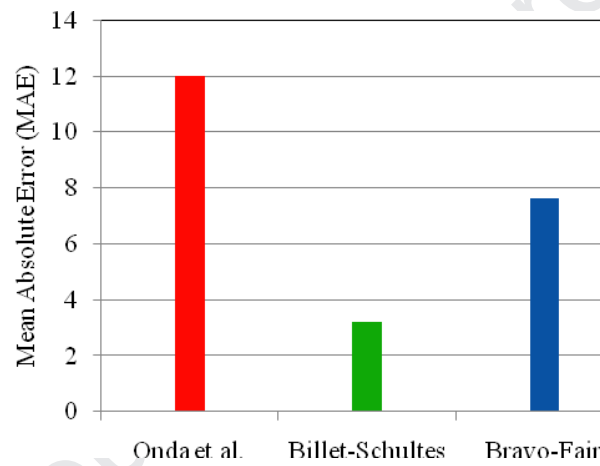
Possibilities	CO ₂ partial pressure (kpa)	Gas flow rate $\times 10^3$ (m ³ min ⁻¹)	Experimental CO ₂ absorption (%)
1	10	5	98.8125
2	10	6	98.8906
3	10	7	98.9718
4	10	8	99.00
5	12	5	99.0015
6	12	6	99.11
7	12	7	99.2013
8	12	8	99.2687
9	15	5	99.4062
10	15	6	99.5
11	15	7	99.5625
12	15	8	99.625

The simulation results of the 12 points presented in Table 7 indicate that Billet-Schultes coefficients have the most accurate predictions for the CO₂ capture process with a Mean Absolute Error (MAE) of 3.2 %. However, MEAs of Onda et al and Bravo-Fair coefficients are 12 % and 7.63 % respectively. Figure 4 compares the three correlations in 12 operational conditions. The calculated absorption percentages of the three correlations are provided in Table1 of the supplementary data. The absorption percentage is obtained from relation 24.

$$\text{Absorption percentage} = \left(\frac{\text{kg CO}_2 \text{ in flue gas} - \text{kg CO}_2 \text{ in outlet gas}}{\text{kg CO}_2 \text{ in flue gas}} \right) \times 100 \quad (24)$$



(a)



(b)

Figure 4- mass transfer coefficients' prediction of CO₂ absorption, a- absorption percentage in 12 possibilities, b- coefficients' mean absolute error

The second validation is executed in 12 points in regards to the changes applied in operational absorption temperature and PZ concentration. Nevertheless, other operational parameters like flue gas's CO₂ concentration, solvent flow rate, and gas flow rate remain constant. The experimental results of these changes are provided in Table 8.

Replacing AMP with PZ in the constant total blend amine concentration (total concentration of AMP+PZ is constant) leads to the elevation of Enhancement Factor. This rise is more intense in smaller quantities of PZ, which is due to the formation of PZ-carbamate and PZ-dicarbamate ions.

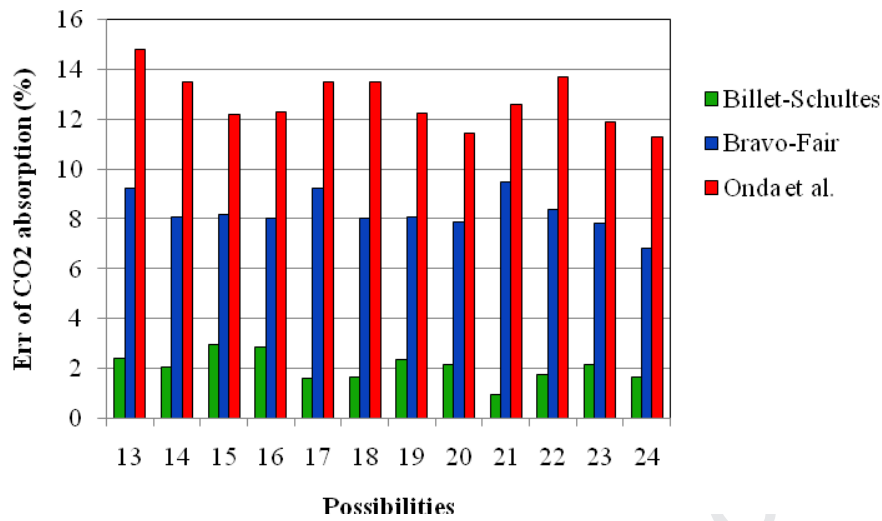
According to the results of Khan et al., Xu et al. [59], Zhang et al. [34], Bishnoi and Rochelle [54], and Sun et al. [36], regarding the usage of PZ as an activator with AMP aqueous solvent, it is deduced that AMP-PZ solvent is the most favorable option in terms of both kinetics and absorption in comparison with benchmark solvents like MEA AND AMP.

These studies indicate that temperature has a positive effect on reaction rate constant and as a result, on the total reaction rate constant in the absorption by PZ aqueous solution. In other words, the temperature rise will result in the total reaction rate constant of CO₂ absorption by AMP+PZ solution to increase, too. When the temperature goes up and PZ concentration (as an activator) is constant, the diffusion and solubility of CO₂ in amine blend will improve. Absorption rate will also increase continuously when temperature rises and PZ concentration and CO₂ partial pressure remain constant, which is due to the fact that temperature rise will cause reaction rate constant and CO₂ diffusion to increase (The reaction rate constants of CO₂ capture by AMP aqueous solvent and by PZ solvent is second-order) [45, 47].

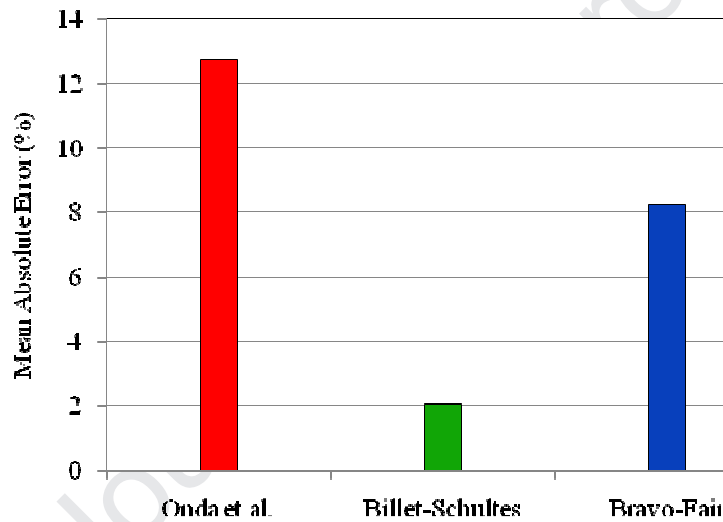
Table 8- Effect of solvent blend and solvent temperature on the percentage of CO₂ absorbed.

Possibilities	Operational absorption temperature (K)	PZ Concentration (wt %)	CO ₂ absorption (%)
13	298	2	94.375
14	298	5	97.125
15	298	8	98.125
16	298	10	98.3837
17	303	2	95.0625
18	303	5	97.25
19	303	8	98.2125
20	303	10	98.5625
21	308	2	96.325
22	308	5	97.875
23	308	8	98.4687
24	308	10	98.76

In the second evaluation (possibilities 13 to 24), Billet-Schultes coefficients own the most accurate prediction of CO₂ absorption compared to the laboratory results. According to this assessment, MAEs of Onda et al, Bravo-Fair, and Billet-Schultes are 12.74 %, 8.26 %, and 2.04 % respectively. The calculated absorption percentages by the three coefficients are given in Table 2 of the supplementary data. Figure 5 compares the coefficients' prediction of CO₂ absorption for the second validation.



(a)



(b)

Figure 5- mass transfer coefficients' prediction of CO₂ absorption, a- absorption percentage in possibilities 13 to 24, b- coefficients' mean absolute error

The third validation is done based on the comparison between the results of three correlations for absorber loading and according to the experimental results. This evaluation is in respect to the changes made in AMP/PZ and CO₂ partial pressure. In the meantime, other operational parameters are kept constant. Khan et al.'s results are presented in Table 9. Absorption column's loading is calculated by relation 25.

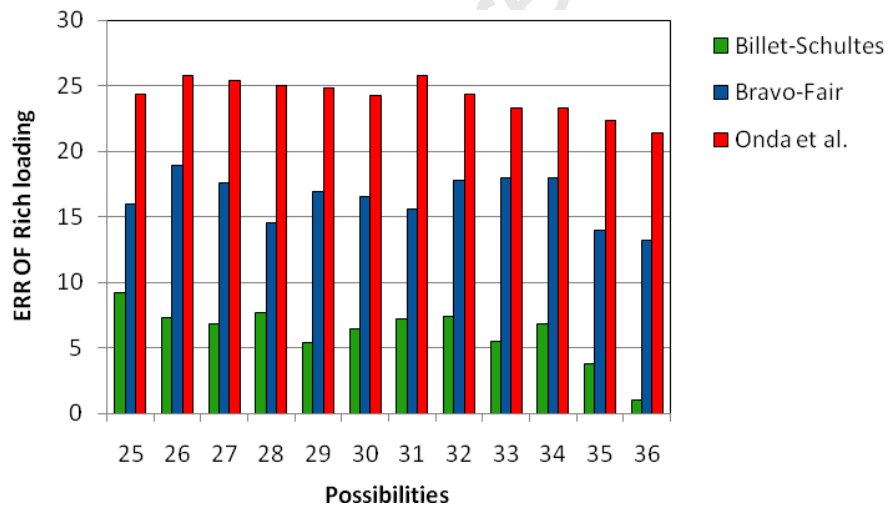
$$\text{Loading} = \left(\frac{\text{molCO}_2 + \text{molHCO}_3^{2-} + \text{molCO}_3^{2-} + \text{molH}^+ \text{PZCOO}^- + \text{molPZCOO}^- + \text{molPZ}(\text{COO}^-)_2}{\text{molAMP} + \text{molAMP}^+ + \text{molPZ} + \text{molPZH}^+ + \text{molHPZCOO} + \text{molPZCOO}^- + \text{molPZ}(\text{COO}^-)_2} \right) \quad (25)$$

Table 9- Effect of AMP to PZ ratio and CO₂ partial pressure on Absorber Loading.

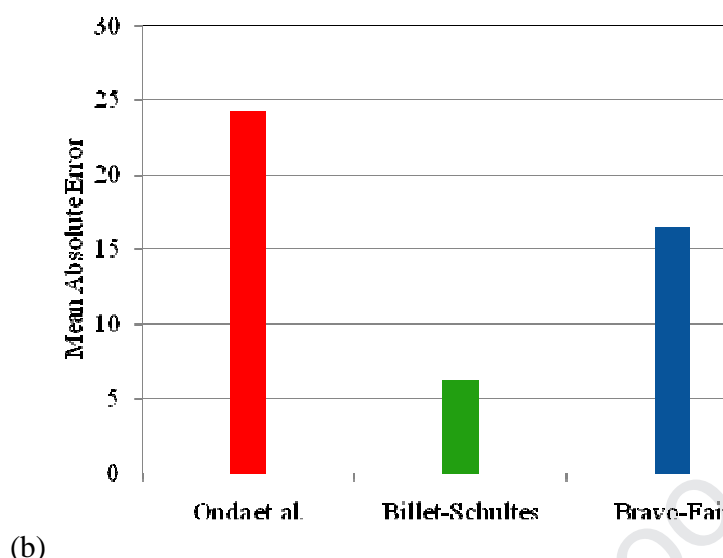
Possibilities	SB = AMP/PZ	CO ₂ partial pressure (kpa)	Absorber Loading (mol of CO ₂ / mole of amine blend)
---------------	-------------	--	---

37	28/2	10	0.8333
38	28/2	12	0.8760
39	28/2	15	0.8980
40	25/5	10	0.8542
41	25/5	12	0.8913
42	25/5	15	0.9113
43	22/8	10	0.8765
44	22/8	12	0.9126
45	22/8	15	0.9386
46	20/10	10	0.9266
47	20/10	12	0.9538
48	20/10	15	0.9800

The third evaluation (possibilities 25 to 36) similarly proves that Billet-Schultes model, with MAE of 6.23 %, gives a more precise prediction of absorber loading in comparison with Bravo-Fair model, with MAE of 16.44 %, and Onda, with MEA of 24.21 %. The calculated absorber loading for coefficients is presented in Table 3 of the supplementary data. Figure 6 compares the correlations' predictions of absorption column's loading for possibilities 24 to 36.



(a)



(b)
Figure 6- comparison between the correlations regarding the prediction of absorption column's loading.
a) For possibilities 25 to 36. b) MEA of each coefficient

Conclusion

The prevalent solvents' disadvantages in CO₂ capture processes, such as their degradability, high energy consumption for solvent recovery, low CO₂ absorption capacity, and corrosive nature have persuaded the scientists to suggest a combination of Alkanolamines to be used in place of the common solvents like MEA. However, this leads to facing some challenges during the simulation processes of the units before the implementation of the operational phase. Thus, it is vital to outline the Rate-Based model's parameters which are able to predict CO₂ capture processes precisely. In the current study and for the first time, Onda et al., Bravo-Fair, and Billet-Schultes correlations have been evaluated with the aim of introducing the best mass transfer coefficients in the processes of CO₂ capture by a-AMP as a solvent. This evaluation has been done in 36 points regarding different operational conditions. The results of the first assessment in 12 points indicate that in comparison with two other models, Billet-Schultes model owns the most suitable prediction of CO₂ absorption in regard to the varying operational parameters of gas flow rate and CO₂ partial pressure. In the first evaluation, MAEs of Onda et al., Bravo-Fair, and Billet-Schultes are 12 %, 7.63 %, and 3.2 % respectively. The second assessment has been performed in 12 points concerning the changes in operational absorption temperature and PZ concentration. Its results also proves that Billet-Schultes model has the least error, i.e. 2.04 %, in predicting CO₂ absorption compared to two other models. The errors of Onda et al. and Bravo-Fair in this assessment have been 12.74 % and 8.26 % respectively. The third evaluation of this study belongs to the rich solvent loading, which has also been done in 12 points. In this assessment, while CO₂ partial pressure and the ratio of AMP to PZ change, the amounts of absorber loading in the laboratory are compared with its simulated results from applying the three mass transfer coefficients in Rate-Based model. The outcomes demonstrate that Billet-Schultes model, with the error of 6.23 %, gives the most exact prediction of the experimental results in comparison with Onda et al. model, with the error of 24.21 %, and Bravo-Fair model, with the error of 16.44 %.

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- Introducing AMP+PZ as a new solvent which can compensate for the drawbacks of benchmark solvents such as MEA.
- Suggesting the Rate-based model and an efficient package of it as an accurate model to simulate and design CO₂ capture units.
- Evaluating various mass transfer coefficients used in the simulation of the CO₂ capture process by AMP+PZ solvent for the first time.
- Recommending Billet-Schultes mass transfer coefficients as the most accurate ones to predict the experimental results of the CO₂ capture process by AMP+PZ solvent.

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