



Content list available at [ICONSMAT](https://www.iconsmat.com.au)

Journal of Construction Materials

Journal homepage: www.iconsmat.com.au/publication

Article history:

Received 20 April 2021
Received in revised form
25 April 2021
Accepted 25 April 2021
Available online
27 April 2021

Assessment of carbon dioxide separation by amine solutions using electrolyte non-random two-liquid and Peng-Robinson models: Carbon dioxide absorption efficiency

Arash Esmaeili^{1*}, Zhibang Liu¹, Yang Xiang¹, Jimmy Yun^{2*}, Lei Shao¹

¹Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, China

²School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

*Corresponding authors: Arash Esmaeili (phone: +8613161777098; e-mail: ar.esmaeili@mail.buct.edu.cn); Jimmy Yun (e-mail: jimmy.yun@unsw.edu.au)

Abstract

A high pressure carbon dioxide (CO₂) absorption from a specific gas in a conventional column has been evaluated by the Aspen HYSYS simulator using a wide range of single absorbents and blended solutions to estimate the outlet CO₂ concentration, absorption efficiency and CO₂ loading to choose the most proper solution in terms of CO₂ capture for environmental concerns. The property package (Acid Gas-Chemical Solvent) which is compatible with all applied solutions for the simulation in this study, estimates the properties based on an electrolyte non-random two-liquid (E-NRTL) model for electrolyte thermodynamics and Peng-Robinson equation of state for the vapor and liquid hydrocarbon phases. Among all the investigated single amines as well as blended solutions, piperazine (PZ) and the mixture of piperazine and monoethanolamine (MEA) have been found as the most effective absorbents respectively for CO₂ absorption with high reactivity based on the simulated operational conditions.

DOI: [10.36756/JCM.v2.3.10](https://doi.org/10.36756/JCM.v2.3.10) ©2021 Institute of Construction Materials



Keywords

Absorption, amine solutions, Aspen HYSYS, carbon dioxide, simulation.

Introduction

The greenhouse gases emission has become one of the most challenging environmental issues during the last few decades and the rising CO₂ concentration in the past 200 years has contributed significantly to the global warming phenomena. A wide range of CO₂ emissions is directly related to consumption of fossil fuels; therefore, invention and development of efficient processes to reduce capital and operational costs as well as the size of equipment for CO₂ capture have attracted wide interest.

Different methods have been developed for CO₂ capture based on chemical reactions between CO₂ and various types of alkanolamines in both conventional columns and rotating packed beds (RPBs). For example, [1]-[3] studied CO₂ absorption by MEA in a conventional column and RPBs, respectively. The most important advantage of absorption is that absorbents can be regenerated by introducing the CO₂-rich absorbents into a stripper where off-gas is removed by rising temperature. The drawbacks of chemical absorption processes include high energy consumption and limited loadings created by heat of reaction and the reaction stoichiometry in addition to the problems of corrosion and degradation with some of the absorbents.

The commonly used absorbents are non-sterically hindered amines (non-SHAs) in aqueous solutions such as MEA and diglycolamine (DGA) as primary amine, diethanolamine (DEA) and diisopropanolamine (DIPA) as secondary amine, methyldiethanolamine (MDEA) and triethanolamine (TEA) as tertiary amine. Sulfinol-D (mixture of DIPA and sulfolane) and Sulfinol-M (mixture of MDEA and sulfolane) as the combination of chemical and physical absorbents have found some significant applications during the last few decades. The blended amine solutions containing SHAs have been also experimented by scientists and industries. For instance, [4] studied CO₂ absorption by 2-amino-2-methyl-1-propanol (AMP); [5] investigated AMP+MEA in a conventional column; [6] evaluated the blended solution of AMP+PZ; [7] conducted experiments on a number of SHAs; [8] published experimental data for CO₂ removal by MEA, DEA, TEA and AMP; [9] and [10] examined CO₂ capture by diethylenetriamine (DETA)+PZ and aqueous DETA solution respectively in an RPB.

The absorption of CO₂ occurs via a two-step mechanism:

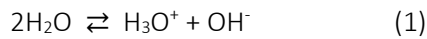
1. the dissolution of CO₂ in the aqueous amine solution, and then,
2. the reaction of the weak acid solution with the weakly basic amine.

The first absorption step is controlled by the partial pressure of the CO₂ in the gas feed. Amines can be classified according to the number of hydrogen atoms that have been substituted, as primary (R-NH₂, where R is a hydrocarbon chain), secondary (R-NH-R') or tertiary (R'-NR-R'') amines [11]. This study investigated the ability of all types of amine solutions as single and blended absorbents to assess their reactivity with CO₂ and select the most appropriate one in terms of absorption efficiency.

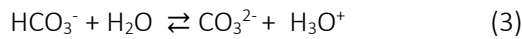
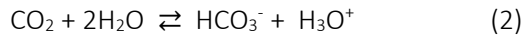
Chemistry of the reaction between CO₂ and Amines

For primary and secondary amines, such as MEA and DEA, the carbamate formation reaction predominates; this reaction is much faster than the CO₂ hydrolysis reaction. The stoichiometry of the carbamate reaction limits the capacity of primary and secondary amines to approximately 0.5 mole of CO₂ per mole of amine. However, DEA-based amine processes can also achieve loadings of more than 0.5 mole of CO₂ per mole of amine through the partial hydrolysis of carbamate (RNHCOO-) to bicarbonate (HCO⁻), which regenerates some free amine [11]. Xiao et al. [5] have reviewed the equilibrium reactions of CO₂ with both primary and secondary amines:

Dissociation of water:



Hydrolysis and dissociation of dissolved CO₂:



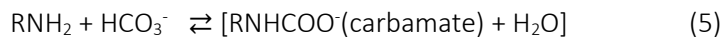
The reaction (R2) is very slow ($k = 0.026 \text{ s}^{-1}$ at 25 °C and may usually be neglected).

Protonation of the amine:

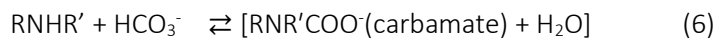


Carbamate formation:

Primary amine:



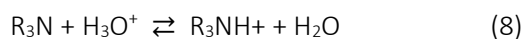
Secondary amine:



And the subsequent removal of the proton by a base B, which could be an amine, OH⁻ or H₂O, from a zwitterion can be shown as:



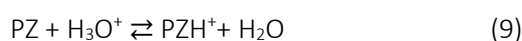
Tertiary amines, such as MDEA, allow higher amounts of CO₂ captured per mole of amine due to a suitable reaction stoichiometry though they present generally a low reaction rate in comparison with primary and secondary amines. This low reaction rate could be associated with a high liquid viscosity that decreases mass transfer rate [12]. The mechanism for the reaction of CO₂ with the tertiary amines is as follows [13], [14]:

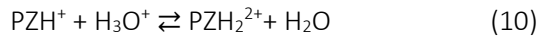


In the case of a SHA such as AMP, the presence of the methyl group significantly reduces the stability of the carbamate bond which results in the preferred formation of the bicarbonate leading to the particularly high loading capacity of these solvents. SHAs demonstrate certain advantages over conventional non-SHA absorbents for CO₂ removal from gases, such as high absorption rate, higher selectivity and resistance to degradation.

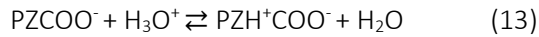
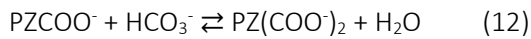
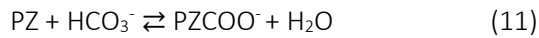
When CO₂ is absorbed in PZ solutions, the zwitterion mechanism used for primary and secondary amines can be adopted to explain the formation of carbamate which is regarded as the result of deprotonation of zwitterion generated through the reaction between CO₂ and PZ, the following equilibrium chemical reactions with the reactions R1 to R3 take place in the liquid phase [15], [16]:

First and second protonation of PZ:





Formation of three carbamate species (PZ carbamate, PZ dicarbamate and protonated PZ carbamate), respectively:



The theory of mass transfer with chemical reaction can be used to analyze the experimental results. The most significant simplification arises from the pseudo-first-order assumption for kinetics. This assumes the concentration of amine to be constant in the liquid boundary layer. Such simplification transforms the second-order reaction expression of CO₂ with an amine to a first-order expression [17]:

$$r_{\text{CO}_2} = k_{2,\text{Am}} [\text{Amine}]([\text{CO}_2] - [\text{CO}_2]^*) \quad (14)$$

$$r_{\text{CO}_2} = k_1([\text{CO}_2] - [\text{CO}_2]^*) \quad (15)$$

where $k_{2,\text{Am}}$ (m³/kmol.s) is the second-order reaction rate constant; [Amine] and [CO₂] are amine and CO₂ concentration (kmol/m².s) respectively, [CO₂]* is the equilibrium concentration of CO₂; k_1 (1/s) is the rate constant for the pseudo-first-order reaction and defined as:

$$k_1 = k_{2,\text{Am}} \cdot [\text{Amine}] \quad (16)$$

The reaction kinetics of CO₂ with MEA has been studied extensively in the literature [1]. Regardless of the experimental techniques and conditions, all the data for the reaction of CO₂ with MEA are in very good agreement. The first-order reaction rate for MEA was suggested as follows for the temperature range of 4.8-35°C and MEA concentration of 0.0152-0.177 M [18]:

$$r_{\text{CO}_2\text{-MEA}} = k_{2,\text{MEA}} [\text{MEA}][\text{CO}_2] \quad (17)$$

$$\log k_{2,\text{MEA}} = 10.99 - 2152/T \quad (18)$$

The reaction rate of CO₂ absorption into a blended amine solution can be considered as a rapid pseudo-first-order reversible reaction and expressed as [19]:

$$N_{\text{CO}_2} = \frac{\sqrt{D_{\text{CO}_2}(k_{2,1\text{st Amine}} \cdot C_{2,1\text{st Amine}} + k_{2,2\text{nd Amine}} \cdot C_{2,2\text{nd Amine}})}}{H_{\text{CO}_2}} (P_{\text{CO}_2,\text{bulk}} - P^*_{\text{CO}_2}) \quad (19)$$

Simulation of CO₂ absorption by amine solutions

The simulation of CO₂ absorption from a specific gas was conducted by different kinds of absorbents in a conventional column with 10 trays using Aspen HYSYS simulator to estimate the outlet CO₂ concentration, absorption efficiency and CO₂ loading so as to choose the most proper absorbent solution in terms of CO₂ absorption rate. Therefore, the studies of required parameters, data and correlations such as Gibbs free energy, binary interaction coefficients and etc., have been avoided by application of the property package of Acid Gas-Chemical Solvent and the main focus of interest is absorption efficiency. The schematic of absorption process is depicted in Fig. 1.

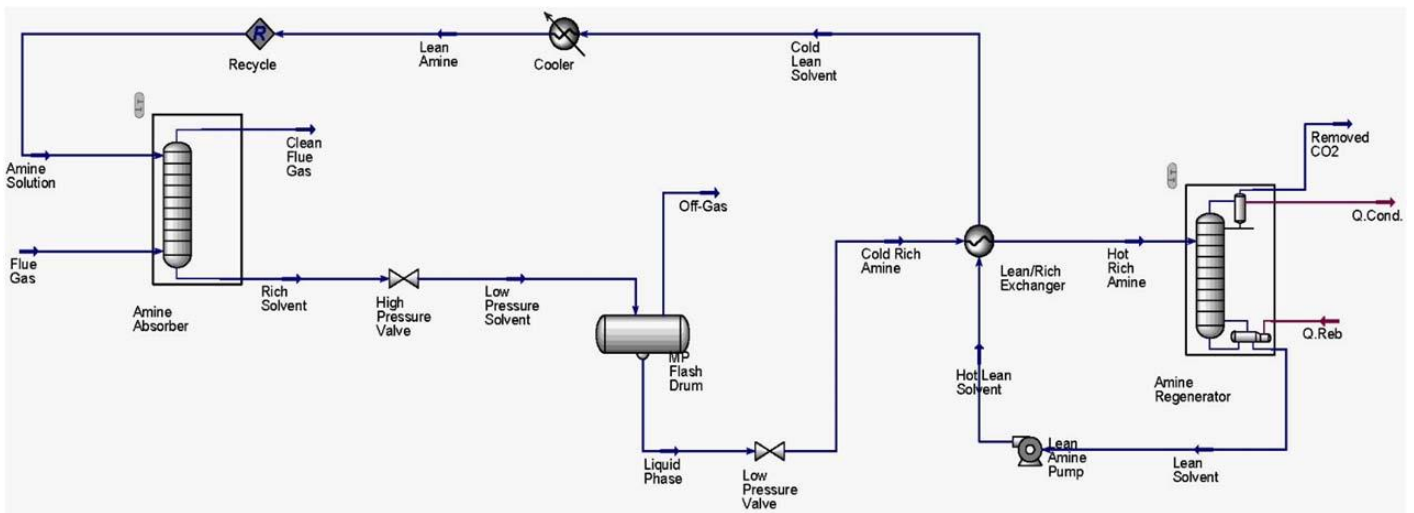


Figure 1 - The schematic CO₂ absorption process by using amine solution in Aspen HYSYS

Nine single amine absorbents and 15 blended amine solutions have been investigated. The single amine solutions include PZ, MEA, DGA, DIPA, DEA, MDEA, TEA, Sulfinol- D (30 wt% DIPA+15%Sulfolane) and Sulfinol-M (30wt% MDEA+15%Sulfolane) while the latter two are considered as a mixture of chemical and physical absorbents. All these solutions were introduced into the column with a concentration of 45 wt% and flow rate of 850 kmol/hr. The appointed concentration of 45 wt% makes the model able to be converged in Aspen HYSYS by all chosen single absorbents. The blended amine solutions are divided into two parts: the first part constitutes PZ+MEA, PZ+DGA, PZ+ MDEA, PZ+DEA, PZ+TEA, MEA+DGA, MEA+MDEA, MEA+DEA and MEA+TEA in contact with the gas separately with a concentration of 30 wt% and flow rate of 500 kmol/hr, the second part comprises DIPA+PZ, DIPA+MEA, DIPA+DGA, DIPA+DEA, DIPA+MDEA and DIPA+TEA which were introduced into the column separately with a concentration of 30 wt% and flow rate of 850 kmol/hr. The second part adopted a higher flow rate because the blended DIPA solutions with a flow rate of 500 kmol/hr could not be converged by Aspen HYSYS in the column including ten trays with the specific gas composition. In this study, absorption efficiency of single absorbents is not compared with that of the blended solutions. Some of these blended solutions, such as PZ+MEA [20], [21] and PZ+MDEA [22-24] have been studied in the literature.

The molar composition of the gas was 27.36% CO₂, 34.73% CO, 37.49% H₂, 0.19% CH₄ and 0.23% H₂O. The gas was introduced into the column in the conditions 35 °C, 58.5 barg and 96.8 kmol/hr while all solutions were introduced into the column in 45 °C, 59.0 barg to investigate CO₂ absorption. The Acid Gas-Chemical Solvent property package is based on the Electrolyte NRTL model for electrolyte thermodynamics [23] and Peng-Robinson equation of state for vapor phase and liquid hydrocarbon phase properties. This property package is based on extensive research and development in rate-based, simulation of chemical absorption process and molecular thermodynamics models for aqueous amine solutions, it contains the parameters identified from regression of thermodynamic and physical property data such as VLE and heat of absorption for amine solutions. It is highly recommended the rate-based model is used instead of equilibrium model for the simulation of CO₂ absorption, the characteristic that distinguishes this model from the equilibrium is the accuracy of results in such a way that the rate-based model considers the following parameters in order to predict the performance of CO₂ absorption process and the required energy of solvent regeneration: mass transfer correlation, thermodynamics and kinetics

model, heat transfer correlation, physicochemical properties (density, viscosity, diffusivity, surface tension, and etc.) and flow model.

The correlations used to simulate the CO₂ absorption are illustrated in Table 1. The investigation and comparison of CO₂ absorption capability with a wide range of amine absorbents has not been conducted in previous studies.

Table 1 - The model and correlations used for simulation of CO₂ absorption by amine solution

Model approach	Used correlation
Flow model	V-plug
Liquid density	Clarke model
Liquid viscosity	Jones-Dole model
Liquid surface tension	Onsager-Samaras model
Binary diffusivity	Nernst-Hartley model
Therman conductivity	Riedel model
Mass transfer	AICHE model
Heat transfer coefficient	Chilton and Colburn
Liquid film resistance	Discrxn model
Vapor fil resistance	Film model

A.Comparison of single amine and blended amine solutions

For the nine single amine solutions with 45 wt% and 850 kmol/hr by considering no lean-CO₂ loading, the following order was obtained from the strongest absorbent to the weakest based on the kinetics parameters which are shown in Tables 2 and 3 for zwitterion and protonated amine formation (reactions 5, 6, 8) as well as electrolytes formation (reactions 2, 11, 12) respectively. This order clearly shows the extent of chemical absorption and reactivity. These results are generally compatible with the previous experimental studies on some of amine absorbents. For instance, [10], [17], [25] and [26] and have carried out experiments and calculated the second order reaction rates for some of single and blended alkanolamines applied in this study and acquired almost the same order and their results verify the model used in this study.

PZ > MEA > DGA > DIPA > DEA > Sulfinol - D > Sulfinol - M > MDEA > TEA

Table 2 - Kinetic parameters of CO₂ absorption by primary, secondary, and tertiary amines

Solvent	Type of reaction	k	E _a (cal/mol)
MEA [27]	forward	9.77E+10	9855.8
	backward	2.18E+18	14138.4
DGA [27]	forward	1.94E+15	15813

	backward	3.0E+26	25287
DIPA [27]	forward	4.09E+9	9563.1
	backward	2.16E+19	15021
DEA [27]	forward	6.48E+16	5072
	backward	1.43E+17	11497
MDEA [28]	forward	6.85E+10	9029
	backward	6.62E+17	22131
TEA [18]	forward	2.02E+11	8837
	backward	5.02E+18	22288

The CO₂ removal by PZ resulted in the off-gas with only 61.2 ppm CO₂ in outlet as this absorbent has the highest reaction rate with CO₂, while such absorption by TEA brought about an outlet CO₂ to concentration of 22184.8 ppm as this solvent is subject to the lowest reaction rate in the same concentration and operational conditions. The reason can be attributed to a higher reactivity resulting from the higher reaction heat of PZ with CO₂.

Table 3 - Kinetics parameters of bicarbonate and species of PZ carbamate formation

Solvent	Type of reaction	k	E _a (cal/mol)
Bicarbonate	forward	1.33E+17	13249
	backward	6.63E+16	25656
PZ carbamate	forward	1.70E+10	319
	backward	3.40E+23	14160
PZ bicarbonate	forward	1.04E+14	8038.3
	backward	3.20E+20	8692

This order can be illustrated as CO₂ absorption efficiency which is depicted in Fig. 2. Efficiency term, η , is defined as the percentage of CO₂ removed from the inlet gas stream of the column by absorption process and expressed as [25]:

$$\eta = \left[1 - \left(\frac{y_{CO_2,out}}{1-y_{CO_2,out}} \right) \left(\frac{1-y_{CO_2,in}}{y_{CO_2,in}} \right) \right] \times 100 = \left[1 - \frac{y_{CO_2,out}}{y_{CO_2,in}} \right] \times 100 \quad (20)$$

Consequently, PZ possesses the highest efficiency of 99.98% for CO₂ removal while TEA has the lowest efficiency of 93.98%; in other words, PZ is able to absorb more CO₂ because of carbamate formation and higher reaction heat; nevertheless, TEA has slower reaction rate due to lowest order of magnitude in its second order reaction rate constant and indirect reaction with CO₂.

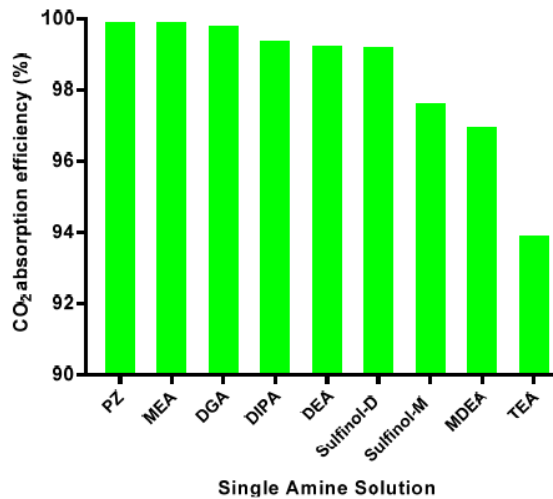


Figure 2 - CO₂ removal efficiency by 45wt% single amine solutions with flow rate of 850 kmol/hr

follows and the detailed data are given in Fig. 3. It is clear that TEA reached the highest CO₂ loading in 0.326 on account of higher reaction stoichiometry, while the minimum CO₂ loading was achieved by MEA in 0.160 owing to having the lowest equilibrium solubility and the fact that its maximum absorption capacity is limited to 0.5 mole CO₂ per mole MEA. Some of these absorbents have been experimentally investigated by [29].

TEA > DIPA > Sulfinol - D > Sulfinol - M > MDEA > DGA > DEA > PZ > MEA

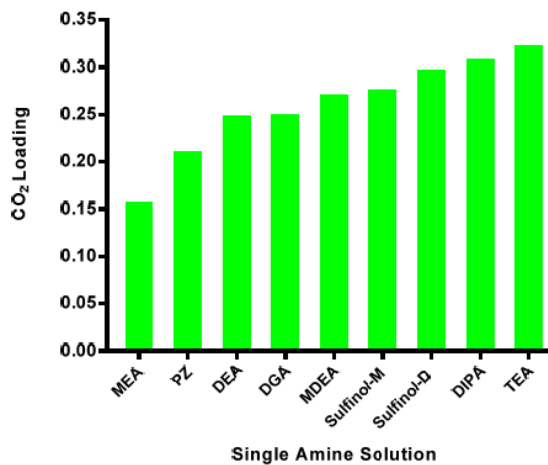


Figure 3 - CO₂ loading in 45wt% single amine solutions with flow rate of 850 kmol/hr

Aroonwilas et al. [25] studied five different single amine solutions as MEA, DEA, AMP, DIPA and MDEA with a constant concentration 3.0 kmol/m³ for CO₂ removal. According to their studies with the mentioned absorbents, MEA has obtained the highest amount of CO₂ absorption while MDEA has attained the lowest in terms of CO₂ absorption efficiency as well as reaction heat which is similar to the achieved results in this study.

The order of CO₂ loading (α) (as molar flow of absorbed CO₂ to molar flow of amine solvent) in the nine absorbents is shown as

The second-order reaction rate constant between amine and CO₂ is independent of absorbent concentration and it is only a function of temperature, so it can be concluded that the reaction between them is a rapid pseudo-first-order reversible reaction [22]. The second order reaction rate constant for PZ [22], DEA [30], DGA [31], MDEA [14] and TEA [13] are as follows, respectively, the values of which are indicated for the mentioned amine absorbents within 305-335 K in Fig. 4.

$$k_{2,PZ}[m^3/kmol.s] = 4.0 \times 10^{10}.exp(\frac{-4059.4}{T}) \quad (21)$$

$$\log k_{2,DEA}[m^3/kmol.s] = 10.4493 - \frac{2274.5}{T} \quad (22)$$

$$k_{2,DGA}[m^3/kmol.s] = 6.66 \times 10^3.exp(-4823.1(\frac{1}{T} - \frac{1}{298})) \quad (23)$$

$$k_{2,MDEA}[m^3/kmol.s] = 5.86 \times 10^6.exp(\frac{-3984}{T}) \quad (24)$$

$$k_{2,TEA}[m^3/kmol.s] = 3.311 \times 10^{10}.exp(\frac{-4089}{T}) \quad (25)$$

The ability of an absorbent to remove CO₂ is dictated by its equilibrium solubility as well as mass transfer and chemical kinetics characteristics [17]. Being a cyclic symmetric diamine, each mole of PZ can theoretically absorb two moles of CO₂ and PZ may favor rapid formation of the carbamates.

The apparent second-order rate constant of PZ has been found to be an order at least higher than that of conventional alkanolamines such as MEA which is shown in Figs. 4 and 5 based on logarithmic-scale. Most of CO₂ is absorbed from the middle to the bottom of column owing to higher driving force between gas and absorbent, the mole fraction of CO₂ in the liquid phase has reached to 6.79 × 10⁻⁶ by PZ on the top of the column while the minimum value of that is about 1.05 × 10⁻⁴ using DIPA which represents two order of magnitudes difference. In other words, PZ has been able to obtain the similar solubility on tray no.7 from the bottom and there has been less CO₂ concentration on the upper stages to be absorbed but such solubility has attained with a slighter slop by DIPA on tray no.10 which proves that CO₂ absorption by DIPA requires an absorber with higher number of stages and height than that of by PZ to achieve the same solubility. The order shown in Fig. 5 is identical to [26] on MEA, DEA and TEA. Whereas PZ is effective in promoting the rate of CO₂ absorption even at its low concentrations in blend with other amine absorbents, it is known as an activator or promoter in industrial processes.

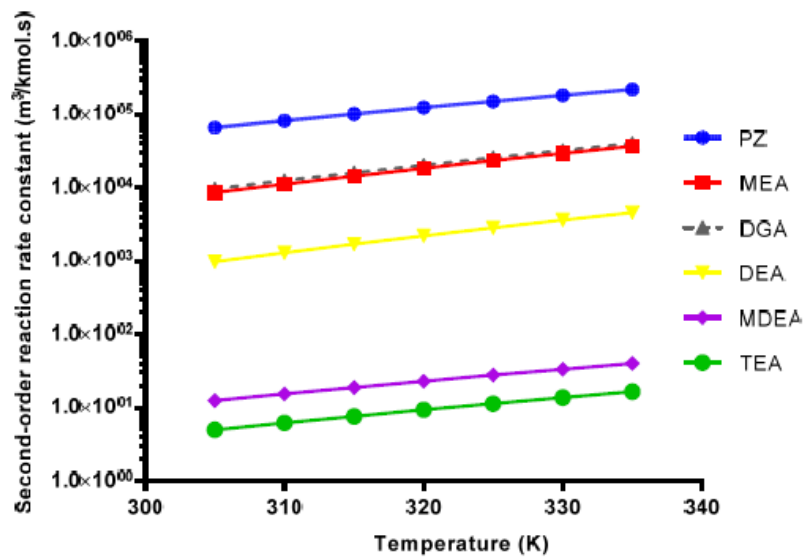


Figure 4 - The estimated values of second-order reaction rate constant for amine absorbents

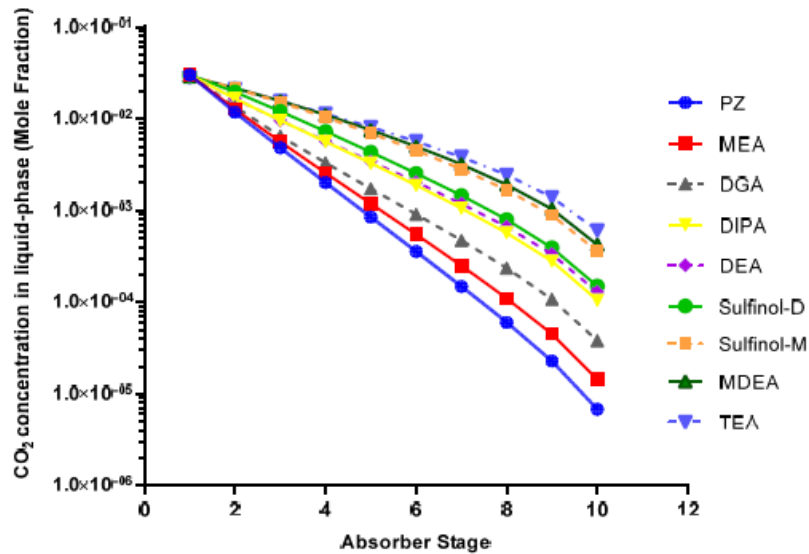


Figure 5 - The values of absorbed CO₂ in 45wt% single amine solutions with flow rate of 85 kmol/hr

For the blended solutions with 30 wt% and 500 kmol/hr, the following order demonstrates CO₂ absorption efficiency of nine different mixtures, and in consequence, solution of PZ and MEA possesses the fastest reaction with CO₂ which can be observed in Figs. 6 and 7. Some of these solutions have been studied before, e.g. [25] reported that MEA+MDEA has much more tendency to absorb CO₂ than DEA+MDEA, and our results confirms that the mixture of DEA and MDEA is subject to the lowest absorption efficiency with the outlet CO₂ concentration varying from 19,618 ppm to 14,220 ppm while DEA concentrations varied between 5 wt% and 25 wt%:

PZ + MEA > PZ + DGA > PZ + MDEA > PZ + DEA > PZ + TEA > MEA + DGA > MEA + MDEA > MEA + DEA > MEA + TEA

Fig. 6 shows the effect of the blended amine solutions with various PZ concentrations on CO₂ removal. PZ was employed as an activator and mixed with five different absorbents to form 30 wt% solutions while the concentration of PZ in each solution varied from 5 wt% to 25 wt%. Exceptionally, TEA solution was evaluated from 10 wt% due to lack of sufficient reactivity in the solution of 5 wt% PZ + 25 wt% TEA with CO₂ to be converged by this model. It is clear that CO₂ removal was improved by increasing PZ concentration, particularly for the amines with slower reaction rate such as DEA and TEA. After the gas was treated by the solution of PZ+TEA, the outlet CO₂ concentration declined by 93% with an increasing PZ concentration from 10 wt% to 25 wt%, while there was only 42% decrease in the outlet CO₂ concentration for the solution of PZ+MEA with 25 wt% PZ in comparison with that of 5 wt% PZ, in such a way the outlet CO₂ concentration by the solution of 5 wt% PZ+25 wt% MEA is around 421 ppm which is comparatively lower than the same PZ concentration blended with other absorbents. Regardless of PZ+MEA solution, PZ+DGA exhibited a higher CO₂ absorption than other mixtures except the case of 5 wt% PZ+ 25 wt% DGA in which the outlet CO₂ concentration reached 1450 ppm compared to 1070.1 by 5 wt% PZ+25 wt% MDEA. TEA demonstrated the lowest absorption ability and the outlet CO₂ concentration was as high as 4412 ppm in the solution of 10 wt% TEA+20 wt% PZ. Similarly, CO₂ removal was simulated by the 30 wt% blended amine solutions with MEA concentration of 5 wt%, 10 wt%, 15

wt%, 20 wt% and 25 wt% and the results are shown in Fig. 7, which illustrates that CO₂ removal performance of MEA with other amines followed the same order as that of PZ with other amines although the outlet CO₂ concentration was 6-8 times higher for the solutions with MEA than those with PZ at the same concentration. The values of CO₂ absorbed by the solutions of MEA+DGA, MEA+MDEA and MEA+DEA were close to each other in the lowest concentration of MEA (5 wt%). These results suggest that the MEA does not influence much at lowest concentration and the effect of those three absorbents (DGA, MDEA and DEA) predominates, while MEA affects CO₂ absorption significantly at higher concentrations (from 10 wt%) and somehow overshadows the effect of the other compounds in the solution.

Fig. 8 depicts CO₂ removal by the blended amine solutions with different concentrations of DIPA as a secondary amine. Contrary to the mixture of PZ with other absorbents that brought about a descending outlet CO₂ concentration with increasing PZ mass ratio, the blended solutions with DIPA demonstrate up or down trends with increasing DIPA concentration depending on their reaction rates with CO₂ as well as CO₂ solubility in these absorbents. Considering the fact that PZ, MEA and DGA have higher reactivity with CO₂ than DIPA, increasing DIPA concentration affected CO₂ absorption reversely and led to a rise in the outlet CO₂ concentration as much as 2.78, 4.86 and 2.15 times, respectively. On the other side, a rise in DIPA concentration in the mixtures of DIPA+DEA caused a slight increase in the outlet CO₂ concentration as 1.11 times because DIPA more promotes CO₂ loading than the reaction rate compared with DEA and finally, brought on higher CO₂ concentration in the outlet gas which has a good consistency with the previous literature [25].

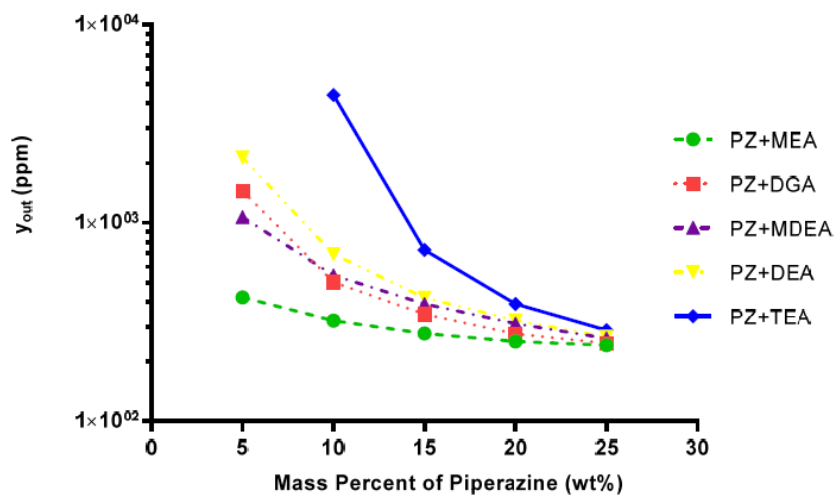


Figure 6 - Comparison of CO₂ absorption by different 30 wt% blended solutions mixed with PZ.

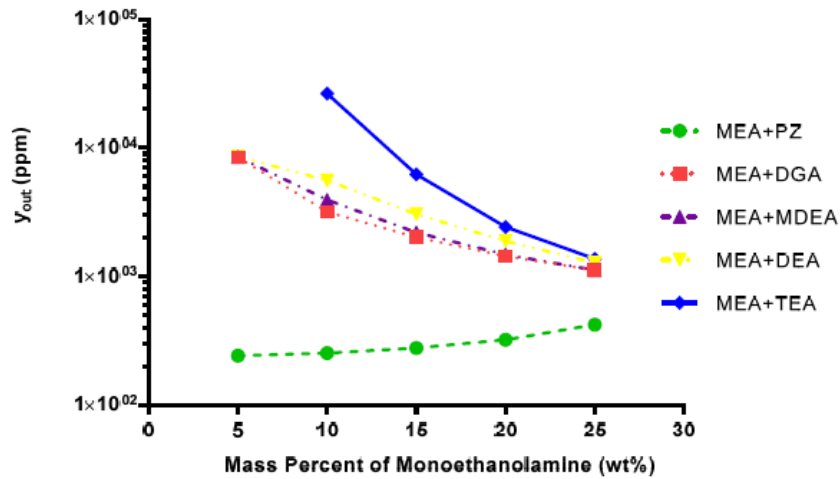


Figure 7 - Comparison of CO₂ absorption by different 30 wt% blended solutions mixed with MEA.

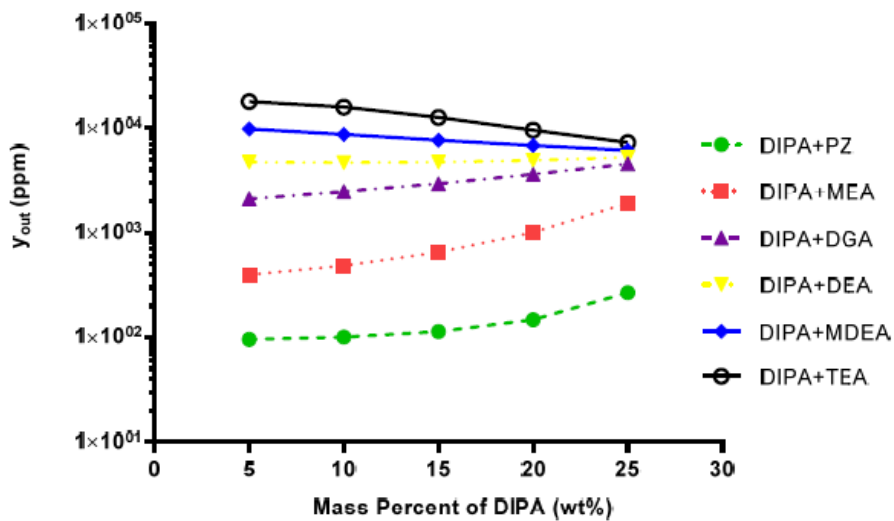


Figure 8 - Comparison of CO₂ absorption by different 30 wt% blended solutions mixed with DIPA

In DIPA+MDEA and DIPA+TEA solutions, both controlling parameters of higher reactivity of DIPA than MDEA and TEA in addition to higher solubility of CO₂ in DIPA compared with MDEA led to the decrease in the outlet CO₂ concentration by 37.6% and 59.5%, respectively. Therefore, DIPA in mixture with tertiary amine solvents makes more efficient blended solutions than that of with other type of amine because it promotes the slow reaction rate of tertiary amine absorbents as an activator in such a way that DIPA worked effectively on the top trays of the column and then higher solubility of CO₂ in MDEA or TEA caused CO₂ reduction on the bottom trays and consequently in the outlet gas. These trends are in good agreement with [25] which shows a mixed kinetic/thermodynamic competition in a blended solution between two reactive components (MEA or DEA and MDEA). Based on their experiments, promoters play a key role in controlling absorption rate in low CO₂ loadings because they react with CO₂ in a faster rate than other amine component to form very stable carbamate components. As CO₂ loading is enhanced, more CO₂ is converted to promoter carbamate resulting in reduction of unreacted promoter to unreacted tertiary amine ratio. Consequently, tertiary amine obtains its role in estimation of CO₂ absorption rate. When blended amines are used, promoters probably act as primary reactant to

absorb CO₂ on upper section of column while the other amine component controls absorption on lower sections.

B. Investigation of operational parameters on CO₂ absorption by PZ+MEA

In order to investigate the effect of operational conditions on CO₂ absorption in the column, five parameters, e.g. solution temperature, gas temperature, solution flow rate, gas flow rate and lean-CO₂ loading for the strongest solution, 25wt%PZ+5wt%MEA, were studied, while the effect of streams temperature was assessed simultaneously and that of streams flow rate was also examined together. Pressure and flow rate of the gas and liquid streams are 58.5 barg and 96.8 kmol/hr as well as 59.0 barg and 500 kmol/hr, respectively.

Fig. 9 represents the effect of PZ+MEA solution temperature on CO₂ absorption. It is clear that rising solution temperature resulted in a higher CO₂ removal because high temperature can enhance the reaction rate between the amine solution and CO₂ and thus increased liquid-side mass transfer coefficient despite the fact that higher temperature causes lower CO₂ solubility in the solution. The effect of gas temperature is shown in Fig. 10, which indicates that increasing gas temperature at a certain amine solution temperature did not affect CO₂ absorption, obviously because the main mass transfer resistance is in liquid film even if gas temperature increase brings about a rising in gas-side mass transfer coefficient. This observation is in agreement with other studies [32]. The temperature over 60 °C is not a good choice for amine solutions based on the operating conditions and recommendations in literature [10], and thus the investigation was performed up to this temperature.

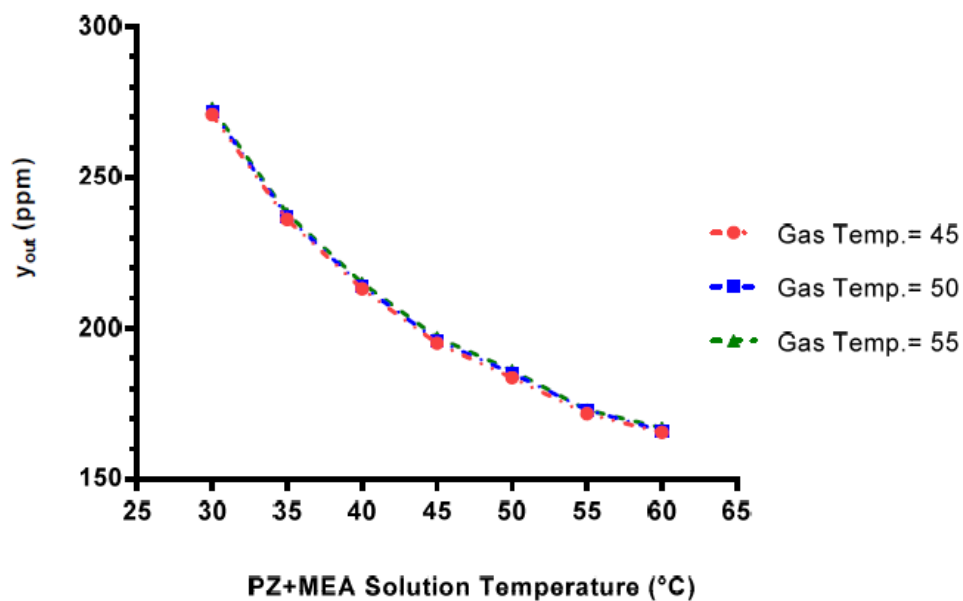


Figure 9 - Outlet CO₂ concentration vs PZ+MEA solution temperature with three different gas temperatures.

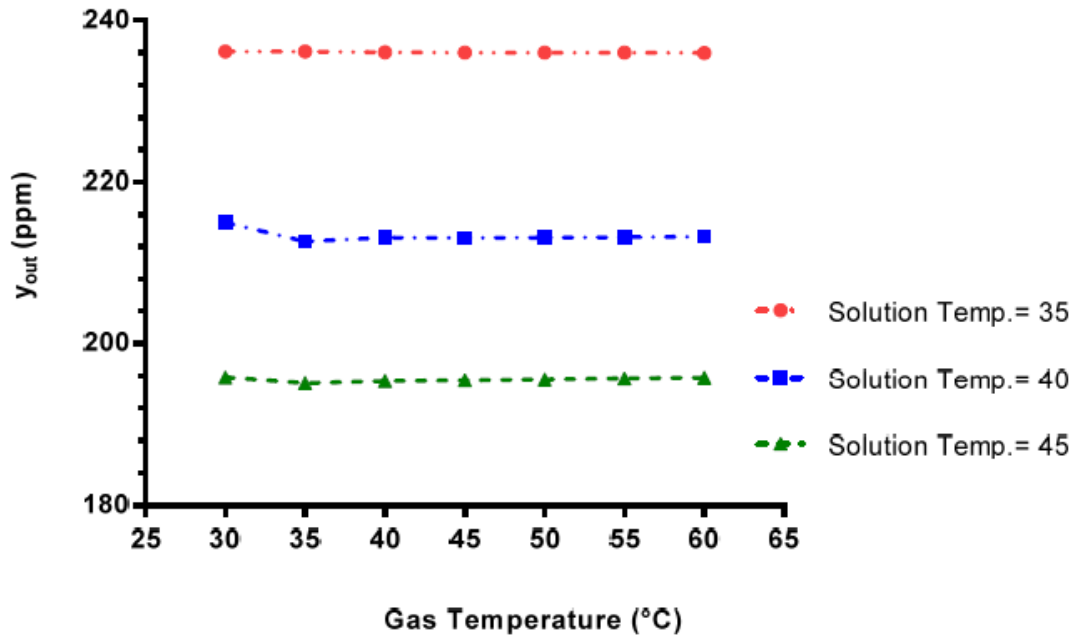


Figure 10 - Outlet CO₂ concentration vs. gas temperature with three different PZ+MEA solution temperatures

The influence of gas flow rate on CO₂ absorption is illustrated in Fig. 11, which shows that higher gas flow rate at a fixed liquid flow rate led to higher outlet CO₂ concentration while the inlet temperature of the gas and absorbent were 35 °C and 45 °C, respectively. A rising gas flow rate from 90 kmol/hr to 130 kmol/hr not only results in higher CO₂ amount per unit time in the column but shortens gas-liquid contact time, thereby causing a lower CO₂ absorption efficiency. Figs. 11 and 12 also indicate that rising PZ+MEA solution flow rate assisted to decrease the outlet CO₂ concentration as a result of higher liquid-side and overall mass transfer coefficients. Furthermore, Fig. 12 clearly indicates that there was negligible difference in the value of absorbed CO₂ with various gas flow rates when PZ+MEA solution flow rate increased from 600 kmol/hr to 900 kmol/hr. Consequently, the flow rate of 600 kmol/hr can be chosen as the minimum required flow of the absorbent where the operating line and the equilibrium curve meet each other.

Fig. 13 illustrates the variation of rich-CO₂ loading (the amount of absorbed CO₂ in rich amine) versus lean-CO₂ loading (the amount of remained CO₂ in lean amine after regeneration) in different solution flow rates. The rich-CO₂ loading increases with rising lean-CO₂ loading up to a specific point depends on the value of solution flow rate, i.e. increasing the amount of CO₂ in lean solution has led to more absorbed CO₂ in rich amine solutions but the maximum solubility is subject to the flow rate so that the minimum flow rate is 600 kmol/hr to achieve rich-CO₂ loading equal to 1.0 and the lower flow rates were not able to reach this amount of rich loading. On the other hand, the rich-CO₂ loading has declined with increasing solution flow rate in a constant lean-CO₂ loading; this trend is in good agreement with the similar work [21]. Fig. 14 depicts the values of outlet CO₂ in the off-gas with the variation of lean-CO₂ loading which has increased in various solution flow rates in such a way that there is no much difference between the values of outlet CO₂ for the flow rates of 600 kmol/hr and 650 kmol/hr from the rich-CO₂ loading of 0.35.

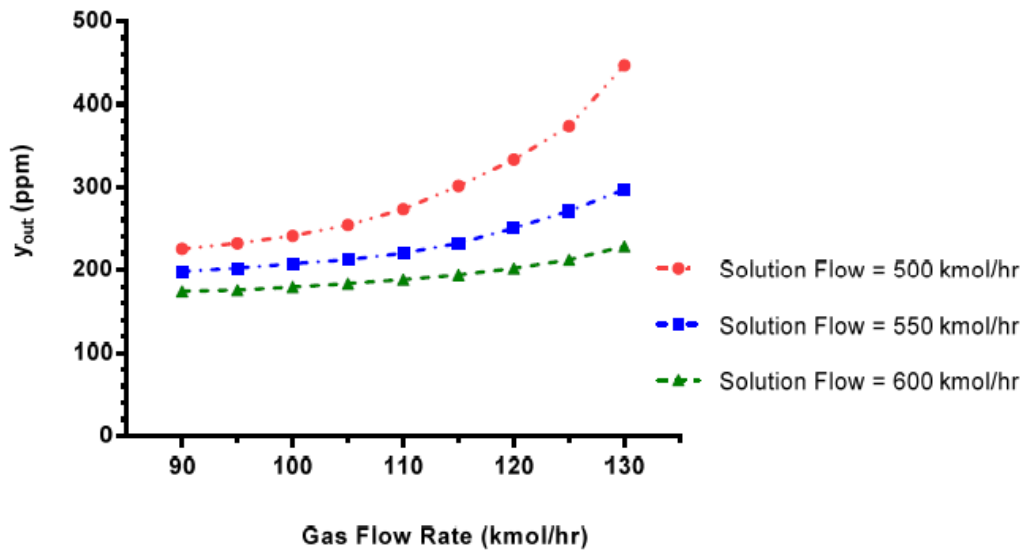


Figure 11 - Outlet CO₂ concentration vs. gas flow rate with three different PZ+MEA solution flow rates.

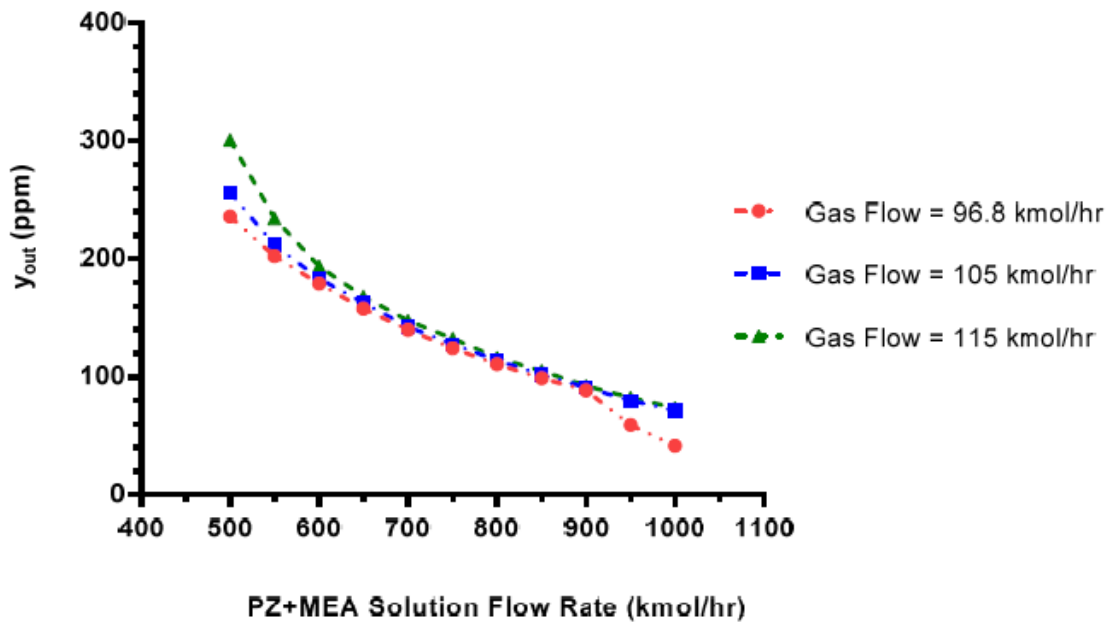


Figure 12 - Outlet CO₂ concentration vs. PZ+MEA solution flow rate with three different gas flow rates.

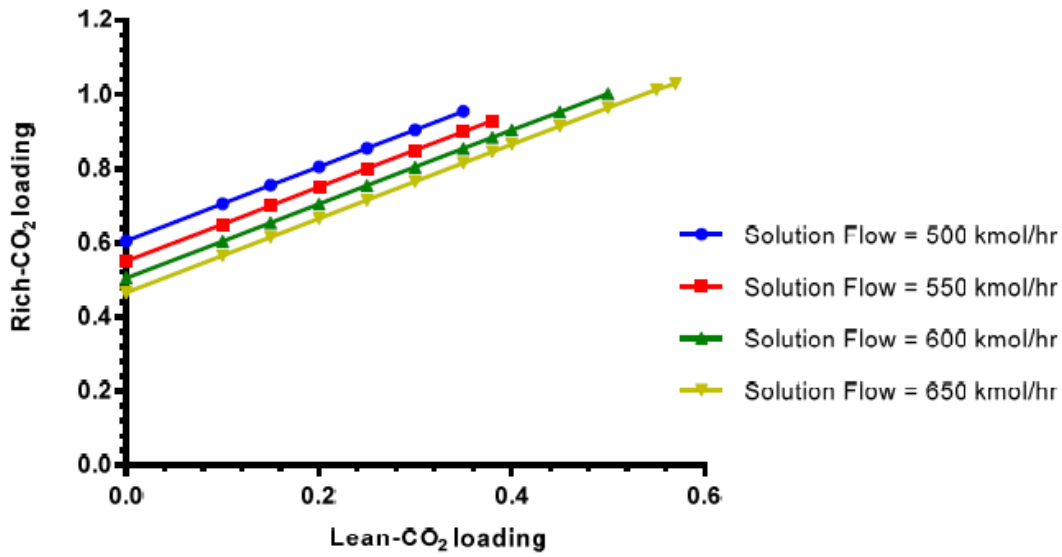


Figure 13 - Rich-CO₂ loading of PZ+MEA solution vs. lean-CO₂ loading with various solution flow rates.

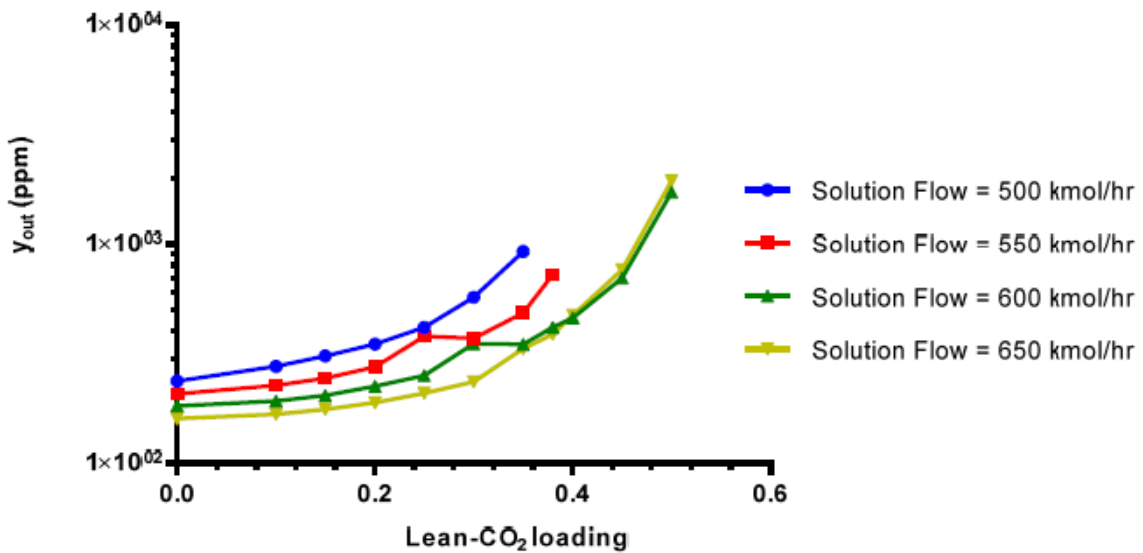


Figure 14 - Outlet CO₂ concentration vs. lean-CO₂ loading with various solution flow rates.

The applications of CO₂ capturing technologies expand to, recently, construction industry as well [33-36]. Proposals had been made to install pilot plants on cement factories which are known to be a major cause of CO₂ emission. Commonwealth Scientific and industrial research Organization (CSIRO) had invested huge amounts in the research and developments associated with this particular topic. However, the economic challenges on the way to a proper commercialized capturing plant is still upheld [36-43].

Conclusion

The conventional absorption column module in Aspen HYSYS was used to investigate CO₂ removal efficiency of a wide range of single and blended aqueous amine solutions, which include PZ, MEA, DEA, MDEA, DIPA, TEA, DGA, Sulfinol-D and Sulfinol-M as well as PZ+MEA, PZ+DGA, PZ+MDEA, PZ+DEA, PZ+TEA, MEA+DGA, MEA+MDEA, MEA+DEA and MEA+TEA; in addition to DIPA+PZ, DIPA+MEA, DIPA+DGA, DIPA+DEA, DIPA+MDEA and DIPA+TEA. It was found that PZ and the mixture of PZ and MEA were the most appropriate solutions for CO₂ absorption among the single amine absorbents and blended solutions owing to the higher order of magnitude in second-order reaction rate constant, fastest reaction rate and highest efficiency, while TEA exhibited the maximum CO₂ loading on account of its higher equilibrium capacity. Furthermore, increasing the amine solution temperature improved CO₂ removal while variation of gas temperature had a negligible effect on CO₂ absorption. An increase in the gas flow rate or decrease in the PZ+MEA solution flow rate resulted in an obvious rise in outlet CO₂ concentration. It was observed that the outlet CO₂ concentration varied a little with the increase of the gas flow rate from 96.8 kmol/hr to 115 kmol/hr at the PZ+MEA solution flow rate in the range of 600 kmol/hr to 900 kmol/hr. Moreover, enhancing lean-CO₂ loading has led to rising the values of CO₂ in the outlet gas and rich solvent, the results of Figs. 12-14 were useful to estimate the minimum required solution flow rate in this model. This work can provide guideline for the selection of suitable absorbents in CO₂ capture.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (No. 21676008).

Nomenclature

Symbols used

[Amine]	[kmol m ⁻³]	Concentration of amine
[CO ₂]	[kmol m ⁻³]	CO ₂ concentration in the liquid bulk
[CO ₂]*	[kmol m ⁻³]	Equilibrium concentration of CO ₂
B	[-]	Base
C	[kmol m ⁻³]	Concentration
D _{G,L}	[m ² s ⁻¹]	Diffusivity of gas in liquid phase
E _a	[cal mol ⁻¹]	Activation energy
N	[kmol m ⁻² s ⁻¹]	Molar mass-transfer flux
P _{CO₂, bulk}	[Pa]	Partial pressure of CO ₂ in the gas bulk
P* _{CO₂}	[Pa]	Equilibrium partial pressure of CO ₂
r	[kmol m ⁻³ s ⁻¹]	Reaction rate
T	[K]	Absolute temperature
y	[-]	Mole fraction of CO ₂
Y	[-]	Molar ration of CO ₂ [y/(1-y)]

Greek symbols

α	[-]	CO ₂ loading
η	[%]	Absorption efficiency of CO ₂

Subscripts

Am	Amine
In	Inlet
Out	outlet

Abbreviations

RNH ₂	Primary amine
RNHR'	Secondary amine
R'NRR''	Tertiary amine

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