

# Simulation and validation of carbon dioxide removal from the ethane stream in the south pars phase 19 gas plant by different amine solutions using rate-based model

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## ABSTRACT

The high pressure absorption of carbon dioxide (CO<sub>2</sub>) from a distilled ethane stream at Phase 19 of South Pars Gas Complex (in Iran) has been simulated by Aspen Plus using non-random two-liquid and Peng-Robinson models in addition to the technical and operational data. The plant employs 40 wt% diethanolamine (DEA) solution as the actual absorbent in a conventional column. The potential single and blended absorbents including methyldiethanolamine (MDEA), piperazine (PZ) + MDEA, and DEA + MDEA have been modelled to estimate the outlet CO<sub>2</sub> and sulfur compounds concentrations, CO<sub>2</sub> loading, reboiler power supply and regeneration heat duty to determine the most efficient substitute. The model is in good agreement with the real data of the plant. The rate-based simulation results reveal that CO<sub>2</sub> and H<sub>2</sub>S concentrations have nearly reached zero while the total sulfur content is below the demanded specification (10 ppm wt) by the application of a blended amine solution with a low PZ concentration as 1 wt% PZ + 39 wt% MDEA in the operational limits of 110–120 ton/hr and 40–55 °C, suggesting that the PZ + MDEA solution can be used as the most appropriate alternative to the 40 wt% DEA solution due to the higher CO<sub>2</sub> concentration (1.950% mole) and CO<sub>2</sub> loading (0.216) of the rich solution as well as the lower required regeneration heat duty (10.590 GJ).

## 1. Introduction

The carbon dioxide emission has become one of the most challenging environmental issues in the last few decades and the reduction in CO<sub>2</sub> emission is an important technological pathway to mitigate the global warming phenomenon. The CO<sub>2</sub> emission is mainly attributed to the combustion of fossil fuels, amongst which the natural gas is known as the cleanest fuel and the emitted CO<sub>2</sub> arising from burning natural gas is less than other fossil fuels. Therefore, the invention and development of more efficient processes to decrease capital and operational costs as well as the size of equipment for CO<sub>2</sub> removal have attracted wide interest. In the recent decades, various types of technology and process such as absorption, adsorption, membrane separation, chemical looping combustion and terrestrial sequestration have been widely applied as effective means for controlling CO<sub>2</sub> emissions. Among the practical CO<sub>2</sub> removal methods, the absorption process by aqueous amine solutions is the dominant technology for the removal of acid gas impurities such as

CO<sub>2</sub> and H<sub>2</sub>S from the exhaust gas streams of power plants and products of refineries. The crucial barrier for the application of absorption/regeneration process of amine solutions on a large-scale is the high capital and operational costs e.g. regeneration heat duty; however, the main reason for the application of absorption process is the cheapness and the simplicity of this technology compared with the other methods (Aghel et al., 2019a). Furthermore, the solvent absorption remains the preferred manner for CO<sub>2</sub> removal which consists of selectively absorbing CO<sub>2</sub> with a given solvent mixture in a gas-liquid contacting system. Regarding solvent selection, alkanolamine-based solvents are the most commonly used due to their high solubility for CO<sub>2</sub> (Aghel et al., 2020).

The commonly used CO<sub>2</sub> absorbents are non-sterically hindered amines (non-SHAs) in aqueous solutions such as monoethanolamine (MEA) and diglycolamine (DGA) as primary amine, diethanolamine (DEA) and di-isopropanolamine (DIPA) as secondary amine, methyl-diethanolamine (MDEA) and triethanolamine (TEA) as tertiary amine.

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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 years. Different technologies have been developed for CO<sub>2</sub> removal based on chemical reactions between CO<sub>2</sub> and various types of amine solutions in both conventional columns and rotating packed beds (RPBs). For instance, Hikita et al. (1979), Aghel et al. (2018) and Jassim et al. (2007) studied CO<sub>2</sub> absorption by MEA in the conventional column, micro-channel reactor and RPB respectively; Rinker et al. (1996) worked on CO<sub>2</sub> removal and absorption kinetics of DEA. Borhani et al. (Borhani and Wang, 2019) evaluated a wide range of solvents with their advantages and drawbacks to select the proper solution for different processes; Bougie et al. (Bougie and Iliuta, 2010) conducted experiments on a number of SHAs; Yu et al. (2012) and Sheng et al. (2018) examined CO<sub>2</sub> removal by aqueous solution of diethylenetriamine (DETA) in an RPB. The blended amine solutions have also been experimented by scientists and industries; Lin et al. (2010) and Xiao et al. (2000) investigated CO<sub>2</sub> absorption by the blended solution of 2-amino-2-methyl-1-propanol (AMP) + MEA in the RPB and conventional column respectively; Dugas et al. (Dugas and Rochelle, 2009, 2011) used the mixture of PZ + MEA for the studies of CO<sub>2</sub> absorption and desorption; Zhang et al., 2001, 2002, 2003 carried out studies on kinetics and reaction rate of PZ + MDEA and DEA + MDEA for CO<sub>2</sub> removal.

There are four major methods to reduce the heat energy consumption which accounts for almost 70% of the overall operational cost in the CO<sub>2</sub> absorption/regeneration processes (Xu et al., 2016): (1) optimization of process configuration; (2) development of process control strategies; (3) improvement of packing and tray performance; and (4) development of alternative solvents with high absorption rate, high absorption capacity, high mass transfer performance, reasonable solvent cost and low heat duty for regeneration. The absorption of acid gases in blended amine solutions has specific advantages over the use of single amines. The application of blended alkanolamine solutions has recently become very attractive because of the complementary advantages of each amine; the fast reactivity from a primary or secondary amine coupled with the high absorption equilibrium capacity and low solvent regeneration cost from a tertiary or sterically hindered alkanolamine. In fact, the ability of a solvent to remove CO<sub>2</sub> is dictated by its equilibrium solubility as well as mass transfer and chemical kinetics characteristics (Bishnoi and Rochelle, 2000). Because PZ is effective in the enhancement of CO<sub>2</sub> absorption rate at much lower concentrations than the primary and secondary amines mixed with MDEA in the absorption columns (such as MEA + MDEA or DEA + MDEA), it is well known as an activator or promoter in the gas treatment (Samanta et al., 2007), and there is a growing interest in the use of MDEA solution activated with PZ (a-MDEA) for the gas treatment processes owing to the fact that the application of a-MDEA simultaneously benefits from the high absorption rate of PZ and the high capacity of MDEA (Aghel et al., 2019b).

In this study, the performance of different amine solutions in CO<sub>2</sub> removal from the ethane stream, which is produced in the distillation columns at Phase 19 gas plant in Iran, is assessed and simulated as rate-based by using electrolyte non-random two-liquid (E-NRTL) model and Peng-Robinson equation of state (EOS) in terms of CO<sub>2</sub> absorption efficiency, CO<sub>2</sub> loading and regeneration heat duty, and a more efficient amine solution than the present solution (40 wt% DEA) for CO<sub>2</sub> removal has been recommended.

## 2. Analytical method and thermodynamics model

The absorption of CO<sub>2</sub> into the aqueous amine solutions follows three mechanisms, i.e. zwitterion mechanism, termolecular mechanism and base-catalyzed hydration. Primary, secondary amine and SHA solutions follow the zwitterion mechanism and in some cases termolecular mechanism, while the reaction of tertiary amines with CO<sub>2</sub> follows base-catalyzed hydration mechanism (Usman, 2012). The principal reaction between CO<sub>2</sub> and a primary or secondary amine (in water) is the

formation of a carbamate, which is typically considered to occur via the formation of a "zwitterion". The main reason that the primary and secondary amine solutions have high CO<sub>2</sub> absorption efficiency is related to the carbamate reactions which take place rapidly. The zwitterion mechanism, originally proposed by Caplow in 1958 and reintroduced by Danckwerts in 1979, is generally accepted as the reaction mechanism for the carbamate formation by CO<sub>2</sub> with primary and secondary amines. The zwitterion mechanism has been successfully employed for aqueous alkanolamine solutions as well as some organic and viscous solutions. Besides the primary and secondary alkanolamines, the zwitterion mechanism has also been found to be appropriate for modeling the CO<sub>2</sub> absorption into piperazine. The stoichiometry of the carbamate reaction limits the capacity of primary and secondary amines to approximately 0.5 mole of CO<sub>2</sub> per mole of amine. However, DEA-based amine processes can achieve loadings of more than 0.5 mole of CO<sub>2</sub> per mole of amine through the partial hydrolysis of carbamate (RNR'COO<sup>-</sup>) to bicarbonate (HCO<sub>3</sub><sup>-</sup>), which regenerates some free amine (Xu et al., 2016). Xiao et al. (2000) have reviewed CO<sub>2</sub> reaction with both primary and secondary amines:

Dissociation (Autoprotolysis) of water:



Formation of bicarbonate and carbonate (dissociation of dissolved CO<sub>2</sub>):

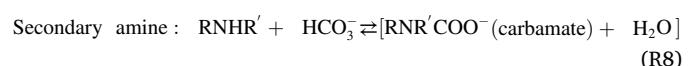
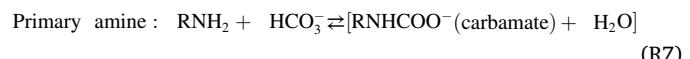


The reaction (R2) is a very slow equilibrium reaction ( $k = 0.026 \text{ s}^{-1}$  at 25°C) (Rinker et al., 1996). The reaction (R3) is also an equilibrium reaction. The reactions (R4, R5) are fast, kinetic type (forward and backward) and can increase mass transfer even when the concentration of hydroxyl ion is low (Xiao et al., 2000). The reactions R2 and R4 are the hydrolysis of carbon dioxide. These above-mentioned reactions (R1-R5) occur in all CO<sub>2</sub> absorption systems with amine solutions. The following reactions exist depending on the type of the amine:

Protonation of amine:



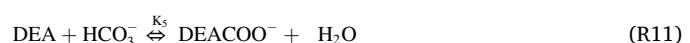
Carbamate formation:

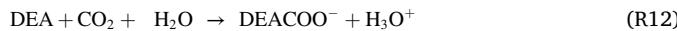


And the subsequent removal of the proton from a zwitterion by a base (B), which can be an amine, OH<sup>-</sup> or H<sub>2</sub>O:



Therefore, the equilibrium reactions (R10, R11) and kinetic reactions (R12, R13) for DEA solution in addition to the reactions R1 to R5 take place in the liquid phase for CO<sub>2</sub> removal from the ethane stream by DEA solution, and these reactions are used as input data in Aspen Plus (Laribi et al., 2019; Austgen and Rochelle, 1989):



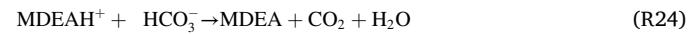
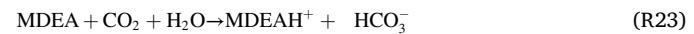
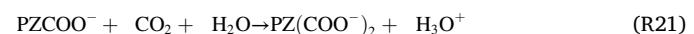
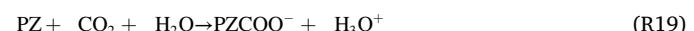
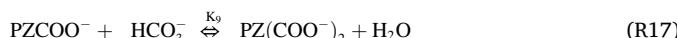
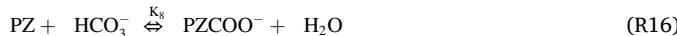
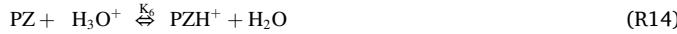


The required data which are used to model  $\text{CO}_2$  removal by DEA solution in Aspen Plus such as Gibbs free energy and enthalpy of formation, ideal gas heat capacity and Henry's constants can be found in Appendix A.

DEA solutions have some significant disadvantages such as great difficulty for reclaiming contaminates such as heat stable salts (HSS), being improper for treatment of gas streams with a high amount of  $\text{CO}_2$  and formation of corrosive degradation products with  $\text{CO}_2$  (Borhani and Wang, 2019). One of the major drawbacks of  $\text{CO}_2$  absorption technology is the degradation of amine solvents due to the high temperature of regeneration and the presence of oxygen. Furthermore, alkanol ammonium cation interacts with anions of organic (products of amine degradation) and inorganic ( $\text{SO}_x$  and  $\text{NO}_x$  presented in the feed gas) acids to form heat stable salts (Grushevenko et al., 2019). As corrosion is an inevitable result of dealing with acid gases, aqueous alkanolamine solutions which contain  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are corrosive to carbon steel and corrosion rates are increased by high alkanolamine concentrations, high acid gas loadings, high temperatures, degradation products and foaming (Abukashabeh et al., 2014). Heat stable salts including chloride, acetate, sulfate and etc. are the impurities in the amine solutions and can help to reduce the amount of required energy to break the bond between the amine and the acid gases in the regenerator if these salts present in very small quantities. However, in larger amounts, these salts can bind with the amine and impede the absorption of the acid gases in the absorber, thereby significantly affecting the performance of the system. As these compounds are heat stable and cannot be fully removed from the amine solutions in the regenerator, other means such as reclaimers or distillation columns are required. It has been reported that primary amines are more corrosive than the secondary amines, which in turn are more corrosive than tertiary amines. MDEA differs from the other amines as it does not produce  $\text{CO}_2$  degradation products. The experimental tests have exhibited that the corrosion rate ranks in the following order: MEA > AMP > DEA > PZ > MDEA (Abukashabeh et al., 2014).

When  $\text{CO}_2$  is absorbed in PZ solutions, zwitterion mechanism can be employed to explain the formation of carbamate, which is regarded as a result of deprotonation of zwitterion generated through the reaction between  $\text{CO}_2$  and PZ and is used as the basis of the reactions of  $\text{CO}_2$  removal in Aspen Plus. Being a cyclic symmetric diamine, each mole of PZ can theoretically absorb 2 moles of  $\text{CO}_2$  and PZ may favor rapid formation of carbamates. The other advantages of using PZ include having double capacity of the concentrated MEA solutions while displaying similar volatility in addition to higher resistance to oxidative and thermal degradation; however, it is not highly soluble (Borhani and Wang, 2019). Recent solid solubility data have shown that PZ has the capability to be used in very high concentrations when it is partially loaded with  $\text{CO}_2$  (Dugas and Rochelle, 2011).

The equilibrium and kinetic reactions of PZ and MDEA with  $\text{CO}_2$  in addition to all the required parameters for modelling of  $\text{CO}_2$  absorption by both amine solutions in Aspen Plus have been thoroughly discussed by Esmaeili et al. (2020):



Tertiary amines such as MDEA, allow greater amounts of  $\text{CO}_2$  removed per mole of amine solvent due to higher reaction stoichiometry in comparison with primary and secondary amines and exhibit a relatively low reaction rate with  $\text{H}_2\text{S}$  and  $\text{CO}_2$  because of unstable carbamate reactions and eventually bicarbonate formation, which limits the reaction rate of  $\text{CO}_2$  with amine. This low reaction rate could be associated with a high liquid viscosity that leads to the decrease in mass transfer rate (Garcia-Abuin et al., 2017). However, MDEA demonstrates the advantages such as being resistant to degradation, applicable in concentrations up to 60 wt% without significant losses, less corrosive with low reaction rates of COS and  $\text{CS}_2$ , and thus offers lower solvent loss (Borhani and Wang, 2019). The reaction equilibrium constants based on the change of Gibbs free energy and defined by the specified coefficients for  $\text{CO}_2$  absorption in DEA, PZ and MDEA are shown in Table 1.

The most important contribution to the fast deprotonation of the zwitterion in solution of PZ + MDEA, comes from PZ and MDEA and to a lesser extent from  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . For the reaction of  $\text{CO}_2$  with aqueous solutions of PZ + MDEA, the reaction of  $\text{CO}_2$  with PZ is considered as the rapid pseudo-first-order reaction in parallel with the reaction of  $\text{CO}_2$  with MDEA. In fact, PZ can be regarded as a catalyst which accelerates the reaction rate between  $\text{CO}_2$  and MDEA. The chemical equilibrium reactions for electrolyte systems are instantaneous and involve only proton transfer (R10-R11 and R14-R18), and such reactions are used in all streams and unit operations of the model. The other chemical reaction set is limited to the absorber because the reactions which occur inside it are both equilibrium and rate-controlled. In the absorber, all reactions are considered to be in chemical equilibrium except those of  $\text{CO}_2$  with  $\text{OH}^-$  (R4-R5),  $\text{CO}_2$  with amine (DEA, MDEA and PZ) and  $\text{CO}_2$  with  $\text{PZCOO}^-$  which are kinetically controlled because of their finite

**Table 1**

Coefficients of chemical equilibrium constants in  $\text{CO}_2$  absorption by DEA, PZ and MDEA (Haji-Sulaiman et al., 1998; Derks et al., 2005; Dash and Bandyopadhyay, 2016; Dash et al., 2011).

Equilibrium constant	Parameter				
	a	b	c	d	T(K)
$K_1$	$1.329 \times 10^2$	$-1.344 \times 10^4$	$-2.247 \times 10$	0.000	273–498
$K_2$	$2.314 \times 10^2$	$-1.209 \times 10^4$	$-3.678 \times 10$	0.000	273–498
$K_3$	$2.160 \times 10^2$	$-1.243 \times 10^4$	$-3.548 \times 10$	0.000	273–498
$K_4$	$-3.071 \times 10^3$	6.777	0.000	$-4.876 \times 10$	273–353
$K_5$	$-1.706 \times 10^4$	$-6.680 \times 10$	0.000	$4.397 \times 10^2$	303–331
$K_6$	$5.143 \times 10^2$	$-3.491 \times 10^4$	$-7.460 \times 10$	0.000	273–323
$K_7$	$4.665 \times 10^2$	$1.614 \times 10^3$	$-9.754 \times 10$	$2.471 \times 10^{-1}$	273–343
$K_8$	6.822	$-6.066 \times 10^3$	$-2.290 \times 10$	$3.600 \times 10^{-3}$	273–343
$K_9$	$-1.156 \times 10$	$1.769 \times 10^3$	$-1.467 \times 10$	$2.400 \times 10^{-3}$	273–343
$K_{10}$	-3.686	$-6.754 \times 10^3$	0.000	0.000	273–328

reaction rates (R12-R13 and R19-R24). These reactions control the absorption rate and enhance mass transfer from the gas phase to the liquid phase in the absorber (Esmaeili et al., 2020). For CO<sub>2</sub> removal, reactive absorption with both rate-controlled and equilibrium reactions occur in the liquid phase. In packed columns, CO<sub>2</sub> absorption is controlled by diffusion with fast chemical reactions in the liquid boundary layer (Pacheco and Rochelle, 1998). The kinetic parameters of the rate-controlled reactions concerned with PZ, DEA and MDEA are given in Table 2.

One of main approaches to calculate vapor-liquid equilibrium (VLE) of amine solutions in process simulation is the  $\gamma - \phi$  (activity-fugacity) approach in which an activity model describes the liquid phase non-idealities and an equation of state estimates the nonidealities of the vapor phase. The process was simulated by Aspen Plus using the property package of E-NRTL model for electrolyte thermodynamics and Peng-Robinson EOS for the properties of vapor and liquid phases of hydrocarbon. The E-NRTL model is the most versatile and suitable electrolyte property method for aqueous amine solution systems since the required data for pure components and binary interaction parameters have been reported in the literature. Furthermore, it has the capability to deal with very low and very high concentrations in aqueous and mixed solvent systems (Esmaeili et al., 2020; Ghanbarabadi et al., 2019). The Peng-Robinson EOS is applicable in the natural gas processes and has reasonable accuracy near the critical point for the calculations of compressibility factor and liquid density. This property package is based on extensive research and development in rate-based simulation of chemical absorption processes and molecular thermodynamics models for aqueous amine solutions and contains the parameters of thermodynamics and physical properties data.

### 3. Process and model description

The main purpose of this study is the comparison of CO<sub>2</sub> absorption efficiency, CO<sub>2</sub> loading and regeneration heat duty of some amine solutions for CO<sub>2</sub> removal from the ethane stream, one of the main products in Phase 19 gas plant located at the South Pars Gas Complex in Iran, to provide a proper alternative to DEA solution to overcome the mentioned drawbacks. The sour natural gas from the South Pars Gas Field is introduced into four identical trains in this plant via two 32 inch sub-sea gas pipelines with the flow rate of 500 MMSCFD for each train to produce methane, ethane, liquefied petroleum gas, condensate and solid sulfur. The ethane stream is separated from propane and the heavier compounds (C3+) into the de-ethanizer column of each train. Then, the ethane streams of two trains are mixed and sent to the ethane treatment unit for CO<sub>2</sub> removal and a limited elimination of sulfur compounds, and there are thus two identical ethane treatment units in this plant.

The mixed ethane stream from the two fractionation units entered the feed gas knock-out drum with the operational conditions of 38 °C, 2440 kPa and 62613 kg/hr and molar composition of 4.3% CO<sub>2</sub>, 0.94%

methane, 94.09% ethane, 0.6% propane and 3.0 ppm butane and the heavier hydrocarbon components (C4+), 49.0 ppm H<sub>2</sub>S and 23.0 ppm carbonyl sulfide (COS), to separate probable solid particles and liquid droplets before introduced into the absorber column. Fig. 1 exhibits the simulated process of CO<sub>2</sub> removal from the ethane stream, which includes a conventional absorber with the diameter of 1.80 m and two packed sections of Mellapak 250X (surface area 256 m<sup>2</sup>/m<sup>3</sup>, void fraction 0.987, and system foaming factor 0.73) with the height of 7.50 m and HETP of 0.9375 m for each one.

Based on the carried out simulation, each packing section was counted as eight stages for modelling the absorber by Aspen Plus. In addition, there are four sieve trays on the top of the packed beds with the system foaming factor 0.75 for water washing (totally 20 stages). The actual absorbent was 40 wt% DEA solution, which flowed into the absorber at 45 °C, 2411 kPa with the flow rate of 128 ton/hr to obtain the maximum mass specifications of 50 ppm CO<sub>2</sub> and 10 ppm total sulfur. Table 3 indicates the operational conditions of inlet streams to the absorber. The washing water was introduced into the column with the operational conditions of 40 °C, 2396 kPa and 4371 kg/hr. The water wash section was used for the cooling of the outlet gas and washing amine droplets entrained in the ethane stream to recycle them to the amine circulation system. A limited part of water entrained in the gas flow was firstly separated by the treated gas knock-out drum before the gas stream was treated by the drying package to obtain the required mass specifications as shown in Table 4.

The rich amine flowed out of the absorber and was introduced into the flash drum after pressure reduction to 801.3 kPa to remove the associated gas, which had 96.09% mole ethane and 0.21% mole CO<sub>2</sub>. This small stream of flash gas (51.2 kg/h) was subsequently treated by DEA in the flash gas absorber on the top of the flash drum to remove CO<sub>2</sub> prior to be used as boiler fuel. The rich amine entered the regenerator after passing the lean/rich amine (plate) heat exchanger with maximum outlet rich solvent temperature of 123 °C to utilize the high temperature of lean amine for the reduction of energy consumption. In order to minimize the regeneration heat duty, the rich solvent must be sent into the stripper at the highest possible temperature, with considering the limitations imposed by the solvent degradation. The liquid portion in the rich solvent stream flowed downward, transferring CO<sub>2</sub> to and receiving water from the upward vapor flow inside the stripper (Kim et al., 2015). The regenerator employed 24 valve trays with the diameter of 1.90 m and the tray spacing of 0.61 m to strip CO<sub>2</sub> from the rich solution. The desorbed CO<sub>2</sub> in high purity can be used in various applications such as well services for enhanced oil recovery, pH reduction to neutralize process and waste water streams, extraction processes as supercritical CO<sub>2</sub> and carbonated beverage in food industry. Then the CO<sub>2</sub>-stripped lean amine solution stream was withdrawn from the reboiler with the average temperature of 132 °C and was reused in the absorber after cooling down to 45 °C.

Five single and blended amine solutions with the concentration of 40%wt including DEA, MDEA, PZ + MDEA with two mass ratios and DEA + MDEA have been evaluated to look into the effect of amine type and absorbent mass ratio on CO<sub>2</sub> absorption efficiency, CO<sub>2</sub> loading and regeneration heat duty (Table 5).

It is recommended that the rate-based model is used instead of the equilibrium model for the simulation of CO<sub>2</sub> absorption because this method offers more rigorous and reliable basis for the evaluation of column performance, particularly for multicomponent separations. The main attribute that distinguishes this model from the equilibrium model is the accuracy of results since the rate-based model considers the following parameters: mass transfer correlations, effective interfacial area, holdup, flooding, thermodynamics and kinetics model, heat transfer correlation, physicochemical properties (density, viscosity and etc.) and flow model (Esmaeili et al., 2020). The equilibrium model assumes that phase and thermal equilibria are achieved between liquid and vapor streams leaving a stage and employs an apparent composition approach which considers that the liquid phase is in chemical

**Table 2**

Kinetics parameters of CO<sub>2</sub> absorption by DEA, MDEA and PZ amine solutions (Borhani et al., 2015; Hemmati et al., 2019; Hikita et al., 1977).

Electrolyte	Type of reaction	k	E <sub>a</sub> (cal/mol)
Bicarbonate	forward	$1.33 \times 10^{17}$	13249
	backward	$6.63 \times 10^{16}$	25656
DEACOO <sup>-</sup>	forward	$6.48 \times 10^{16}$	5072
	backward	$1.43 \times 10^{17}$	11497
MDEAH <sup>+</sup>	forward	$6.85 \times 10^{10}$	9029
	backward	$6.62 \times 10^{17}$	22131
PZ carbamate	forward	$1.70 \times 10^{10}$	319
	backward	$3.40 \times 10^{23}$	14160
PZ bicarbamate	forward	$1.04 \times 10^{14}$	8038
	backward	$3.20 \times 10^{20}$	8692

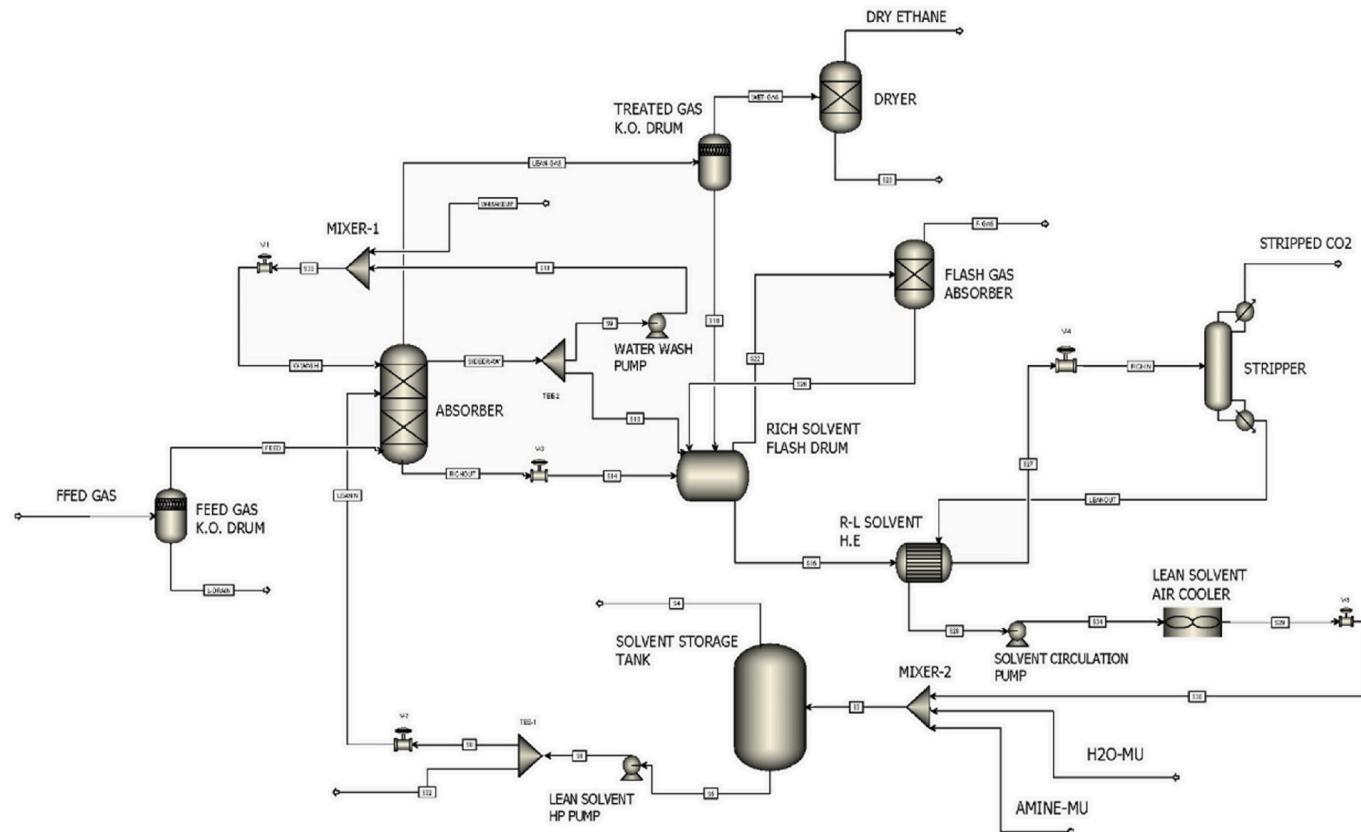


Fig. 1. Schematic of CO<sub>2</sub> absorption process from ethane by using amine solution in Aspen Plus.

**Table 3**  
Operational conditions of inlet stream of ethane, aqueous amine solutions and washing water.

Parameter	Ethane	Amine solution	Washing water	Water make-up
Temperature (°C)	38	45	40	40
Pressure (kPa)	2440	2411	2396	2861
Mass flow rate (kg/h)	62613	128000	4371	370

**Table 4**  
Mass composition of inlet gas into the absorber and the required specifications of dry ethane.

Component	Feed to the absorber	Required specifications
CO <sub>2</sub>	6.18%	50 ppm Max.
Methane	0.49%	1% Max.
Ethane	92.38%	98% Min.
Propane	0.94%	1% Max.
C4+	5.69 ppm	Traces
H <sub>2</sub> S	54.52 ppm	10 ppm as total sulfur
COS	45.11 ppm	

(molecular and ionic) equilibrium. On the other side, the rate-based model assumes that phase and thermal equilibria are attained in the vapor-liquid interface while there are transfer resistances in the vapor and liquid films. Moreover, the rate-based model employs a true composition approach and includes equilibrium and rate-limiting kinetic reactions directly. Both methods are based on the two-film theory in Aspen Plus.

There are various flow models defined in Aspen Plus by which the flow pattern in tray and packing is modelled. In general, the mixed flow

model is recommended for trays and defined on equilibrium stage as the bulk properties for each phase are assumed to be the same as the outlet conditions for that phase leaving that stage; the countercurrent flow model employs the average of inlet and outlet conditions for gas and liquid phases, and is used for binary distillation simulations and recommended for packings; VPlug is applied to the acid gas removal by amine or caustic solution as it treats the liquid phase as well-mixed fluid and the vapor as in plug flow (Hanley and Chen, 2012). The VPlug model considers that outlet conditions are used for the liquid and the average between inlet and outlet conditions are applied to the vapor at the outlet pressure. This model is recommended for both columns with trays and those with packing. Table 6 shows the models used to simulate the process by Aspen Plus.

For packed columns, some correlations are required to estimate absorption efficiency such as mass transfer coefficients ( $k_x$  and  $k_y$ ), effective surface area contributing to mass transfer ( $a_m$ ), two-phase pressure drop and flood capacity of the column. Hanley et al. (Hanley and Chen, 2012) suggested new correlations for the packing of pall ring, metal IMTP, the sheet metal structured packings of Mellapak/Flexipac type and metal gauze structured packings in the X configuration. The recommended correlations are more appropriate than the previously presented correlations for the mentioned packing types and can be utilized for a wide domain of chemical systems and column operational conditions including distillation and acid gas removal by amine solutions. The Hanley's correlations for Mellapak family packings are as follows:

$$k_x = 0.33 Re_L \cdot Sc_L^{1/3} \left( \frac{C_L \cdot D_L}{d_e} \right) \left( \frac{\cos(\theta)}{\cos(\pi/4)} \right)^{4.078} \quad (1)$$

$$k_y = 0.0084 Re_G \cdot Sc_G^{1/3} \left( \frac{C_G \cdot D_G}{d_e} \right) \left( \frac{\cos(\theta)}{\cos(\pi/4)} \right)^{-3.072} \quad (2)$$

**Table 5**

Parameters of the studied amine solutions at the inlet of the absorber.

Parameter	Actual conditions	Simulation by Aspen Plus					
		Single solutions		Blended solutions			
		DEA	MDEA	PZ + MDEA (1)	PZ + MDEA (2)	DEA + MDEA	
Mass Percent of solvent (%)	40	40	40	1	39	2	38
Mole Percent of solvent (%)	10.25	10.25	9.16	0.32	8.92	0.64	8.68
Mass flow rate of solvent (kg/hr)	51200	48000	48000	1200	46800	2400	45600
Molar flow rate of lean solution (kmol/hr)	4750.03	4453.15	4399.42	4403.28		4407.14	4406.13
Molecular weight (kg/kmol)	26.95	26.95	27.28	27.25		27.23	27.23
Density (kg/m <sup>3</sup> )	1040.03	1040.03	1023.69	1023.40		1023.09	1028.08
Viscosity (cp)	2.73	2.73	2.64	2.67		2.70	2.64

**Table 6**Models and correlations used for simulation of CO<sub>2</sub> absorption in amine solutions.

Model approach	Used correlation
Flow model for tray	Mixed
Flow model for packing	VPlug
Mass transfer for sieve tray	AICHE
Mass transfer for valve tray	Scheffe
Mass transfer for packing	Hanley-Chen
Interfacial area for sieve tray	Zuiderweg
Interfacial area for valve tray	Scheffe
Interfacial area for packing	Hanley-Chen
Holdup for tray	Bennett
Holdup for packing	Bravo-Fair
Flooding	Fair
Liquid film resistance	Discrnx
Vapor film resistance	Film
Heat transfer coefficient	Chilton and Colburn
Liquid density	Clarke model
Liquid viscosity	Jones-Dole model
Liquid surface tension	Onsager-Samaras model
Binary diffusivity	Nernst-Hartley model
Thermal conductivity	Riedel model

$$\frac{a_m}{a_d} = 0.539 Re_G^{0.145} \cdot Re_L^{-0.153} \cdot We_L^{0.2} \cdot Fr_L^{-0.2} \left( \frac{\rho_G}{\rho_L} \right)^{-0.033} \left( \frac{\mu_G}{\mu_L} \right)^{0.090} \quad (3)$$

The Radfrac module in Aspen Plus is employed to calculate the reaction rate in film, mass transfer between phases, electrolyte chemistry and hydrodynamics by mass and heat correlations. In this study, VPlug flow model for CO<sub>2</sub> absorption as well as Hanley-Chen correlations for the calculation of mass transfer coefficients and effective interfacial area in Mellapak type packings have been used for all amine solutions because the combination of VPlug model and Hanley-Chen correlations is more appropriate than other models and correlations for the CO<sub>2</sub> absorption using Mellapak packing.

#### 4. Results and discussion

The second-order reaction rate constant (k<sub>2</sub>) between amine and CO<sub>2</sub> is independent of absorbent concentration and can be regarded as a rapid pseudo-first-order reversible reaction for the studied solvents in this work (Zhang et al., 2001). The second-order reaction rate constant of PZ is at least an order higher than that of conventional alkanolamines such as DEA and MDEA. The second-order reaction rate constant of PZ (Zhang et al., 2001), DEA (Kierzkowska-Pawlak and Chacuk, 2010), MDEA (Xu et al., 1992) in the temperature range of 303–333 K are presented in Fig. 2 and can be expressed by Eqs. (4)–(6).

$$k_{2,PZ} [\text{m}^3 / \text{kmol.s}] = 4.0 \times 10^{10} \cdot \exp \left( \frac{-4059.4}{T} \right) \quad (4)$$

$$\ln k_{2,DEA} [\text{m}^3 / \text{kmol.s}] = 24.515 - \frac{5411.3}{T} \quad (5)$$

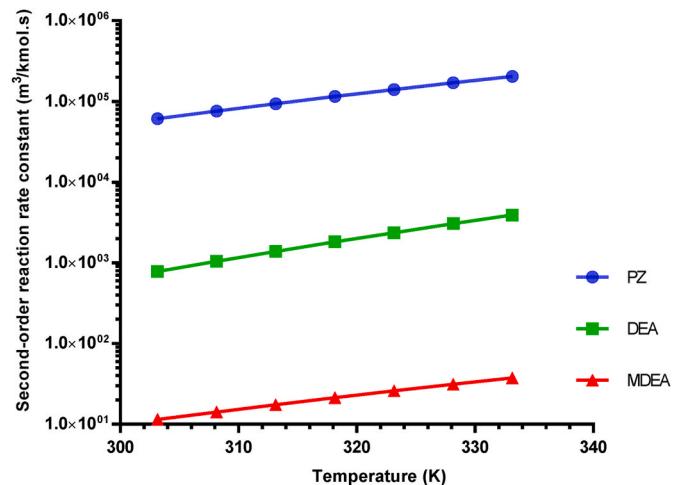


Fig. 2. Second-order reaction rate constant of PZ, DEA and MDEA at 303–333 K.

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

The absorption and stripping columns are often designed for the gas pressure drop of 0.2–0.4 bar per meter of packing. There is usually less pressure drop per theoretical stage in packed columns, which can be crucial for low pressure operations. This kind of columns possess higher capacity for the systems with a high liquid to gas ratio. In order to estimate the height of a packed column, HETP is required. HETP is the height of packing that will give the same separation effect as an equilibrium stage and is a function of the system, devices geometry and mechanical factors. Liquid distribution is one of critical considerations in packed beds and can result in significant efficiency loss as long as it is not executed properly. The pressure drop is caused in gas stream as it flows through the bed because of (1) both skin friction and form friction, (2) frequent changes in the flow direction and (3) expansion and contraction. Maximum area for gas flow is available if the packing is dry, i.e. if there is no liquid throughput. When liquid flows through the bed, part of the open space of the bed is occupied by the liquid (called liquid holdup in the bed) and the area available for gas flow decreases. This is the reason why the pressure drop of the gas increases with rising liquid throughput. If the gas flow rate is increased at a constant liquid rate, the drag of the gas impedes the downward liquid velocity and the liquid holdup in the bed is consequently increased. Therefore, either gas or liquid gas flow rate is increased, the liquid holdup and the pressure drop through the height of bed can be enhanced.

If the gas flow rate is further increased, the liquid accumulation rate in the upper region increases very sharply and leads to preventing the flow of gas. This steady increase in the pressure drop brings to loading. Loading point is often defined as the gas velocity at which the pressure

drop first becomes proportional to the gas velocity raised to the power of 2 for a fixed liquid rate. As the gas flow rate is increased above the loading point (on the same liquid rate), a point is finally reached where the same curve turns abruptly into almost vertical line. This point is the limiting condition of operation or flooding point. The bed becomes flooded when the voids in the bed is full of liquid and the liquid becomes the continuous phase with increasing pressure drop and loss of mass transfer efficiency (Dutta, 2009). Flooding velocities are a function of the liquid and gas flow rates, the physical properties of the two fluids, and the characteristics of the packing material. Table 7 illustrates the hydrodynamic data achieved for different amine solutions with 63.37% of the maximum capacity which is located below 80% of the considered maximum capacity in this study. Fig. 3 indicates the flooding curve of the absorber using DEA on the stage of 5 (the first packing stage from the top) according to Fair correlation.

#### 4.1. The comparison of absorption efficiency

In this study, the simulation was initially conducted with the incumbent amine solution (40 wt% DEA), which is already used in Phase 19 gas plant, to assess the models shown in Table 6 and verify the validity of the simulation data in comparison with the actual data. Then, the process was simulated with four other amine solutions in the same mass concentration and the flow rate of 120,000 kg/h to determine the compositions and operating conditions along the absorber. The simulation results show that the solution of 40 wt% DEA reached the specified targets with CO<sub>2</sub> absorption efficiency (Eq. (7)) of 100% using the considered mass flow rate which is 6.25% less than the operating one. The mass concentration of the impurities in the dry ethane stream by the

conducted simulation are  $3.42 \times 10^{-3}$  ppm CO<sub>2</sub>,  $6.10 \times 10^{-9}$  ppm H<sub>2</sub>S and  $4.05 \times 10^{-6}$  ppm COS that are in good agreement with the average actual data of Phase 19, which have been reported around 3.50 ppm CO<sub>2</sub> and total sulfur of 3–4 ppm. Moreover, the estimated flow rate of water make-up on the top of absorber is 411 kg/hr which is injected to the washing water. On the other hand, the single solution of 40 wt% MDEA was not able to achieve the targets and the CO<sub>2</sub> absorption efficiency was only 67.74% due to the lower second-order reaction rate constant compared to those of PZ and DEA illustrated in Fig. 2, in addition to the slower mass transfer rate between CO<sub>2</sub> and MDEA. Therefore, the single solution of 40 wt% MDEA cannot be considered as a suitable solution to remove CO<sub>2</sub> from the ethane stream based on the defined process conditions. However, the simulation data reveal that the addition of 1-2 wt % PZ or 5 wt% DEA as promoter to MDEA solution has a significant effect on the CO<sub>2</sub> absorption because the reaction of CO<sub>2</sub> with PZ is much faster than that of CO<sub>2</sub> with the conventional carbamate-forming amines (Bishnoi and Rochelle, 2000). Table 8 exhibits the operational conditions of rich amine solution to the stripper as well as the mass flow rate of the treated dry ethane stream and the composition of each component.

Although PZ has a low solubility in aqueous solution and its price is relatively expensive, adding a limited amount of PZ into MDEA solution can greatly increase the absorption rate of CO<sub>2</sub> as well as the absorption capacity with the CO<sub>2</sub> molar concentration of 1.95% in the rich solution. As MDEA is considerably less corrosive than other conventional amine solutions such as MEA and DEA and has the lowest heat of reaction among the studied absorbents, it can be used as the major amine and then activated by a strong promoter. Therefore, all chosen blended amine solutions can remove CO<sub>2</sub> and sulfur components effectively and meet all required specifications mentioned in Table 4. The results also depict that the performance of 5 wt% DEA +35 wt% MDEA is located either between each of parent solvent or the same as 40 wt% DEA in terms of the absorption efficiency, the molar flow of rich amine and mass fraction of the dry gas stream compositions, which are compatible with the experimental data reported by Aroonwilas et al. (Aroonwilas and Veawab, 2004). Table 9 demonstrates the CO<sub>2</sub> absorption efficiency of each amine solution with the operational conditions of 45°C, 2411 kPa and 120 ton/hr.

Fig. 4 indicates the values of CO<sub>2</sub> vapor pressure (solubility) in each solution, and Fig. 5 reveals that the amount of CO<sub>2</sub> loading in the rich amine solutions (Eq. (8)) is directly proportional to CO<sub>2</sub> vapor pressure and depends on molar flow rate of amine solvents and the thermodynamic limitation of each amine. As this study has assessed a brownfield process unit where operating conditions such as amine solution flow rate should comply with the existing absorber column to prevent flooding and high pressure drop, CO<sub>2</sub> loading more than 0.216 could not be reached. An increase in PZ mass concentration of PZ + MDEA solution brings on the decrease in molecular weight of solution, leading to rise in the molar flow rate of solution and drop in CO<sub>2</sub> loading which can be seen in comparison between the solutions 1 wt% PZ + 39 wt% MDEA and 2 wt% PZ + 38 wt% MDEA. It is obvious that the amine solutions of 1 wt% PZ + 39 wt% MDEA and 5 wt% DEA +35 wt% MDEA have attained the highest values of vapor pressure and CO<sub>2</sub> loading compared with other single and blended amine solutions.

$$\eta_{\text{abs.}} = \left[ 1 - \left( \frac{Y_{\text{CO}_2,\text{out}}}{1 - Y_{\text{CO}_2,\text{out}}} \right) \left( \frac{1 - Y_{\text{CO}_2,\text{in}}}{Y_{\text{CO}_2,\text{in}}} \right) \right] \times 100 = \left[ 1 - \frac{Y_{\text{CO}_2,\text{out}}}{Y_{\text{CO}_2,\text{in}}} \right] \times 100 \quad (7)$$

$$\text{CO}_2 \text{ loading} = \frac{\text{absorbed moles of CO}_2 (\text{molar flow})}{\text{moles of absorbent} (\text{molar flow})} \quad (8)$$

Fig. 6 exhibits the temperature profile of CO<sub>2</sub> absorption along the column using five different solutions. The results are in good agreement with the actual temperature profile with the maximum average absolute deviation (AAD) of 3.78% due to the difference between the actual and

**Table 7**  
Hydrodynamic characteristics of the top and bottom packed sections using different amine solutions.

Packing section	Parameter	Amine solution (40 wt%)				
		DEA	MDEA	PZ + MDEA (1)	PZ + MDEA (2)	DEA + MDEA
Top Packed Bed	Max. Capacity (%)	58.89	62.80	61.01	61.04	61.25
	Max. Capacity Factor (m/s)	0.035	0.037	0.036	0.036	0.036
	Section Pressure Drop (mbar)	27.58	27.50	27.60	27.60	27.46
	Pressure Drop/Height (mbar/m)	3.68	3.67	3.68	3.68	3.66
	Max. Stage Liquid Holdup (m <sup>3</sup> )	0.223	0.223	0.224	0.225	0.223
	Max. Liquid Superficial Velocity (m <sup>3</sup> /hr.m <sup>2</sup> )	45.58	46.52	46.42	46.44	46.37
	Max. Capacity (%)	60.60	63.37	62.81	62.95	62.87
	Max. Capacity Factor (m/s)	0.037	0.038	0.037	0.037	0.038
	Section Pressure Drop (mbar)	27.47	27.67	27.54	27.54	27.10
	Pressure Drop/Height (mbar/m)	3.66	3.69	3.67	3.67	3.61
Bottom Packed Bed	Max. Stage Liquid Holdup (m <sup>3</sup> )	0.223	0.226	0.224	0.225	0.217
	Max. Liquid Superficial Velocity (m <sup>3</sup> /hr.m <sup>2</sup> )	46.22	46.64	46.72	46.76	46.68

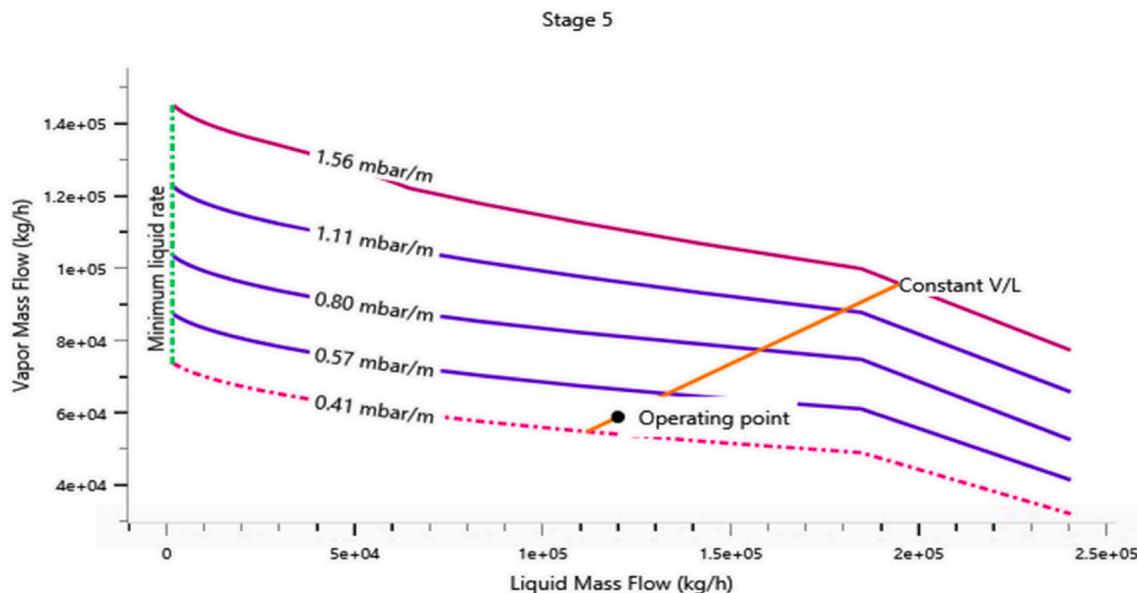


Fig. 3. Flooding curve of the absorber in contact with DEA solution on the stage of five .

**Table 8**  
Operational conditions of rich amine solutions and treated dry ethane stream.

Parameter and Component	Amine Solutions				
	40 wt% DEA	40 wt% MDEA	PZ + MDEA (1)	PZ + MDEA (2)	5 wt% DEA + 35 wt% MDEA
Molar flow rate of rich solution (kmol/hr)	4557.27	4475.09	4507.50	4511.39	4510.30
Mole percent of CO <sub>2</sub> in rich solution	1.930	1.329	1.950	1.948	1.949
Amine Efficiency	5.19	6.77	4.63	4.67	4.66
Mass flow rate of dry gas (kg/hr)	58653.24	59874.08	58598.07	58597.53	58604.43
CO <sub>2</sub> (ppm wt)	3.42E-3	20893	0.00	0.00	3.67
Methane (wt %)	0.525	0.514	0.525	0.525	0.525
Ethane (wt%)	98.47	96.41	98.47	98.47	98.47
Propane (wt %)	0.997	0.977	0.997	0.997	0.997
C4+ (ppm wt)	6.00	6.00	6.00	6.00	6.00
H <sub>2</sub> S (ppm wt)	6.10E-9	1.57E-2	0.00	0.00	0.00
COS (ppm wt)	4.05E-6	21.89	4.56	4.59	4.65

**Table 9**  
CO<sub>2</sub> absorption efficiency of the amine solutions based on the similar operating conditions.

Amine Solution				
40 wt% DEA	40 wt% MDEA	PZ + MDEA (1)	PZ + MDEA (2)	5 wt% DEA + 35 wt% MDEA
100%	67.74%	100%	100%	99.98

simulated flow rates. The 40 wt% DEA has the highest absorption temperature of 59.66 °C on the stage of 20 in the absorber (the lowest stage); 1 wt% PZ + 39 wt% MDEA and 2 wt% PZ + 38 wt% MDEA

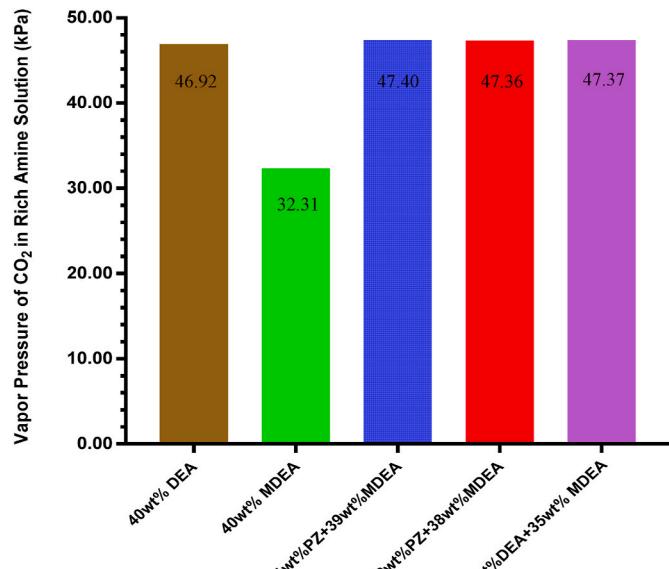


Fig. 4. Vapor pressure of CO<sub>2</sub> in various rich amine solutions.

solutions have the maximum absorption temperature of 56.83 and 57.46 °C respectively on the stage of 19, while the solution of 5 wt% DEA + 35 wt% MDEA has reached the peak temperature of 61.68 °C on the stage of 18. Therefore, the solution of 1 wt% PZ + 39 wt% MDEA has shown the lowest temperature bulge among the blended solutions. As CO<sub>2</sub> is absorbed in the solvent, temperature in the down-coming solution increases and water is vaporized. Because of the combination of absorption and water vaporization, a temperature bulge will appear in the absorber. When the bulge is located on the top or bottom of the column, the magnitude is close to the limiting values of the temperature in the liquid and gas respectively. The magnitude is maximized when the bulge is located approximately in the middle of the column. The absorber performance seems to be independent of the bulge location when it is located in the top or bottom of the column but it might be affected when the bulge is located in the middle (Kvamsdal and Rochelle, 2008). The temperature bulge is located on the bottom for all the studied amine solutions, as exhibited in Fig. 6.

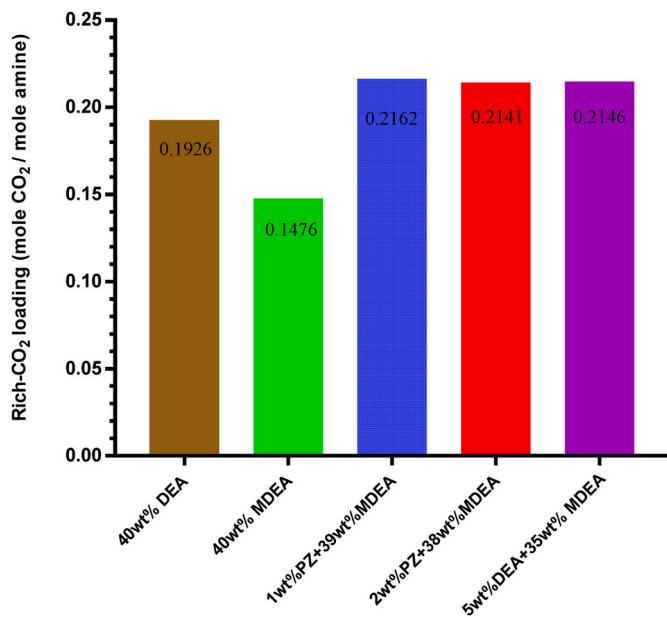


Fig. 5. Rich-CO<sub>2</sub> loading in various rich amine solutions.

The profile of CO<sub>2</sub> mole fraction in vapor phase along the absorber is shown in Fig. 7. Because of higher driving force between the rich gas and amine solution at the bottom of absorber, higher mass transfer rate and CO<sub>2</sub> loading are achieved in this region and most of CO<sub>2</sub> is absorbed in this part. The solutions with higher reactivity and mass transfer rate are able to reduce the CO<sub>2</sub> concentration in vapor phase with a higher slope and obtain the required specifications on the lower stages in such a way that the outlet CO<sub>2</sub> mole fraction from the absorber has almost reached the required target on the stage of 16 by both PZ + MDEA solutions using 1 and 2 wt% PZ. Fig. 7 also demonstrates that the solution of 40 wt% MDEA has the minimum slope in CO<sub>2</sub> absorption due to its lowest reactivity and temperature bulge (54.84 °C) among the studied amine solutions with the associated water concentration of 0.25 wt% in the wet ethane stream; thus the required targets were not attained by the single amine solution of 40 wt% MDEA and this absorbent cannot be considered as a proper solution for this purpose.

The solution of 5 wt% DEA +35 wt% MDEA presents the profile between that of 40 wt% DEA and 40 wt% MDEA as reported in the literature (Aroonwilas and Veawab, 2004), and has gained the specified targets on the stage of 8 considering the fact that the profile is closer to

that of the solution of 40 wt% MDEA because of higher ratio of MDEA to DEA. Therefore, the blended solution of DEA + MDEA has the highest absorption temperature compared with the other solutions and has reached the target on the upper section of packing. These trends exhibit that the profile of CO<sub>2</sub> concentration is close to the promoter (PZ or DEA) profile at low CO<sub>2</sub> loadings and then moves toward MDEA profile; additionally, it shows a mixed competition of kinetic/thermodynamic in a blended solution between two reactive components. At lower CO<sub>2</sub> loadings (the upper section of column), promoters play a notable role in controlling absorption rate because their reaction with CO<sub>2</sub> is faster than that of MDEA with CO<sub>2</sub>. As CO<sub>2</sub> loading is enhanced (the bottom section of column), more CO<sub>2</sub> is converted to PZ or DEA carbamate, resulting in reduction of the ratio of unreacted promoter to unreacted MDEA. When blended solutions are used, promoters probably act as primary reactant to absorb CO<sub>2</sub> in the upper section of column while MDEA controls absorption in the lower section. As CO<sub>2</sub> concentration in vapor phase decreases from bottom to top, ethane concentration rises in the same direction, while CO<sub>2</sub> solubility in the amine solutions increases from top to bottom (Figs. 8 and 9). The maximum mass concentration of wet ethane in contact with 40 wt% DEA and all the blended amine solutions has reached 98.24% while this is 96.17% by the solution of MDEA with the flow rate of 120 ton/hr as shown in Fig. 8. The mole fraction of CO<sub>2</sub> in an amine solution is directly concerned with both the reaction rate and equilibrium capacity of CO<sub>2</sub> in the absorbent. As the studied blended amine solutions have the combination of the absorbents with high reactivity (PZ or DEA) and high capacity (MDEA), the mole percent of 1.95 for CO<sub>2</sub> in liquid-phase has been obtained for all those blended solutions compared to 1.94 and 1.33 for 40 wt% DEA and 40 wt% MDEA respectively as depicted in Fig. 9.

From the absorption point of view, two blended solutions 1 wt% PZ + 39 wt% MDEA and 2 wt% PZ + 38 wt% MDEA are comparable with the actual solution of 40 wt% DEA in terms of absorption temperature profile along with CO<sub>2</sub> and ethane profiles in the absorber with the average associated water concentration of 0.25 wt%. However, the solutions of 1 wt% PZ + 39 wt% MDEA and 5 wt% DEA +35 wt% MDEA have achieved the required targets of CO<sub>2</sub> removal coupled with the highest treated dry gas mass flow rates and CO<sub>2</sub> loadings. Therefore, all the investigated blended amine solutions can be considered as appropriate alternatives to the solution of 40 wt% DEA in terms of reactivity and solubility for CO<sub>2</sub> and sulfur compounds removal in this process, and other factors need to be evaluated to choose the most efficient absorbent.

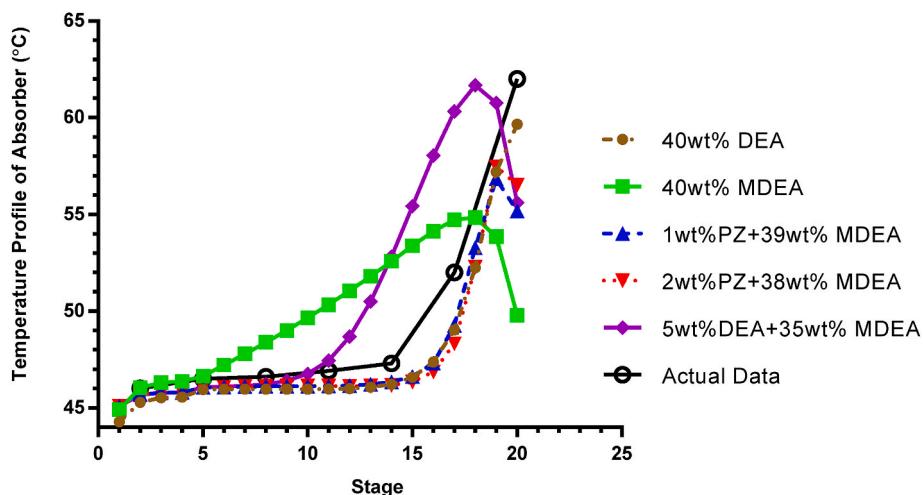


Fig. 6. Temperature profile vs. column stages for various amine solutions.

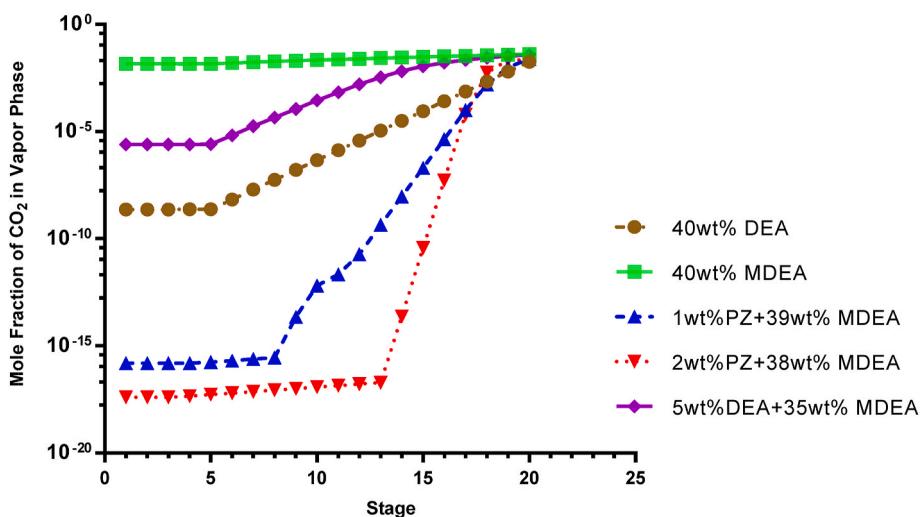


Fig. 7. Profile of  $\text{CO}_2$  mole fraction in vapor phase vs. column stages for various amine solutions.

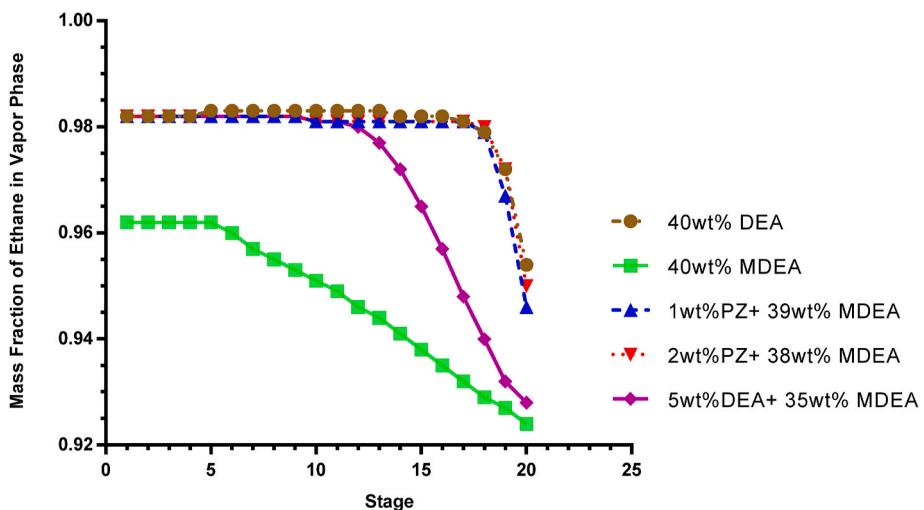


Fig. 8. Profile of ethane mass fraction in vapor phase vs. column stages for various amine solutions.

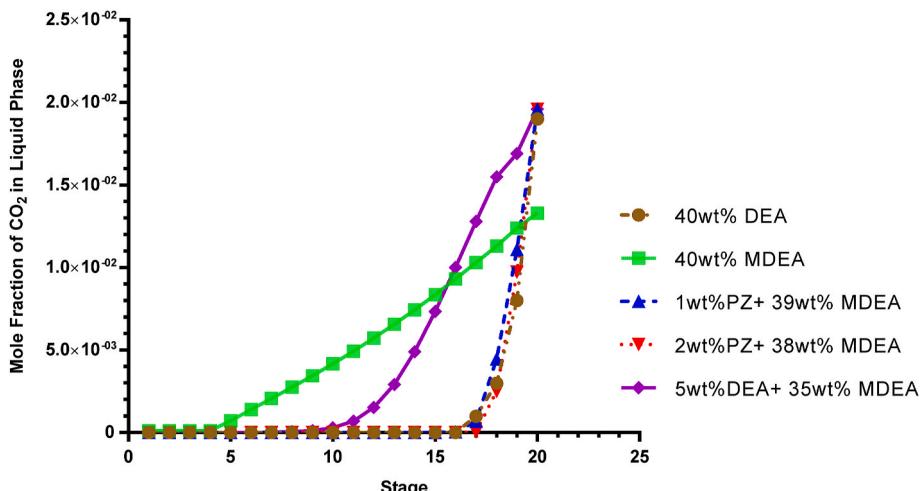


Fig. 9. Profile of  $\text{CO}_2$  mole fraction in liquid phase vs. column stages for various amine solutions.

#### 4.2. The comparison of regeneration heat duty

Although the regeneration of tertiary amines requires less heat duty than primary and secondary amines, low reaction rates with CO<sub>2</sub> make tertiary amines difficult to use for CO<sub>2</sub> removal (Chowdhury et al., 2013). By increasing the absorption rate of tertiary amines efficiently and maintaining low reaction heat, the absorption/regeneration process could be largely optimized. Gao et al. (2017) noticed the blends of MEA and tertiary amines are more attractive than aqueous MEA solution. Idem et al. (Idem et al. (2006)) reported that a significant reduction in the regeneration heat duty can be obtained by using a mixed MEA + MDEA solution compared with MEA solution. Oyenekan et al. (Oyenekan and Rochelle, 2007) also reported that tertiary amine (MDEA) solvents promoted by PZ achieved 15–22% energy savings and the reaction rate of CO<sub>2</sub> with MDEA can be enhanced by the addition of PZ. To investigate all single and blended amine solutions in the similar conditions, regeneration efficiency ( $\eta_{reg}$ ) defined by Eq. (9), is considered as one hundred percent for the simulation of all amine solutions, and it is assumed that all the absorbed CO<sub>2</sub> is recovered by the stripper and no CO<sub>2</sub> exists in the lean solution. Thus, lean-CO<sub>2</sub> loading is regarded as zero (Bougie and Iliuta, 2010).

$$\eta_{reg} = \frac{\alpha_{rich} - \alpha_{lean}}{\alpha_{rich}} \times 100\% \quad (9)$$

The regeneration (reboiler) heat duty (kJ/kg<sub>CO<sub>2</sub></sub>) is defined as the net power supply per mass flow rate of CO<sub>2</sub> and is a function of various operating parameters, such as rich-CO<sub>2</sub> loading, lean-CO<sub>2</sub> loading, solution molar flow rate, feed temperature, type of amine solution, concentration as well as mass ratio (of two amine species) in blended solutions:

$$q_{reg.} = \frac{H_{reb.} - H_{loss}}{n_{rich}(\alpha_{rich} - \alpha_{lean})M_{CO_2}} \quad (10)$$

Generally, the primary amines require the highest regeneration heat duty followed by the secondary and then tertiary amines as a result of two reasons. The first one is that PZ and DEA have higher heat of reaction with CO<sub>2</sub> than MDEA, and the second one is the heat of water vaporization which is associated with the operating CO<sub>2</sub> partial pressure. PZ and DEA demand a lower operating CO<sub>2</sub> partial pressure in comparison with MDEA to establish the driving force for CO<sub>2</sub> stripping. Consequently, greater amount of water vapor must be produced for PZ and DEA solutions, causing higher energy consumption for water vaporization. Table 10 shows the required power for each of the devices in this gas treatment unit based on various amine solutions.

The addition of promoter such as PZ to the MDEA solution with a low ratio not only leads to the increase in the reactivity but brings on the

**Table 10**  
Required power of the devices in this process with different amine solutions.

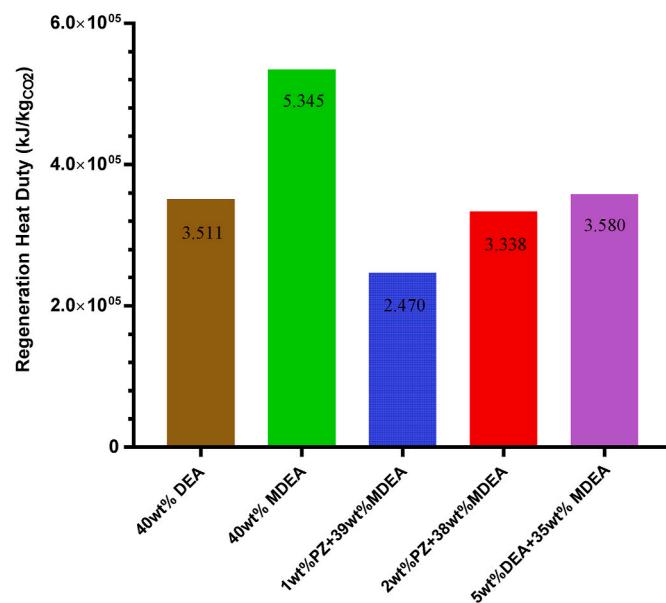
Equipment	Amine Solution				
	40 wt% DEA	40 wt% MDEA	PZ + MDEA (1)	PZ + MDEA (2)	5 wt% DEA + 35 wt% MDEA
Reboiler	1.356 × $10^{10}$	1.554 × $10^{10}$	1.059 × $10^{10}$	1.419 × $10^{10}$	$1.525 \times 10^{10}$
Air Cooler	1.171 × $10^7$	5.568 × $10^6$	7.273 × $10^6$	8.052 × $10^6$	$7.241 \times 10^6$
Lean solvent	6.166 × $10^5$	6.263 × $10^5$	6.265 × $10^5$	6.267 × $10^5$	$6.237 \times 10^5$
HP pump	6.596 × $10^3$	6.600 × $10^3$	6.597 × $10^3$	6.597 × $10^3$	$6.597 \times 10^3$
Water wash pump	5.044 × $10^4$	5.093 × $10^4$	5.104 × $10^4$	5.112 × $10^4$	$5.078 \times 10^4$
Solvent circulation pump					
Total	1.358 × $10^{10}$	1.555 × $10^{10}$	1.060 × $10^{10}$	1.420 × $10^{10}$	$1.526 \times 10^{10}$

higher CO<sub>2</sub> loading of rich amine than that of MDEA solution in such a way that the solution of 1 wt% PZ + 39 wt% MDEA needs 32% lower reboiler power supply (kJ/hr) than the solution of 40 wt% MDEA. On the other hand, the solution of 5 wt% DEA + 35 wt% MDEA requires the reboiler power supply higher than DEA and lower than MDEA of 40 wt% respectively and shows the behavior between its parent solvents.

The previous studies show that the regeneration heat duty decreased with the rising lean-CO<sub>2</sub> loading in view of less required CO<sub>2</sub> recovery from amine solution and reduction in water partial pressure for vapor-liquid equilibrium. On the other side, the CO<sub>2</sub> loading of rich solution also has a significant effect on the regeneration heat duty since a reduction in rich-CO<sub>2</sub> loading causes a sharp increase in the regeneration heat duty. This impact is mainly related to the differences in equilibrium CO<sub>2</sub> partial pressure at various rich-CO<sub>2</sub> loadings, which suggests that stripping CO<sub>2</sub> from the solutions with lower rich-CO<sub>2</sub> loadings requires much greater amount of water vapor generated from the reboiler, bringing about a remarkable increase in regeneration heat duty as depicted in Fig. 10. Although the solution of 40 wt% DEA demands lower reboiler power supply ( $1.356 \times 10^{10}$  kJ/hr) than the solution of 2 wt% PZ + 38 wt% MDEA, 40 wt% DEA has the lower CO<sub>2</sub> loading compared to the mentioned solution and thus the higher regeneration heat duty ( $3.511 \times 10^5$  kJ/kg<sub>CO<sub>2</sub></sub>). The solution of 5 wt% DEA + 35 wt% MDEA demands the regeneration heat duty ( $3.580 \times 10^5$  kJ/kg<sub>CO<sub>2</sub></sub>) between that of 40 wt% DEA and 40 wt% MDEA solutions which has been reported in the previous studies (Hemmati et al., 2019); however, it requires the highest reboiler power supply and regeneration heat duty amongst the studied blended amine solutions, while the solution of 1 wt% PZ + 39 wt% MDEA has gained the lowest values of reboiler power supply ( $1.059 \times 10^{10}$  kJ/hr) and regeneration heat duty ( $2.470 \times 10^5$  kJ/kg<sub>CO<sub>2</sub></sub>) compared with the investigated single and blended amine solutions. Therefore, the solutions of 2 wt% PZ + 38 wt% MDEA and 5 wt% DEA + 35 wt% MDEA are not considered as suitable alternatives to the actual absorbent.

Due to the slight loss of the amine solution in the absorption/regeneration processes, the make-up streams have been added into the circulated absorbents to compensate for the loss the amine solution flow rate and concentration, as shown in Table 11.

In a final analysis, the solutions of 1 wt% PZ + 39 wt% MDEA is determined as the most efficient solution among the studied blended amine absorbents on account of the highest CO<sub>2</sub> absorption efficiency



**Fig. 10.** Regeneration heat duty of CO<sub>2</sub> removal from various rich amine solutions.

**Table 11**  
Make-up of the amine solutions (kg/hr).

Make-up solvent	Amine Solution				
	40 wt% DEA	40 wt% MDEA	PZ + MDEA (1)	PZ + MDEA (2)	5 wt% DEA + 35 wt% MDEA
DEA	0.000	0.000	0.000	0.000	0.013
PZ	0.000	0.000	0.011	0.015	0.000
MDEA	0.000	0.131	0.222	0.060	0.151

and CO<sub>2</sub> loading as well as the lowest reboiler power supply and regeneration heat duty. Furthermore, this solution can achieve the demanded specifications in addition to the lowest temperature bulge (56.83 °C) which is in favor of the forward reactions of CO<sub>2</sub> removal.

#### 4.3. The effect of operational parameters

As the solution of MDEA is not applicable for removing CO<sub>2</sub> from the ethane stream because the required specifications are not achieved, the investigation on the effect of operational parameters was conducted only for the actual and blended amine solutions. Fig. 11 exhibits the variation of outlet CO<sub>2</sub> mass fraction from the absorber versus the temperature of lean amine solution. The increase in amine solution temperature from 40 to 55 °C has led to decrease as much as 90% and 62.3% in the CO<sub>2</sub> mass fraction from the absorber for the solutions of 40 wt% DEA and 5 wt% DEA + 35 wt% MDEA respectively. On the other side, the blended solutions of PZ + MDEA present opposite behaviors in such a way that rising temperature from 40 to 55 °C has caused increase in the outlet CO<sub>2</sub> concentration by 53.9% for the solution of 1 wt% PZ + 39 wt% MDEA and 2.71 times for the solution of 2 wt% PZ + 38 wt% MDEA.

It is known that increasing temperature leads to a decrease in equilibrium absorption capacity according to the exothermic nature of absorption but an increase in reaction rate according to the Arrhenius equation (Yu et al., 2012). Generally, increasing liquid temperature enhances the second-order reaction rate constant and reduce the viscosity of amine solution which are beneficial to the mass transfer phenomena. An increase in CO<sub>2</sub> removal with rise in solution temperature seems to be more affected by an increase in reaction rate than by a decrease in equilibrium capacity at higher temperatures which has taken place in the solutions of DEA and DEA + MDEA. However, the increase in temperature results in enhancement of CO<sub>2</sub> partial pressure and reduction of the gas solubility, causing a drop in the gas-side mass transfer driving force. Furthermore, the reaction of PZ with CO<sub>2</sub> is

exothermic and thus higher temperatures expedite the reverse reaction. Sheng et al. recommended the temperature over 60 °C is not a good choice for CO<sub>2</sub> absorption (Sheng et al., 2018). Joel et al. (2014) mentioned that CO<sub>2</sub> removal level increases significantly with rising lean amine temperatures from 25 °C to 50 °C, but further rise above 50 °C has no significant impact on the CO<sub>2</sub> removal level.

Fig. 12 illustrates the effect of lean solution mass flow rate on the outlet CO<sub>2</sub> mass fraction at the temperature of 45 °C. Because of the increase in mass flow rate and decrease in the contact time between CO<sub>2</sub> and lean amine solution, the reaction rate has decreased for DEA and to some extent for the blended amine solutions despite the required specifications were achieved. However, the reduction of lean solution flow rate is not always an advantage in particular for the brownfield plants where hydrodynamic characteristics such as flooding must be reconsidered. Increasing liquid velocity (flow rate) leads to an increase in gas-liquid contact area in the absorber and finally liquid-side and overall mass transfer coefficients as well as decrease in CO<sub>2</sub> loading. Moreover, a higher liquid flow rate provides more absorption solution per unit of gas to absorb more CO<sub>2</sub>. The outlet CO<sub>2</sub> mass fraction shows the fluctuating trend for the blended solutions, in such a way that the decrease in the contact time has predominated up to the flow rate of 105 and 110 ton/hr for the solution of 2 wt%PZ+38 wt%MDEA and 5 wt%DEA+35 wt%MDEA respectively but the further amounts of amine solution per unit mass of gas have shown downward trend for the CO<sub>2</sub> concentration levels.

Fig. 13 also reveals that increase in lean-CO<sub>2</sub> loading is positively related to the rise in outlet CO<sub>2</sub> concentration from the absorber due to the decrease in the equilibrium capacity of amine solution. Increasing lean-CO<sub>2</sub> loading causes reduction in overall and liquid-side mass transfer coefficients. In fact, the CO<sub>2</sub> loading of the lean solutions reflects the concentration of the remaining active amines which are able to react with CO<sub>2</sub> and sulfur components, and is important to the absorption. Increasing the lean-CO<sub>2</sub> loading leads to greater Henry's constant and viscosity of lean amine solution, lower CO<sub>2</sub> diffusivity in liquid and enhancement factor, which are unfavorable for the CO<sub>2</sub> absorption process. Nevertheless, the values of lean-CO<sub>2</sub> loading up to 0.015 and 0.020 are acceptable for the solutions of PZ + MDEA with 1 and 2 wt% PZ respectively to be introduced into the absorber because the required specifications can be reached at the temperature of 45 °C with the flow rate of 120 ton/hr.

The influence of amine mass concentration on outlet CO<sub>2</sub> mass fraction at the temperature of 45 °C with the flow rate of 120 ton/hr without lean-CO<sub>2</sub> loading has been assessed in Fig. 14. The range of amine solution varies from 25 wt% to 45 wt% by considering the fact

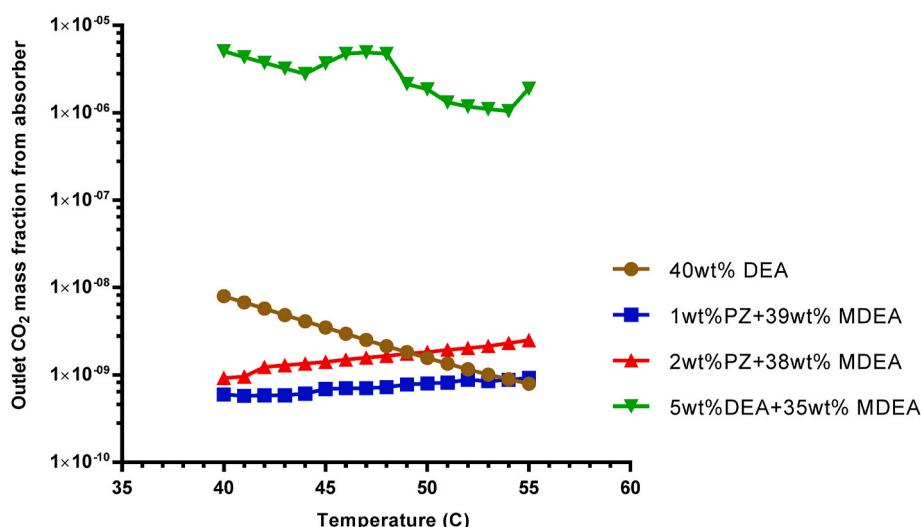


Fig. 11. Outlet CO<sub>2</sub> concentration from absorber vs. lean amine solution temperature.

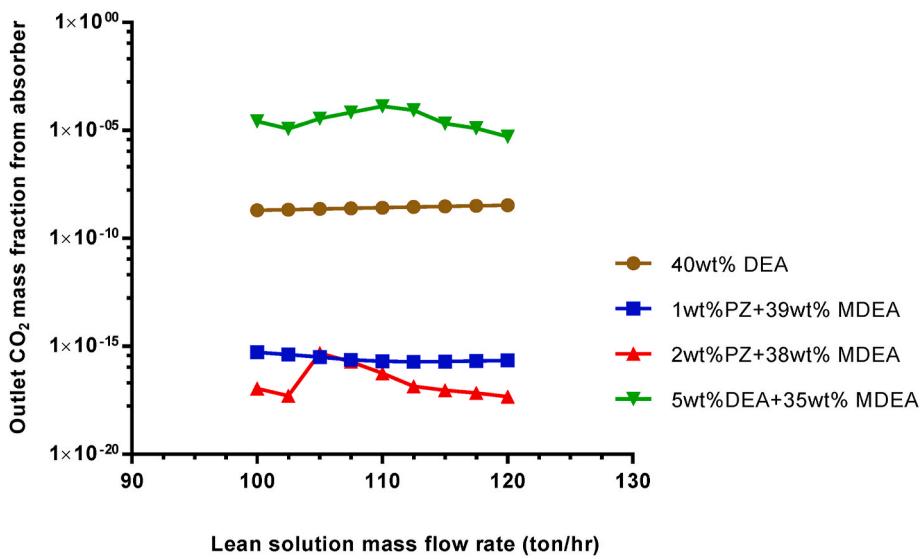


Fig. 12. Outlet CO<sub>2</sub> concentration from absorber vs. lean amine solution flow rate.

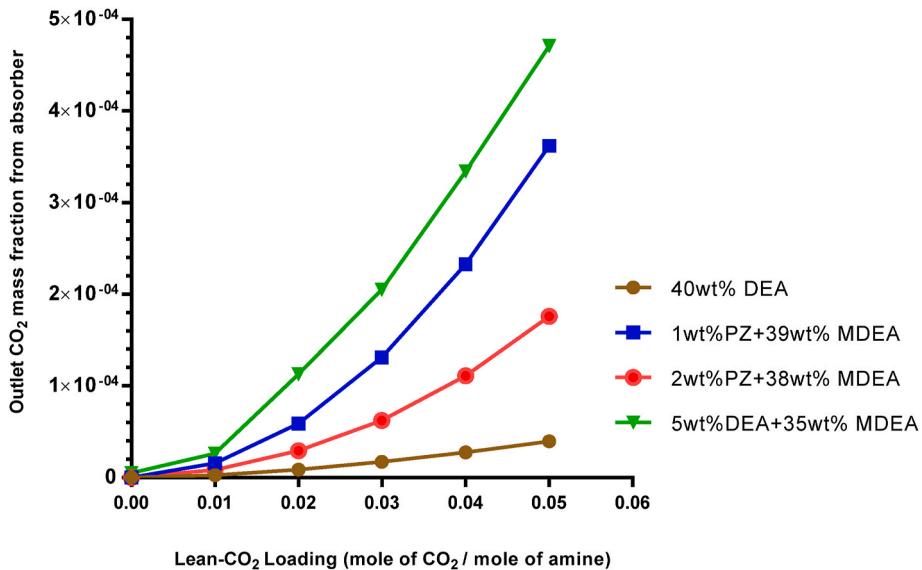


Fig. 13. Outlet CO<sub>2</sub> concentration from absorber vs. lean-CO<sub>2</sub> loading.

that the concentration of activator is constant for each run of the blended solutions and only the concentration of MDEA has changed. For instance, the mass concentration of MDEA has altered from 24 to 44 wt% in the solution with 1 wt% PZ. It is obvious that the increase in the mass concentration of amine solution has brought forth the decrease in the outlet mass fraction of CO<sub>2</sub> by using the solutions of DEA and PZ + MDEA owing to the higher reaction and mass transfer rates. On the other hand, increasing MDEA concentration from 34 to 44 wt% in the solution of DEA + MDEA has caused the rise in viscosity of the amine solution and reduction in CO<sub>2</sub> diffusivity in liquid and overall mass transfer coefficient, thus increase in outlet CO<sub>2</sub> mass concentration. The most efficient and cost-effective mass concentrations are 39% and 38% for MDEA with 1 and 2 wt% PZ respectively in the solution of PZ + MDEA since the required targets have been achieved and higher amine concentration is not necessary.

## 5. Conclusion

The CO<sub>2</sub> absorption from a fractionated ethane stream in Phase 19 gas

plant (Kangan county, Iran) has been simulated by five single and blended amine solutions containing DEA, PZ and MDEA using Aspen Plus based on the rate-based model to evaluate CO<sub>2</sub> absorption efficiency, CO<sub>2</sub> loading and regeneration heat duty in order to find an effective alternative to the solution of 40 wt% DEA which is employed in that plant. The model was validated by the required specifications and the existing actual data. The comparison was made in terms of the above-mentioned three parameters to choose the most applicable solution with the highest reaction rate and solubility in addition to the lowest regeneration heat duty.

Among the studied amine solutions, three blended solutions have achieved the required specifications with the CO<sub>2</sub> absorption efficiency about 100% and low concentrations of sulfur components in the outlet gas stream while the solution of 40 wt% MDEA has not reached the specified targets. Amongst the three blended solutions with PZ or DEA as promoter, the solutions of 1 wt% PZ + 39 wt% MDEA and 5 wt% DEA + 35 wt% MDEA have gained the highest CO<sub>2</sub> loading and CO<sub>2</sub> vapor pressure in the rich amine solutions. The comparison between these two amine absorbents reveals that the solution of 1 wt% PZ + 39 wt% MDEA

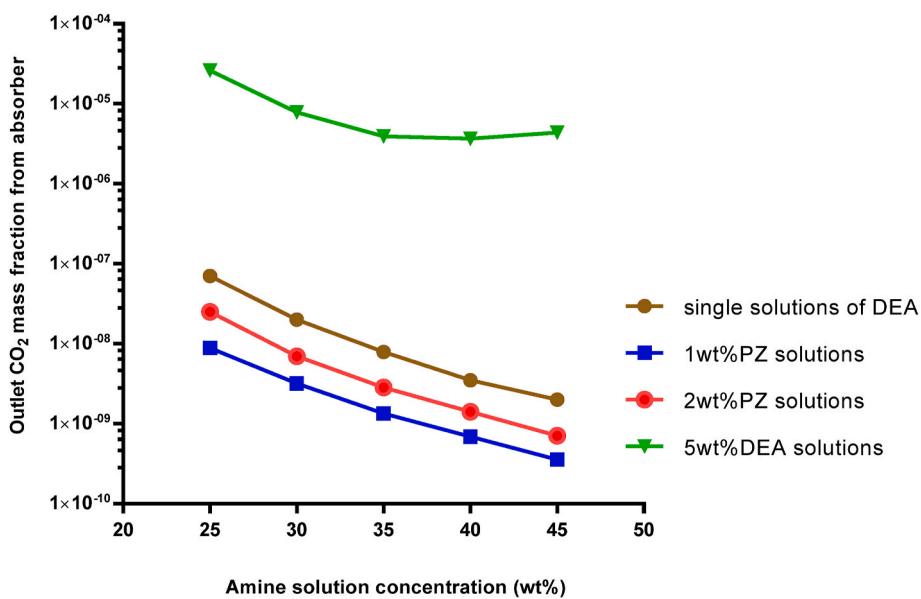


Fig. 14. Outlet CO<sub>2</sub> concentration from absorber vs. amine solution mass concentration.

presents the lowest absorption temperature, reboiler power supply and regeneration heat duty which are in favor of equilibrium reactions in the absorber and energy consumption in the stripper. In consequence, the solution of 1 wt% PZ + 39 wt% MDEA with the lean solution temperature of 40–55 °C, the mass flow rate of 110–120 ton/hr coupled with the maximum lean-CO<sub>2</sub> loading of 0.015 can be applied to the CO<sub>2</sub> removal from the ethane stream of this processing unit in the future.

#### Declaration of competing interest

The authors declare that they have no known competing financial

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jngse.2021.104030>.

#### Nomenclature

##### Symbols Used

- $a_d [\text{m}^2 \text{m}^{-3}]$  dry specific surface area of packing
- $a_m [\text{m}^2 \text{m}^{-3}]$  effective surface area of packing
- $B [-]$  base
- $C [\text{kmol m}^{-3}]$  concentration
- $D_L [\text{m}^2 \text{ s}^{-1}]$  binary diffusivity of liquid-phase
- $D_G [\text{m}^2 \text{ s}^{-1}]$  binary diffusivity of gas-phase
- $d_e [\text{m}]$  equivalent diameter
- $E_a [\text{cal mol}^{-1}]$  activation energy
- $Fr [-]$  Froude number
- $H [\text{m}^3 \text{ Pa mol}^{-1}]$  Henry's constant
- $HETP$  height of packing equivalent to a theoretical plate
- $H_{loss} [\text{kJ h}^{-1}]$  loss of reboiler power supply
- $H_{reb.} [\text{kJ h}^{-1}]$  reboiler power supply
- $k [-]$  pre-exponential factor
- $k_2 [\text{m}^{-3} \text{ kmol}^{-1} \text{ s}^{-1}]$  second-order reaction rate constant
- $k_x [\text{mol m}^{-2} \text{s}^{-1}]$  liquid-side mass transfer coefficient based on mole fraction
- $k_y [\text{mol m}^{-2} \text{s}^{-1}]$  gas-side mass transfer coefficient based on mole fraction
- $M [\text{kg kmol}^{-1}]$  molecular weight
- $n [\text{kmol h}^{-1}]$  molar flow rate

interests or personal relationships that could have appeared to influence the work reported in this paper.

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$q_{reg}$	[kJ kg $_{CO_2}^{-1}$ ]	regeneration heat duty
$Re$	[—]	Reynolds number
$Sc$	[—]	Schmidt number
$T$	[K]	absolute temperature
$We$	[—]	Weber number
$y_{CO_2}$	[—]	$CO_2$ mole fraction
$Y$	[—]	molar ratio of $CO_2$ [ $y/(1-y)$ ]

**Greek Symbols**

$\alpha$	[—]	$CO_2$ loading of amine solution
$\eta$	[—]	efficiency
$\theta$	[rad]	corrugation inclination angle from the vertical
$\mu$	[kg m $^{-1}s^{-1}$ ]	viscosity
$\rho$	[kg m $^{-3}$ ]	mass density
$\tau$	[—]	electrolyte-molecule ternary interaction parameter

**Subscripts**

$abs.$	absorption
$CO_2$	carbon dioxide
$G$	gas-side
$L$	liquid-side
$reg.$	regeneration

**Abbreviations**

<b>AMP</b>	2-amino-2-methyl-1-propanol
<b>DEA</b>	diethanolamine
<b>DETA</b>	diethylenetriamine
<b>DGA</b>	diglycolamine
<b>DIPA</b>	di-isopropanolamine
<b>E – NRTL</b>	electrolyte non-random two-liquid
<b>MDEA</b>	methyldiethanolamine
<b>MEA</b>	monoethanolamine
<b>MMSCFD</b>	million standard cubic feet per day
<b>PZ</b>	piperazine
<b>RNH<sub>2</sub></b>	primary amine
<b>RNHR'</b>	secondary amine
<b>RPB</b>	rotating packed bed
<b>SHA</b>	sterically hindered amine
<b>TEA</b>	triethanolamine

**Author statement**

Arash Esmaeili: Conceptualization, Simulation, Validation, Writing Zhiabng Liu: Modelling analysis, Literature review Yang Xiang: Simulation advice, Investigation Jimmy Yun: Methodology, Visualization Lei Shao: Project administration, Supervision, Review & Editing.

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