Simulation and Assessment of Carbon Dioxide Separation by Piperazine Blended Solutions Using E-NRTL and Peng-Robinson Models: A Study of Regeneration Heat Duty

Arash Esmaeili, Zhibang Liu, Yang Xiang, Jimmy Yun, Lei Shao

Abstract—High pressure carbon dioxide (CO_2) absorption from a specific off-gas in a conventional column has been evaluated for the environmental concerns by the Aspen HYSYS simulator using a wide range of single absorbents and piperazine (PZ) blended solutions to estimate the outlet CO_2 concentration, CO_2 loading, reboiler power supply and regeneration heat duty to choose the most efficient solution in terms of CO_2 removal and required heat duty. The property package, which is compatible with all applied solutions for the simulation in this study, estimates the properties based on electrolyte non-random two-liquid (E-NRTL) model for electrolyte thermodynamics and Peng-Robinson equation of state for vapor phase and liquid hydrocarbon phase properties. The results of the simulation indicate that PZ in addition to the mixture of PZ and monoethanolamine (MEA) demand the highest regeneration heat duty compared with other studied single and blended amine solutions respectively. The blended amine solutions with the lowest PZ concentrations (5wt% and 10wt%) were considered and compared to reduce the cost of process, among which the blended solution of 10wt%PZ+35wt%MDEA (methyldiethanolamine) was found as the most appropriate solution in terms of CO_2 content in the outlet gas, rich-CO_2 loading and regeneration heat duty.

Keywords—Absorption, amine solutions, Aspen HYSYS, CO_2 loading, piperazine, regeneration heat duty.

I. INTRODUCTION

THE global warming due to ever-increasing CO_2 content in the atmosphere as a result of the combustion of fossil fuels and development of industries is one of the most crucial challenges in the recent century, and reduction of the elevated CO_2 emissions in anthropogenic activities is thus of great importance. Among different CO_2 removal processes, the absorption process by aqueous amine solutions is a promising technology for the removal of acid gas impurities such as CO_2 and H_2S from the exhaust gas streams of power plants and refineries; however, the main barrier for the application of absorption/regeneration of amine solutions on a large-scale is the high capital cost and operating cost. Two major costs in CO_2 absorption processes are (1) the required absorbent circulation rate which is determined by the amount of CO_2 that must be removed from the feed gas and the CO_2 loading capacity of the absorbent and (2) the required power of reboiler to regenerate the absorbent which is most costly parameter in absorption/ regeneration processes. Therefore, the demanded reboiler heat duty is a key factor to design, implement and operate the CO_2 absorption units.

The non-sterically hindered amines (non-SHAs) in aqueous solutions have been widely evaluated for CO_2 removal, such as MEA and diglycolamine (DGA) as primary amine, diethanolamine (DEA) and di-isopropanolamine (DIPA) as secondary amine, MDEA and triethanolamine (TEA) as tertiary amine. A broad range of studies has been conducted to investigate CO_2 removal by various single and blended alkanolamine solutions. The studies [1] and [2] have worked on CO_2 absorption by MEA, [3] stated the results of experiments on CO_2 removal by aqueous DGA solution, [4] studied kinetics of CO_2 absorption by MDEA and [5] estimated CO_2 solubility and diffusivity in TEA, [6] represented the second-order reaction rate constant for three alkanolamine solvents. Some authors have conducted CO_2 absorption by blended amine solutions; [7] and [8] have used the mixture of PZ+MEA for the studies of CO_2 absorption and desorption, [9]-[11] have undertaken study on kinetics and reaction rate of PZ+MDEA and DEA+MDEA for CO_2 removal and [12] has also assessed reaction rate of CO_2 with the blend of MEA+AMP.

There are four major methods to decline heat energy consumption which accounts for almost 70% of the whole operational cost in this process as [13] mentioned: (1) optimization of process configuration; (2) development of process control strategies; (3) improvement of packing 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. In this study, the last method by various PZ blended amine solutions is used to remove CO_2 from a specific gas for the environmental concerns and the required regeneration heat duty is minimized by most efficient aqueous amine solution. Very few data on reboiler heat duty for CO_2 removal by aqueous amine solutions blended with PZ have been reported in the literature.

Lei Shao is with Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, China (corresponding author, phone: +8613641092152; e-mail: shaol@mail.buct.edu.cn).

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II. CONCEPT OF CO_2 ABSORPTION IN (ALKANOL) AMINE SOLUTIONS

In order to design an absorption/regeneration unit properly, different required data on the mass transfer coefficients, gas-liquid contact area and reaction kinetics, physicochemical properties such as solubility (H_{CO_2}) and diffusivity (D_{CO_2}) of CO_2 in the various amine solutions are essential to model the rate of absorption. Due to the chemical reaction between CO_2 and amine absorbents, neither the free-gas solubility nor the diffusivity of CO_2 in amine solutions can be measured directly. As a result, a non-reacting gas such as NO_2 can be used as a surrogate to CO_2 in estimating the physical solubility of CO_2 in these solvents. The N_2O analogy has been frequently used to estimate the solubility and diffusivity of CO_2 in amine solutions based on the following correlations [14]:

$$H_{CO_2-AM} = H_{N_2O-AM} \times \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{\text{in water}} \quad (1)$$

$$D_{CO_2-AM} = D_{N_2O-AM} \times \left(\frac{D_{CO_2}}{D_{N_2O}}\right)_{\text{in water}} \quad (2)$$

Versteeg et al. [15] proposed four convenient equations based on the available solubility and diffusivity data of N_2O and CO_2 in water:

$$H_{N_2O-H_2O} \left(\frac{m^3.Pa}{mol}\right) = 8.547 \times 10^6.\exp\left(\frac{-2284}{T}\right) \quad (3)$$

$$H_{CO_2-H_2O} \left(\frac{m^3.Pa}{mol}\right) = 2.825 \times 10^6.\exp\left(\frac{-2044}{T}\right) \quad (4)$$

$$D_{N_2O-H_2O} \left(\frac{m^2}{s}\right) = 5.07 \times 10^{-6}.\exp\left(-\frac{2371}{T}\right) \quad (5)$$

$$D_{CO_2-H_2O} \left(\frac{m^2}{s}\right) = 2.35 \times 10^{-6}.\exp\left(-\frac{2119}{T}\right) \quad (6)$$

The results for the Henry's constant of N_2O and CO_2 in water as well as diffusivity of N_2O and CO_2 in water for the temperature range of 298 to 333 K are illustrated in Figs. 1 and 2. Henry's constant shows the ascending order because of increase in partial pressure ($m^3.Pa/mol$) by temperature rise. The solubility of N_2O in some pure alkanolamine solvents was measured and correlated by [16] over the range from 20 °C to 85 °C at atmospheric pressure which is shown in Fig. 3, the solubility order of MEA, DEA and TEA does not show regularity according to the number of the ethanol group on volumetric basis ($m^3.Pa/mol$) while the order of MDEA > TEA > DEA > MEA is obtained for the capacity absorption of N_2O per kilomole of pure amines as mole basis.

Jassim et al. [17] proposed a first-order fast reaction for CO_2 absorption by MEA solution based on fast reaction in the boundary layer, the absorption rate for the pseudo-first-order reaction of this liquid-side-resistance-controlled process can be expressed as:

$$N_{CO_2} = k_L.\left(C_{CO_2,bulk} - C_{CO_2-Am}\right).\sqrt{1+Ha^2} =$$
$$k_L.\frac{\left(P_{CO_2,bulk} - P_{CO_2-Am}\right)}{H_{CO_2-AM}} \cdot \sqrt{1 + \frac{k_{ov}.D_{CO_2-AM}}{k_L^2}} \quad (7)$$
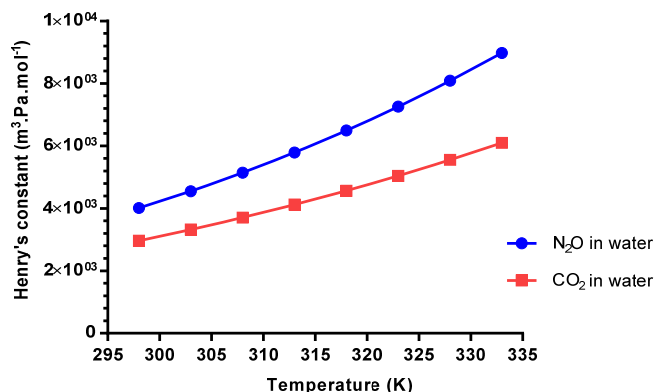

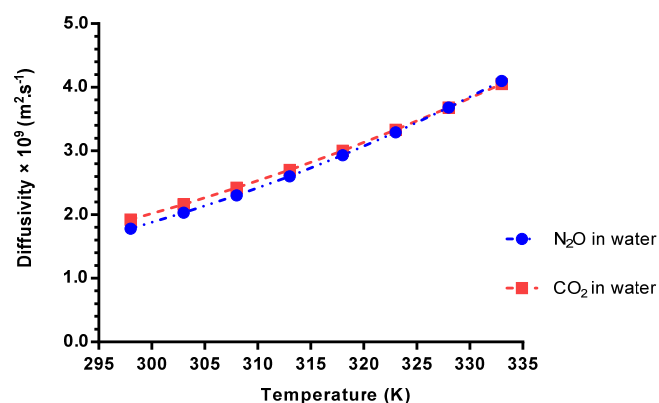Fig. 1 Henry's constant of N_2O and CO_2 in water ($m^3.Pa.mol^{-1}$)

Fig. 2 Diffusivity of N_2O and CO_2 in water ($m^2.s^{-1}$)
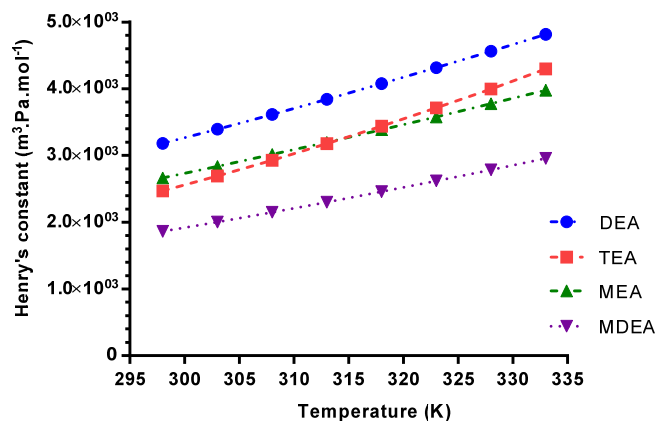
Fig. 3 Henry's constant N_2O in pure alkanolamine solvents ($m^3.Pa.mol^{-1}$)

$$N_{CO_2} = K_G.\left(P_{CO_2,bulk} - P_{CO_2-Am}\right) = K_G.P\left(y_{CO_2,bulk} - y_{CO_2-Am}\right) \quad (8)$$

where k_1 is the rate constant for the pseudo-first-order reaction, C_{CO_2-Am} or $[CO_2]^*$ is the equilibrium concentration of carbon dioxide in the amine solution, $C_{CO_2,bulk}$ is concentration of CO_2 in the bulk of the amine solution, D_{CO_2} is diffusivity of CO_2 in amine solution and estimated by (2) and Ha is Hatta number which compares the rate of reaction in a liquid film to the rate of diffusion through the film. The fast reactions ($Ha > 3$) are considered to proceed predominantly near the gas-liquid

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interface, while the slow reactions ($Ha < 3$) are considered to occur mainly in the liquid bulk.

$$Ha = \frac{\left(k_{ov} . D_{G,L}\right)^{1/2}}{k_L} \qquad (9)$$

$$k_1[1/s] = k_{2,Am} . C_{Am} \qquad (10)$$

where $k_{2,Am}$ is the second-order reaction rate constant. Equation (7) can be simplified because the second term under the square root is much more than unity at the high enhancement factors [18]. Furthermore, the equilibrium partial pressure of CO_2 (P_{CO_2-Am}) will approach zero since the solution loading is low what conducted in most experiments. Because of the fast reaction rate between CO_2 and aqueous amine solution, the absorbed CO_2 in the solution is consumed immediately in the process; therefore, y_{CO_2-Am} can be considered to be zero. In consequence, the equality of (7) and (8) result in:

$$N_{CO_2} = K_G . P . y_{CO_2,bulk} = \frac{\sqrt{\frac{k_{ov} . D_{CO_2-AM}}{H_{CO_2-AM}}}}{} . P_{CO_2,bulk} \qquad (11)$$

It can be assumed that amine concentration remains constant in the liquid boundary layer because of an excess of amine. Thus, the second-order reaction of CO_2 with an amine can be presented by a simplified first-order expression [18]:

$$r_{CO_2} = k_1 \left(C_{CO_2,bulk} - C_{CO_2-Am}\right) = K_G . a . P . y_{CO_2,bulk} = k_L . a . C_{CO_2,bulk} \sqrt{1 + Ha^2} \qquad (12)$$

III. Concept of Regeneration of (Alkanol) Amine Solutions

In absorption/stripping processes, an optimum solvent flow rate should be calculated to achieve the defined CO_2 removal requirements. If the solvent flow rate is too low, there is not enough capacity for absorption, unless the rich solvent is regenerated to a very low lean-CO_2 loading. On the other side, if the solvent flow rate is too high, an excess amount of sensible heat is required to cope with the temperature difference between absorption and stripping columns. This problem can be solved by using a solvent for CO_2 removal with high CO_2 capacity, high absorption rate (reaction rate) and low heat of absorption to decrease the cost of the whole process. The reactions which occur in stripper are the reverse reactions of what take place in absorber, the generated heat to absorb CO_2 molecules into absorbent is similar to the required heat to perform the reverse reaction in the regeneration step as [19] mentioned. The reboiler power supply (kJ/h) provided by hot stream passing through a reboiler at the bottom of a stripping column is the total energy for amine solution regeneration and can be estimated based on the mass and energy balance in the regeneration system, which is expressed as [20]:

$$H_{reb.} = m_h . C_{p,h} (t_{in,h} - t_{out,h}) \qquad (13)$$

where m_h, C_{ph}, $t_{in,h}$ and $t_{out,h}$ are the mass flow rate (kg/h), heat capacity (kJ/kg.°C), inlet temperature and outlet temperature (°C) of heating fluid, respectively.

The regeneration (reboiler) heat duty (kJ/kg$_{CO2}$) is defined as the net power supply per mass flow rate of CO_2 and is a function of various operating parameters, such as rich-CO_2 loading, lean-CO_2 loading, solution molar flow rate, feed temperature, type of amine solution, concentration as well as mass ratio (of two amine species) in blended solutions [13]:

$$q_{reg.} = \frac{H_{reb.} - H_{loss}}{n_{rich} (\alpha_{rich} - \alpha_{lean}) M_{CO_2}} \qquad (14)$$

The difference between these two parameters ($\alpha_{rich} - \alpha_{lean}$) also determines CO_2 cyclic capacity and the amine solution circulation rate for a given CO_2 absorption efficiency, which represents the capacity of the solvent over multiple cycles and depicts the true net CO_2 mole removal per amine mole after each absorption/regeneration cycle. The required total energy for regeneration is summation of three different parameters [19]:

$$q_{reg.} = q_{sens.} + q_{vap,water} + q_{des,CO_2} \qquad (15)$$

where $q_{sens.}$ is sensible heat defined as the required heat to increase the temperature of the rich absorbent in stripper to regeneration heat (boiling point); however, the regeneration process is usually implemented at a temperature in excess of the boiling temperature. Generally, regeneration occurs in high temperatures, 373 K at least, and consequently solution evaporates and vaporization heat of water ($q_{vap,water}$) is created, which is the required energy to produce the water vapor to establish an operating CO_2 partial pressure needed for CO_2 stripping. The vaporization heat depends on the water concentration in amine solution; therefore, comparison of the blended amine solutions with the same concentration shows no difference in their vaporization heat of water [21]. When solution temperature reaches regeneration temperature, binding between solvent and CO_2 is broken. The desorption heat (q_{des,CO_2}) indicates the necessary thermal energy to remove binding between amine and carbon dioxide carrying species (carbamate, bicarbonate and carbonate) formed during the amine-CO_2 reactions. This heat can be estimated quite accurately using the Gibbs-Helmholtz equation and a limited number of vapor-liquid equilibrium (VLE) data [22]. It is very crucial to take into account the contribution of heat of desorption, sensible heat and heat of vaporization to reduce the regeneration heat duty in order to optimize the process [21]. Moreover, the calculations for desorption energy are very difficult and complicated since the heat-associated data are lacking and the reboiler heat duty for solvent regeneration can be greatly influenced by both amine type and operating conditions. The level of reboiler heat duty is directly related to the quantity of CO_2 stripped from the regeneration column and quality of lean solution returned to the absorption column. Therefore, higher heat duty in a constant amine solution flow rate and concentration results in larger amount of desorbed CO_2

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and a leaner solution leaving the regeneration column [20].

$$q_{sens.} = \frac{\rho_{rich} \cdot C_{p,rich} \, (t_{reb.} - t_{in})}{C_{rich} \, (\alpha_{rich} - \alpha_{lean}) M_{CO_2}} = \frac{\rho_{rich} \cdot V_{rich} \cdot C_{p,rich} \cdot (t_{reb.} - t_{in,rich})}{n_{rich} \, (\alpha_{rich} - \alpha_{lean}) M_{CO_2}} \quad (16)$$

$$q_{vap,water} = \Delta H_{vap,water} \cdot \frac{P_{H2O}}{P_{CO_2}} \cdot \frac{1}{M_{CO_2}} \quad (17)$$

$$q_{des,CO_2} = \Delta H_{abs,CO_2} = -R \frac{d(\ln P_{CO2})}{d(1/T)} = \sum_{i=1}^{m} \frac{C_i}{C_{rich}} \Delta H_{abs,i} \quad (18)$$

Several experimental and simulation works have been conducted for the calculation of regeneration heat duty for CO_2 absorption by different types of amine solutions [13], [20], [22]-[26]; however, the regeneration of a broad range of blended PZ solutions has not been evaluated and there are relatively less information concerned with the CO_2 desorption process from PZ blended amine absorbents.

IV. PROCESS AND MODEL DESCRIPTION

The main purpose of this study is comparison of CO_2 absorption efficiency from a specific off-gas in one natural gas plant located at South Pars Gas Complex in Iran and regeneration heat duty with application of a wide range of single amine absorbents in addition to blended solutions with PZ. The process was simulated by Aspen HYSYS based on the property package of the Electrolyte-NRTL (E-NRTL) model for electrolyte thermodynamics and Peng-Robinson equation of state for vapor and liquid hydrocarbon phase properties. This property package is based on extensive research and development in rate-based, simulation of the chemical absorption process and molecular thermodynamics models for aqueous amine solutions, it contains the parameters identified from the regression of thermodynamic and physical properties data such as VLE and heat of absorption for amine solutions. It is highly recommended that the rate-based model is used instead of the equilibrium model for the simulation of CO_2

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 the CO_2 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 six single amine absorbents including PZ, MEA, DGA, DEA, MDEA and TEA as well as five blended solutions as PZ+MEA, PZ+DGA, PZ+DEA, PZ+MDEA and PZ+TEA in various concentrations have been studied to investigate the effect of amine type, absorbent mass ratio and flow rate on regeneration heat duty to choose the most efficient solution for CO_2 removal in terms of consumed energy and cost. Fig. 4 exhibits the simulation of CO_2 removal conducted in a conventional absorber with 10 trays, the off-gas which is vented to the atmosphere after pressure drop is considered to be introduced into the column in the operational conditions 45 ℃, 6000 kPa and 100 kmol/h and molar composition of 27.36% CO_2, 34.73% CO, 37.49% H_2, 0.19% CH_4 and 0.23% H_2O while amine solutions flowed into the column at 35 ℃ and 5950 kPa and the flow rate of 1000 kmol/h which are shown in Table I. A broad range of concentration between 15-45 wt% for the single amine solutions as well as a total concentration of 45 wt% in various mass ratios for the blended PZ absorbents were evaluated. Xu et al. [13] declared that the minimum amine concentration in a typical industrial CO_2 removal process is around 15 wt% which is followed in this simulation.

TABLE I
OPERATIONAL CONDITIONS OF INLET GAS AND AQUEOUS AMINE SOLUTIONS IN THE COLUMN

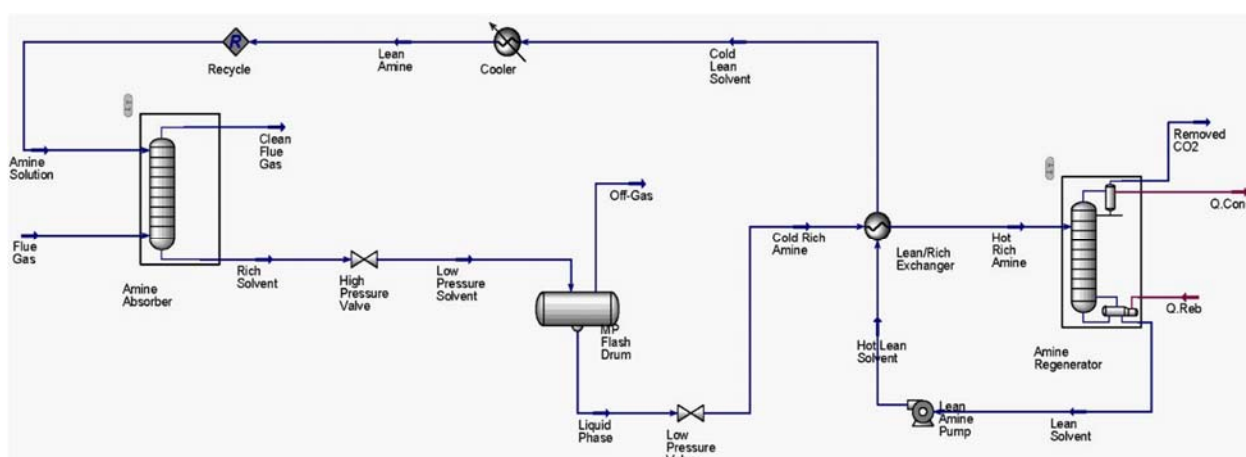| Parameter	Inlet Gas	Amine solution
Temperature (℃)	45	35
Pressure (kPa)	6000	5950
Molar flow rate (kmol/h)	100	1000

Fig. 4 The schematic CO_2 absorption process by using amine solution in Aspen HYSYS

The rich amine flows out the absorber and after pressure drop by a valve, it is introduced to the flash drum to remove a small part of CO_2 and water. The rich amine enters the regenerator after passing the lean/rich amine exchanger with minimum

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temperature approach of 5 ℃ to utilize the heat of lean amine for 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, taking into account the limitations imposed by the minimum temperature approach in the cross heat exchanger and the solvent degradation [27]. To meet this requirement, the minimum inlet temperature to the stripper in this simulation has been considered between 93-100 ℃ for different amine solutions to decrease steam flow rate inside the reboiler.

The regenerator employed 10 trays to strip CO_2 from the rich solution which was thus converted into the lean amine solution to reuse in the absorber. Tables II-IV show the models used to simulate the process and the kinetic parameters for carbamate formation of different amine solvents.

TABLE II
THE MODELS AND CORRELATIONS USED FOR SIMULATION OF CO_2 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
Thermal conductivity	Riedel model
Mass transfer	AICHE model
Heat transfer coefficient	Chilton and Colburn
Liquid Film resistance	Discrxn model
Vapor film resistance	Film model

TABLE III
KINETICS PARAMETERS OF BICARBONATE AND SPECIES OF PZ CARBAMATE FORMATION [28]

Type of Electrolyte	Type of reaction	k	E_a (cal/mol)
Bicarbonate	forward	1.33E+17	13,249
	backward	6.63E+16	25,656
PZ carbamate	forward	1.70E+10	319
	backward	3.40E+23	14,160
PZ bicarbamate	forward	1.04E+14	8038.3
	backward	3.20E+20	8692

TABLE IV
KINETICS PARAMETERS OF CO_2 ABSORPTION BY PRIMARY, SECONDARY AND TERTIARY AMINES [6], [28], [29]

Solvent	Type of reaction	k	E_a (cal/mol)
MEA	forward	9.77E+10	9855.8
	backward	2.18E+18	14138.4
DGA	forward	1.94E+15	15813
	backward	3.0E+26	25287
DEA	forward	6.48E+16	5072
	backward	1.43E+17	11497
MDEA	forward	6.85E+10	9029
	backward	6.62E+17	22131
TEA	forward	2.02E+11	8837
	backward	5.02E+18	22288

V. RESULTS AND DISCUSSION

To investigate all single and blended amine solutions in the similar conditions, regeneration efficiency ($\eta_{reg.}$) defined as the following term is considered 100% for the simulation of all amine solutions and it is assumed that all the absorbed CO_2 is recovered by the stripper and no CO_2 exists in the lean solution thus lean-CO_2 loading is taken account into zero [30].

$$\eta_{\text{reg.}} = \frac{\alpha_R - \alpha_L}{\alpha_R} \times 100\% \qquad (19)$$

Bougie et al. [30] have compared the regeneration efficiency between PZ and MEA with SHAs amine solvents and recognized that the presence of carbamate influences the regeneration efficiency of alkanolamine solutions. The stable carbamates are difficult to revert to fresh amine, causing the longer regeneration time and more energy consumption. Compared with conventional primary and secondary amines like MEA and DEA, SHAs form unstable carbamates due to the hindrance of the bulky group adjacent to the amino group. Hydrolysis of the voluminous carbamates leads to a preferential bicarbonate formation process and it is expected that a solution containing a greater proportion of bicarbonate undergoes desorption with less required energy and produces a lean solution containing less physically and chemically absorbed CO_2.

Water vapor including up to 10% of the off-gas stream composition has a negligible effect on alkanolamine processes since the amine solution contains a large amount of water. In contrast, it has been reported that water can enhance the CO_2 absorption capacity as a result of the formation of bicarbonate, which is a main species formed in CO_2 removal in an aqueous amine process [31]. Therefore, the water composition in the studied off-gas does not affect CO_2 removal in the evaluated simulation; however, the CO_2 solubility as the term of rich loading is assessed with variation of the water concentration in the aqueous amine solutions.

A. Single Amine Solutions

For the first step, the required power supply and reboiler heat duty of single amine solutions were evaluated. Figs. 5 and 6 indicate the effect of amine concentration on CO_2 absorption efficiency (20) and rich-CO_2 loading (21) of the amine solutions respectively. The enhancement of the amine concentration has brought about the reduction of CO_2 content in the outlet gas and drop in the rich-CO_2 loading, the highest CO_2 absorption efficiency from the treated gas and rich-CO_2 loading is concerned with PZ and TEA solutions respectively. Furthermore, the lower concentrations for the promoters such as PZ and MEA can be more beneficial, these two types of amine in the lower concentrations demonstrate a high CO_2 absorption efficiency accompanied by their highest CO_2 loading and lowest required heat duty under such circumstances.

$$\eta_{\text{abs.}} = \left[1 - \left(\frac{y_{CO_2,out}}{1-y_{CO_2,out}}\right)\left(\frac{1-y_{CO_2,in}}{y_{CO_2,in}}\right)\right] \times 100 = \left[1 - \frac{Y_{CO_2,out}}{Y_{CO_2,in}}\right] \times 100 \qquad (20)$$

$$CO_2 \text{ loading} = \frac{\text{absorbed moles of } CO_2 \text{ (molar flow)}}{\text{moles of absorbent (molar flow)}} \qquad (21)$$

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In contrast, MDEA and TEA do not exhibit high reaction rate to reduce CO_2 content in the outlet gas and the rise in their concentration only results in CO_2 loading reduction, increase in the outlet CO_2 concentration and excess regeneration heat because the higher solubility in tertiary amines is not able to compensate their slow reaction rate and the optimum concentration is 20 wt% where the outlet CO_2 content has decreased by 11% and 56% for MDEA and TEA, respectively, compared with the 15 wt% solutions. The order of CO_2 content in the outlet gas as a function of reaction rate and CO_2 loading which is in good agreement with [32] studies based on the simulation by Aspen HYSYS are as follows:

Outlet CO_2 Content: PZ < MEA < DGA < DEA < MDEA < TEA
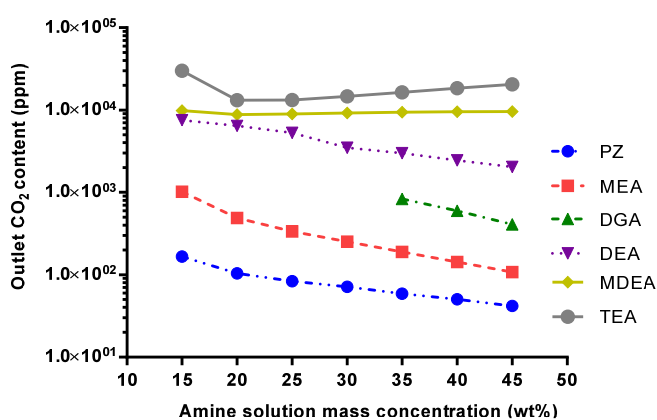
Rich − CO_2 Loading: TEA > MDEA > DGA, DEA > PZ > MEA

Fig. 5 Outlet CO_2 content in the treated gas by various single amine solutions in 1000 kmol/h
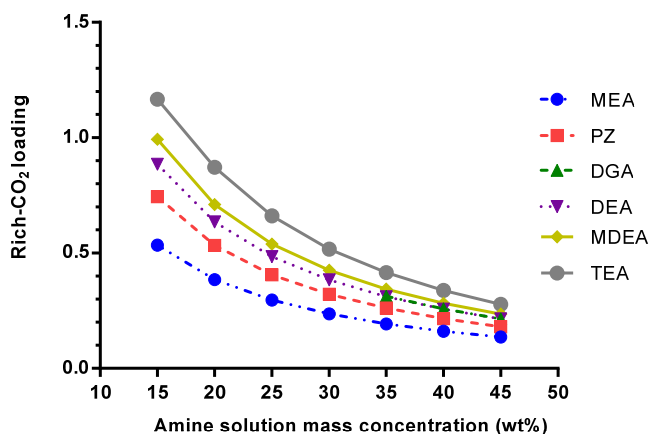

Fig. 6 Rich-CO_2 loading of various single amine solutions in 1000 kmol/h

Figs. 7 and 8 reveal the influence of amine concentration on reboiler power supply and heat duty. The flow rate of the amine solutions was considered 1000 kmol/h and the mass concentration is in the range of 15-45%, DGA was only studied in 35-45 wt% because the model was not converged in the concentration below 35 wt% with the mentioned operational conditions. It is apparent that increase in the concentration of

amine solution leads to the decrease of required power supply and rise in the regeneration heat duty in such a way that, PZ requires the highest power supply and regeneration heat duty, and it is followed by primary, secondary and tertiary amine solutions, respectively. The increase in amine mass concentration has caused the rise in the heat of absorption (CO_2 partial pressure) and sensible heat while the decrease has occurred in the vaporization heat of water. It contributes in the reduction in water concentration (partial pressure), drop in the reboiler power supply and rise in the heat duty of single amine solutions because of descending order of rich-CO_2 loading.
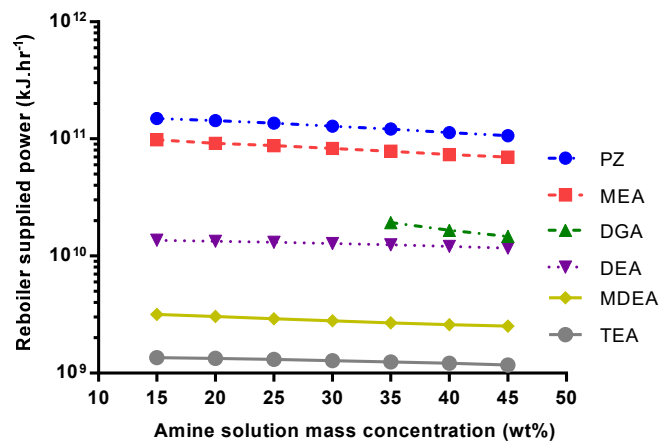

Fig. 7 Reboiler power supply of various single amine solutions in 1000 kmol/h
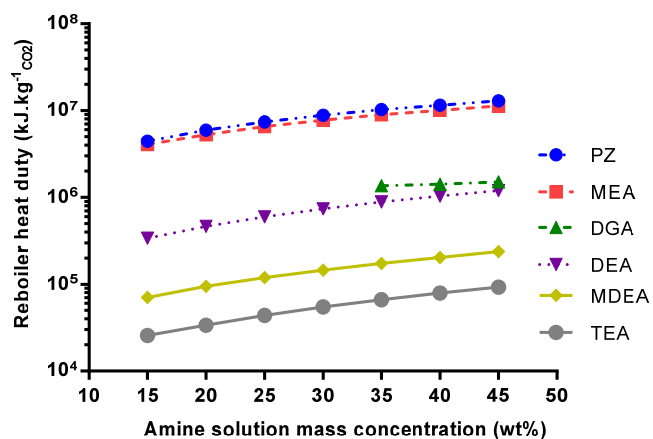

Fig. 8 Reboiler heat duty of various single amine solutions in 1000 kmol/h

As mentioned, the primary and secondary amines form a quite stable carbamate component and only half a mole of CO_2 is absorbed per mole of amine while each mole of PZ can theoretically absorb two moles of CO_2. The carbamate is dissociated to produce CO_2 and amine in the stripping step and consumes lots of energy to break the bonds because of stability in the formed carbamate during absorption. Xu et al. [13] mentioned that tertiary amines have a higher theoretical capacity of one mole of CO_2 per mole of amine and form an unstable carbamate as tertiary amines cannot directly react with CO_2 which leads to the formation of bicarbonate ions, thus

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brings on the lower regeneration energy consumption than primary and secondary amines which validates the results in Fig. 8. This order in the vertical axis is attributed to three main factors; the first factor is the reaction heat value of amine solutions (q_{des,CO_2}) with CO_2, PZ and primary amine solutions have the highest reaction heat with CO_2 compared with secondary and tertiary as explained. The second factor is the vaporization heat of water ($q_{vap,water}$) associated with the operating CO_2 partial pressure. This parameter is mainly related to the difference in magnitude of equilibrium CO_2 partial pressure at various rich-CO_2 loadings. PZ and the primary amines demand the lowest operating CO_2 partial pressure in comparison with other amine solutions in the similar mass concentrations to establish the driving force for CO_2 stripping. Thus, CO_2 stripping from the lower rich-CO_2 loading in the same amine concentrations requires larger amount of water vapor generated from the reboiler and higher vaporization heat of water [20]. The third factor is the sensible heat which has increased owing to decrease in the rich-CO_2 loading of amine solution. Therefore, CO_2 loading of rich solution has a significant effect on the reboiler heat duty and sensible heat according to (14) and (16). Consequently, the reboiler heat duty declines from PZ and MEA to the tertiary amines due to drop in all three main heat components as illustrated in Table V and Fig. 8 in the logarithm-scale.

Power supply and Regeneration heat duty: PZ > MEA > DGA > DEA > MDEA > TEA

TABLE V
THE VARIATION OF RELEVANT PARAMETERS TO REBOILER HEAT DUTY IN A CONSTANT CONCENTRATION OF THE SINGLE AMINES

Solvent	MEA	PZ	DGA, DEA	MDEA	TEA
MW (mol/g)	61.08	86.14	105.1	119.2	149.2
Solution mass flow rate (kg/h)	Increase				→
Solvent mole fraction	Decrease				→
Solvent molar flow rate (kmol/h)	Decrease				→
CO_2 Loading	Increase				→
Sensible heat (kJ/kg$_{CO2}$)	Decrease				→
Vaporization heat of water (kJ/kg$_{CO2}$)	Decrease				→
Desorption heat (kJ/kg$_{CO2}$)	Decrease				→

B. Blended Amine Solutions with PZ

Although the regeneration of tertiary amines requires less heat duty than primary and secondary amines, low reaction rates with CO_2 make tertiary amines difficult to use for CO_2 removal [33]. By increasing the absorption rate of the tertiary amines efficiently and maintaining low reaction heat, the regeneration heat duty could be largely decreased. Gao et al. [23] noticed that the blends of MEA and tertiary amines are more attractive than aqueous MEA solution. Idem et al. [34] 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. [35] also represented that tertiary amine (MDEA) solvents promoted by PZ achieved 15-22% energy savings and the reaction rate of CO_2 with MDEA can be enhanced by the addition of PZ. In recent years, interest in use of blended amine absorbents e.g. mixture of primary and tertiary amines (such as MEA and MDEA) or secondary and tertiary amines (such as DEA and MDEA) has increased which combine the higher equilibrium capacity of tertiary amines with the higher reaction rate of primary or secondary amines. The second part of this study is dedicated to a wide range of blended solutions with PZ and compares their regeneration heat duties.

The variation of outlet CO_2 concentration with increasing PZ mass ratio is illustrated in Fig. 9, the effect of high reaction rate of PZ with CO_2 on tertiary amines is significant, the rise from 5 wt% PZ to 10 wt% PZ has decreased the outlet CO_2 concentration by 32% and 68% for the blended solution with MDEA and TEA, respectively, while it has only declined by 19% in the mixture with MEA. Similarly, a sharp drop is observed in 5 wt% PZ blended with 40 wt% other amine solvents compared to 45 wt% single solutions in such a way that the outlet CO_2 content has plunged by 72.1 and 62.1 times for the PZ blended solution with MDEA and TEA, respectively, and the reaction rate with CO_2 has increased drastically.
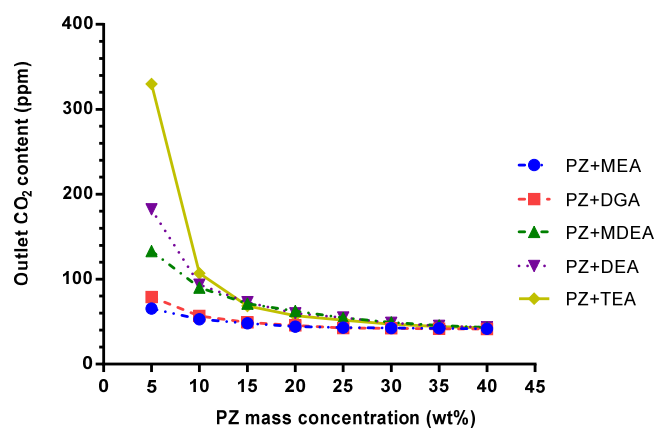

Fig. 9 Outlet CO_2 content in the treated gas by various blended amine solutions with PZ in 1000 kmol/h

Fig. 10 illustrates the effect of PZ mass ratio on rich-CO_2 loading of the blended solutions. The CO_2 loading of PZ+MEA has different trend than the other solutions. The increase in PZ/MEA mass ratio has led to increase the molecular weight (and mass flow rate) of solution, the molar concentration and molar flow of solvents decrease because of constant solution mass concentration (45 wt%); therefore, rich-CO_2 loading rises. Contrarily, the molecular weight of other blended solutions decreases with rising PZ mass ratio in the secondary and tertiary amine solutions which results in higher molar concentration and molar flow of solvents and consequently rich-CO_2 loading decreases. The lowest drop in rich-CO_2 loading for 5 wt% PZ

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with other solvents compared to 45 wt% single solutions is subject to MDEA by 1.3%. The orders of CO_2 content in the outlet gas and rich-CO_2 loading by PZ blended solutions similar to that of single amine solutions are as follows:

Outlet CO_2 Content: PZ + MEA < PZ + DGA < PZ + DEA < PZ + MDEA < PZ + TEA
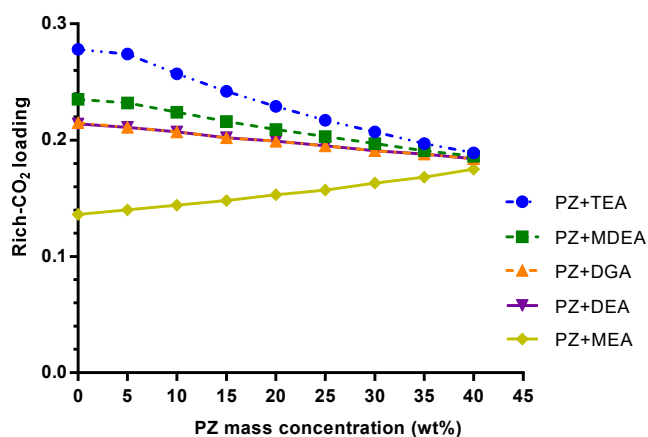
Rich CO_2 Loading: PZ + TEA > PZ + MDEA > PZ + DGA, PZ + DEA > PZ + MEA

Fig. 10 Rich-CO_2 loading of various blended amine solutions with PZ in 1000 kmol/h

Fig. 11 reveals the effect of PZ mass ratio of the blended amine solutions on the reboiler power supply. The total concentration of the blended amine solutions was considered 45 wt%. The reboiler power supply increases with rising PZ concentration for all blended solutions in the flow rate of 1000 kmol/h due to increase in desorption heat of solutions. However, the sensible heat has increased for PZ+MEA solutions and decreased for other amine solutions but the sensible heat has the lowest effect on reboiler power supply [20].
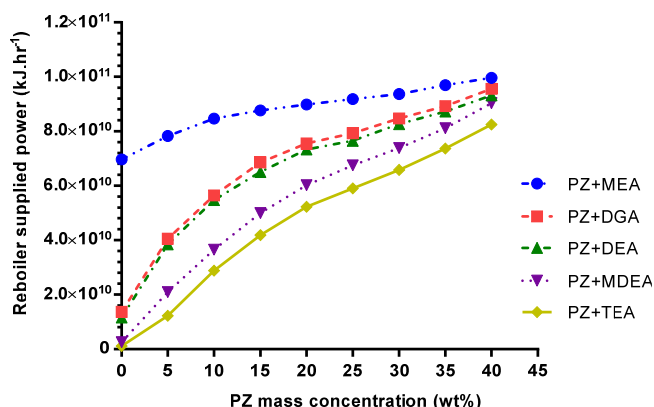

Fig. 11 Reboiler power supply of various blended amine solutions with PZ in 1000 kmol/h

It can be observed from Fig. 12 that regeneration heat duty declines for PZ+MEA solution (PZ > 15 wt%) but increases for other solutions with the enhancement in PZ concentration as rich-CO_2 loading has different behavior for PZ+MEA solution than other PZ blended solutions according to Fig. 10. It is obvious that the CO_2 loading of the rich solution has a significant effect on the regeneration heat duty [20]. The reduction in rich-CO_2 loading at a constant lean-CO_2 loading with increase in PZ mass concentration causes decrease in water partial pressure at the blended PZ solutions with the secondary and tertiary amines and more water vapor required to be supplied by the reboiler and the regeneration heat duty rises sharply which is exhibited for PZ+DGA, PZ+DEA, PZ+MDEA and PZ+TEA solutions. Reversely, rise in rich-CO_2 loading at a constant lean-CO_2 loading leads to increase in water partial pressure and drop in the heat duty which has occurred for PZ+MEA solution. Aroonwilas et al. [20] demonstrated that the decline in reboiler heat duty of blended amines is not proportional to the increasing MDEA or TEA. This illustrates a nonlinear relationship between the mass ratio and the reboiler heat duty which is shown in Fig. 12. At the lower PZ concentrations (≤ 10wt%), the blended solutions PZ+MDEA and PZ+TEA have the minimum regeneration heat duties and high absorption efficiency owing to combination of both higher reactivity and solubility. The reboiler heat duty declines from PZ blended solutions with the primary amine to the tertiary amines (in constant lean-CO_2 loading and PZ mass concentration) because of decrease in two main heat components (q_{des,CO_2} and $q_{vap,water}$) as a result of increase in water partial pressure which is illustrated in Table VI and Fig. 12.

Power supply and Regeneration heat duty : PZ + MEA > PZ + DGA > PZ + DEA > PZ + MDEA > PZ + TEA
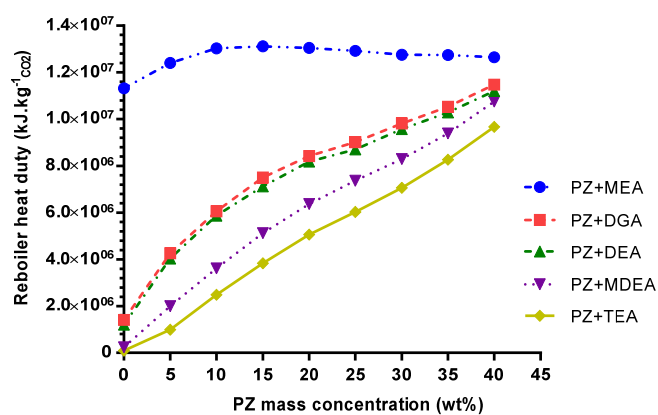
Fig. 12 Reboiler heat duty of various blended amine solutions with PZ in 1000 kmol/h

In order to compare the performance of different blended amine solutions containing the lowest PZ mass concentration, three parameters such as regeneration heat duty, CO_2 content in the outlet gas and rich-CO_2 loading of the solutions have been evaluated simultaneously. As a case study, 100 ppm CO_2 in the outlet gas was considered as the required specification in this study and the most efficient solution was determined based on

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the lowest heat duty and CO_2 content in the outlet gas and highest rich-CO_2 loading. The results are given in Table VII. Based on such comparison, five different blended solutions with the lowest PZ concentrations (5 wt% and 10 wt%) have been chosen, while each one has various outlet CO_2 content, rich-CO_2 loading and regeneration heat duty. It is evident that the most suitable solution can be 10wt%PZ+35wt% MDEA which has reached the required target with as lowest heat duty and highest CO_2 loading as possible.

TABLE VI
THE VARIATION OF RELEVANT PARAMETERS TO REBOILER HEAT DUTY IN CONSTANT PZ MASS CONCENTRATIONS

Solvent	PZ+MEA	PZ+DGA	PZ+DEA	PZ+MDEA	PZ+TEA
MW (mol/g)					
Solvent mole fraction			Increase		
Solvent molar flow rate (kmol/h)			Decrease		
CO_2 Loading			Decrease		
Sensible heat (kJ/kgCO2)			Increase		
Vaporization heat of water (kJ/kgCO2)			Increase		
Desorption heat (kJ/kgCO2)			Decrease		
			Decrease		

TABLE VII
COMPARISON OF FIVE BLENDED SOLUTIONS CONTAINING 5WT% AND 10WT% PZ IN THE FLOW RATE OF 1000 KMOL/H

PZ concentration (wt%)	Amine concentration (wt%)	CO_2 Content (ppm)	Rich-CO_2 Loading	Reg. Heat Duty × 10^{-6} (kJ/kg$_{CO2}$)
5	40% MEA	65.4	0.140	12.4
	40% DGA	79.1	0.211	4.26
	40% DEA	182.4	0.211	4.03
	40% MDEA	133.3	0.232	2.00
	40% TEA	329.8	0.274	0.99
10	35% MEA	52.9	0.144	13.0
	35% DGA	56.8	0.207	6.05
	35% DEA	93.5	0.207	5.87
	35% MDEA	90.1	0.224	3.62
	35% TEA	106.9	0.257	2.48

VI. CONCLUSION

The CO_2 absorption by six single amine absorbents and five blended amine solutions containing PZ have been simulated and compared in Aspen HYSYS with a rate-based model to evaluate the values of CO_2 absorption efficiency and regeneration heat duty in this work. Among the single amine solutions, PZ concentrations of 25 wt% and higher have reached the specified target of CO_2 content in the outlet gas with the highest power supply and regeneration heat duty compared with other single absorbents. Despite the fact that PZ and TEA are able to absorb the highest and lowest values of CO_2, the maximum and minimum power supply and regeneration heat

duty are concerned with them respectively. On the other side, MEA and TEA solutions have the lowest and highest rich-CO_2 loading in the studied concentrations respectively. All three components of reboiler heat duty declined in the single amine solutions from the lowest molecular weight to the highest, while increase in the amine mass concentration in a constant lean-CO_2 loading brings about rise in the heat duty due to descending order of rich-CO_2 loading.

Among the blended amine solutions, PZ+MEA achieved the lowest CO_2 content in the outlet gas and rich-CO_2 loading while it requires the highest power supply and regeneration heat duty in all mass ratios. On the other hand, PZ+TEA obtained the maximum outlet CO_2 content (PZ ≤ 10wt%) besides the highest rich-CO_2 loading compared with the other blended solutions; however, it demands the minimum power supply and regeneration heat duty in various PZ concentrations. Generally, the blends of PZ with primary amines require the highest regeneration heat duty followed by secondary and tertiary amines. The solution of PZ+MDEA has represented the most efficient mixture, the specific solution of 10wt%PZ+35wt%MDEA has particularly obtained the targeted outlet CO_2 with the lowest regeneration heat duty and the highest rich-CO_2 loading.

NOMENCLATURE

Symbols Used

C [kmol m^{-3}]	concentration
C_{Am} [kmol m^{-3}]	concentration of the amine solution in the bulk of the liquid
C_{CO_2-Am} [kmol m^{-3}]	equilibrium concentration of CO_2 in the amine solution
$C_{CO_2,bulk}$ [kmol m^{-3}]	CO_2 concentration in the bulk of the amine solution
C_p [kJ kg^{-1}°C^{-1}]	heat capacity
$D_{G,L}$ [m^2 s^{-1}]	diffusivity of gas in liquid phase
E_a [cal mol^{-1}]	activation energy
Ha [−]	Hatta Number
H_{abs,CO_2} [kJ h^{-1}]	reaction heat of CO_2 in blended amine solution
$H_{abs,i}$ [kJ h^{-1}]	reaction heat of CO_2 in single amine solution
H [m^3 Pa mol^{-1}]	Henry's constant
H_{loss} [kJ h^{-1}]	loss of reboiler power supply
$H_{reb.}$ [kJ h^{-1}]	reboiler power supply
$H_{vap,water}$ [kJ h^{-1}]	enthalpy of water vaporization
k_1 [s^{-1}]	pseudo-first-order reaction rate constant
k_2 [m^3 kmol^{-1} s^{-1}]	second-order reaction rate constant
K_G [kmol m^{-2} s^{-1} pa^{-1}]	overall gas-phase mass transfer coefficient
k_{OH^-} [m^3 kmol^{-1} s^{-1}]	CO_2 hydration reaction rate constant
k_{ov} [s^{-1}]	overall pseudo-first-order reaction rate constant
k_L [m s^{-1}]	liquid-side mass transfer coefficient
K_L [m s^{-1}]	overall liquid-phase mass transfer coefficient
m [kg h^{-1}]	mass flow rate
M [kg kmol^{-1}]	molecular weight
n [kmol h^{-1}]	molar flow rate

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N [kmol m^{-2} s^{-1}]	molar mass-transfer flux
P [Pa]	pressure
P_{CO_2-AM} [Pa]	equilibrium partial pressure of CO_2 in the bulk of the amine solution
$P_{CO_2,bulk}$ [Pa]	partial pressure of CO_2 in the bulk of the gas
$q_{reg.}$ [kJ kg$^{-1}_{CO_2}$]	regeneration heat duty
$q_{sens.}$ [kJkg$^{-1}_{CO_2}$]	sensible heat duty
$q_{vap,water}$ [kJ kg$^{-1}_{CO_2}$]	vaporization heat of water
q_{des,CO_2} [kJ kg$^{-1}_{CO_2}$]	desorption heat
r [kmol m^{-3} s^1]	reaction rate
R [J mol^{-1} K^{-1}]	gas constant
T [K]	absolute temperature
t [°C]	temperature
V [m^3 h^{-1}]	volumetric flow rate
y_{CO_2-Am} [$-$]	equilibrium mole fraction of CO_2 in the bulk of the amine solution
$y_{CO_2,bulk}$ [$-$]	CO_2 mole fraction in the bulk of the gas
y_{CO_2} [$-$]	CO_2 mole fraction
Y [-]	molar ratio of CO_2 [$y/(1-y)$]

Greek Symbols

α [$-$]	CO_2 loading of amine solution
η [$-$]	efficiency
ρ [kg m^{-3}]	mass density

Subscripts

abs.	absorption
Am	amine solution in bulk
CO_2	carbon dioxide
h	heating fluid
in	inlet
lean	lean amine solution
out	outlet
Reb.	reboiler
reg.	regeneration
rich	rich amine solution

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