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Capacity Utilization of Aqueous 2-amino-2-methyl-1-propanol (AMP) and Methyl Diethanolamine (MDEA) for CO_2 Capture with Piperazine (PZ)

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Abstract. The current study emphasized the CO_2 capturing performance of two activated blends such as (AMP+PZ) and (MDEA+PZ) in a pilot plant like set-up. The experimental investigation was conducted in a packed column at varying mass proportion ratios of amines, absorption temperature and CO_2 concentration in addition to viscosity and density measurement of the blended solvent. The impacts of several process parameters were assessed to substantiate CO_2 sorption characteristics of the engineered blends. The specific absorption rate of aqueous (AMP+PZ) and (MDEA+PZ) blends were estimated to be (16.7- 35.7) $\times 10^{-6}$ and (13.2- 33.5) $\times 10^{-6}$ kmol m^{-2} s^{-1} respectively. Regeneration efficiency of (AMP+PZ) blend was ranging from 90.8- 98.93% while 84.28–93.64% for (MDEA+PZ). The required heat towards solvent regeneration for (AMP+PZ) and (MDEA+PZ) was 3.4–4.7 MJ per kg CO_2 and 3.0–4.1 MJ per kg CO_2 respectively in comparison with conventional 30 wt% MEA (3.8-4.8 MJ per kg CO_2).

Keywords: CO_2 capture; Sorption study; (AMP+PZ) blend; (MDEA+PZ) blend; Flue gas from customized unit.

INTRODUCTION

The continuous progression of atmospheric carbon dioxide (CO_2) in the environment has caused serious environmental problems like melting of glaciers; land degradation and extreme weather conditions (Xiao et al., 2016). Scientists and researchers around the world are working towards the mitigation of this global threat. Although the emission of GHGs (greenhouse gases), for instance methane (CH_4) and nitrogen dioxide (NO_2) in the atmosphere is also responsible for the greenhouse effect yet, the contribution of CO_2 is utmost significant (Dutcher et al., 2013). The Global Carbon Budget report of 2018 showed that CO_2 emitted from the consumption of oil, gas and coal for combustion-related activities increased by 2.7 % to record levels in 2018. According to the report, China was the highest contributor of CO_2 emissions along with India behind it. The CO_2 emissions in China rose up to 4.7 % in 2018 and accounted for more than a quarter of such global emissions. Loss of control and weak regulations on new coal-fired power plants due to the economic downturn were suggested to be the reason for such increased emissions in China. In order to bring power to regions that never had electricity before, India had the second largest gains in GHG emissions (Report; Evarts E.C., 2019b). Therefore, the stabilization of GHG emissions aiming at 450 ppm (parts per million) CO_2-e (carbon dioxide equivalent) through continuous efforts is the need of the hour.

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The chemical absorption techniques have already been established by some industries like gas processing units, coal-fired power station, and cement production plants (Norouzbahari et al., 2016). Due to the ready availability and relatively lower price of MEA having the highest stoichiometric loading of 0.5 moles CO_2 for each mole of amine, it is the most preferred conventional industrial absorbent for CO_2 capture (Mandal et al., 2003; Freguia and Rochelle, 2003). Moreover MEA also has some major drawbacks as an absorbent like a high energy intensive regeneration method, extremely corrosive in nature with a greater degree of degradation (Aronu et al., 2009). In recent years, attention moved towards the development of activated aqueous solutions of tertiary or hindered amines like MDEA and AMP with polyamines like PZ. These solvents possessed attractive sorption potentials viz. improved sorption capacity, higher stoichiometric CO_2 loading, reasonable sorption rate kinetics, reduced energy intensive solvent regeneration, a lesser degree of solvent degradation and deterioration. While PZ further boosts the rate of absorption by increased rate of reaction and thereby enhancing the reaction kinetics (Khan et al., 2019). Substantial research work on several amines and also their combination perform as a capturing agent towards CO_2 absorption has been published but literature on detailed assessment and application of aqueous (MDEA + PZ) and (AMP + PZ) blend as a significant capturing element for CO_2 removal (real flue gas generated from a customized coal-fired boiler unit) is very limited.

The present research work focuses on the detailed evaluation of CO_2 absorption to be associated with solvent regeneration of (MDEA+ PZ + H_2O) and (AMP+PZ+ H_2O) towards the removal of CO_2 discharge from a customized coal-fired boiler through CO_2 capture scheme (post-combustion) in a packed absorption column. The important solvent characteristic property like density and viscosity has been analysed over the variation of temperature and different blending mass ratio. Absorption investigation have been performed at four distinct temperatures viz. 300, 305, 310 and 315 K with four diverse mass proportion combinations of (MDEA+PZ) and (AMP+PZ). The specific absorption rate of CO_2 has been analyzed through the relative mass concentration i.e. (wt%: wt%) of both (MDEA+PZ) and (AMP+PZ) blends by means of 26:4, 22:8, 20:10 and 18:12 respectively. The impacts of numerous experimental variables on absorption rate of CO_2 were detected during absorption process. Solvent regeneration efficiency, regeneration temperature, residual CO_2 retain in regenerated amine blend and heat duty requirement for solvent regeneration all together were characterized the regeneration performance of specific amine blend through various regeneration temperature. After the successful completion of every absorption and desorption cycles of each (MDEA+PZ+H_2O) and (AMP+PZ+H_2O) blends, the cyclic CO_2 loading capacities were determined through a desorption-cell study. The essential heat load needed towards solvent regeneration of CO_2 rich solvent blend was also determined.

THEORETICAL BACKGROUND

Absorption Mechanism of (AMP+PZ+H_2O)

In case of hindered amine AMP, the significant reaction with CO_2 is a hydration of CO_2 which is catalyzed by AMP and formed bicarbonate ion. However, the development of carbamate is very less related to the bicarbonate because of the least carbamate stability constant of AMP. Therefore it can be overlooked as well.

The feasible reaction accompanying to CO_2 and PZ comprises of two steps: one is the zwitterion complex creation trailed by base catalyzed zwitterion deprotonation (Dash et al., 2011; Bishnoi, and Rochelle, 2000; Derks et al., 2006; Samanta and Bandyopadhyay, 2007). Zwitterion mechanism is firstly specified by Caplow, 1968 and recreated by Danckwerts, 1979; which mention that zwitterions deprotonation can occur by prevailing base in the aqueous solution. In (AMP+PZ+H_2O), presence of additional AMP percentage catalyzes the reaction involving CO_2 and PZ.

Reaction Mechanism of (MDEA+PZ+H_2O)

A base-catalyzed hydration reaction occurs between CO_2 with tertiary amines MDEA suggested by Donaldson and Nguyen, 1980. The mechanism reveals that there is no direct interaction between MDEA with CO_2. Physical absorption is the only option when CO_2 capture takes place into MDEA but with non-aqueous medium according to (Versteeg and Van Swaaij, 1988). The projected reaction scheme is involving CO_2 and PZ consists of a zwitterions trailed by the zwitterions deprotonation by a base to obtain PZ-carbamate and protonated base. Formation of zwitterions should be the rate controlling stage in case of PZ, however the deprotonation stage comprises simply a proton transmission and is predicted to be very fast.

Regeneration Reaction Method of CO_2 Rich Amine Solution

The thermal breakdown of carbamate formed and various absorption derivative discharges CO_2 from the CO_2 loaded rich solvent. Carbamate ($RNHCOO^-$) is converted into amine and CO_2. The required heat for CO_2 discharge from loaded solution is subject to the intensity of carbamate structure. The structural arrangement of AMP is hindered type, and carbamates formed detaches effortlessly in contrast with others. In view of tertiary amine like MDEA the heat energy for separation is comparatively small since the formation of only bicarbonate with CO_2 and could dissociates readily with temperature effect. In view of PZ the liberation of CO_2 from rich amine complex structure needs more thermal energy towards breakdown the stable carbamate and dicarbamate dissociation.

Specific Rate of Absorption

A proposed relationship recommended by Billet (1995) was applied towards determine the specific absorption rate of blended absorbent involving gas-liquid interaction and related mass transfer in a packed absorber which represented by following equation (1).

$$\frac{a_{eff}}{a_p} = 3 \times (\varepsilon)^{0.5} \times (Re_L)^{-0.2} \times (Fr_L)^{-0.45} \times (We_L)^{0.75} \quad (1)$$

where, a_{eff} indicates specific effective area of absorption, m2, a_P designates specific dry packing area, $m^2.m^{-3}$, ε specifies void fraction, Re_L indicates Reynolds Number, Fr_L signifies Froude Number and We_L denotes Weber Number.

$$Re_L = \frac{u_L}{a_P} \times \frac{\rho_L}{\mu_L} \quad (2)$$

$$Fr_L = \frac{u_L^2 a_p}{g} \quad (3)$$

$$We_L = \frac{u_L^2 \rho_L}{\sigma_L a_p} \quad (4)$$

$$u_L = \frac{v}{a} \quad (5)$$

Here; v =Volumetric flow rate, m^3s^{-1}; a = Tower cross section area, m^2, u_L= Superficial liquid velocity, ms^{-1}, ρ_L= Liquid density, $kg.m^{-3}$, σ_L = Liquid surface tension, $mN.m^{-1}$, g= acceleration due to gravity, $kg.m^{-2}$, μ_L= Liquid viscosity, mPa.s.

$$Volumetric\ rate\ of\ absorption = G_s(Y_{inlet} - Y_{outlet}) \quad (6)$$

$$G_s = G_m(1 - y) \quad (7)$$

where, Y_{inlet} = Initial CO_2 concentration on inert basis; Y_{outlet} = Outlet CO_2 concentration in inert basis; G_m = Total flow rate of gas; and G_s = Inert flow rate of gas.

$$Specific\ absorption\ rate = \frac{Volumetric\ rate\ of\ absorption}{a_{eff} \times p} \quad (8)$$

Applying the ideal gas law transformation volumetric flow rate was transformed into molar volume ($kmol\ s^{-1}$) and the unit of specific absorption rate becomes ($kmol\ m^{-2}s^{-1}$).

$$Percentage\ of\ CO_2 absorbed = \frac{n_1 - n_2}{n_1 y_1} \times 100 \quad (9)$$

Where n_1 signifies moles of gas mixture present before absorption, n_2 represents moles of gas mixture after absorption and y_1 symbolizes the CO_2 mole fraction in inlet flue gas.

Regeneration Efficiency Determination

To examine the regeneration criteria of (AMP+PZ+H_2O) and (MDEA+PZ+ H_2O) towards CO_2 removal, regeneration efficiency of each blended solution has been determined. The regeneration studies have been conducted at temperatures of 373, 380, 385 and 390 K. The CO_2 loading capabilities of each blended solution were analysed using the sample taken after absorption as well as regeneration completion of individual blended solution. The regeneration of each blended solution was carried out for 2.5 to 3 hours.

$$Regeneration\ efficiency = 1 - \frac{Lean\ solvent\ loading\ after\ stripping}{Rich\ solvent\ loading\ before\ stripping} \times 100\% \quad (10)$$

MATERIALS AND METHODS

Formulation of Solution Blend

In the current analysis, PZ activated AMP and MDEA blends were studied as CO_2 capturing agents throughout the sorption process. The reagent category of MDEA, AMP, and PZ was purchased from Sigma- Aldrich, Germany possessing above 98% purity. Aqueous solution of (AMP+PZ) and (MDEA+PZ) were prepared in varied mass proportion ratios such as (26:4, 22:8, 20:10 and 18:12) using laboratory grade double distilled water. Mettler Toledo mass balance, model ML204/A01 along with ±0.01 % precision was used for quantifying the exact mass proportion blend preparation. To determine the precise strength of each and every blended amine solution titration process was applied. Laboratory category hydrochloric acid (HCl, 37%) delivered by Merck, India and methyl orange indicator were utilized in the process.

Formation and Assessment of Generated Flue Gas

The exhaust flue gas (source of CO_2) was produced from a customized coal-fired boiler and analysed by a flue gas analyser (TESTO 350-S, Germany) (Khan et al., 2016; Khan et al., 2017; Khan et al., 2019). Pure CO_2 was mixed with the flue gas to attain the desired CO_2 percentage by operating a mass flow meter arrangement. The pressure of flue gas on collection from boiler stack was nearly equal to atmospheric pressure and the gas temperature was on the scale of 110-115°C. After that the flue gas was passed through the water scrubbing unit towards lowering the temperature between 40-45°C. Finally the flue gas was accumulated in a gas storage balloon (10 m^3 in size) and utilized as working absorbate (flue gas). Table 1 represent the generated flue gas composition from customized unit.

TABLE 1. Generated flue gas composition from customized coal-fired boiler unit

Gas composition	% or ppm
CO_2	10-15%
O_2	8-10%
N_2	74-76%
CO	750-1050ppm
NOx	150-350 ppm
SOx	400-650 ppm

Physicochemical Characteristics of (AMP+PZ+ H_2O) and (MDEA+PZ+H_2O)

Determination of physicochemical behaviour such as density and viscosity of each and every blended amine solvent is essential to be familiarized with thermodynamics, hydrodynamics, and optimal operational activities of the CO_2 sorption process. These solvent properties are also important for designing and optimizing the gas capturing process units for smooth operation.

Density Measurement of Blended Solution

The density measurement of each and every formulated blended amine solvent was performed by a 25 ml Gay-Lussac pycnometer. The density factors were measured for each amine blends across a temperature span of 300-315 K in a thermostat water bath retaining a fixed temperature along with ±0.2 K accuracy. The measured density of the reference solvent (water) was procured from the textbook (Geankoplis, 2003). The density values of aqueous blended solvent of (AMP+PZ) and (MDEA+PZ) was analysed with varying temperature along with various mass proportion of amine blend. Table 2 represent the density data of each and every amine blend along with their possible effect of temperature on it.

Viscosity Measurement of Blended Solution

The viscosity data was determined in an Ostwald viscometer within a temperature span of 303-315 K for every distinct aqueous blended solvent of (AMP+PZ) and (MDEA+PZ) with varied weight proportion combinations such as (26:4, 22:8, 20:10 and 18:12). The viscometer was dipped into a constant temperature thermostat water bath conserving with accurateness of ±0.2 K. Laboratory grade doubly purified water was considered as a reference standard. The different viscosity data of water was obtained from the book (Geankoplis, 2003). The viscosity data of aqueous blended solvent of (AMP+PZ) and (MDEA+PZ) was calculated with changing temperature along with various mass percentages of amine blends. Table 2 characterize the viscosity value of each blended combination along with their related influence of temperature on it.

TABLE 2. Different physicochemical property of (AMP+PZ+H_2O) and (MDEA+PZ+H_2O) and effects of temperature

Aqueous amine solvent	T (K)	Density (kg m^{-3})	Viscosity (mPa.s)	Surface tension (mNm^{-1})
26% A+ 4% B	300	999.8	3.824	46.84
	305	997.6	3.052	45.21
	310	994.8	2.636	43.78
	315	992.8	2.064	42.25
22% A+8% B	300	1002.5	4.172	47.21
	305	999.6	3.576	45.88
	310	995.3	2.938	44.63
	315	992.8	2.234	43.22
20% A+ 10% B	300	1005.6	4.283	47.84
	305	1003.1	3.783	47.03
	310	999.9	3.152	46.32
	315	997.4	2.686	45.14
18% A+ 12% B	300	1007.9	4.412	48.82
	305	1005.4	3.918	47.71
	310	1002.5	3.412	46.67
	315	1000.6	3.132	44.89
26% C+ 4% B	300	1028.4	2.867	60.12
	305	1025.2	2.413	59.63
	310	1020.9	2.078	58.88
	315	1016.4	1.782	58.14
22% C+ 8% B	300	1022.4	3.768	58.75
	305	1020.3	3.412	57.82
	310	1015.2	2.542	56.45
	315	1012.6	2.348	55.37
20% C+ 10% B	300	1020.0	3.905	56.92
	305	1018.8	3.612	55.66
	310	1014.2	2.693	54.23
	315	1011.1	2.466	53.11
18% C+ 12% B	300	1017.2	4.128	54.25
	305	1015.1	3.787	53.08
	310	1012.2	3.198	51.87
	315	1010.1	2.755	50.97
MEA 30 %	300	1003.9	1.95	59.51
	305	1002.1	1.78	58.08
	310	1001.2	1.65	56.92
	315	999.7	1.51	55.89

A: AMP, B: PZ, C: MDEA

Experimental Arrangement and Procedure

CO_2 absorption investigation was achieved in a packed absorber represented in Figure 1 containing distinct mass proportions of aqueous (MDEA +PZ) and (AMP+PZ) as capturing agent and pilot plant generated flue gas (source of CO_2) as an working gas. Material of construction of both absorber and stripper are made-up of glass. Entire length of the absorber and stripper was 1.3 m with effective packing length of 0.84 m and having the inner diameter of 0.04 m. A randomly distributed metal HELI-PAK was introduced as a packing substance for the absorber and stripping unit. A liquid distributor was fixed on top of the column for the proper dispersal of solvent throughout the absorber. The process variables for instance, blended solution flow rates (1.5×10^{-4}, 2×10^{-4}, 2.5×10^{-4} and 3×10^{-4} m^3 min^{-1}), absorbate gas flow rates (5×10^{-3}, 6×10^{-3}, 7×10^{-3} and 8×10^{-3} m^3 min^{-1}), varied initial CO_2 concentration (10, 12 and 15 kPa) and process temperatures of (300, 305, 310 and 315 K) were maintained throughout the experiment. A flue gas analyser was employed to estimate the concentration of CO_2 before and after absorption all through the experimental run. The regeneration activity of working solution was carried out in a stripping unit maintaining the temperatures of (373, 380, 385, and 390 K) with process duration of 2.5-3 hrs. The stripping performance was conducted at 50–55 kPa (vacuum) and controlled by a needle valve functioning in the bypass route of water ring vacuum pump. The cyclic CO_2 loading capabilities of aqueous (MDEA+PZ) and (AMP+PZ) were estimated after completion of each single cycle run of absorption and regeneration in a desorption chamber.

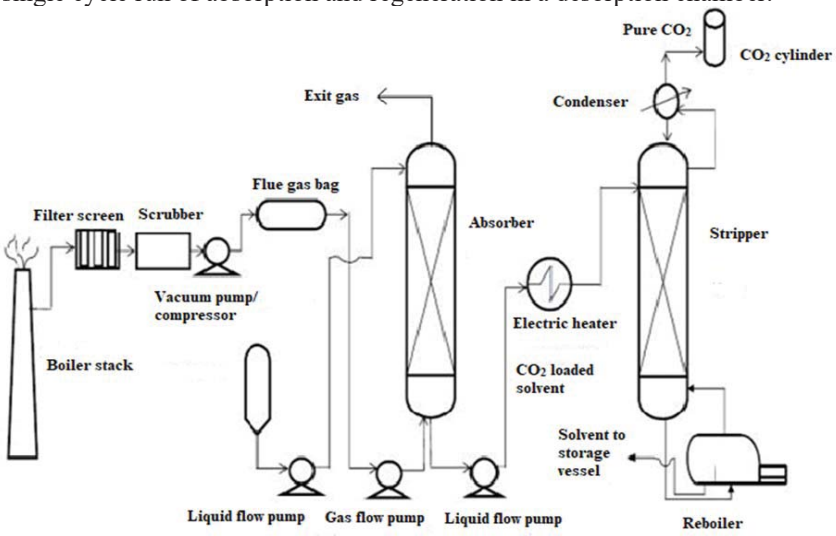

FIGURE 1. Experimental Setup.

RESULTS AND DISCUSSION

These experimental outcomes focused on CO_2 sorption phenomena in a packed absorber considering two distinctive active amine blends i.e. (AMP +PZ+H_2O) and (MDEA+PZ+ H_2O) with proposed mass fraction combination. Five experimental process factors such as gas flow rate, blending mass proportion ratio, absorption temperature, absorbent flow rate, and CO_2 concentration has efficiently measured the absorption performance. Regeneration efficiency, cyclic CO_2 loading capabilities, residual CO_2 retain in the regenerated blended solution and reboiler heat energy requisite for solvent regeneration effectively influence the regeneration characteristics of both operative amine blends. Regeneration temperature and regeneration time have an absolute effect on regeneration performance. Table 3 represents the characteristic performance of both working amine blends.

TABLE 3. Characteristic performance of (AMP +PZ+H_2O) and (MDEA+PZ+ H_2O)

Aqueous amine solvent	Specific absorption rate at 15 kpa ($kmol.m^{-2}.s^{-1}$)	CO_2 loading capacity (mol CO_2/ mole of amine)	T (K)	Residual CO_2 retain (mol CO_2 per mole of amine)	Regeneration efficiency (%)	Reboiler heat duty (MJ per kg CO_2)
26% A+ 4% B	22.6×10^{-6}	0.891	373	0.026	94.54	3.4
			390	0.030	98.93	4.1
22% A+8% B	27.1×10^{-6}	0.909	373	0.032	93.10	3.8
			390	0.039	97.51	4.2
20% A+ 10% B	31.8×10^{-6}	0.938	373	0.050	91.82	4.1
			390	0.058	96.66	4.5
18% A+ 12% B	35.7×10^{-6}	0.978	373	0.061	90.80	4.3
			390	0.072	95.32	4.7
26% C+ 4% B	19.4×10^{-6}	0.635	373	0.044	88.34	3.0
			390	0.053	93.64	3.5
22% C+ 8% B	24.6×10^{-6}	0.723	373	0.051	86.84	3.3
			390	0.063	91.68	3.8
20% C+ 10% B	28.8×10^{-6}	0.804	373	0.058	85.24	3.4
			390	0.069	89.58	3.9
18% C+ 12% B	33.5×10^{-6}	0.875	373	0.067	84.28	3.6
			390	0.077	88.45	4.1
MEA 30 %	18.4×10^{-6}	0.486	373	0.092	74.15	3.8
			390	0.114	82.15	4.8

A: AMP, B: PZ, C: MDEA

Determination of Specific Absorption Rate

Considering the (AMP+PZ+H_2O) blends it has been discovered from the experimental outcomes that with gradual escalation in weight fraction of PZ content i.e. 4-12 wt% in (AMP+PZ+H_2O) blend maintaining the overall strength of 30 wt%, specific rate of CO_2 absorption appreciably enhances accordingly within the range of (16.7-35.7)$\times10^{-6}$ kmol m^{-2} s^{-1}. The resultant enhancement of CO_2 absorption rate was experienced for the reason that the construction of stable PZ-dicarbamate along with the AMP catalyzed PZ- carbamate since PZ weight percentage steadily increases in blended solution of (AMP+PZ). In solvent absorption technique CO_2 concentration is one of the most substantial factor, Figure 2 displays the impact of initial CO_2 concentration on CO_2 absorption rate and it indicates that the rate steadily rises according to the gradual escalation of CO_2 concentration from 10-15 kPa with a rate of 35.6×10^{-6} kmol m^{-2} s^{-1} for the blending mass proportion of (AMP 18wt%+ PZ 12 wt %). Subsequently, in any liquid gas absorption arrangement, the concentration of a gaseous constituent (CO_2 intensity) is higher; the elimination of gaseous concentration will also be more and directs towards the better capture. In case of (MDEA+PZ+H_2O), progressive outcome of CO_2 absorption rate was attained with gradual addition of PZ in the blended solution from 4 wt% to 12 wt% with resulting value of (13.2-33.5) $\times10^{-6}$ kmol m^{-2} s^{-1}. The higher rate of absorption was achieved because of gradual accumulation of rate accelerator PZ (4, 8, 10 and 12 wt %) in the amine blend which implies the higher rate since, fundamentally two nitrogen atoms present in the PZ structure and development of stable PZ-dicarbamate through faster reaction rate with CO_2. The CO_2 absorption rate steadily improves for each mass combination of (MDEA+PZ) with an upsurge in the mass proportion of PZ from 4 wt % to 12 wt% with an escalation of CO_2 concentration from 10–15 kPa which displayed in Figure 2. The faster rate of CO_2 absorption took place because of more CO_2 molecular transformation from the bulk gas stream to the gas-liquid interface since steady increase of CO_2 intensity in the inlet gas stream.

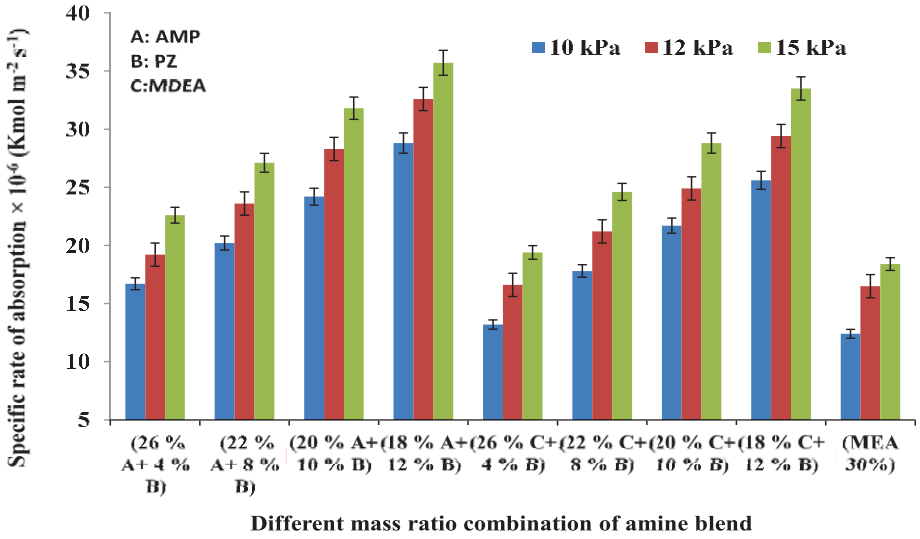

FIGURE 2. Specific CO_2 absorption rate using (AMP+PZ+H_2O) and (MDEA+PZ+H_2O) blend

Assessment of Cyclic CO_2 Loading Capacity

The CO_2 loading capability signifies one of the most important features of solvent characteristics towards post-combustion CO_2 removal by two distinct blends of amine and the investigated data are represented in Table 3. In case of (AMP+PZ+H_2O) blend, from Figure 3 it can be observed that with the gradual enhancement of PZ weight fraction from 4-12 wt % in the solvent blend the resultant CO_2 loading capability progressively rises from 0.881 to 0.978 moles CO_2. The enhanced result was attained since the cyclic diamine characteristics of PZ molecule along with two nitrogen attachments and the steric hindrance effect of AMP in the blended solvent. In view of (MDEA+PZ+H_2O), the improved CO_2 loading characteristics were accomplished within 0.486 to 0.875 moles CO_2 with the steady addition of PZ percentage from 4-12 wt % in the blend with escalating CO_2 concentration from 10-15 kPa which is represented in Figure 3. Structural advantage of PZ is responsible for the enhancement of CO_2 loading capability during the capture procedure with rising quantity of PZ in the blend since the physical characteristics of MDEA (tertiary amine) i.e. exclusion of any hydrogen group connection with nitrogen leads relatively poor loading performance.

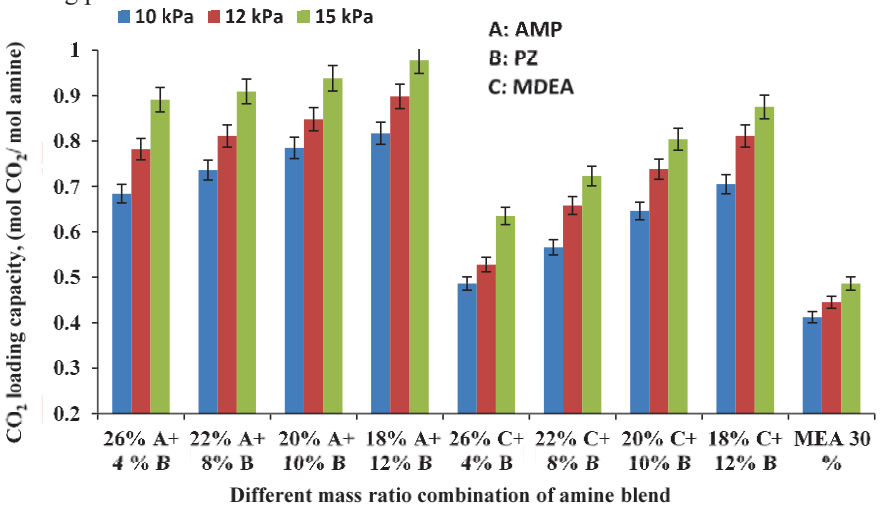

FIGURE 3. Cyclic CO_2 loading capability of (AMP+PZ+H_2O) and (MDEA+PZ+H_2O) blend

Assessment of Regeneration Performance

Regeneration efficiency and excess CO_2 retained in regenerated blended solution after stripping of CO_2 rich amine blend collectively represent the solvent regeneration characteristics. Regeneration temperature and requisite time for solvent regeneration of CO_2 enriched solvents are the important parametric conditions to be considered towards regeneration performance. Considering (AMP+PZ+H_2O) blend, maximum regeneration efficiency has been attained with the blend having the lowest proportion of PZ specifically (26 wt % AMP+ 4 wt% PZ) and the estimated values are within a range of 94.54 to 98.93% with the steady temperature rise from 373-390 K as represented in Figure 4. The residual CO_2 retain following stripping operation offers a significant indication of better solvent property which is shown in Figure 5. It shows the superiority of (26 wt % AMP+ 4 wt% PZ) blend with lesser quantity i.e. 0.026 moles of CO_2 per mole of blended solution over (18 wt% AMP+ 12 wt% PZ) blend with 0.072 moles of CO_2. Table 3 illustrates the investigated data of regeneration efficiency and the residual amount of CO_2 retain after the stripping study of both the considered amine blend with corresponding mass fraction arrangement. Taking into consideration of (MDEA+PZ+H_2O), the regeneration efficiency steadily rises with a rise in regeneration temperature. The regeneration temperature is responsible for the required heat energy of separation towards CO_2 liberation from the CO_2 rich aqueous blend and it is subject to the strength of carbamate formation. From Figure 4 it can be observed that with a steady escalation of regeneration temperature from 373 to 390 K the regeneration efficiency also increases. The maximum regeneration efficiency was attained for the blend of (26 wt % MDEA+ 4 wt% PZ) amongst all the four different combinations with the corresponding value ranges of 86.72 to 92.24 %. Figure 5 displays the residual CO_2 retains in regenerated solvent after desorption study and it shows a reduced value (0.044-0.053 moles) containing minimum PZ presence i.e. 4 wt% in the aqueous MDEA blend which implies the improved regeneration characteristics as compared to maximum PZ concentration i.e. 12 wt% in the measured MDEA blend with detected values of (0.067-0.077) moles of CO_2.

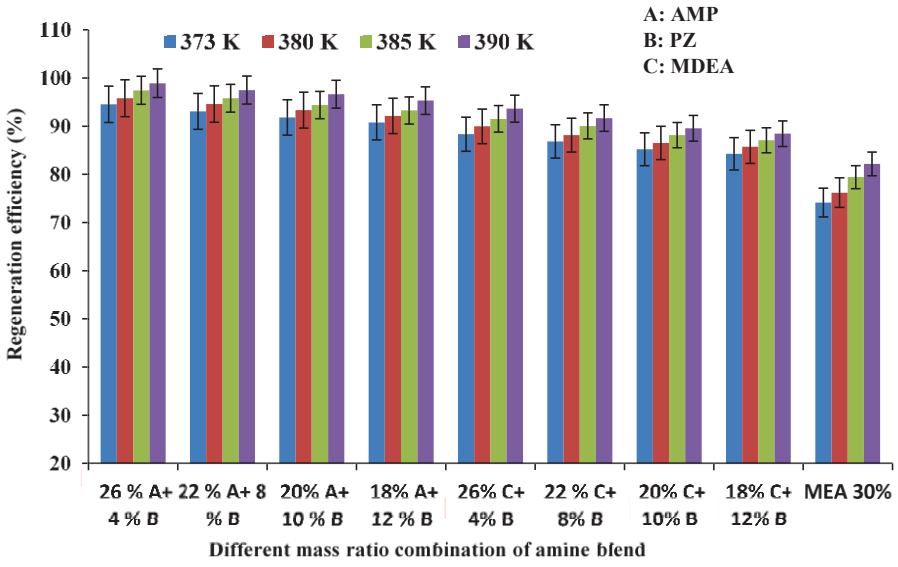

FIGURE 4. Regeneration efficiency of (AMP+PZ+H_2O) and (MDEA+PZ+H_2O)

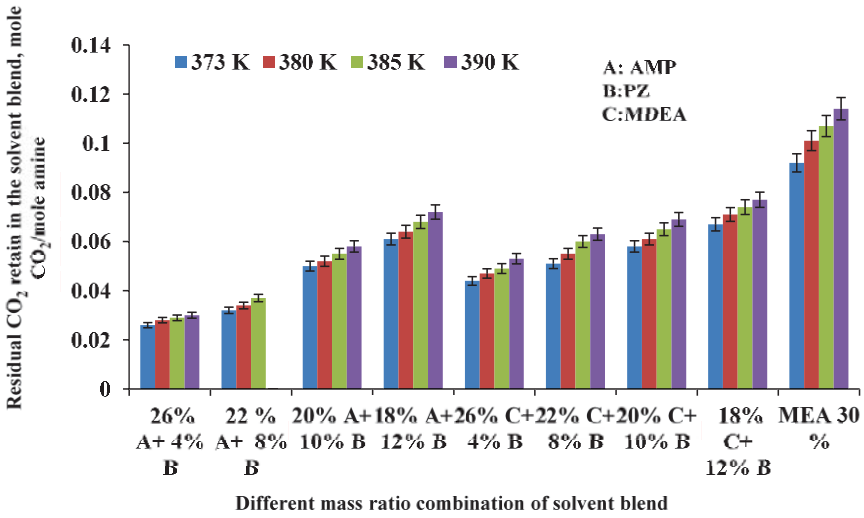

FIGURE 5. Residual CO_2 retains in the solvent blend after stripping operation of (AMP+PZ+H_2O) and (MDEA+PZ+H_2O)

Reboiler Heat Energy Requirement

Reboiler heat energy requirement is an intense measure towards CO_2 capture operation by blended amine solution. The regeneration characteristics of CO_2 enriched aqueous blends around stripping column segment has been estimated by creating heat energy balance over reboiler and stripping section through the supply of required heat energy. The requisite thermal energy in the reboiler section strongly depends on three dependable constituents: sensible heat ($Q_{sensible}$) signifies the energy required for heating up the CO_2 loaded solvent to expected reboiler temperature; required heat for CO_2 desorption ($Q_{desorption}$) implies the essential enthalpy to breakdown the CO_2/amine complex created through the CO_2 capture method; heat of vaporization ($Q_{vap, H2O}$) signifies the latent heat of vaporization for the production of accompanying water vapours through CO_2 rejection in the desorber. Figure 6 symbolizes the regeneration temperature dependency of reboiler heat load for assessment of both working blended amine solution. Considering the aqueous (AMP+PZ) blend, the heat energy requirement steadily escalates with the gradual rise in PZ proportion (4wt%< 8 wt% < 10 wt% <12 wt %) in blended solution. The calculated reboiler heat load values are varying from 3.4 to 4.7 MJ per kg CO_2 for four different aqueous (AMP+PZ) combinations which shown in Table 3. The steady upsurge in PZ percentage in the blended solution recorded higher reboiler heat energy requirement since, the heat of absorption (kJ per mol CO_2) of PZ is high compared to AMP. Subsequently, additional energy towards breaking up of AMP-PZ complex will be necessary during the regeneration process. As the regeneration temperature escalates step by step from 373 to 390 K the requirement of reboiler heat energy also enhances because the escalation of temperature initiates more CO_2 and water evaporation owing to their improved vapor pressure. The amount of CO_2 present in blended solution steadily dropped with rising temperatures through the heat capacity enhancement of each distinct amine blends with increasing temperature. The recorded reboiler heat energy data gradually accelerates with improved PZ mass proportion in the aqueous solution viz. (4wt%< 8 wt%<10 wt%<12 wt%). The required heat energy values are in a scale of 3.0 to 4.1 MJ per kg CO_2 for four (MDEA+PZ) blends which were displayed in Table 3. The higher reboiler heat duty was experienced since the heat of absorption of PZ is relatively larger compared to MDEA and additional heat will be essential for breakdown the MDEA-PZ compound over regeneration process. The essential reboiler heat requirement of both the investigated amine blends with four individual mass proportions has correlated with conventional 30 wt% MEA, which varies from 3.8 to 4.8 MJ per kg CO_2.

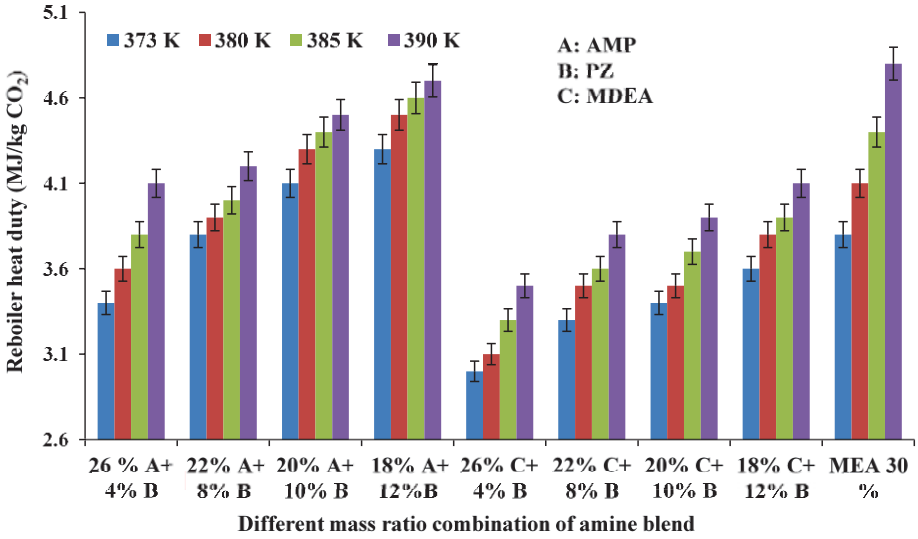

FIGURE 6. Reboiler heat energy requirement for (AMP+PZ+H_2O) and (MDEA+PZ+H_2O)

CONCLUSION

The present investigation highlights the influence of rate accelerating agent PZ on aqueous AMP and MDEA blend towards CO_2 sorption characteristics considering; specific rate of CO_2 absorption, CO_2 cyclic loading capability, solvent regeneration efficiency, residual CO_2 retain after stripping operation and reboiler heat energy estimation. Both the inspected blend experienced an enhancement of the rate of absorption, CO_2 capture capability, and regeneration ability compared to their individual performance along with comparatively lower heat energy requirement for solvent regeneration compared to conventional 30 wt% MEA. It can be summarized from the entire capturing performance (absorption and desorption) that both the amine blends could be considered as a promising agent for capturing CO_2 from flue gas. Considering the (AMP+PZ) blend, the specific rate of CO_2 absorption as well as regeneration performance was attractively far better than the conventional aqueous MEA (30 wt%) solution. In view of (MDEA+PZ) blend, the required heat duty for solvent regeneration was considerably very less along with reasonably improved rate of absorption characteristics.

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