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Carbon dioxide absorption using monoethanolamine, piperazine and n-metil-2-pirolidon solvents under counter current regime in packed column reactor

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ABSTRACT

In this research the carbon dioxide absorption using Monoethanolamine (MEA), Piperazine (PZ) and N-Metil-2-pirolidon (NMP) solvents and their different blends (MEA/NMP, PZ/NMP, MEA/PZ) in packed column reactor filled with Raschig rings was investigated and compared for efficient carbon dioxide absorption. The process was followed in a countercurrent regime under a liquid flow rate of 200 mL/min, gas flow rate of 2.5 L/min, and CO_2 concentration of 50,000 ppm. Carbon dioxide removal efficiency (%), absorption capacity (mol CO_2/mol solvent), overall mass transfer coefficient (1/min) and absorption rate (mol/l.s) were monitored. The highest obtained values for carbon dioxide removal efficiency, absorption capacity and overall mass transfer coefficient were 57.5%, 0.148 mol CO_2/mol solvent and 2.178 min^{-1} respectivelly when 0.03 M MEA/0.07 M PZ in a hybrid system was used. It was concluded that PZ blends with MEA were successful absorbent as the organic physical solvent whereas NMP didn't show improving effect in blends with MEA on the absorption efficiency.

1. Introduction

Nowadays, the increasing demand for energy is being mainly supplied from fossil resources, which is the major cause of the increase in carbon levels in the atmosphere. Statistical data published by Mauna Loa Observatory show that the carbon dioxide concentration in the Earth's atmosphere peaked at 418.51 ppm in September 2023 (Mauna Loa, 2023). Carbon dioxide has attracted attention because it is the main greenhouse gas affecting global warming. CO_2 removal is essential for carbon capture and storage, reducing emissions from industrial factories and power plants (Karlsson et al, 2020). Pre-combustion, post--combustion, and oxy-fuel combustion are the three main methods of reducing CO_2 emissions (He et. al., 2023). Various methods have been studied to reduce post-combustion CO_2 emissions, such as chemical absorption (Shen et. al., 2023; Zhao et al., 2011), membrane separation (Fu et. al., 2022), adsorption (Qie et. al., 2022), cryogenic separation (G. De Guido, 2023) and algal system (Smerigan et. al., 2023).

Chemical post-combustion CO_2 capture using aqueous alkanolamines is considered the most practical approach to control CO_2 emissions from industrial flue gases, where the amine-based chemical absorption process is considered the most mature method for post-combustion CO_2 capture (Zhang et. al., 2023-c). During the chemical process, carbon dioxide is removed from the flue gas through a chemical reaction with a solvent. High absorption efficiency, low energy consumption, high economic value, easy operation and mature technology are all advantages of this method (Peng et. al., 2012). The technologies rapid development is considered essential for preventing global warming and associated climatic changes (Chen et. al., 2022; Zhang et. al., 2023-a).

The use of aqueous MEA has some significant disadvantages, including the energy-intensive regeneration of the sorbent, which accounts for over 70% of the total operating costs and must be reduced to achieve commercial viability, as well as the high degradation rate of the sorbent amine solution and equipment corrosion (Chen et. al., 2022; Li et al., 2023).

Alkanolamines have the potential to be combined in such a way that their benefits are maximized, resulting in highly efficient sorbents for CO_2 capture. These sorbents demonstrate superior performance compared to aqueous MEA under similar operating conditions (Chen et. al., 2022). Searching for higher solvent performances for CO_2 capture

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are followed by introduction of new formulas by combining different amines. Several researchers have focused their research in this area with the aim of developing and testing new sorbents with lower energy requirements, such as new synthetic solvents and aqueous amine mixtures for CO_2 capture (Zhong et . al., 2023; Zhang et. al., 2023-b), including N-methyl-2-pyrrolidone (NMP), monoethanolamine (MEA) (Yuan and Rochelle, 2018; Yeh et. al., 2001) Triethanolamine (TEA) (Rubia et. al., 2010), methyldiethanolamine (MDEA) and piperazine (PZ) (Ali and Aroua, 2004; Pashaei,et, al., 2017), diethylethanolamine (DEEA) and ethylethanolamine (EEA) (Vaidya and Kenig, 2009; Chen, et. al., 2014), alkaline solutions (Chen, et. al., 2014; Tippayawong and Thanompongchart, 2010) and ammonia solution (Ma, et al, 2016).

Recently, research on hybrid solvents increased where combination of MEA and NMP (Tan et. al., 2015) in packed absorption column; MEA and NMP in wetted wall column (Yuan and Rochelle, 2018); AMP and NMP in a static-synthetic apparatus (Pakzad et. al., 2018); PZ and AMP in packed absorption column (Halim et. al., 2015); NMP and six different chemical solvents in a bubble column (Eskandari et. al., 2022) were studied.

To date, only a few experimental studies on the absorption capabilities of NMP in packed countercurrent columns have been published (Tan et. al., 2015; Qi et. al., 2023; Liu et. al., 2023; Wang et. al., 2021). Tan et al., investigated MEA/NMP hybrid solution on CO_2 removal efficiency in a countercurrent packed column (Tan et. al., 2015). Qi et al., used EMEA/NMP hybrid solution on CO_2 removal efficiency and regeneration energy in a countercurrent packed column (Qi et. al., 2023; Liu et. al., 2023). Wang et al., investigated carbon dioxide capture by non-aqueous blend in rotating packed bed reactor. AMP/AEEA/NMP tri-solvent blend is used for determining CO_2 capture efficiency and overall volumetric mass transfer coefficient (Wang et. al., 2021). A challenge in the post-combustion CO_2 capture from natural gas power plants is the large flow of flue gas with low CO_2 content (~3-4%vol.) (Diego et. al., 2017; Jiang et. al., 2019), and low pressure which is not sufficient to overcome the pressure drop inside absorbers. In this work, a CO_2 concentration of 50,000 ppm in a packed bed counter current absorber is tested.

Primary amine MEA has a high reaction rate, but on the other hand, its absorption capacity is low. In this study, aiming the increase of absorption capacity, dual systems with PZ solvent and NMP solvent, which are activators, were prepared. Two single amines including PZ, MEA and three amine mixtures such as MEA+NMP, PZ+NMP, MEA+PZ were proposed and their performance was compared. Specifically, low concentration of these absorbents (< 0.1 M) where used to maintain low pressure drop and well mixing in the reactor. Carbon dioxide absorption experiments performed at atmospheric pressure and room temperature. NMP was chosen as an organic physical solvent due to its low viscosity, being completely miscible in water, and capability of mixing completely with other solvents in this study. This feature would make pumping easier and use less power during the process.

1.1. Absorption Capacity Calculations

The area over the CO_2-time profile graph (Fig. 1) corresponds to the total absorbed CO_2. The input flow rate of CO_2 was known from the total flow rate and the inlet concentration. The outlet flow rate of CO_2 was calculated based on the fixed flow rate of N_2 that was an inert compound and the read CO_2 concentration. The following equation was used to calculate the CO_2 outlet flow.

$$Q_{CO_{2_{out}}} = Q_{total_{in}} \times y_{N_{2_{in}}} \left(\frac{y_{CO_{2out}}}{y_{N_{2out}}} \right) \quad (1)$$

In this equation, $Q_{CO_{2_{out}}}$ is the outlet carbon dioxide flow rate (l/min); $Q_{total_{in}}$ is the total flow rate (l/min); $y_{N_{2_{in}}}$ is N_2 mole fraction in the gas inlet; $y_{CO_{2out}}$ is CO_2 mole fraction in the gas outlet; $y_{N_{2out}}$ is N_2 mole fraction in the gas outlet.

Using conversion factors and the assumption that each mole at a standard temperature and pressure (STP) of 1 atm and 273 K occupies 22.4 liters, the volumetric flow rates were converted to molar mass flow rates. This volumetric flow rates were corrected for adjusted temperature. Then, the concentration (ppm)-time graph was replotted for mass flow rate vs time.

The rate of absorbed CO_2 at each reading interval was then calculated using the following equation;

$$R_{CO_2} = \dot{M}_{CO_{2_{in}}} - \dot{M}_{CO_{2out}} \quad (2)$$

Where; Rco_2 is the rate of absorbed CO_2 (l/min); $\dot{M}_{CO_{2_{in}}}$ and $\dot{M}_{CO_{2out}}$ are the mass flow rate of CO_2 in the gas inlet and outlet respectively.

The amount of absorbed CO_2 for each time period was determined using the equation below:

$$M_{CO_{2_{ab}}} = R_{CO_2} \times (t_2 - t_1) \quad (3)$$

Where;

M_{CO2} is the mass of absorbed CO_2 (mol CO_2); Rco_2 is the rate of

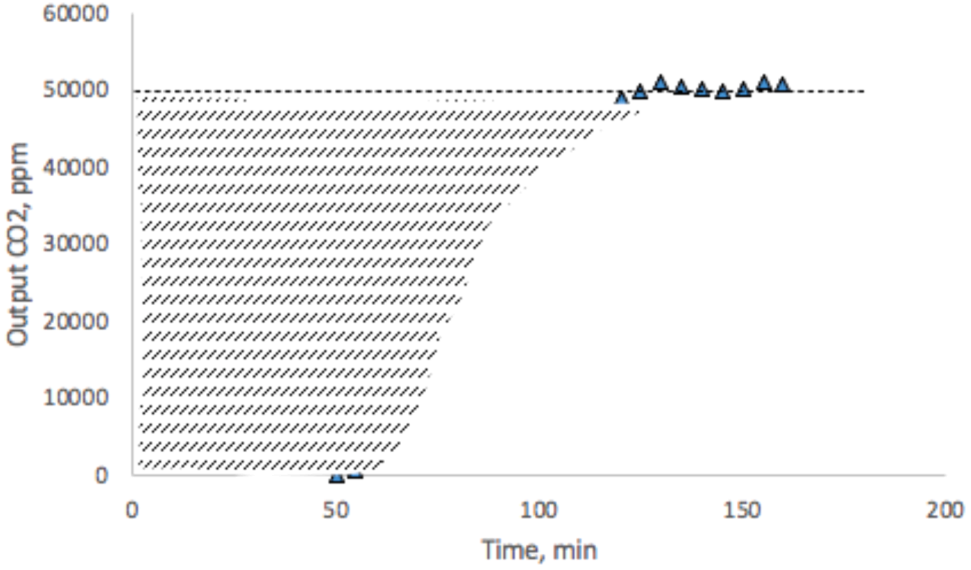

Fig. 1. A sample of the CO_2 concentration profile at the output (Gül et. al., 2023).

absorbed CO_2 (l/min).

The absorption capacity of the absorbent was calculated using equation given below;

$$Ab.Cap = \frac{\sum_1^n M_{CO_{2_{ab}}}}{M_{MEA}} \tag{4}$$

Where n is the number of time intervals, M_{CO2} is the mass of absorbed CO_2 and M_{MEA} is the mass of MEA in the solution.

Spreadsheets in MS Excel were used for calculation procedures.

1.2. Overall Mass Transfer ($K_G a$) calculation

In many separation processes, the material diffuses from one phase to the other (Fig. 2). It is assumed that the two-film model is used to determine the mass transfer coefficient and to define the mass transfer of CO_2. Two-film model assumes equilibrium at interface. According to two film models, the local absorption rate, expressed as total mass transfer coefficients, on both the gas and liquid side at a local point, can be written as follows;

$$r_A = (K_G a)(C_g - HC_L) \tag{5}$$

We assume a plug flow for the gas phase and well-mixed flow for liquid phase, steady state, mass equilibrium with z;

Mass balance over ΔZ:

$$(U_g C_g)_z^S - (U_g C_g)_{z+\Delta z}^S = r_A \Delta V \tag{6}$$

$$\Delta V = \Delta Z.S \tag{7}$$

Where S is the column cross-sectional area

Combining Eq 5 & Eq 6;

$$(U_g C_g)_z.S - (U_g C_g)_{z+\Delta z}.S = K_G a.(C_g - HC_L)(\Delta Z.S) \tag{8}$$

$$\frac{S.U(C_{g_z} - C_{g_{z+\Delta z}})}{\Delta z} = K_G a.(C_g - HC_L).S \tag{9}$$

$$HC_L \simeq 0$$

$$S.U\frac{dC}{dz} = S.K_G a.(C_g) \tag{10}$$

$$Q\frac{dC}{C} = S.K_G a.dz \tag{11}$$

$$Q\int_{Cin}^{Cout}\frac{dC}{C} = \int_0^L S.K_G a.dz \tag{12}$$

$$\mathbf{K_G a} = \frac{\mathbf{Q_g \ln \frac{C_0}{C}}}{\boldsymbol{L.S}} \tag{13}$$

Where C_g, CO_2 gas concentration in gas phase(mol/L), C_L, CO_2 gas concentration in liquid phase(mol/L), r_A is absorption rate (mol/L.min), $K_G a$ is overall mass-transfer coefficient (1/min), S is the column cross section area (cm^2), U is gas superficial velocity (m/s) and Q is the gas flowrate (l/min).

1.3. Chemical reaction mechanism

The reaction mechanism in a ternary system of H_2O-CO_2-amine differs based on the number of amine functionality. These reactions, which are equilibrium reactions have been suggested for single amine functionality as for MEA (Aronu, et. al., 2011):

Water dissociation:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \tag{14}$$

Carbon dioxide dissociation:

$$2H_2O + CO_2 \rightleftharpoons H_3O^+ + HCO_3^- \tag{15}$$

Bicarbonate dissociation:

$$H_2O + HCO_3^- \rightleftharpoons H_3O^+ + CO_3^{2-} \tag{16}$$

Dissociation of protonated MEA:

$$H_2O + RNH_3^+ \rightleftharpoons H_3O^+ + RNH_2 \tag{17}$$

Carbamate reversion to bicarbonate:

$$H_2O + RNHCOO^- \rightleftharpoons RNH_2 + HCO_3^- \tag{18}$$

Reactions for PZ that occur in the liquid phase are given below (Ramezani et. al., 2017). Reaction mechanism for PZ-CO_2-H_2O system;

Piperazine protonation:

$$PZ + H_2O \leftrightarrow PZH^+ + OH^- \tag{19}$$

$$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+ \tag{20}$$

Piperazine deprotonation:

$$PZH_2^+ + H_2O \leftrightarrow PZH^+ + H_3O^+ \tag{21}$$

Carbamate formation:

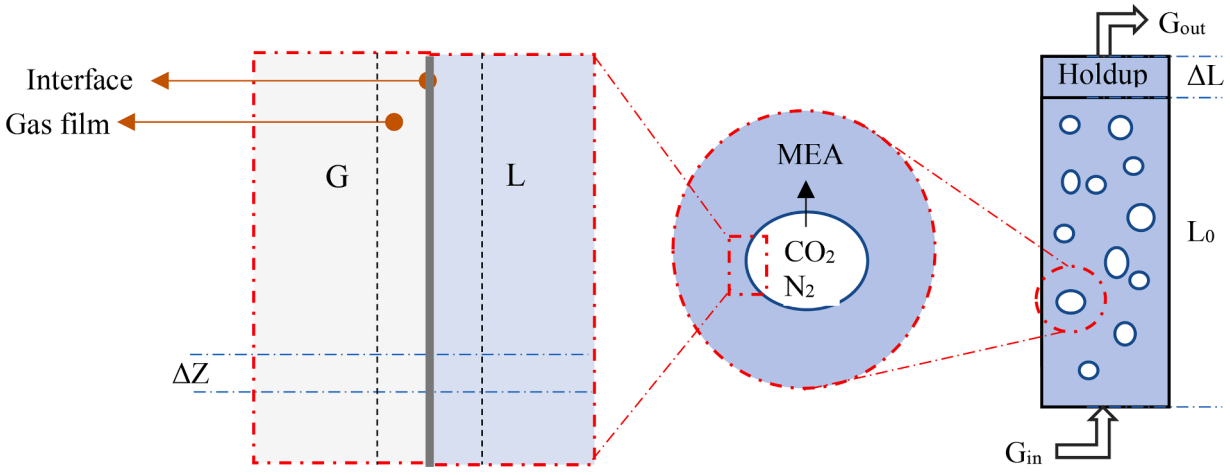

Fig. 2. The schematic of two film theory for CO_2 absorption in MEA.

$$PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+ \quad (22)$$

$$PZH^+ + H_2O + CO_2 \leftrightarrow H^+PZCOO^- + H_3O^+ \quad (23)$$

$$PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+ \quad (24)$$

Manocarbamate protonation:

$$H^+PZCOO^- + H_2O \leftrightarrow PZCOO^- + H_3O^+ \quad (25)$$

1.4. Chemical reaction mechanism for mixtures

Natural gas, synthetic gas, and hydrogen can all be processed using monoethanolamine (MEA), a reasonably strong base with a quick reaction rate. Its high capacity for CO_2 absorption results from its low molecular weight. High energy consumption and heat generation are disadvantages of solvent regeneration in boilers due to exothermic carbon dioxide absorption in MEA solutions. A diamine molecule known as piperazine (PZ) has two nitrogen atoms in its structure, allowing it to absorb two moles of CO_2 per mole. When interacting with CO_2, PZ produces less heat than MEA. Mixing two solvents improves the MEA's fast reaction kinetics, higher CO_2 capacity, and lower PZ reaction heat. The amount of packing required in the absorber may be reduced by faster solvents.

CO_2 absorption in aqueous MEA-PZ blended amine solution triggers numerous chemical reactions. The chemical reactions are listed below (Mirzaei and Ghaemi, 2018).

$$\text{Ionization of water} : 2H_2O \overset{K1}{\longleftrightarrow} H_3O^+ + OH^- \quad (26)$$

$$\text{Dissociation of carbon dioxide} : 2H_2O + CO_2 \overset{K2}{\longleftrightarrow} H_3O^+ + HCO_3^- \quad (27)$$

$$\text{Dissociation of bicarbonate} : H_2O + HCO_3^- \overset{K3}{\longleftrightarrow} H_3O^+ + CO_3^{2-} \quad (28)$$

$$\text{Dissociation of protonated MEA} : H_2O + MEAH^+ \overset{K4}{\longleftrightarrow} H_3O^+ + MEA \quad (29)$$

The reactions shown above occur very fast and are assumed instantaneous with respect to mass transfer. MEA reacts directly with CO_2 to form a stable carbamate. Zwitterion formation is the first step in the amines' zwitterion mechanism for absorbing CO_2.

$$\text{Formation of MEA carbamate} : H_2O + MEA + CO_2 \overset{K5}{\longleftrightarrow} H_3O^+ + MEACOO^- \quad (30)$$

$$\text{Dissociation of protonated PZ} : H_2O + PZH^+ \overset{K6}{\longleftrightarrow} H_3O^+ + PZ \quad (31)$$

$$\text{Formation of PZ carbamate} : H_2O + PZ + CO_2 \overset{K7}{\longleftrightarrow} H_3O^+ + PZCOO^- \quad (32)$$

$$\text{Formation of PZ dicarbamate} : H_2O + PZCOO^- + CO_2 \overset{K8}{\longleftrightarrow} H_3O^+ + PZCOO^- \quad (33)$$

$$\text{Di} - \text{protonation of PZ} : PZH^+ + H_3O^+ \overset{K9}{\longleftrightarrow} PZH_2^{2+} + H_2O \quad (34)$$

$$\text{Protonation of PZ carbamate} : PZCOO^- + H_3O \overset{K10}{\longleftrightarrow} PZH^+COO^- + H_2O \quad (35)$$

PZ solutions containing tertiary or hindered amines absorb CO_2 more quickly than MEA and have a higher CO_2 cycle capacity (Zhang et al., 2018; Gordesli and Alper.,2011). When compared to MEA, CO_2 reaction rates for PZ are approximately 2-3 times faster (Dugas and Rochelle, 2009). It was thought desirable to look into PZ derivatives such NMP given that the PZ has a fast reaction rate (Gordesli and Alper., 2011).

2. Materials and Method

2.1. Chemicals

Three solvents were employed in this investigation. MEA (≥98%), NMP (99.5%) and PZ (99%) were supplied by Sigma (Germany). Deionized water was supplied using a Thermo Scientific, German unit with ultra-pure filters. N_2 (> 99.99 %, 200 bar) and CO_2 (> 99.95%, 150 bar) gas cylinders were purchased from Oksangas, Turkey.

3. Experiment

In this study, monoethanolamine (MEA), piperazine (PZ) and N-methyl-2-pirolidone (NMP) as solvents and their different blends (MEA/NMP, PZ/NMP, MEA/PZ) were used in a Raschig ring filled packed column reactor and the efficiency of CO_2 removal (%), the absorption capacity (mol CO_2 / mol solvent), the total mass transfer coefficient (1/min) and the absorption rate (mol/l.s) were calculated and compared with regard to efficient carbon dioxide absorption . The solvents and mixture concentrations are given in Table 1. Specifically low concentration of solvents where used for mainly two reasons; First, to maintain a low viscosity solution with well wetting property on the fillings surface and second, high concentrations of solvents result in almost full absorbtion and zero output concentration in gas phase which halts calculation of K_Ga at different concentrations of absorbent.

The absorption column of this study is shown in Fig. 3. It was made of a 100-cm-high Plexiglas cylinder with a 5.0-cm diameter that was equipped with a jacket for temperature control. The gas absorption column was randomly packed with ceramic Raschig rings (0.4 mm×0.4 mm) at 70 cm height. The gas/liquid interaction in the absorption column was significantly enabled by packing.

The process run in a countercurrent flow mode (Fig. 2 & 3). Desired solvent was prepared in a feed tank with 2.5 L volume and replenished during process when needed. A micro gear liquid pump (LP-WT3000) was used to obtain a smooth 200 ml/min flow rate. Experiments were conducted at room temperature. The gas mixture was supplied using two separate mass flow controllers (ALICAT Scientific Mass Flow Controller, Range:0-10 L/min, accuracy % 0.2 of full-scale) for nitrogen and carbon dioxide. The gas mixture was first sent directly to CO_2 analyzer to ensure initial 50000 ppm concentration then the main line valves were opened and gas mixture directed to the column filled with MEA solution. The gas mixture was bubbled first in a humidifier where its temperature was controlled/adjusted by a heat exchanger in a closed loop. A dry gas flow would change the concentration of the amine solution by evaporation from liquid to gas phase and humidification minimizes this effect. The humidified/saturated gas mixture was bubbled using diffuser in the column and the carbon dioxide concentration in the gas phase in the output was monitored using a Vernier CO_2 gas sensor (USA). The process continued until there was no change in the output CO_2 gas concentration. This process was confirmed by the concentration/time profile as shown in Fig. 1 for a specific run.

4. Results and Discussion

The absorption performance of CO_2 gas in aqueous solvent (MEA,

Table 1
Solvent concentrations.

Solvent and Mixtures	Solvent Concentration (M)
MEA	0.025, 0.05, 0.1
PZ	0.025, 0.05, 0.1
MEA-NMP	0.05-0.05
PZ-NMP	0.05-0.05
MEA-PZ	0.05-0.05
	0.07-0.03
	0.03-0.07

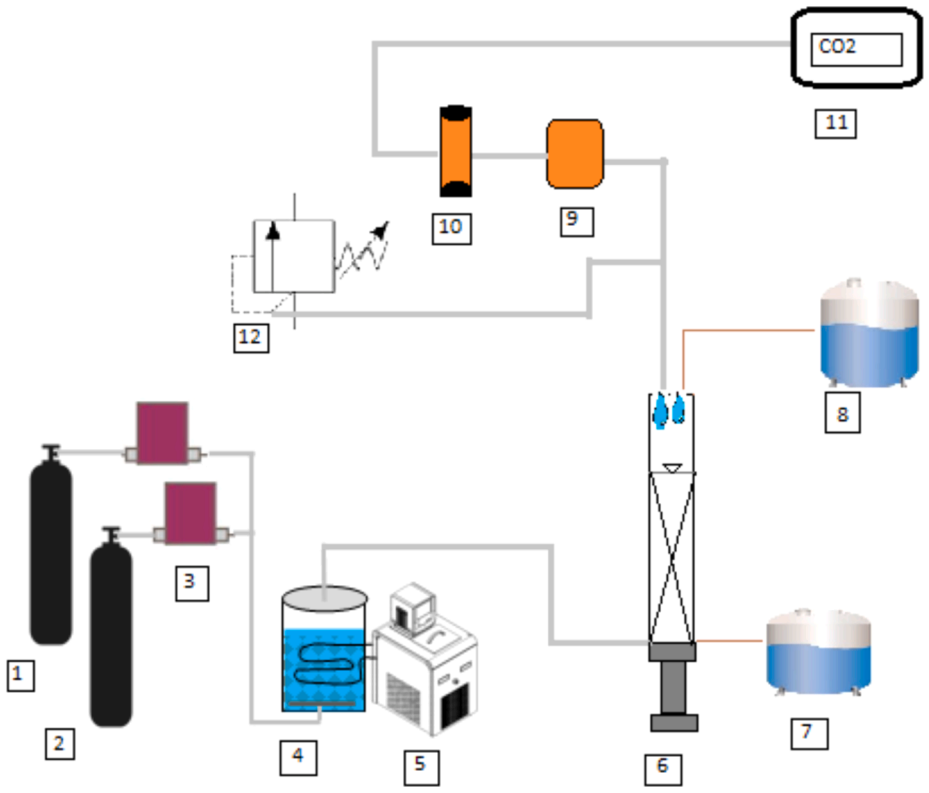

Fig. 3. The experimental setup: 1: CO_2 cylinder, 2: N_2 cylinder, 3: Mass flow controller, 4: Humidifier, 5: Heat exchanger, 6: Column, 7: Waste tank, 8: Solvent tank, 9: Dehumidifier gas regulator, 10: Dehumidifier, 11: CO_2 Analyzer (10.000-100.000ppm), 12: Relief valve.

PZ) and three binary solvent (MEA+NMP; PZ+ NMP; MEA+PZ) is evaluated based on CO_2 removal efficiency, absorption capacity (mol CO_2 / mole solvent), mass transfer coefficient and absorption rate.

4.1. CO_2 Removal Efficiency

Fig. 4 shows the effect of the MEA, PZ and MEA+NMP; PZ+ NMP; MEA+PZ blends (Table 1) at different concentrations on CO_2 removal efficiency (%). As can be seen from the figure, when the MEA solvent increases from 0.025 to 0.1M, the carbon dioxide removal efficiency increase by 20%, the carbon dioxide removal efficiency increased by 38.5% with the PZ solvent. CO_2 reaction rates for PZ were 2–3 times faster than MEA solutions showing that PZ is very effective solvent for CO_2 absorption (Dugas and Rochelle, 2009).

While 0.05 M MEA absorb 25% carbon dioxide, the removal efficiency was 28% when 0.05 NMP was added. Contrary to this Tan et al, reported that at 0.1 MPa and 1 MPa working pressures, MEA aqueous solution had better CO_2 removal performance compared to MEA hybrid solution (Tan et.al., 2015). The reaction rate of MEA was not affected by the addition of physical solvent as reported in (Gordesli and Alper, 2011). While the carbon dioxide removal efficiency of 0.05 M PZ solvent was 36%, when 0.05 M NMP was added, the removal efficiency remained almost the same as 37%.

The highest carbon dioxide removal efficiency of 57.5% was

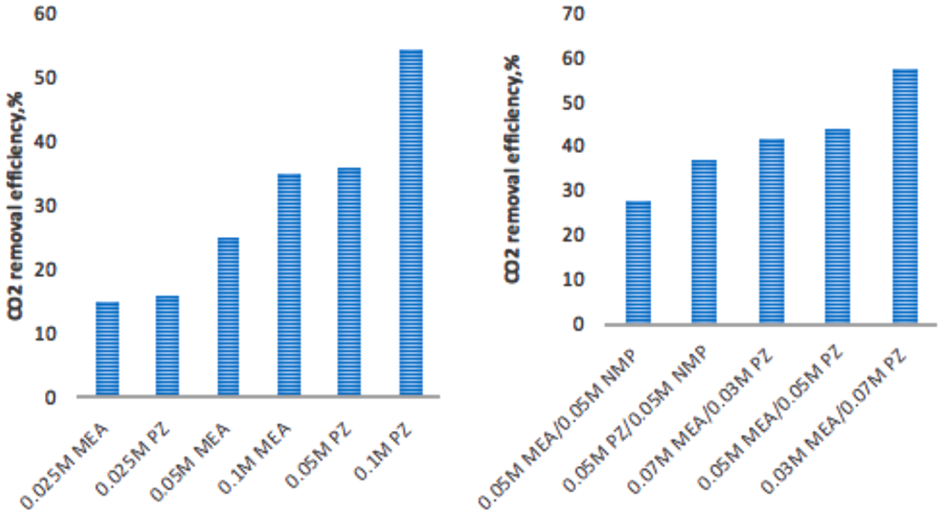

Fig. 4. The effect of solvent concentrations on carbon dioxide removal efficiency (2.5 L.min^{-1} gas flow rate, 200 mL.min^{-1}solvent concentration, 5% CO_2 ppm).

obtained with 0.03 M MEA / 0.07 M PZ solvent in hybrid systems. When the PZ solvent is increased from 0.03 M to 0.07 M, it has been observed that PZ increases the carbon dioxide removal efficiency which can be related to its high absorption rate. PZ solvent has twice the absorption capacity and absorption rate than MEA, and it is mixed with other amine solvents due to its higher regeneration efficiency with an average of 15% lower energy requirement.

Considering the synergistic effects of the mixed solvents; while the expected value of single 0.05 M MEA and 0.05 M PZ solvents (Fig. 4 left) were 25 and 36 % respectivelly, the carbon dioxide removal efficiency of 44% was obtained when used together in a hybrid system (Fig. 4 right). It confirms that the hybrid solution has a synergistic effect.

4.2. Absorption Capacity

A packed column's capacity to remove CO_2 while using an aqueous amine blend depends on its CO_2 absorption capacity, which may be expressed as the amount of CO_2 that is absorbed per mole of amine solution. Fig. 5 represents the experimental outcome of CO_2 loading characteristics of three different aqueous amine blends (MEA+NMP; PZ+ NMP; MEA+PZ) and two different single absorbents (MEA; PZ). The absorption process has been executed with constant process variables including liquid flow rate of 200 mL min^{-1}, gas flow rate of 2.5 L min^{-1}. The highest absorption capacity achieved was 0.217 mol of CO_2 per mole of aqueous 0.05 M PZ in single system. The highest absorption capacity is obtained as 0.148 mol CO_2/mol 0.03 M MEA/ 0.07 M PZ in hybrid system. The absorption capacity decreases per unit mole of absorbent for both MEA and PZ. It may be related to higher amount of unreacted molecules at higher concentrations probably for being trapped in dead zones inside the reactor.

4.3. Overall Mass Transfer

Understanding mass-transfer characteristics like the interfacial area and mass-transfer coefficient thoroughly is necessary to comprehend the processes connected to gas-liquid absorption with chemical reactions. Because there are more solvent molecules per unit volume available to absorb more CO_2 at the gas-liquid interface and more opportunities for CO_2 to come into contact and interact with the active absorbent, a high absorbent concentration enhances the mass transfer coefficient (Tan et. al., 2012). Dugas et al. indicated that overall mass transfer incorporates terms that are strongly amine concentration dependent. MEA or PZ as a promoter has no effect on the solvent's inherent capacity, but it does improve the rate of CO_2 absorption. According to their findings, PZ reacted with CO_2 about ten times faster than MEA (Dugas et al, 2009).

Fig. 6 shows the effect of solvents on overall mass transfer coefficient. The highest overall mass transfer coefficient is achieved to be 2.004 min^{-1} with 0.1 M PZ in single system. The highest overall mass transfer coefficient is obtained to be 2.178 min^{-1} with 0.03 M MEA/ 0.07 M PZ in hybrid system. In comparison, Lin Chang et al., obtained 0.008 min^{-1} overall mass transfer coefficient at 4.4 L/min gas flow rate, 42 ml/min liquid flow rate and 2M MEA using rotate-packed bed reactor (Lin Chang et. al., 2003).

4.4. Absorption Rate

One of the most important factors in calculating the capital cost and energy cost of an amine solvent for CO_2 capture is CO_2 absorption rate. Faster absorption rates require less packing to remove the same amount of CO_2, which lowers the cost of the absorber.

According to the results in Fig. 7, while the absorption rate of 0.1 M MEA is 0.156 $mol.l^{-1}.s^{-1}$, absorption rate of hybrid 0.05 M MEA/0.05 M PZ solution is 0.185 $mol.l^{-1}.s^{-1}$. According to Zhang et al., blends of primary/secondary and tertiary amines can react with CO_2 faster than single tertiary amines and consume less energy than single primary/ secondary amines (Zhang et al., 2017). Bishnoi et al. (Bishnoi et al., 2000) reported the rate constant of PZ with CO_2 is one order of magnitude larger than that of MEA with CO_2. Therefore, a mixture of MEA and PZ should absorb CO_2 more quickly than MEA alone. (Fig. 7). A high removal capacity (mol CO_2/mol absorbent) along with high rate means that for the same amount of CO_2 load, lower volume of absorbent will be required, therefore, regeneration phase will demand less amount of energy where stripping happens upon heating.

5. Conclusion

Chemical absorption is highly effective method for CO_2 capture. Historically, amines have been used in single or blended form due to their high absorption/desorption efficiency. In this study, carbon dioxide absorption using MEA, PZ and NMP and binary solvents (MEA+NMP, PZ+NMP, MEA+PZ) in packed column reactor filled with Raschig ring was investigated. The experiment was operating under counter current regime that had a higher conversion than the co-current operation. NMP was selected as the organic physical solvent because of its low viscosity, being completely miscible in water, and capable to completely mix with different solvents.

The result shows that compared with the single absorbents, blended solvents show better absorption performance because of their synergic

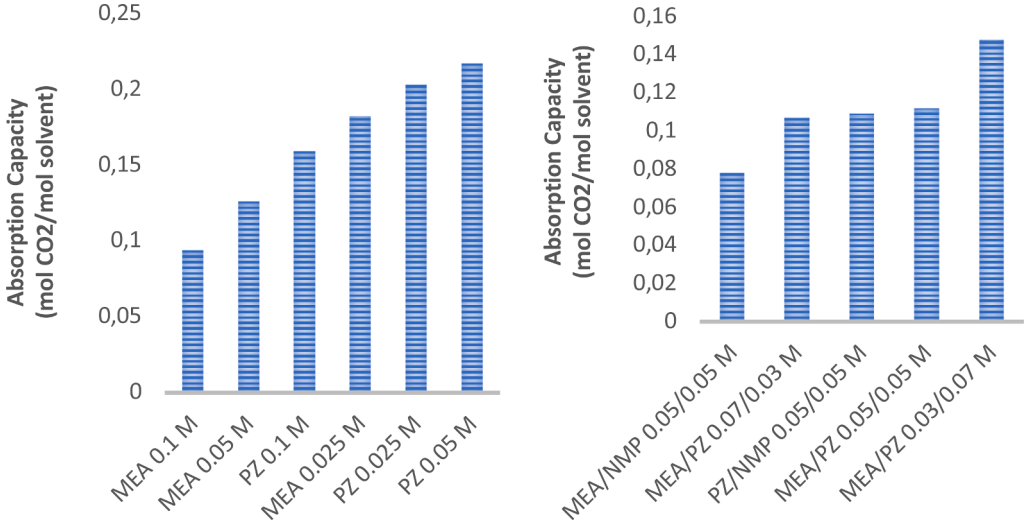

Fig. 5. The effect of solvent concentrations on absorption capacity (2.5 L.min^{-1} gas flow rate, 200 mL.min^{-1} liquid flow rate, 5% CO_2 ppm).

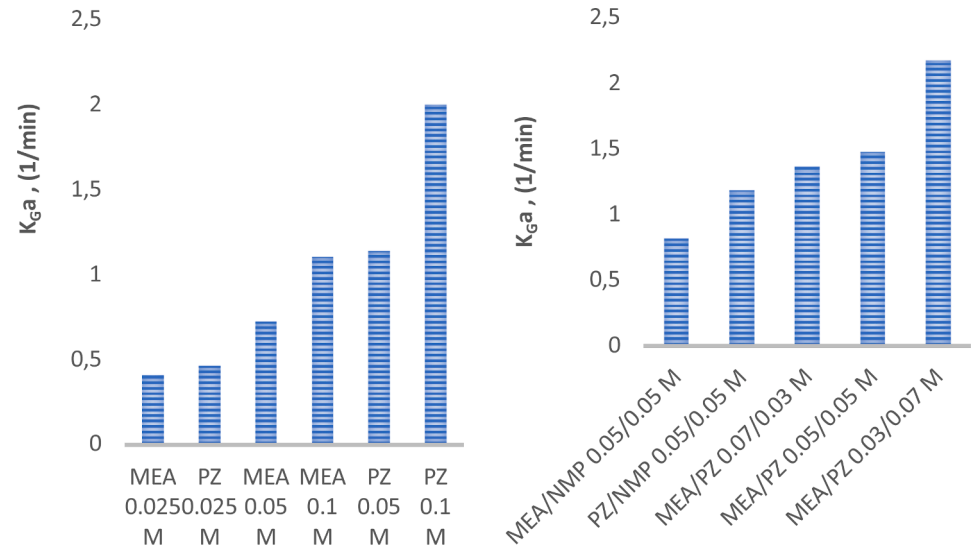

Fig. 6. The effect of solvent concentrations on overall mass transfer coefficient (K_Ga) at (2.5 L.min^{-1} gas flow rate, 200 mL.min^{-1} liquid flow rate, 5% CO_2 ppm).

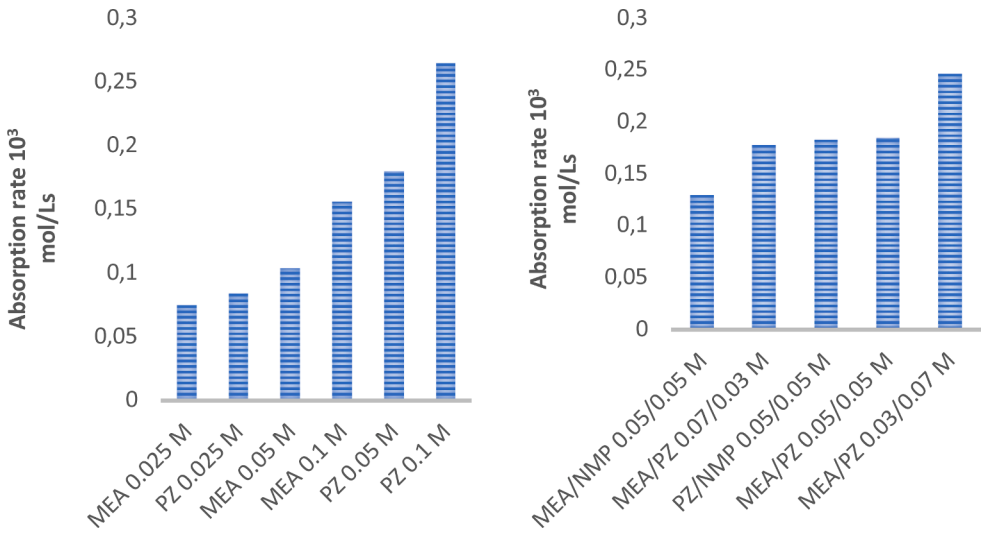

Fig. 7. The effect of solvent concentrations on absorption rate (2.5 L.min^{-1} gas flow rate, 200 mL.min^{-1} solvent concentration, 5% CO_2 ppm).

enhancement effect which could be related to the availability of more than two pathways that can happen in the case of hybrid systems. It was concluded that mixing MEA solvent with PZ solvent improves absorption performance, whereas NMP organic solvent has no effect. The highest absorption capacity with 0.148 mol CO_2/mol solvent, the highest mass transfer coefficient with 2.178 1/min, and the highest absorption rate with 0.247 mol/Ls is obtained with using 0.03 M MEA/0.07 M PZ in hybrid system. The effectiveness of the blends for removal of CO_2 in low concentrations would facilitate low cost capture processes. A packed bed reactor generally causes lower pressure drop comparing with a bubble column reactor where the gas phase needs to overcome a static pressure.

Contribution to the literature can be made by studying the cost analysis of the mixture of PZ and NMP, experimental studies under higher pressure, and its effects on the environment.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Ayse Gul reports financial support was provided by Anadolu University. Ayse Gul reports a relationship with Anadolu University that includes: funding grants. Ayse Gul has patent #project no. 1706F386 issued to Assignee.

Data availability

The data that has been used is confidential.

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Statement of novelty

The novelty of the work is the application of different absorbents in low concentration (< 0.1 M) where some of them like NMP has not been studied well in a countercurrent packed column in open literature. This study is important also showing the performance of hybrid absorbents when challenging low CO_2 concentration (5%) capture is sought.

Additionally, PZ and NMP mixture experiment has not been presented in the literature. The outcomes are very interesting for researchers in the field of carbon dioxide capturing and clean energy.

References

Ali, B.S., Aroua, M., 2004. Effect of piperazine on CO 2 loading in aqueous solutions of MDEA at low pressure. Int. J. Thermophys. 25 (6), 1863–1870.

Aronu, U.E., et al., 2011. Solubility of CO2 in 15, 30, 45 and 60 mass% MEA from 40 to 120°C and model representation using the extended UNIQUAC framework. Chem. Eng. Sci. 66 (24), 6393–6406.

Bishnoi, S., Rochelle, G.T., 2000. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. Chem. Eng. Sci. 55, 5531–5543.

Chen, P.C., Liao, C.C., 2014. A study on CO2 absorption in bubble column using DEEA/EEA mixed solvent. Int. J. Eng. Pract. Res.

Chen, G., Chen, G., Peruzzini, M., Zhang, R., Barzagli, F., 2022. Understanding the potential benefits of blended ternary amine systems for CO2 capture processes through 13C NMR speciation study and energy cost analysis. Sep. Purif. Technol. 291 (120939), 120939.

De Guido, G., 2023. Cryogenic CO2 capture from oxy-combustion flue gas by a hybrid distillation + physical absorption process. Chem. Eng. Res. Des.

Diego, M.Elena, Bellas, J.M., Pourkashanian, M., 2017. Process analysis of selective exhaust gas recirculation for CO2 capture in natural gas combined cycle power plants using amines. J. Eng. Gas Turbine Power 139 (12), 121701.

Dugas, R., Rochelle, G., 2009. Absorption and desorption rates of carbon dioxide with monoethanolamine and piperazine. Energy Procedia 1, 1163–1169.

Eskandari, M., Elhambakhsh, A., Rasaie, M., Keshavarz, P., Mowla, D., 2022. Absorption of carbon dioxide in mixture of N-Methyl-2-Pyrrolidone and six different chemical solvents. J. Mol. Liq. 364 (119939), 119939.

Fu, H., Xue, K., Li, Z., Zhang, H., Gao, D., Chen, H., 2022. Study on the performance of CO2 capture from flue gas with ceramic and PTFE membrane contactors. Energy, 125677.

Gül, A., et al., 2023. Optimization of carbon dioxide absorption in a continuous bubble column reactor using response surface methodology. Environ. Qual. Manage. 33 (1), 79–93.

Gordesli, P.F., Alper, E., 2011. The kinetics of carbon dioxide capture by solutions of piperazine and N-methyl piperazine. Int. J. Global Warming 3 (Nos. 1/2).

Halim, H.N.A., Shariff, A.M., Bustam, M.A., 2015. High pressure CO2 absorption from natural gas using piperazine promoted 2-amino-2-methyl-1-propanol in a packed absorption column. Sep. Purif. Technol. 152, 87–93.

He, X., He, H., Barzagli, F., Amer, M.W., Li, C., Zhang, R., 2023. Analysis of the energy consumption in solvent regeneration processes using binary amine blends for CO2 capture. Energy (Oxf.) 270 (126903), 126903.

Jiang, L., Gonzalez-Diaz, A., Ling-Chin, J., Roskilly, A.P., Smallbone, A.J., 2019. Post-combustion CO2 capture from a natural gas combined cycle power plant using activated carbon adsorption. Appl. Energy 245, 1–15.

Karlsson, H., Sanku, K., Svensson, M.G.H., 2020. Absorption of carbon dioxide in mixtures of N-methyl-2 pyrrolidone and 2-amino-2-methyl-1-propanol. Int. J. Greenhouse Gas Control 95.

La Rubia, M.D., et al., 2010. Interfacial area and mass transfer in carbon dioxide absorption in TEA aqueous solutions in a bubble column reactor. Chem. Eng. Process. 49 (8), 852–858.

Li, T., et al., 2023. Energy efficient catalytic CO2 desorption: mechanism, technological progress and perspective. Carbon Capture Sci. Technol. 6 (100099), 100099.

Lin Chang, C., Tzong Liu, W., Sung Tan, C., 2003. Removal of Carbon Dioxide by Absorption in a Rotating Packed Bed. Ind. Eng. Chem. Res. 42, 2381–2386.

Liu, F., Qi, Z., Fang, M., Ding, H., 2023. Pilot test of water-lean solvent of 2-(ethylamino) ethanol, 1-methyl-2-pyrrolidinone, and water for post-combustion CO2 capture. Chem. Eng. J. 459 (141634), 141634.

Ma, S., et al., 2016. Mass transfer of ammonia escape and CO2 absorption in CO2 capture using ammonia solution in bubbling reactor. Appl. Energy 162, 354–362.

Mauna Loa, 2023 July https://gml.noaa.gov/ccgg/.

Mirzaei, F., Ghaemi, A., 2018. An experimental correlation for mass transfer flux of CO2 reactive absorption into aqueous MEA-PZ blended solution. Asia Pacific J. Chem. Eng. 13, 6. https://doi.org/10.1002/apj.2250.

Pakzad, P., Mofarahi, M., Izadpanah, A.A., Afkhamipour, M., Ha Lee, C., 2018. An experimental and modeling study of CO_2 solubility in a 2-amino-2-methyl-1-propanol (AMP) + N-methyl-2-pyrrolidone (NMP) solution. Chem. Eng. Sci. 175, 365–376.

Pashaei, H., Ghaemi, A., Nasiri, M., 2017. Experimental investigation of CO2 removal using Piperazine solution in a stirrer bubble column. Int. J. Greenhouse Gas Control 63, 226–240.

Peng, Y., Zhao, B., Li, L., 2012. Advance in post-combustion CO2 capture with alkaline solution: a brief review. Energy Procedia 14, 1515–1522.

Qi, Z., Liu, F., Ding, H., Fang, M., 2023. Bench-scale CO2 capture using water-lean solvent of 2-(ethylamino) ethanol, 1-methyl-2-pyrrolidinone, and water. Fuel (Lond.) 350 (128726), 128726.

Qie, Z., Wang, L., Sun, F., Xiang, H., Wang, H., Gao, J., Zhao, G., Fan, X., 2022. Tuningporosity of coal-derived activated carbons for CO2 adsorption. Front. Chem. Sci. Eng. 16, 1345–1354.

Ramezani, R., Mazinani, S., Felice, R.D., Darvishmanesh, S., Bruggen, B.V., 2017. Selection of blended absorbents for CO_2 capture from flue gas: CO_2 solubility, corrosion and absorption rate. Int. J. Greenhouse Gas Control 62, 61–68.

Shen, Y., Gong, Y., Sun, L., Chen, P., Zhang, Q., Ye, J., Wang, L., Zhang, S., 2023. Machine learning-driven assessment of relationship between activator properties in phase change solvent and its absorption performance for CO2 capture. Sep. Purif. Technol. 309, 123092.

Smerigan, A., Uludag-Demirer, S., Cutshaw, A., Marks, A., Liao, W., 2023. High-efficiency carbon dioxide capture using an algal amino acid salt solution. J. CO2 Util. 69 (102394), 102394.

Tan, L.S., Shariff, A.M., Lau, K.K., Bustam, M.A., 2012. Factors affecting CO2 absorption efficiency in packed column: A review. J. Ind. Eng. Chem. 18 (6), 1874–1883.

Tan, L.S., Shariff, A.M., Lau, K.K., Bustam, M.A., 2015. Impact of high pressure on high concentration carbon dioxide capture from natural gas by monoethanolamine/N-methyl-2-pyrrolidone solvent in absorption packed column. Int. J. Greenhouse Gas Control 34, 25–30.

Tippayawong, N., Thanompongchart, P., 2010. Biogas quality upgrade by simultaneous removal of CO2 and H2S in a packed column reactor. Energy 35 (12), 4531–4535.

Vaidya, P.D., Kenig, E.Y., 2009. CO2 capture by Novel Amine Blends. In: Alfadala, H.E., Rex Reklaitis, G.V., El-Halwagi, M.M. (Eds.), Proceedings of the 1st Annual Gas Processing Symposium. Elsevier, Amsterdam, pp. 239–246. Editors.

Wang, Y., et al., 2021. Carbon dioxide capture by non-aqueous blend in rotating packed bed reactor: Absorption and desorption investigation. Sep. Purif. Technol. 269 (118714), 118714.

Yeh, J.T., Pennline, H.W., Resnik, K.P., 2001. Study of CO2 absorption and desorption in a packed column. Energy Fuels 15 (2), 274–278.

Yuan, Y., Rochelle, G.T., 2018. CO2 absorption rate in semi-aqueous monoethanolamine. Chem. Eng. Sci. 182, 56–66.

Zhang, R., Zhang, X., Yang, Q., Yuc, Hai, Lianga, Zhiwu, Luo, Xiao, 2017. Analysis of the reduction of energy cost by using MEA-MDEA-PZ solvent for post-combustion carbon dioxide capture (PCC). Appl. Energy 205, 1002–1011.

Zhang, T., Yu, Y., Zhang, Z., 2018. " An interactive chemical enhancement of CO_2 capture in the MEA/PZ/AMP/DEA binary solutions". Int. J. Greenhouse Gas Control 74, 119–129.

Zhang, R., Liu, R., Barzagli, F., Sanku, M.G., Li, C., Xiao, M., 2023b. CO2 absorption in blended amine solvent: Speciation, equilibrium solubility and excessive property. Chem. Eng. J. 466 (143279), 143279.

Zhang, R., et al., 2023a. Investigation of the improvement of the CO2 capture performance of aqueous amine sorbents by switching from dual-amine to trio-amine systems. Sep. Purif. Technol. 316 (123810), 123810.

Zhang, R., et al., 2023c. Energy-saving effect of low-cost and environmentally friendly sepiolite as an efficient catalyst carrier for CO2 capture. ACS Sustain. Chem. Eng. 11 (11), 4353–4363.

Zhao, X., Smith, K.H., Simioni, M.A., Tao, W., Kentish, S.E., Fei, W., Stevens, G.W., 2011. Comparison of several packings for CO2 chemical absorption in a packed column. Int. J. Greenhouse Gas Control 5, 1163–1169.

Zhong, X., Li, C., Hu, X., Zhang, R., 2023. A modified semi-empirical model for correlating and predicting CO2 equilibrium solubility in aqueous 2-[2-(dimethylamino)ethoxy]ethanol solution. Sep. Purif. Technol. 323 (124364), 124364.