

## Selection of efficient absorbent for CO<sub>2</sub> capture from gases containing low CO<sub>2</sub>

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**Abstract**—Amine-based absorption processes are widely used in natural gas processing, but recently they have been considered for CO<sub>2</sub> capture from flue gas emitted from thermal power plants. The main issue of amine used in the CO<sub>2</sub> capture process is the high cost of solvent regeneration. So, this issue can be solved by using efficient amine absorbent. The amine type absorbents employed in the experimentation were an aqueous blend of 2-(Diethylamino)ethanol (DEEA) with different types of diamine activators such as piperazine (PZ), 2-(2-aminoethylamino)ethanol (AEEA), hexamethylenediamine (HMDA), ethylenediamine (EDA), and 3-(Dimethylamino)-1-propylamine (DMAPA). An absorption experiment was performed to evaluate the CO<sub>2</sub> absorption performance in terms of CO<sub>2</sub> loading, absorption capacity, and absorption rate. The experiment was performed to assess the CO<sub>2</sub> desorption performance in terms of desorption capacity, desorption rate, cyclic capacity, and regeneration efficiency. From the results of absorption-desorption and comparison with benchmark amine absorbent MEA, the aqueous blend of DEEA and HMDA indicated the best performance for CO<sub>2</sub> capture applications among all the tested amine blends.

**Keywords:** CO<sub>2</sub> Loading, Absorption-desorption Rate, Cyclic Capacity, Regeneration Efficiency, 2-(Diethylamino) Ethanol, Diamine

### INTRODUCTION

The global energy demand has been increasing due to rapid industrialization and urbanization, which has created various environmental problems, such as global warming and climate change due to the continuous release of prime greenhouse gas CO<sub>2</sub> into the atmosphere by various industries. The CO<sub>2</sub> present in the gas stream has been released from industries like fossil-fuel based thermal power plants for electricity generation, iron and steel industry, cement production, natural gas processing, oil refinery, chemical, and petrochemical manufacturing units. In which, the fossil-fuel based thermal power plants industries are mainly responsible for CO<sub>2</sub> emission as it contributes approximately 40% of total CO<sub>2</sub> emission in the world. Among fossil-fuel based power plants, coal-fired thermal power plants have a significant role in the global CO<sub>2</sub> emission of approximately 31% [1]. The coal-fired thermal power plants release a large amount of exhaust gas, which contains 12-16% CO<sub>2</sub> [2]. However, the global CO<sub>2</sub> emission has increased up to 70% from 1971 to 2002, and also the energy-related CO<sub>2</sub> emissions in the world are increasing at a rapid rate of about 2.1% per year, which has made the emphasis on the reduction of CO<sub>2</sub> emission at the global scale [3].

Currently, carbon capture and sequestration (CCS) is the best option for removing the CO<sub>2</sub> from a different gas stream such as flue gas, natural gas, refinery gas, and blast furnace gas. Several types of separation technologies, such as absorption, adsorption, cryogenic, membrane separation, and chemical looping, have been used

for CO<sub>2</sub> removal from different gas streams. Among these, absorption technology using amine-based solvent has been widely used because it has good absorption efficiency, is capable of removing lean CO<sub>2</sub> level present in the gas stream, has a large volume of exhaust gas conditioning capacity [4], retrofitting option, cost-effectiveness, and an option for solvent regeneration [5,6]. Therefore, amine absorbents such as alkanolamine and polyamine have been used in the removal of CO<sub>2</sub> from a gas stream. The different types of amine absorbents such as primary amine monoethanolamine (MEA), secondary amine diethanolamine (DEA), tertiary amine N-methyl diethanolamine (MDEA), sterically-hindered amine 2-amino-2-methyl-1-propanol (AMP), and polyamine piperazine (PZ) are widely used in the removal of CO<sub>2</sub> from different gas streams [7].

Several researchers measured the CO<sub>2</sub> capture performance of different tertiary amines, such as 3-dimethylamino-1-propanol (DMAP-31) [8,9], 2-(Diethylamino)ethanol (DEEA) [8], 2-(2-(dimethylamino) ethoxy) ethanol (DMAEOE) [9], 1,2-bis (dimethylamino) ethane (TEMED) [9], methyl-4-morpholine [9], pyridine [9], 2-(Dimethylamino)ethanol (DMEA) [8,10], ethyldiethanolamine (EDEA) [11] and butyldiethanolamine (BDEA) [11], in terms of CO<sub>2</sub> loading, overall mass transfer coefficient, physical solubility, absorption rate, desorption rate, and cyclic capacity at various operating conditions using laboratory scale setup. Also, various researchers measured the performance of different single polyamines such as 1, 3-diaminopropane (DAP) [12,13], ethylenediamine (EDA) [13], N-methylethylenediamine (MEDA) [13], N-methylpropane-1, 3-diamine (MAPA) [13], 2-Dimethylaminoethylamine (DMAEA) [13], 3-Dimethylaminopropylamine (DMAPA) [13], diethylenetriamine (DETA) [14], triethylenetetramine (TETA) [14], tetraethylene-pentamine (TEPA) [14] and 1-(2-aminoethyl)piperazine (AEP) [15] for CO<sub>2</sub> capture.

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The polyamine performance was measured in terms of CO<sub>2</sub> loading, absorption capacity, absorption rate, desorption rate, apparent absorption rate, overall mass transfer coefficient, ions species concentration and cyclic capacity at various operating conditions by using different experimental apparatus. Liu et al. [16] studied eleven different single amines using novel screening method and selected secondary amine 2-(methylamino)ethanol and (MAE) 2-(ethylamino)ethanol (EAE) as a potential solvent for CO<sub>2</sub> capture. Among these single amine absorbents, MEA has been widely used in the industries for CO<sub>2</sub> removal from a several gas stream [17], but its major drawbacks include low absorption capacity [18], high regeneration energy, high thermal degradation [19], and corrosive behavior at higher concentrations more than 30 wt% [20]. The drawback of secondary amine is the limited CO<sub>2</sub> absorption capacity. Also, the tertiary amine has a low CO<sub>2</sub> absorption rate as the main drawback. Sterically hindered amine such as AMP precipitated at higher concentration (above 3M), resulting from clogging in a pipe used in the CO<sub>2</sub> capture process [21].

To overcome these drawbacks of single amine absorbent, researchers have been attracted to the development of amine blend absorbent to improve the existing solvent performance for CO<sub>2</sub> capture. The first researcher [22] suggested alternative absorbent as an amine blend of tertiary amine or sterically-hindered amine with primary or secondary amine for the improvement of CO<sub>2</sub> capture from a gas stream. Consequently, significant efforts have been made for improving the CO<sub>2</sub> absorption performance [23,24], showing that a blend of amines of MDEA and/or AMP [25,26] and MEA or DEA [27] has better absorption performance than single amine MEA, DEA, MDEA, and AMP [28,29]. But recently, the aqueous blend of tertiary amine DEEA and polyamine has attracted more for CO<sub>2</sub> capture because DEEA has better absorption performance than conventional tertiary amine MDEA, and it can be prepared from renewable sources like agricultural residue or waste products [30,31]. Also, polyamines show better CO<sub>2</sub> absorption than primary and secondary monoamines due to the presence of multiple reaction sites available to absorb a large amount of CO<sub>2</sub> in the solvent [15]. However, a single polyamine solvent used at high concentration showed degradation behavior and also has a high material cost, so it may not be preferred for CO<sub>2</sub> capture at industrial scale [32,33].

At a low partial pressure of CO<sub>2</sub> in the gas stream, the absorption capacity and absorption rate of diamine are more than primary/secondary/tertiary/sterically hindered amine. Also, the diamine shows low thermal degradation behavior and material cost comparison to triamine and tetramine. Therefore, researchers used different laboratory scale apparatus for testing the potential of individual DEEA based aqueous amine blend for CO<sub>2</sub> capture by adding different diamines such as Piperazine [34], N-Methyl-1,3-diaminopropane [35,36], 1,4-Butanediamine [37], 2-(2-aminoethyl amino) ethanol [38], 1,6-hexanediamine [39]; and capture performance has been evaluated in terms of CO<sub>2</sub> loading, absorption capacity, absorption/desorption rate, cyclic capacity, absorption heat, mass transfer coefficient, and reaction rate constant of CO<sub>2</sub>. Researchers [40] have also selected an efficient solvent among various DEEA based amine blends by using different types of additives as a primary amine (MEA), secondary amine (DEA), sterically-hindered amine (AMP, EAE), diamine (PZ, AEEA), triamine (DETA), tetra-

mine (TETA) with the help of the absorption-desorption screening experiments.

Several researchers developed advanced solvent systems such as liquid biphasic solvents [41,42] and catalyzed the solvent system by using carbonic anhydrase enzyme [43,44] for CO<sub>2</sub> capture process to reduce the regeneration heat duty and improve capture performance. Consequently, Zhang et al. studied the different liquid biphasic solvents [45] for CO<sub>2</sub> capture and reported a comprehensive list of absorbents. But, liquid biphasic solvent required unconventional handling cost and catalyzed solvent system required temperature limitation for CO<sub>2</sub> capture process [46]. Also, little information is available on an amine blend of DEEA with diamine absorbent promising for the CO<sub>2</sub> capture [47]. So, due to drawbacks of liquid biphasic solvent, catalyzed solvent system and limited information on DEEA+diamine solvent, the present work focused on the selection of the potential solvent for CO<sub>2</sub> capture among various DEEA based amine blend using five different types of diamines such as PZ, AEEA, HMDA, EDA, and DMAPA. Because, a potential absorbent has a significant role in the design and selection of absorption-desorption column, heat exchanger, and pump applied in the CO<sub>2</sub> capture process.

In the present work, five amine blends such as DEEA+PZ, DEEA+AEEA, DEEA+HMDA, DEEA+EDA, and DEEA+DMAPA have been proposed for selecting efficient absorbent for CO<sub>2</sub> capture. The CO<sub>2</sub> absorption-desorption experiments were performed at atmospheric pressure. The absorption experiment was conducted at 313.15 K and CO<sub>2</sub> partial pressure 20.26 kPa to evaluate the absorption performance parameters. A desorption experiment was conducted at 363.15 K to evaluate desorption performance parameters. Among the proposed amine blends, the best amine blend was selected based on evaluation of performance parameters concerning CO<sub>2</sub> loading, absorption rate, desorption rate, cyclic capacity, and regeneration efficiency. The performance of amine blends was also compared with that of benchmark absorbent MEA as well as DEEA to see the potential of different diamine blended in DEEA solution.

## EXPERIMENTAL

### 1. Materials

The analytical grade chemicals 2-(Diethylamino)ethanol (SD-Fine Chem. Ltd., Mumbai), hexamethylenediamine (Tokyo Chemical Industries Co. Ltd., Japan), 2-(2-Aminoethylamino) ethanol (SD-Fine Chem. Ltd., Mumbai), Ethylenediamine (Sisco Research Laboratories Pvt. Ltd., Mumbai), 3-(Dimethylamino)-1-propylamine (Sigma-Aldrich Chemicals Pvt. Ltd., Bangalore) and anhydrous piperazine (SD-Fine Chem. Ltd., Mumbai) with minimum mass purity of 98% were used without any further purification. Monoethanolamine (SD-Fine Chem. Ltd., Mumbai) with purity greater than 99% was used as a reference amine for validation and comparison with all proposed amine blends studied in the present work. Hydrochloric acid with 37% mass purity without any further purification was used in the measurement of amine solution concentration and determination of CO<sub>2</sub> loading in all amine solutions. The required concentration of amine blend solution for the experiment was prepared by dissolving in double distilled water. The

total concentration of final prepared amine blend solution was analyzed by titrating with 1 M HCl solution to check the accuracy of solution concentration. The pH of prepared amine solutions was measured by microprocessor-based pH meter (Elico, accuracy:  $\pm 0.02$ ). Two commercial grade gas cylinders, first containing a composition of 20% CO<sub>2</sub> balanced with N<sub>2</sub> gas and second containing 99.99% N<sub>2</sub> were supplied by Narayan Gas Company, India. The CO<sub>2</sub> simulated gas stream of desired concentration was prepared with the help of simulating gas chamber made of stainless steel and gas flow rotameter (Alicat, range: 0-3 LPM) to set at a fixed flow rate. A portable infrared flue gas analyzer (Gasboard-3800P, CO<sub>2</sub> range: 0-100% by volume) with an accuracy of  $\pm 0.2\%$  was used for the analysis of CO<sub>2</sub> in the gas phase. Thermometers with temperature subdivisions of 0.1 K were used to measure the water and oil bath temperature as well as solutions placed in the bubble column and flask. The temperature programmed hot-plate magnetic stirrer (range: 0-473.15 K, accuracy:  $\pm 0.01$  K) was used to heat solutions present in the flask.

## 2. Experimental Set-up and Procedure

### 2-1. CO<sub>2</sub> Absorption Experiment

A schematic diagram of the experimental set-up for absorption studies is shown in Fig. 1. The little-modified absorption setup as compared to our previous work [38] was used in the present work. This experimental setup operating at atmospheric pressure was used for determination of absorption performance parameters such as CO<sub>2</sub> loading, absorption capacity, and absorption rate. In this setup, a borosilicate glass bubble column having a liquid holding capacity of 250 ml was kept inside temperature maintained water circulating bath. Then, the desired concentration of amine blend of 150 ml solution was loaded in the column. After that, nitrogen

gas was passed at a low flow rate of approximately 15 min throughout the whole gas-liquid system to remove previously present trace gases with the starting of each experiment. Then, CO<sub>2</sub> simulated gas stream fixed concentration of 20% v/v and flow rate of 250 ml/min. was passed through water saturation column to bubble column for the absorption of CO<sub>2</sub> in the amine solution. After the gas-liquid contact, bubbles were formed in the liquid bed of the column during the continuous flow of CO<sub>2</sub> gas stream and outlet gas stream emitted from the column was passed through silica bed column to absorb moisture present in the gas stream. The concentration of the dried gas stream was measured by using a portable flue gas analyzer at a regular time interval of 5 min. The gas flow was continued until the CO<sub>2</sub> concentration in outlet gas stream became equal to the inlet gas stream, a phenomenon also known as gas-liquid equilibrium. However, for evaluating the absorption performance parameters, partially absorbed CO<sub>2</sub> solution sample was collected at a regular time of interval of 10 min up to 60 min during the experiment for measuring the absorption rate. Finally, for evaluating the CO<sub>2</sub> loading and absorption capacity with time, a fixed volume (1 ml) of saturated and partial CO<sub>2</sub> absorbed solutions, respectively, were titrated with 1 M HCl solution, and the volume of evolved CO<sub>2</sub> was measured using water-displacement column (its details are provided in the previously studied work [48]).

### 2-2. CO<sub>2</sub> Desorption Experiment

A schematic diagram of the experimental set-up for desorption studies is shown in Fig. 2. A desorption setup operating at atmospheric pressure was used for determination of performance parameters such as desorption capacity, desorption rate, and cyclic capacity of CO<sub>2</sub>. A four-necked round bottom flask made up of a borosilicate glass, having a liquid holding capacity of 250 ml was used in

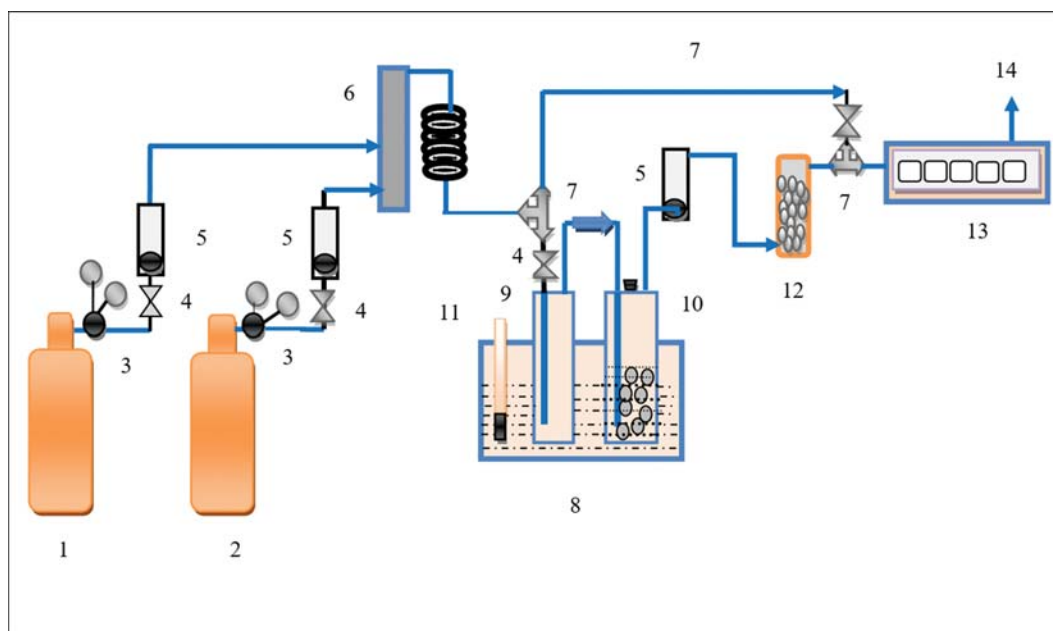


Fig. 1. Schematic diagram of absorption set-up.

- |                             |                                    |                                      |                                      |
|-----------------------------|------------------------------------|--------------------------------------|--------------------------------------|
| 1. CO <sub>2</sub> cylinder | 5. Gas-flow rotameter              | 9. Water saturator                   | 12. Silica bed column                |
| 2. N <sub>2</sub> cylinder  | 6. Gas simulation chamber          | 10. Bubble column fitted with septum | 13. Portable multi-flue gas analyzer |
| 3. Pressure regulator       | 7. Glass tee                       | 11. Thermometer                      | 14. Exhaust                          |
| 4. Stainless steel valve    | 8. Constant temperature water bath |                                      |                                      |

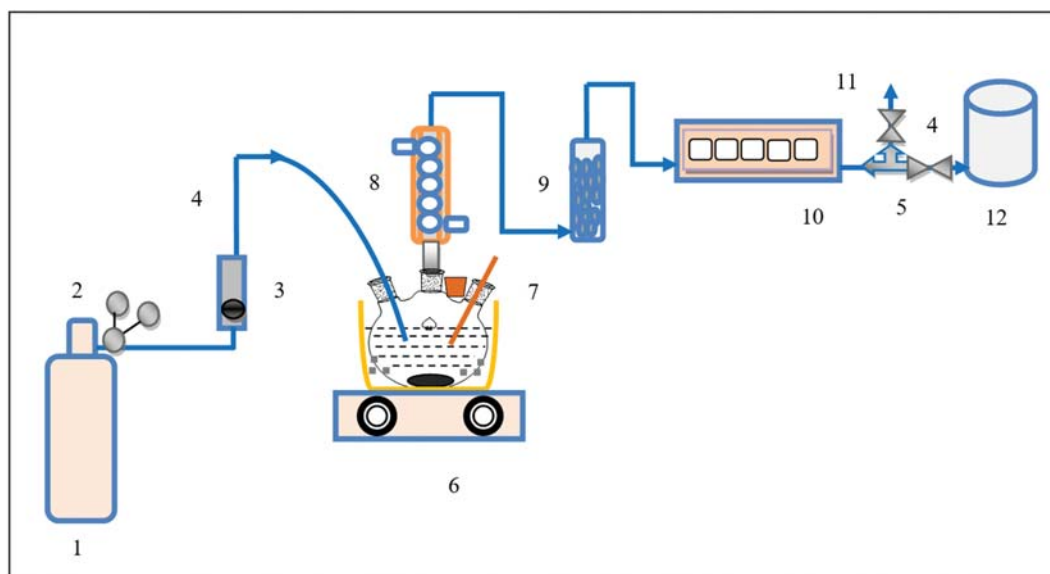


Fig. 2. Schematic diagram of desorption set-up.

- |                            |                                       |                                      |
|----------------------------|---------------------------------------|--------------------------------------|
| 1. N <sub>2</sub> cylinder | 6. Heating and magnetic stirrer       | 9. Silica bed column                 |
| 2. Pressure regulator      | 7. Four necked round bottom flask     | 10. Portable multi-flue gas analyzer |
| 3. Gas flow meter          | placed in silicon oil bath and fitted | 11. Exhaust                          |
| 4. Stainless steel valve   | with septum and thermometer           | 12. Gas storage tank                 |
| 5. Glass tee               | 8. Condenser                          |                                      |

the desorption process. A flask fitted with a condenser, septum, and thermometer dipped in an oil bath was placed on the temperature programmed hot plate magnetic stirrer heater and the stirring speed was set at 600 rpm. The previous CO<sub>2</sub> saturated amine solution was further used for desorbing CO<sub>2</sub>. A carbonated amine blend solution of 100 ml was filled in the flask, and before starting the experiment N<sub>2</sub> gas with a flow rate of 1,000 ml/min was continuously purged in an entire gas-liquid system to remove the trace gases present in the system. The heater was started and maintained the temperature required for the desorption process. The dissolved CO<sub>2</sub> gas was released continuously after heating, and the outlet vapor stream was passed through a condenser to prevent losses of amine solution. The discharged vapor stream was passed through a silica bed column for absorbing moisture present in the stream. The final outlet gas stream was passed through portable flue gas analyzer for measuring the concentration of CO<sub>2</sub> at a regular time interval of 5 min. A fixed amount of partial desorbed solution was collected with a syringe at a regular time intervals of 5 min up to 60 min, and it was required for the evaluation of the desorption rate. The desorption process was stopped when the outlet concentration of CO<sub>2</sub> was less than 1% by volume. After desorption of CO<sub>2</sub>, a fixed amount (1 ml) of the desorbed solution was titrated with 1 M HCl solution to calculate the desorption capacity as well as desorption rate as described in the earlier section. Finally, at room temperature and pressure, three successive analyses of the entire absorbed and desorbed samples were performed to calculate the CO<sub>2</sub> loading at rich and lean conditions, and the results were found to be reproducible within 1.0% error.

### 2-3. Calculation of CO<sub>2</sub> Loading

The amount of CO<sub>2</sub> absorbed in amine solution is called CO<sub>2</sub>

loading. It is expressed by the ratio of a mole of CO<sub>2</sub> to the mole of amine. The CO<sub>2</sub> loading is determined by direct-titration methods [49]. Mathematically, it follows as:

$$\text{CO}_2 \text{ loading } (\alpha_{\text{CO}_2}) = \frac{V_{\text{CO}_2} - V_{\text{HCl}}}{22.4 \times M_{\text{sample}} \times V_{\text{sample}}} \times \frac{273.15}{373.15 + T_{\text{RT}}} \quad (1)$$

where,  $\alpha_{\text{CO}_2}$  is the CO<sub>2</sub> loading in mol CO<sub>2</sub>/mol amine,  $V_{\text{CO}_2}$  is the volume of CO<sub>2</sub> evolved in ml,  $V_{\text{HCl}}$  is the volume of HCl in ml,  $M_{\text{sample}}$  is the molarity of amine sample in M,  $V_{\text{sample}}$  is the volume of amine sample in ml,  $T_{\text{RT}}$  is the room temperature in K.

### 2-4. Calculation of Absorption and Desorption Rate

It may be determined by the linear slope of plot drawn by CO<sub>2</sub> loading versus absorption or desorption time, and is also called apparent absorbent or desorption rate. It is expressed as the ratio of mole of CO<sub>2</sub> to the product of volume of amine as well as absorption or desorption time. The unit of absorption or desorption rate is mol CO<sub>2</sub>/L solution.s.

### 2-5. Calculation of Cyclic Capacity and Regeneration Efficiency

Regeneration performance of amine blend solution was evaluated in terms of CO<sub>2</sub> cyclic capacity. It is defined as the difference between absorption capacity and desorption capacity. Regeneration efficiency is represented as the percentage ratio of the cyclic capacity of CO<sub>2</sub> to the absorption capacity or CO<sub>2</sub> loading at absorption condition.

Mathematically, it follows as:

$$\begin{aligned} \text{Cyclic capacity (mol of CO}_2\text{/L solution)} \\ = \text{Absorption capacity (mol of CO}_2\text{/L solution)} \\ - \text{Desorption capacity (mol of CO}_2\text{/L solution)} \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Regeneration efficiency (\%)} \\ = (\text{Cyclic capacity/Absorption capacity}) \times 100 \end{aligned} \quad (3)$$

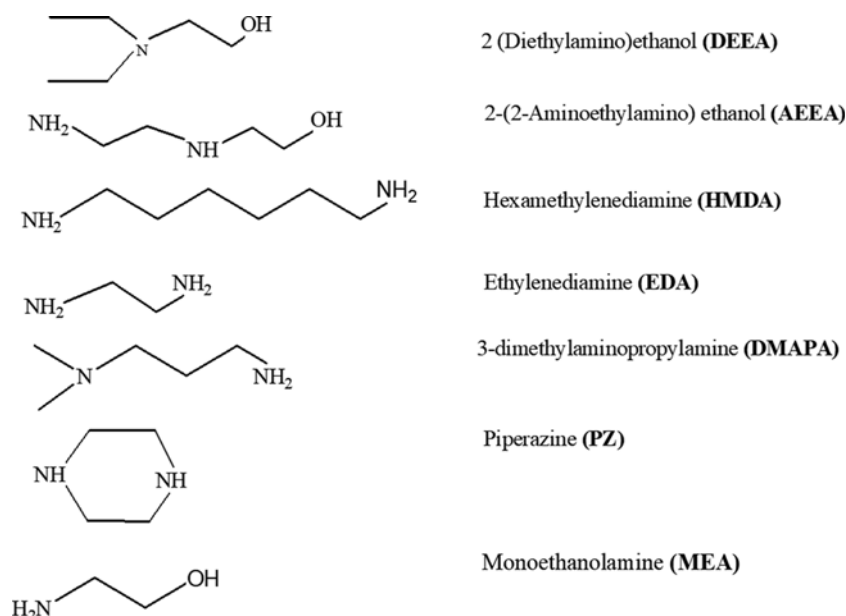


Fig. 3. Chemical structure of alkanolamines and diamines used in present work.

## RESULTS AND DISCUSSION

### 1. Validation

The concentration of the amine solution was taken in molarity (M) unit, because the chemical reaction occurred on a mole basis. The concentration of all the proposed amine blend solution was taken as 2.5 M along with 2 M concentration of DEEA and 0.5 M concentration of each diamine (PZ, AEEA, HMDA, EDA, and DMAPA), because the aqueous solution of DEEA blend concentration more than 3 M showed the worst performance in terms of CO<sub>2</sub> loading at a low concentration of CO<sub>2</sub> (20%v/v) in the gas stream corresponding to 20.27 kPa CO<sub>2</sub> partial pressure [38,39]. The total concentrations of all amine blend solutions was between 27.5 wt% and 30.52 wt%, and we know that the 30 wt% concentration is favorable for the industrial point of view in the CO<sub>2</sub> capture applications [7]. The chemical structures of base absorbent (DEEA), benchmark absorbent (MEA) and diamine activators (PZ, AEEA, HMDA, EDA, and DMAPA) are shown in Fig. 3 to see the effect of diamine activator after blending with DEEA solution.

Before measuring the aqueous amine blend potential for CO<sub>2</sub> capture, the reliability of the experimental apparatus was validated by measuring the CO<sub>2</sub> loading in MEA solution at temperature 313.15 K. The present, and previous data of several authors [50-52] on CO<sub>2</sub> loading is represented in Fig. 4. After the comparison, the measurement techniques used in this work are reliable and acceptable for the further measurement of CO<sub>2</sub> loading in proposed amine blend solution.

### 2. CO<sub>2</sub> Loading

CO<sub>2</sub> loading is the most significant absorption performance parameter because CO<sub>2</sub> loading data are used in the development of an empirical model which is further applied for the design of absorption-desorption column used in the CO<sub>2</sub> capture process [53]. An absorbent having higher CO<sub>2</sub> loading requires a smaller column for the same amount of CO<sub>2</sub> absorption, which can reduce

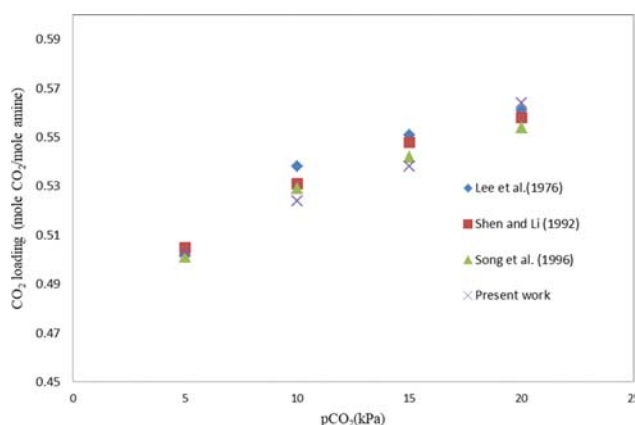


Fig. 4. CO<sub>2</sub> loading in 2.5 M MEA solution at temperature 313.15 K.

the capital cost of the absorption column. CO<sub>2</sub> loading is the maximum absorption capacity of CO<sub>2</sub> in an absorbent, which is expressed in terms of a mole of CO<sub>2</sub> absorbed per mole of the absorbent. Therefore, for measuring the CO<sub>2</sub> loading in various amine solutions, an absorption experiment was performed at a 313.15 K and 20.26 kPa of CO<sub>2</sub> partial pressure. The results of CO<sub>2</sub> loading in MEA, DEEA, and five proposed amine blends DEEA+PZ, DEEA+AEEA, DEEA+EDA, DEEA+HMDA, DEEA+DMAPA solution are shown in Fig. 5. From Fig. 5, the CO<sub>2</sub> loading in single amine solution and blend solution follows the order as DEEA+HMDA > DEEA+EDA ≈ DEEA+PZ > DEEA+AEEA > DEEA+DMAPA > MEA > DEEA. The results show that the entire proposed amine blends had better absorption performance than DEEA and the benchmark absorbent MEA. Interestingly, a drastic increase in the CO<sub>2</sub> loading in the entire blends was observed because the activators present in DEEA blend solutions provided multiple reaction sites leading to absorbing more CO<sub>2</sub> in blend solutions. However, a significant enhancement of CO<sub>2</sub> absorption in amine blends was found

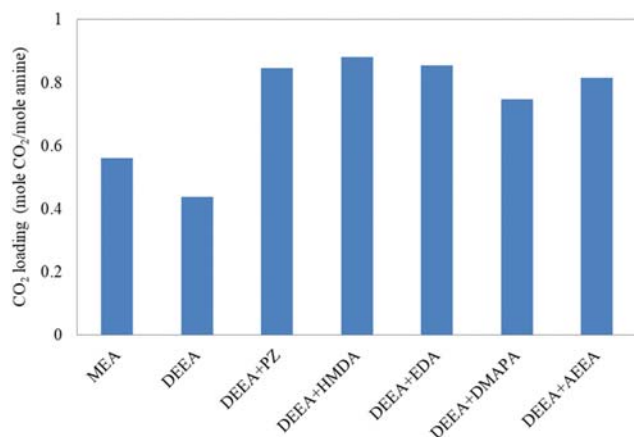


Fig. 5. CO<sub>2</sub> loading in various amine solutions of total concentration of 2.5 M.

by HMDA, EDA, PZ, and AEEA activator but little enhancement by DMAPA. Mainly, DEEA+HMDA blend showed the best absorption performance in terms of CO<sub>2</sub> loading among the entire blends because HMDA has two primary amines as well as a long linear carbon chain in the structure, so it provides extra reactive sites than other diamines [12]. But, the amine blends DEEA+EDA, and DEEA+PZ showed similar absorption performance because EDA has only a primary amine group in the chemical structure, and PZ has only secondary amine groups in the chemical structure, a known fact that reactivity of primary amine is more than the secondary amine. In the case of DEEA+AEEA blend, AEEA diamine contains a primary amine, a secondary amine, and a hydroxyl group in the chemical structure, but the hydroxyl group reduces the absorption capacity of diamine. Low absorption capacity was shown by DEEA+DMAPA blend, and DMAPA contains primary and tertiary amine, but at a low pressure of CO<sub>2</sub> tertiary amine has lower absorption capacity than primary amine as well as a secondary amine. The primary and secondary amine directly react with CO<sub>2</sub> to form carbamate ions and tertiary amine react with CO<sub>2</sub> to form bicarbonate. So, DMAPA component present in amine blend solution provides an extra tertiary amino group, which decreases the absorption capacity of DEEA+DMAPA blend.

### 3. Absorption Rate

The absorption performance of an absorbent in terms of absorption rate has a significant role in the CO<sub>2</sub> capture process. The fast absorption rate requires a smaller size of the absorption column, which corresponds to reducing the capital cost of the CO<sub>2</sub> capture process [54]. The absorption profile in terms of absorption capacity versus time is shown in Fig. 6 to investigate the effect of different types of diamine activator in an aqueous solution of DEEA. From Fig. 6, the entire amine solutions system shows a similar pattern in their profiles of absorption capacity with respect to time. It is also clear that the absorption capacity of CO<sub>2</sub> significantly increased with increase in time within 60 min and then slowly achieved a constant value. The enhanced absorption capacity of CO<sub>2</sub> was attributed to the addition of diamine activators, which can be further used to prove the worth of the acquisition. Finally, after blending diamine activators HMDA, EDA, PZ, AEEA, and DMAPA in

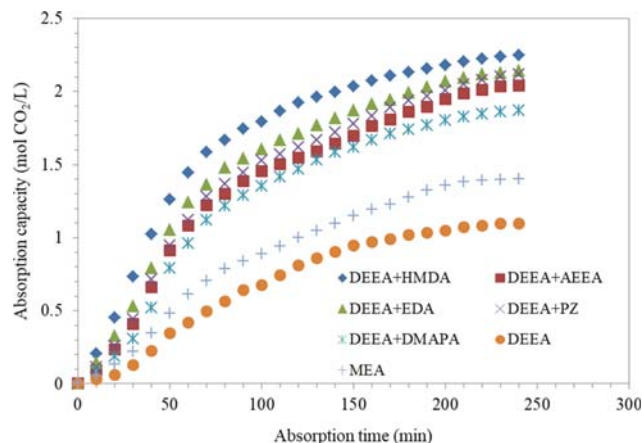


Fig. 6. Absorption profile of CO<sub>2</sub> in various amine solutions at temperature 313.15 K and total concentration of 2.5 M.

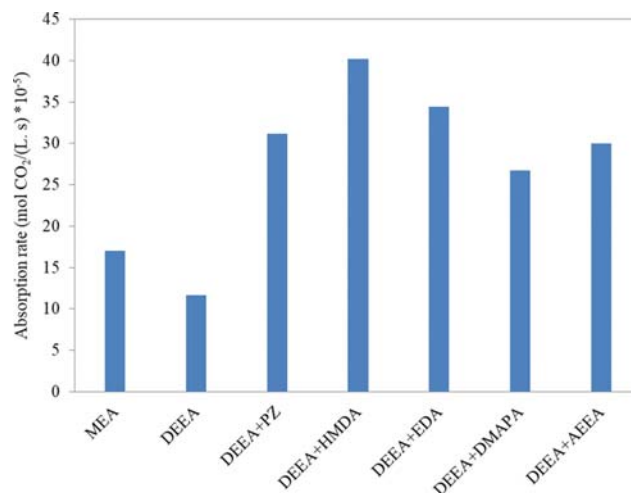


Fig. 7. Absorption rate of CO<sub>2</sub> in various amine solutions of total concentration of 2.5 M.

DEEA solution, the absorption performance in terms of absorption capacity was increased by 100.09%, 94.99%, 92.94%, 85.88% and 70.39%, respectively, to single amine solution of DEEA; and the absorption capacity increased by 57.22, 52.58, 50.98, 45.41 and 33.33, respectively, with respect to single solution of benchmark absorbent MEA. The initial absorption rate of CO<sub>2</sub> was calculated with the help of the graph shown in Fig. 6, and a plot of the absorption rate of amine solutions is illustrated in Fig. 7. In Fig. 7, the order of initial absorption rate of amine solution follows as: DEEA+HMDA > DEEA+EDA > DEEA+PZ > DEEA+AEEA > DEEA+DMAPA > MEA > DEEA. All the DEEA blends have different types of diamine activators, which indicates that all the activators have two amine group providing more reaction sites, and they are successful in increasing the absorption rate. Also, from the absorption data, a plot of absorption rate with an absorption capacity of entire amine solutions is presented in Fig. 8. From Fig. 8, the amine blend DEEA+HMDA, shows the best absorption performance in the proposed amine blend and MEA. Also, the amine blend DEEA+PZ and DEEA+EDA shows similar absorption per-

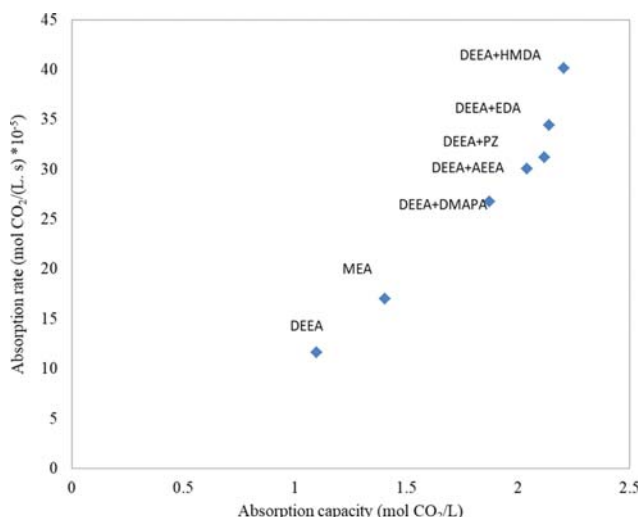


Fig. 8. Plot of absorption rate versus absorption capacity in various amine solutions at temperature 363.15 K and the total concentration of 2.5 M.

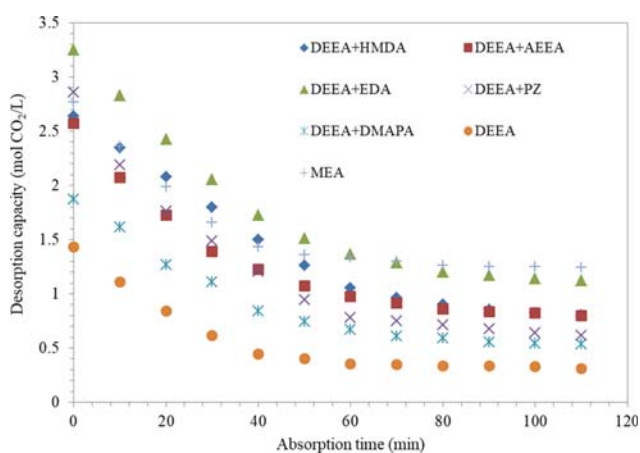


Fig. 9. Desorption profile of CO<sub>2</sub> from various carbonated amine solutions at temperature 363.15 K and total concentration of 2.5 M.

formance but better than DEEA+AEEA. Finally, the blend DEEA+DMAPA shows lower absorption performance but better than MEA and DEEA.

#### 4. Desorption Rate

As already known, the reuse of absorbent is one of the most reliable ways to reduce the capital cost of CO<sub>2</sub> capturing industry; therefore, desorption of CO<sub>2</sub> from amine solution is of utmost importance in a continuous process plant. Fig. 9 shows the variation of CO<sub>2</sub> desorption capacity of the amine with stripping time, and it depicts a similar pattern like absorption. After the CO<sub>2</sub> was released from carbonated amine solution, desorption capacity significantly decreased within 60 min and then became constant with time. Further, the initial desorption rate of tested amine blend was obtained by the slope of linear portion of plot between desorption capacity with time and represented in Fig. 10. The initial desorption rate of all the tested amine blends follows the pattern as:

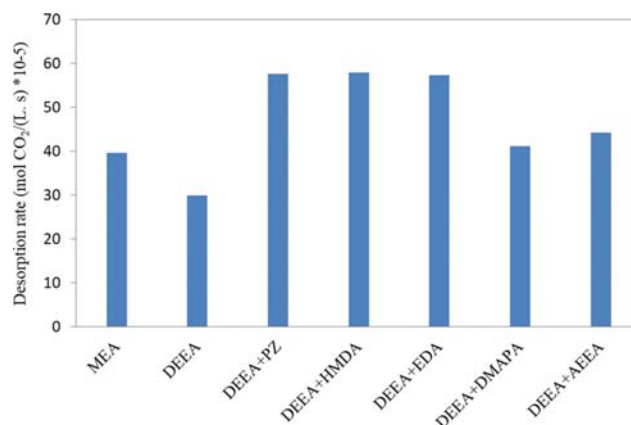


Fig. 10. Desorption rate CO<sub>2</sub> in various amine solutions of total concentration of 2.5 M.

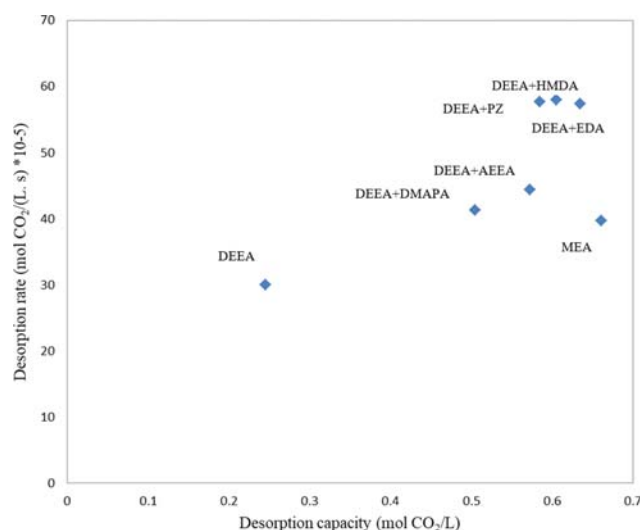


Fig. 11. Plot of stripping rate versus desorption capacity from various amine solutions at temperature 363.15 K and the total concentration of 2.5 M.

DEEA+HMDA>DEEA+PZ>DEEA+EDA>DEEA+AEEA>DEEA+DMAPA>MEA>DEEA. So, the results show that the addition of diamine activators in DEEA solution significantly increased the desorption performance of the tested entire amine blend. The absorbent DEEA+HMDA exhibited the best desorption performance among the entire amine blends because HMDA has long carbon chain in chemical structure [55]. DEEA showed the lowest initial desorption rate. For more clarification, a plot of desorption rate versus desorption capacity is also shown in Fig. 11. As we know, any absorbent is excellent for CO<sub>2</sub> capture when it has low desorption capacity and high desorption rate, but from Fig. 11 it is clear that the amine blend, particularly DEEA+HMDA, has high desorption rate because it is present in the upper right corner in the Fig. 11. So, absorbent represents the best desorption characteristics and it was further characterized by the evaluation of CO<sub>2</sub> cyclic capacity and regeneration efficiency.

#### 5. Cyclic Capacity and Regeneration Efficiency

In the regeneration process, the absorbent continuously flows

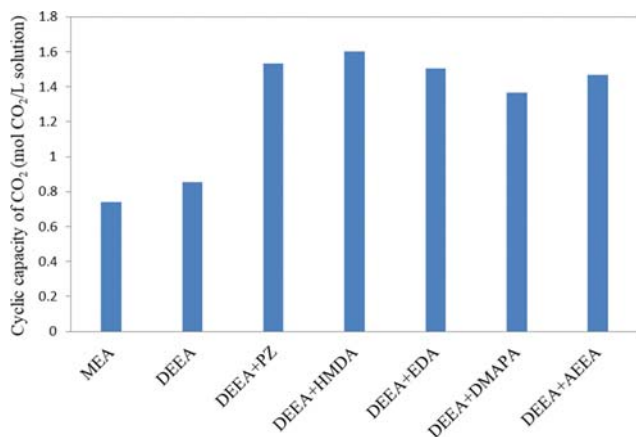


Fig. 12. Cyclic capacity of CO<sub>2</sub> in various amine solutions.

from an absorption column to the desorption column in the CO<sub>2</sub> capture process. The absorbent having more cyclic capacity desired for less amount corresponds to low recirculation of absorbent through pumps and heat exchanger system, which can reduce the operating cost of the CO<sub>2</sub> capture process. Therefore, for the selection of absorbent for CO<sub>2</sub> capture application, an evaluation of the cyclic capacity of absorbent is a required process parameter. The cyclic capacity was evaluated by the difference of CO<sub>2</sub> absorption capacity and desorption capacity at absorption-desorption conditions. The evaluated values of cyclic capacity of amine solutions are presented in Fig. 12. From Fig. 12, the order of CO<sub>2</sub> cyclic capacity is DEEA+HMDA>DEEA+PZ>DEEA+EDA>DEEA+AEAA>DEEA+DMAPE>DEEA>MEA. It can be concluded that the cyclic capacity of the entire amine blend is more than single absorbent DEEA and benchmark absorbent MEA. Particularly, DEEA+HMDA blend showed the best regeneration performance in terms of cyclic capacity among the amine solutions because HMDA blended solution showed highest CO<sub>2</sub> absorption capacity and low desorption capacity of CO<sub>2</sub>. The regeneration efficiency of CO<sub>2</sub> is represented as the percentage ratio of the cyclic capacity of CO<sub>2</sub> to the absorption capacity of CO<sub>2</sub>. So in the evaluation of amine blend performance for continuous process, the regeneration efficiency of the studied amine blends for capturing CO<sub>2</sub> was investigated in

five consecutive cycles using an absorption-desorption experiment. The absorption and desorption experiments were performed within 60 min to see the effect of the number of cycles, and results are shown in Fig. 13. It was observed that the regeneration efficiency of all amine blend decreased slightly from one cycle to another cycle and followed the same order as cyclic capacity of CO<sub>2</sub>. Therefore, it can also be concluded that the studied amine blend can be considered for the continuous process used in CO<sub>2</sub> capture applications.

## CONCLUSION

Different types of diamine activators PZ, EDA, AEAA, HMDA, and DMAPE were added into DEEA solution, making amine blend solution of 2.5 M total concentration. The relative comparison of amine blends for CO<sub>2</sub> capture was investigated by absorption-desorption experiments at an absorption temperature of 313.15 K and desorption temperature 363.15 K with low partial pressure of CO<sub>2</sub> (20.26 kPa), and its capture performance was evaluated in terms of CO<sub>2</sub> loading, absorption/desorption rate, cyclic capacity, regeneration efficiency and number of regeneration cycles. The CO<sub>2</sub> loading drastically increased after the addition of diamine activator in single DEEA solutions and showed better capture performance than benchmark amine MEA and single amine DEEA. The absorption/desorption rate decreased with an increase in time, but both the rates were significantly improved after the addition of diamine activator in DEEA solutions. The cyclic capacity of CO<sub>2</sub> followed the order as: DEEA+HMDA>DEEA+PZ>DEEA+EDA>DEEA+AEAA>DEEA+DMAPE>DEEA>MEA. Among all the tested amine blend and compared to MEA, the DEEA+HMDA solution showed good potential for absorption, desorption and regeneration, indicating that this absorbent could be considered as an efficient solvent for CO<sub>2</sub> capture at low pressure of CO<sub>2</sub> applications.

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## NOMENCLATURE

3DMA1P	: 3-dimethylamino-1-propanol
AEP	: 1-(2-aminoethyl)piperazine
AMP	: 2-amino-2-methyl-1-propanol
BDEA	: butyldiethanolamine
CA	: carbonic anhydrase
DAP	: 1, 3-diaminopropane
DEA	: diethanolamine
DEEA	: 2-(diethylamino)ethanol
DETA	: diethylenetriamine
DMAEA	: 2-dimethylaminoethylamine
DMAEOE	: 2-(2-(dimethylamino)ethoxy) ethanol
DMAPE	: 3-dimethylaminopropylamine
DMEA	: 2-(dimethylamino)ethanol

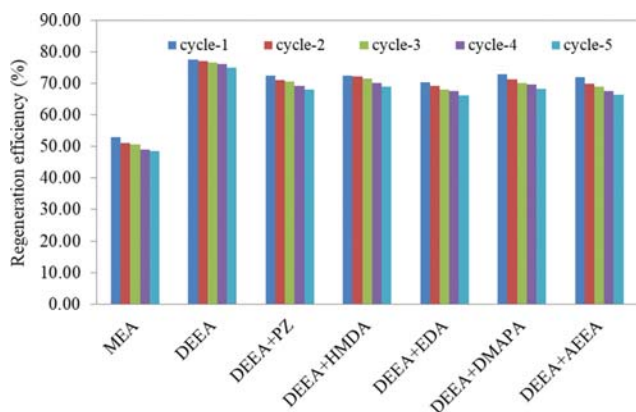


Fig. 13. Regeneration efficiency of amine blends in different cycle.

EAE	: 2-(ethylamino)ethanol
EDA	: ethylenediamine
EDEA	: ethyldiethanolamine
MAPA	: N-methyl propane-1, 3-diamine
MAE	: 2-(methylamino)ethanol
MDEA	: N-methyl diethanolamine
MEA	: monoethanolamine
MEDA	: N-methylethylenediamine
PZ	: piperazine (PZ)
TEMED	: 1, 2-bis (dimethyl amino) ethane
TEPA	: tetraethylenepentamine (TEPA)
TETA	: triethylenetetramine

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