Chapter 2

Literature Review and Objectives

Many investigations have been conducted over various amines and their different blends to obtain an improved amine-based solvent for CO_2 capture. 30 wt% MEA is regarded as a benchmark for the CO_2 capture process due to its high reactivity and fast kinetics; however, it exhibits a few significant challenges, such as it is a highly degradable, corrosive, high vapor pressure and costly regeneration process [1-8]. The challenges were minimized by exploring various amine blends. These amine blends are prepared by mixing either primary or secondary amines with tertiary or sterically hindered amines. In this chain, the tertiary amine, i.e., 2-Dimethylaminoethanol (DMAE), and its different amine blends were widely explored by various researchers for capturing CO_2 from the flue gas stream. Therefore, reviewing the previous work carried out by different researchers on DMAE and its various blends used to capture CO_2 is critical. The selection of amine is challenging since it requires lots of attention and different theoretical aspects to improve CO_2 capture performance. This chapter reviews the screening of tertiary amines and the selection of DMAE and DMAE-based amine blends for post-combustion CO_2 capture.

2.1 Amine solvents for CO_2 capture

The post-combustion is a highly developed and mature technique, and its commercialization has already started. It can easily retrofit with the existing production units in which different amine blends are used to enhance the overall efficiency in terms of CO_2 capture [3]. Therefore, based on such marvelous benefits of the post-combustion technique, the amine-based solvent is a fruitful concept that can be employed

for CO_2 capture systems. Some of the very famous traditional amines for CO_2 capturing are primary amine: Monoethanolamine (MEA), secondary amine: Diethanolamine (DEA), tertiary amine: Methyldiethanolamine (MDEA), sterically hindered amine: 2-Amino-2-methyl-1-propanol (AMP), and cyclic amine: Piperazine (PZ) [1-3,9-13]. Amongst all these conventional amines, MEA with 30 wt% composition has been regarded as a benchmark because of its high reactivity towards CO_2, commendable absorption capacity, good solubility, economical price, etc. [14-17]. However, the biggest drawback of MEA is its high viscosity and elevated regeneration energy demand ($\approx$ 3.7 GJ/ton CO_2) [18-21]. Therefore, researchers and scientists are preparing various amine blends in order to overcome such challenges. Amine blending is a fascinating task that improves the performance of CO_2 capture loading and reduces regeneration energy demand [5,11,22]. Different classes of amines can be blended so that the disadvantage of one amine is balanced by the benefit of another [23,24]. Primary amine + tertiary amine, secondary amine + tertiary amine, and primary amine + hindered amine are some examples of amine blend preparation. Few of those amine blends show biphasic behavior after successful CO_2 absorption, and they have the advantage of reduced regeneration energy as juxtaposed to MEA.

Primary and secondary amines are high kinetics solvents and are referred to as activators (Heat of CO_2 absorption, $\Delta H_{abs} \approx 80$ kJ/mol CO_2), while tertiary or hindered amines are low kinetics solvents are known as promoters ($\Delta H_{abs} \approx 60$ kJ/mol CO_2) [16,25-27]. Activators form carbamates, while promoters produce bicarbonates in reaction to CO_2. The heat of absorption of activators is greater than that of promoters. It simply means that the energy requirement for breaking off the carbamates is greater than bicarbonates [28]. Based on the

experimental analyses, most of the literature concluded that the regeneration energy cost is 70–80% of the entire operational cost [25,27-29]. Activators have disadvantages such as high regeneration energy demand, low absorption capacity, equipment degradation, corrosiveness, etc. On the other hand, tertiary amines have a higher CO_2 absorption capacity and a lower regeneration energy requirement [29-32]. Therefore, amine blending, i.e., a concoction of activators with promoters, enhances the overall property of the amine blend and simultaneously finds a tremendous reduction in regeneration energy [33]. Based on these theoretical concepts, researchers are extensively exploring tertiary amines for CO_2 capture due to their advantageous performance. Therefore, screening of tertiary amines is the first important step in the CO_2 capture process, and based on the available literature, screening of tertiary amines is discussed in detail in the next section.

2.2 Screening of tertiary amine for post-combustion CO_2 capture

In their investigation, Liu et al. [34] targeted chain structure and intramolecular hydrogen bonds of eleven different tertiary alkanolamines to select the most efficient tertiary amine for post-combustion CO_2 capture. Firstly, they prepared a 2.5 M concentration of each tertiary amine to examine their water solubilities and estimated boiling point and vapor pressure for every single tertiary amine. CO_2 absorption (setup: vapor-liquid equilibrium - VLE) and desorption investigations have been done over the tertiary amines to judge their performance. pH determination, equilibrium CO_2 solubility, rate constant, cyclic capacity, and dissociation constant were the prime aspects of the entire investigation. 2.5 M fresh solution of 1-Diethylamino-2-propanol (1DEA2P) solution and CO_2-loaded of 2.5 M concentration of 4-Diethylamino-2-butanol (4DEA-2B) solution showed biphasic behavior. A low boiling point and high vapor pressure were observed in

the case of 1-Dimethylamino-2-propanol (1DMA2P) and 1DEA2P due to the presence of intramolecular hydrogen bonds. Their investigation revealed that amines with linear alkanol chains reacting with CO_2 showed high basicity, absorption capacity, and reaction rate. It was due to the fact that the effect of intramolecular hydrogen bond's influence is lesser in linear alkanol chains than in branched alkanol chain amines. Further, the CO_2 capture performance based on cyclic capacity, molar Gibbs free energy change (ΔrGm) and molar reaction enthalpy (ΔrHm) confirmed that linear alkanol chain amines are better than branched alkanol chain amines. Based on the entire investigation conducted over 11 tertiary amines, the linear alkanol chain amines, i.e., 3-Dimethylamino-1-propanol (3DMA1P) and 3-Diethylamino-1-propanol (3DEA1P) performed commendably. Therefore, researchers concluded that for the selection of tertiary amines, i.e., linear alkanol chain amines must be preferred over branched chain amines to get superb CO_2 capture performance for industrial processes.

In their investigation, Chowdhury et al. [30] focused on twenty-five different broad-range structures of tertiary amines to select the cost-effective high-performance CO_2 capture absorbent that is capable of reducing regeneration energy demand. The CO_2 absorption rate, loading capacity, and heat of reaction were considered during the investigation, and the chosen tertiary amine's performance was compared with the traditional N-methyldiethanolamine (MDEA). The researchers primarily conducted CO_2 absorption and desorption experiments to evaluate the performance of different amines. Thirteen out of twenty-five chosen amines showed promising results in terms of higher CO_2 absorption rate and lower heat of reaction than conventional MDEA. The reaction rate of tertiary amines Dimethylethanolamine (DMAE), Diethylethanolamine (DEAE), 3-

Diethylamino-1,2-propanedio (3DEA-1,2-PD), N,N,N',N'-Tetramethyl-1,4-butanediamine (TM-1,4-DAB), TEDAM, 2-[2-(Dimethylamino)ethoxy] Ethanol (DMAE-EO) and 2-[2-(Diethylamino)ethoxy]ethanol (DEAE-EO) increased many times with the reduction of heat of reaction than MDEA. Methyl and ethyl groups were the most suitable groups found in all the thirteen amines that showed better CO_2 absorption rates and heat of reaction. Further, they concluded that increasing hydroxyl groups adversely affects the absorption rate and CO_2 loading capacity.

In their investigation, Chowdhury et al. [35] selected twenty-four tertiary amines, including twenty-one commercial amines and three structures-modified synthetic amines. Every solvent with 30 wt% amine concentration was used to conduct CO_2 absorption and desorption investigations to judge the CO_2 capture performance, and the results were compared with traditional MDEA. Cyclic CO_2 capacity, absorption rate, amount of CO_2 absorbed, and heat of reaction were the prime research objectives for every selected solvent. The performance of seven solvents, including one synthetic amine solvent, was higher in absorption rates, heat of reaction, and cyclic capacities than conventional MDEA. Further, they concluded that low reaction enthalpy and high CO_2 absorption rates decrease the regeneration energy demand. Therefore, 3-Diethylamino-1,2-propanediol (DEA-1,2-PD) (DEA-1,2-PD) and 1-Methyl-2-piperidineethanol (1M-2PPE) outperformed in terms of the above-mentioned research objectives.

Muchan et al. [16] screened different primary, secondary, and tertiary aqueous alkanolamine for post-combustion CO_2 capture. The authors chose nine different amines, including three tertiary amines, and compared the results with traditional 5 M MEA. They targeted different hydroxyl groups to examine the amine's performance regarding initial

CO_2 absorption and desorption rate. pKa value, equilibrium CO_2 loading, heat duty requirement, and heat of CO_2 absorption were mainly focused on while investigating different amines. They concluded that the presence of a large number of hydroxyl groups results in a negative electron withdrawing tendency, which diminishes the CO_2 capture performance. Therefore, they selected amines that comprised only one hydroxyl group, i.e., 2-mino-2-methyl-1-propanol (AMP), 2-(Ethylamino) ethanol (EAE), and 2-(Dimethylaminoethanol) (DMAE) to prepare amine blends. Two binary amine blends, such as AMP+DMAE and EAE+DMAE, and one tertiary amine blend of AMP+EAE+DMAE were prepared and tested on the laboratory scale. All the tested amine blends showed commendable performance compared to 5 M traditional MEA. AMP (2.5 M) + DMAE (2.5 M) showed best performance and exhibited equilibrium CO_2 loading of 0.56 mol CO_2/mol amine, initial absorption rate of 0.26×10^{-2} mol CO_2/min, initial desorption rate of 2.62×10^{-2} mol CO_2/min, and heat duty of 53.81 kJ/mol.

Xiao et al. [36] performed amine absorbent screening on ten different tertiary amines by conducting CO_2 absorption and desorption tests. The suitable tertiary amine was selected by performing CO_2 absorption rate, equilibrium CO_2 loading, pKa, and heat of CO_2 absorption experiments. Their investigations have revealed that any electron-donating group that is directly attached to the nitrogen atom increases CO_2 reactivity. Good water solubility and steric hindrance availability lead to high CO_2 solubility, whereas the presence of the hydroxyl group influences CO_2 reactivity. Further, they concluded that the regeneration energy demand is directly correlated with the hydroxyethyl group present in the amine. The regeneration energy demand is directly proportional to the presence of the

hydroxyethyl group, i.e., when such group increases, the regeneration heat duty also increases and vice-versa for the opposite case.

Gao et al. [37] blended 5 M MEA solution with ten different tertiary amines to select the most efficient amine blend for post-combustion CO_2 capture. Equilibrium CO_2 loading, absorption and desorption rates, and cyclic capacity were mainly focused on evaluating the performance of different amine blends by rapid screening method. MEA+1DEA2P showed the highest equilibrium CO_2 loading of 0.5548 mol CO_2/mol amine. The faster CO_2 absorption and desorption rates were achieved from MEA+1DMA2P aqueous amine blend and their experimental investigations provided the sequence of cyclic capacity as: MEA+2DMA2M1P < 5 M MEA < MEA+TEA < MEA+1DEA2P < MEA+3DMA1P < MEA+DEEA < MEA+DMEA < MEA+MDEA < MEA+1DMA2P. The highest CO_2 cyclic capacity of the MEA+1DMA2P amine blend was found to be 1.6710 mol CO_2/L.

Gao et al. [38] reported that tertiary amines provide high equilibrium CO_2 loading and low heat of CO_2 absorption (ΔH_{abs}) as compared to primary and secondary amines. Therefore, their investigation targeted the relationship between tertiary amine's molecular configuration with equilibrium CO_2 loading and ΔH_{abs} value. The trend of ΔH_{abs} value as per their investigation: 1-Diethylamino-2-Propanol (1DEA2P) > 3-(Diethylamino)-1,2-propanediol (DEA-1,2-PD) >Diethylaminoethanol (DEEA) > 3-Diethylamino-1-Propanol (3DEA1P) > 1-Dimethylamino-2-propanol (1DMA2P) > 3-Dimethylamino-1-propanol (3DMA1P) > 2-Dimethylaminoethanol (DMEA) > Methyldiethanolamine (MDEA) > Triethanolamine (TEA). A microcalorimeter was employed to measure the CO_2 absorption heat of nine different tertiary amines with high accuracy. Natural population analysis and dual descriptor analysis were used to visualize the effect of electron density and steric

hindrance of tertiary amine, respectively. The electron-donating effect of the ethyl group is higher than that of the methyl group, resulting in higher reactivity of the tertiary amines. Further, they pointed out that the existence of methyl group on the side chain of tertiary amine increases the CO_2 reactivity. A large number of hydroxyl groups create the steric hindrance in the amine, which is highly discouraged from the reactivity point of view. Their experimental investigation revealed that the availability of hydrogen bonds increases the equilibrium CO_2 loading and also reduces the heat of CO_2 absorption.

Most of the researchers have conducted several screening investigations on tertiary amines, as discussed above. In this chain, Baltar et al. [39], Shen et al. [40], Singto et al. [41], Kumar et al. [9], Narku-Tetteh et al. [42], etc., have deeply investigated various tertiary amines and targeted different aspects of CO_2 absorption and desorption parameters. The investigations conducted over various tertiary amines by researchers have been presented in Table 2.1. Based on the entire screening investigation of tertiary amine used for post-combustion CO_2 capture, DMAE showed commendable performance in CO_2 absorption and desorption behavior. Therefore, the next section comprises a detailed description of DMAE and the screening of DMAE-based amine solvents for CO_2 capture.

Table 2.1 Investigation conducted by various researchers for screening of tertiary amines for post-combustion CO_2 capture.

S. No.	Total Absorbents Screened/ used	Best Absorbent and Equilibrium CO_2 loading (α)	Apparatus used	Absorption Temperature (℃)	Regeneration Temperature (℃)	Operating Conditions	References
1.	11	3DMA1P and 3DEA1P; α (3DMA1P) and α (3DEA1P) ≈ 0.8–0.9 mol CO_2/mol amine; α (DMAE) ≈ 0.65–0.7 mol CO_2/mol amine.	VLE setup	40	80	CO_2 partial pressure (P_{CO2}): 15 kPa; Operating pressure: 1 atm; Amine concentration: 2.5 M; Amine volume: 0.3 L; Total gas flow rate: 1 L/min; N_2 flow rate for desorption = 0.85 L/min,	Liu et al. [34]
2.	25	DMAE; DEAE; 3DEA-1,2-PD; TM-1,4-DAB; TEDAM; DMAE-EO and DEAE-EO; α (DMAE), α (DEAE), α (3DEA-1,2-PD), α (TM-1,4-DAB), α (TEDAM), α (DMAE-EO), and α (DEAE-EO) = 2.27, 2.16, 2.05, 2.36, 2.59, 1.32, and 1.63 mol CO_2/L.Sol, respectively.	VLE setup	40	70	P_{CO2}: 20 kPa; Absorption time: 60 min; Amine concentration: 30 wt%; Amine volume = 50 mL; Total gas flow rate = 700 mL/min; Operating pressure: 1 atm; and Desorption time = 60 min.	Chowdhury et al. [30]
3.	24	DEA-1,2-PD and 1M-2PPE; α (DEA-1.2-PD) and α (1M-2PPE) = 1.66 and 1.75 mol	VLE setup	40	70	P_{CO2}: 20 kPa; Operating pressure: 1 atm; Amine volume = 50 mL; Total gas flow rate = 700 mL/min; Amine concentration	Chowdhury et al. [35]

		CO_2/L. Sol, respectively.				= 30 wt%; Absorption and desorption time = 60 min.	
4.	8 (Including 3 tertiary amines)	AMP (2.5 M) + DMAE (2.5 M); α (AMP+DMAE) = 0.48–0.56 mol CO_2/mol amine.	Bubble column reactor; Hot plate desorption setup	40	90	Operating pressure: 1 atm; P_{CO2}: 15 kPa; Total gas flow rate = 160 mL/min; Amine volume = 75 mL; CO_2 absorption time = 4–6 h; Heat output by hot plate = 1500 W.	Muchan et al. [16]
5.	10	DMEA and DEEA; α (DMEA) and α (DEEA) = 0.664 and 0.824 mol CO_2/mol amine, respectively.	VLE setup	20–40	-	Amine volume = 20 mL; P_{CO2}: 8.1–60.8 kPa; Operating time: 8 h; Amine concentration: 2 mol/L; Total gas flow rate: 250 mL/min.	Xiao et al. [36]
6.	10	MEA+1DEA2P and MEA+1DMA2P; α (MEA+1DEA2P) = 0.5548 mol CO_2/mol amine; α (MEA+1DMA2P) = 0.5500 mol CO_2/mol amine	Bubble colum reactor	40	80	Operating pressure: 1 atm; P_{CO2}: 15 kPa; Operating time: 90 min; Amine volume = 20 mL; N_2 flow rate for desorption = 850 mL/min; Desorption time = 90 min.	Gao et al. [37]
7.	9	3DMA1P, 3DEA1P, and DEA-1,2-PD; α (3DMA1P), α (3DEA1P), and α (DEA-1,2-PD) = 0.776, 0.891, 0.748 mol CO_2/mol amine,	Bubble column reactor	40	80	Amine volume = 100 mL; Amine concentration = 2 mol/L; Total gas flow rate = 1000 mL/min; Desorption stirring speed = 800 rpm; N_2 flow rate for desorption = 850 mL/min; P_{CO2}: 15 kPa.	Gao et al. [38]

		respectively.					
8.	2	DMEA and DEEA; α (DMEA-based solvents) = 1.07 mol CO_2/mol amine and α (DEEA-based solvents) = 1.10 mol CO_2/mol amine	Square bubble column reactor; Desorption setup	22	100	Amine concentration for desorption = 0.3 mol/L; Desorption gas flow rate = 0.3 L/min; NMR investigation conducted; Amine concentration = 0.1–1 mol/L.	Baltar et al. [39]
9.	40 (Including blends)	TETA + N,N,N',N'-Tetramethyl-1,3-propanediamine (TMPDA); α (TETA+TMPDA) ≈ 0.83 mol CO_2/mol amine.	Double stirred cell reactor;	40, 50, 60	-	CO_2 gas flow rate: 200 ml/min; Solution concentration: 4 Molar (1:3); Absorption time: 90 min.; Stirring speed: 250 rpm; P_{CO2}: 1.3 and 13 kPa;	Shen et al. [40]
10.	7	4- (Dimethylamino)-2-butanol (DMAB), 4-((2-Hydroxyethyl)(methyl)amino)-2-butanol (HEMAB), and 4-((2-Hydroxyethyl)(ethyl)amino)-2-butanol (HEEAB); α (DMAB) = 0.82–0.98 mol CO_2/mol amine;); α (HEMAB) = 0.43–0.91 mol CO_2/mol amine; α (HEEAB)	Bubble column reactor; Hot plate desorption setup	25	90	Amine volume = 25 mL; Amine concentration = 2 mol/L; P_{CO2}: 3–100 kPa; CO_2 flow rate = 200 mL/min; Absorption time = 20–22 h; Desorption amine volume = 100 mL; Agitation speed = 300 rpm; Desorbed amine collection time = 15, 30, and 45 min.	Singto et al. [41]

		= 0.61–0.95 mol CO_2/mol amine.					
11.	7 (Including 2 tertiary amines)	DEEA + HMDA; α (DEEA+HMDA) = 0.932 mol CO_2/mol amine.	Bubble column reactor; Chittick apparatus; Hot plate desorption setup	40	90	Operating pressure: 1 atm; P_{CO2}: 20.26 kPa; Amine volume = 150 mL; Total flue gas flow rate = 250 mL/min; Absorption and desorption time = 60 min; Desorption stirring = 600 rpm; Desorption amine volume = 100 mL; N_2 purging before desorption = 1000 mL/min.	Kumar et al. [9]
12.	10	BEA (2 M) + AMP (2 M); α (AMP) ≈ 0.7 mol CO_2/mol amine; α (BEA) ≈ 0.6–0.63 mol CO_2/mol amine	Chittick apparatus; Desorption setup	40	90	Amine concentration = 2 mol/L; Stirring speed = 600 rpm; Absorption time = 6 h; Amine volume = 100 mL; Total flue gas flow rate = 200 mL/min; Desorption amine volume = 76 mL.	Narku-Tetteh et al. [42]

2.3 2-Dimethylaminoethanol (DMAE) tertiary amine for CO_2 capture

2-Dimethylaminoethanol (DMAE) is a tertiary amine-containing 2 methyl groups attached to nitrogen atoms and 1 hydroxyethyl group present in its molecular structure [29,43]. The properties of DMAE, such as molecular weight, density, boiling point (B.P.), and initial purity, are 89.138 g/mol, 890 kg/m^3, 134.1 ℃, and ≥ 98%, respectively. It is chemically synthesized by adding an equal percentage of ethylene oxide and dimethylamine. Amine blends of DMAE are becoming popular nowadays in CO_2 capture since DMAE is a novel amine that is obtained from renewable energy resources, which is replacing most conventional tertiary amines due to its superior behavior [24,31]. High equilibrium CO_2 loading, good degradation resistance, low viscosity, fabulous thermal stability, and more pK_a value are the major advantages of DMAE. The majority of the literature also reported that DMAE also offered excellent absorption and desorption rate, low heat of CO_2 absorption (ΔH_{abs} < 70 kJ/mol), and lower desorption enthalpy than conventional MEA [20,24,30,32,44-48]. The chemical structure of DMAE is shown in Figure 2.1.

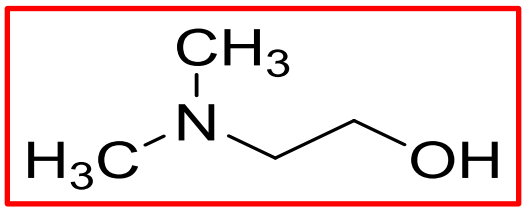

Figure 2.1 Chemical structure of DMAE

Chowdhury et al. [30] have evaluated the performance of some tertiary amines to judge their performance for post-combustion CO_2 capture. During their entire investigation, CO_2 absorption capacities, reaction rate, and heat of CO_2 absorption of DMAE were found to be

better than traditional MDEA. Their screening investigation over tertiary amines (including DMAE) has already been discussed in Table 2.1. Buvik et al. [49], in their investigation, selected 19 different amines and performed oxidative degradation, thermal degradation, and biodegradation tests. Loss of alkalinity correlated with the oxidative degradation of specific amine. Based on experimental results, they concluded that every tertiary amine tolerates high oxidation. DMAE outperformed all other amines by having the lowest amine loss of 4 %, being thermally stable, and being highly biodegradable. Brúder et al. [50] prepared two amine blends of DMAE (3M) + 3-Methylaminopropylamine (MAPA) (2M) and DMAE (5M) + MAPA (1M) for screening and VLE equilibrium measurement. They reported that their amine blends did not show solid precipitation while loading CO_2.

Zhang et al. [51] selected DMAE and AMP and blended them with piperazine (PZ) to evaluate their performance for CO_2 capture. DMAE, AMP, AMP+PZ, and DMAE+PZ amine blends were tested for flue gas emitted from natural gas power plants. The chosen power plant emits low CO_2 and high O_2 concentrations. They significantly targeted CO_2 loading of the amine absorbent for absorption investigation. The researchers have also targeted density (Anton Paar DMA 5000 M) and viscosity of such amine blends to evaluate their mass transfer and fluid dynamics performance. Further, they reported that DMAE and 2-Diethylaminoethanol (DEAE) show slow reaction kinetics while reacting with CO_2. PZ exhibits commendable properties such as fast reaction kinetics, high CO_2 loading, and good chemical stability; therefore, the researchers blended DMAE with PZ to overcome the individual disadvantages of DMAE. They reported that the DMAE+PZ blend enhanced CO_2 loading, improved regenerability, and reduced solution viscosity.

Xiao et al. [43] targeted five different aqueous tertiary amines to check the effect of activity-structure on a molecular level for the estimation of equilibrium CO_2 loading. Triethanolamine (TEA), N-methylethanolamine (MDEA), 2-(Dimethylamino)ethanol (DMEA), 3-Dimethyl-amino-1-propanol (3DMA1P), and Diethylethanolamine (DEEA) were the selected tertiary amines. The researchers have used the modified Kent-Eisenberg (M-KE) model for the tertiary amine+H_2O+CO_2 system to validate the experimental work. As per the experimental study, the percentage average absolute relative deviation (% AARD) was found to be 2.5, 3.3, 1.3, 1.0, and 0.8 % for TEA, MDEA, DMAE, and DEEA, respectively. The prime objective of their investigation included equilibrium CO_2 loading, second-order reaction rate constant, and heat of CO_2 absorption (ΔH_{abs}). The Clausius-Clapeyron equation was employed to determine the ΔH_{abs} value. Their experimental results confirm that the equilibrium CO_2 loading of 3DMA1P, DMAE, and DEEA was higher than MEA and DEA. Further, they reported that the equilibrium CO_2 loading increases with an increase in CO_2 partial pressure, whereas loading decreases with an increase in temperature.

Hadri et al. [29] performed solvent screening on thirty aqueous tertiary amines by solvent screening setup. Different classes of amines, such as linear, non-linear, polyamines, and sterically hindered amines, were adopted to check their structural behavior on CO_2 capture. They primarily focused on CO_2 loading and calculated absorption performance at a temperature of 313.15 K, 30 wt % amine concentration, 15 vol % of CO_2 and 85 vol % of N_2 in the flue gas composition, 1 bar operating pressure, and 12 hours of absorption time. Their screening investigation by stopped-flow apparatus revealed that Hexamethylenediamine (HMDA) resulted in a maximum CO_2 loading of 1.35 mol CO_2/mol amine, whereas Triethanolamine (TEA) provided the least CO_2 loading of 0.39

mol CO_2/mol amine. Six out of thirty amines, i.e., 2-Ethylaminoethanol (2EAE), N-Methyldiethanolamine (MDEA), 1-Dimethylamino-2-propanol (1DMA2P), 2-Dimethylaminoethanol (2DMAE), 3-Dimethylamino-1-propanol, (3DMA1P) and N,N,N',N'-Tetramethyl-1,3-propanediamine (TMPDA) showed promising results in terms of CO_2 loading and heat of CO_2 absorption aspects. The heat of CO_2 absorption and CO_2 loading of such 6 amines fall in the range of -68.95 to -52.51 kJ/ mol of CO_2 and 0.52 and 1.16 mol CO_2/mol amine. As per the outcomes of the thermodynamics and kinetic properties, 2DMAE+2EAE, 2EAE+MDAE, 2EAE+1DMA2P, 2EAE+3DMA1P, and 2EAE+TMPDA were the emerging amine blends for enhancing the CO_2 capture performance. For post-combustion CO_2 capture, the various research findings on DMAE-based amine blends done by different researchers have been incorporated in Table 2.2. It was found that DMAE performed commendably well when blended with activators (primary or secondary amine) while investigating DMAE-based amine solvents. Therefore, DMAE seems to be the potential amine solvent that can be further utilized to capture CO_2.

Table 2.2 Literature related to DMAE-based amine solvents for post-combustion CO_2 capture.

S. No.	Total Absorbents Screened/ used	Best Absorbent and Equilibrium CO_2 loading (α)	Apparatus used	Absorption Temperature (℃)	Regeneration Temperature (℃)	Operating Conditions	References
1.	2	DMAE (3M)+MAPA (2M); α (DMAE+MAPA) = 0.58 mol CO_2/mol amine.	VLE Setup	40	80	CO_2 flow rate = 0.5 NL/min; N_2 flow rate = 4.5 NL/min; Amine volume = 750 mL.	Brúder et al. [50]
2.	6 (Including two amine blends)	DMAE+PZ; α (DMAE+PZ) ≈ 0.55–0.65 mol CO_2/mol amine.	Static-analytic apparatus	40	120	Total operating pressure = up to 1 MPa; Temperature range for density = 25–80 ℃; P_{CO2}: 4 and 12 kPa.	Zhang et al. [51]
3.	7	DMAE, 3DMA1P, and DEEA; α (DMAE) = 0.563–0.853 mol CO_2/mol amine; α (3DMA1P) = 0.641–0.887 mol CO_2/mol amine; α (DEEA) = 0.673–0.898 mol CO_2/mol amine.	VLE Setup; Chittick apparatus	25–40	120	Amine concentration = 2 mol/L; P_{CO2}: 8.1–60.8 kPa; Total gas flow rate = 250 mL/min; Amine volume = 20 mL.	Xiao et al. [43]
4.	30	2DMAE, MDEA,	Stop-flow	40	-	Amine concentration = 30 wt%; Pressure	Hadri et al. [29]

		1DMA2P, 3DMA1P, TMDPA, and 2EAE; α (2DMAE), α (MDEA), α (1DMA2P), α (3DMA1P), α (TMDPA), and α (2EAE) = 0.73, 0.52, 0.72, 0.89, 1.16, and 0.67, respectively.	equipment; Microreaction calorimeter			range = 0–6 bar; Stirring speed = 500 rpm; P_{CO2}: 15 kPa; Total gas flow rate = 15 L/h; Operating time = 12 h; Condenser temperature = 6.5 ℃; Reactor's pressure = 1bar.	
5.	4	DMAE+PZ and 2EAE+PZ	-	-	-	Molecular dynamic simulation investigation; Solvent concentration = 30 wt%; Temperature = 40 ℃; Operating pressure = 0.1 Mpa;	Sharif et al. [32]
6.	3	DMAE	Stirred cell reactor (Jacketed stirred glass reactor)	20–60		P_{CO2}: 6–20 kPa; DMAE concentration = 1–4 kmol/m^3; Liquid flow rate = 3.90–11.70 m^3/m^2-h; Inert gas flow = 26.11–43.52 kmol/m^2-h; Surface area of packing = 900 m^2/m^3; Packing height = 1.25 m; Absorption column height = 1.7 m; and absorption column diameter = 0.028 m.	Ling et al. [31]
7.	2	DMAE+MEA	Hollow fiber	40	80	Molecular dynamic simulation study;	Sharif et al. [45]

			membrane contractor; Chittick apparatus; VLE apparaus			Membrane module dimensions: internal diameter = 18 mm, packed height = 0.20 m, and total height = 0.60 m; Hollow fibers used = 20; Amine volume = 300 mL; Operating pressure = 1 atm; P_{CO2}: 15 kPa; Total gas flow rate = 1000 mL/min; and solution concentration = 2 mol/L.	
8.	3	-	Stopped flow apparatus	20–40	-	DMAE and DEEA concentration = 0.075–0.175 kmol/m^3; MEA concentration = 0.0075–0.0175 kmol/m^3; and Absorption time = 0.5 h.	Jiang et al. [48]
9.	3	-	Densimeter; viscometer; and calorimeter			Thermophysical properties were estimated at temperature = 20–80 ℃; Pressure = 0.1–30 MPa, and mass fraction (TEA, MDEA, and DMAE) = 0.1–0.4.	Concepcion et al. [52]
10.	3	DMAE+EG (Ethylene glycol); α = 0.72 mol CO_2/mol amine.	Dual vessel absorption system; Density meter; Viscometer	20 and 50	30 and 60	Quantity of absorbent = 1 g; Absorption time = 30 min; Catalytic hydration is used during the experiments.	Chen et al. [20]

11.	2	DMAE +2-(Ethylamino) ethanol (EAE); α (DMAE+EAE) = 0.108–0.675 mol CO_2/mol amine	Autoclave setup; Setup for enthalpy of absorption	40, 55, 70, and 85	-	Pressure range = 6.5–236 kPa; Amine blend volume = 50 mL.	Delavari et al. [53]
12.	30	3,3'-Diamno-N-Methyldipropylamine, DAMDPA; α (DAMDPA) = 1.4846 mol CO_2/mol amine	Bubble column reactor	40	80	Chiller temperature = 0 ℃; Total gas flow rate = 2 L/min; Amine volume = 100 mL; Solution concentration = 30 wt%; CO_2 concentration = 15 vol %; Absorption time = 90 min.	Kim et al. [54]
13.	11 (Including 6 amine blends	DMAE+MAPA; α (DMAE+MAPA) = 0.274–4.563 mol CO_2/kg solution	Autoclave absorption setup	40	-	Density and viscosity temperature range = 30–80 ℃; Amine volume = 50 mL; Operating pressure < 0.6 kPa; Tertiary amine concentration = 40 %; Activator concentration (AEEA or MAPA) = 5 %.	Rahimi et al. [55]

2.4 Research gap / scope of the present work

Based on the solvent screening study, the scope of this work is to select the efficient tertiary amine and prepare novel aqueous amine blends to conduct CO_2 absorption and desorption investigation. As per the literature review, DMAE is a tertiary amine, and it is used as an alternative to MDEA for post-combustion CO_2 capture due to its commendable performance. DMAE can be prepared from renewable resources, its performance is better than traditional MDEA, and its toxicity is lesser than most of the previously reported amines and its various blends. In this chain, scanty work has been carried out by using DMAE for post-combustion CO_2 capture. Therefore, the aqueous amine blend of BAE+DMAE, HMDA+DMAE, and TETA+DMAE is entirely novel, least hazardous and no research work has been conducted before these experimental investigations. Since the amine blends were novel; therefore, their reaction mechanism with CO_2 was suggested, and the same was authenticated by ^{13}C NMR and FTIR characterization. Thermophysical property such as density was determined for CO_2-unloaded, CO_2-loaded, and CO_2-regenerated samples for the first time for the novel aqueous HMDA+DMAE amine blend. Optimization of process parameters has never been attempted in the selected operating conditions. The environmental impact of amine blend, i.e., toxicity assessment, has been evaluated for BAE+DMAE and HMDA+DMAE amine blends for the first time.

2.5 Objective of the research work

This thesis aims to select novel aqueous amine blends and study their performance for post-combustion CO_2 capture. The overall point-wise objectives of this thesis work are as follows:

- The prime objective of this thesis work is to evaluate CO_2 absorption-desorption performance for the selected novel aqueous amine blends of BAE+DMAE, HMDA+DMAE, and TETA+DMAE for post-combustion CO_2 capture.
- The first objective is validating the experimental setup and estimating equilibrium CO_2 loading during CO_2 absorption investigation.
- Analyzing the effect of process parameters on equilibrium CO_2 loading as per the chosen range of operating conditions.
- Developing an empirical model for the validation of CO_2 absorption results.
- To evaluate the cyclic capacity, cyclic equilibrium CO_2 loading, heat duty, and regeneration efficiency of the novel blends and their comparison with the benchmark MEA during the CO_2 desorption study.
- To examine pH, density, CO_2 absorption and desorption rates.
- Proposing reaction mechanism for novel aqueous amines of BAE+DMAE, HMDA+DMAE, and TETA+DMAE when reacting with CO_2 and their validation by ^{13}C NMR and FTIR characterization.
- To study the heat of CO_2 absorption (ΔH_{abs}) for all novel aqueous amine blends.
- Modeling and optimization of equilibrium CO_2 loading by the RSM software.
- To study the toxic behavior of the chosen novel amine blends.

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