

## Comprehensive technical analysis of CO<sub>2</sub> absorption into a promising blended amine of DEEA-HMDA

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### ABSTRACT

Comprehensive technical analysis is vital for the large-scale industrialization of a certain potential amine solvent. This paper proposes a technical evaluation method to assess amine-based CO<sub>2</sub> capture processes thoroughly. The method's validity was also verified by using the DEEA-HMDA as an example, compared with various conventional amine solutions in terms of the above three technical properties. Based on the technical properties analysis, a new rapid screening assessment method for amines based on technical indicators proposed. In addition, eight conventional amine solvents selected to calculate the technical indicators (including packed column design, solvent consumption, and regeneration energy consumption) reflected by these three technical properties. The packed column volume (44.5 m<sup>3</sup>), solvent consumption (2.28 kg/tCO<sub>2</sub>), and regeneration energy consumption (18.64 KW·h/tCO<sub>2</sub>) of using DEEA-HMDA as a CO<sub>2</sub> absorbent were lower than the most commonly used MEA. In conclusion, the blended amine DEEA-HMDA is a potential carbon capture alternative solvent.

### 1. Introduction

CO<sub>2</sub> released from burning fossil fuels significantly contributes to climate change (Friedlingstein et al., 2022). Thus, limiting the atmospheric buildup of CO<sub>2</sub> and reducing global warming is crucial (Gao et al., 2020). CO<sub>2</sub> capture is usually done by absorption, adsorption, membrane, cryogenic, and so on (Chen et al., 2020; He et al., 2020; Wang et al., 2021a; Wu et al., 2014; Yang et al., 2021). Among them, the use of amine solvents for CO<sub>2</sub> capture has high selectivity, fast reaction rate, wide industrial application, and is a common method of CO<sub>2</sub> emission reduction (El Hadri et al., 2017). Amine solution with different structure and composition have different effects on CO<sub>2</sub> capture (Wei et al., 2022). The commonly used amine solutions include primary amine (MEA, AMP), secondary amine (DEA, PZ), tertiary amine (DEEA, TEA, 1DMA2P) and some newly proposed amines ((DETA) (Afkhamipour and Mofarahi, 2018b; Ghiasi et al., 2017; Han and Wee, 2021; Li et al., 2021). Among them, the CO<sub>2</sub> capture mechanism by secondary and primary amines is amphoteric ions, which transfer the generated protons to amines to form amine carbamate and have a high reaction rate (Crooks and Donnellan, 1989). Particularly, MEA aqueous solution and its methanol solution are considered excellent CO<sub>2</sub> absorbents (Naami et al., 2012; Sema et al., 2012; Shi et al., 2021), which have a fast

absorption rate, and stable chemical properties of amino acetate generated after absorption. But the stable carbamate regeneration requires more regeneration energy consumption. In addition, the MEA solution is corrosive, which will damage the pipeline, device, pump valve, and so on (Chakravarty et al., 1985). On the contrary, the stability of tertiary amine reaction products is poor, easier than secondary amine desorption, and the desorption energy consumption is the lowest (Bai et al., 2022; Laddha and Danckwerts, 1981). Besides, tertiary amines have lower CO<sub>2</sub> reactivity than secondary/primary amines (Barth et al., 1984). For example, MDEA has an outstanding CO<sub>2</sub> absorption capacity, low desorption energy consumption, and high degradation resistance. Therefore, one of the key research areas in recent years is developing and designing of CO<sub>2</sub> capture solvents with high reaction kinetics, high CO<sub>2</sub> absorption and low regeneration consumption. The blended amine is another novel solvent with exciting possibilities (Wang et al., 2021b). And they are usually obtained by mixing two or more primary/secondary amines and tertiary amines, combining the CO<sub>2</sub> absorption rate of primary/secondary amines with the low energy consumption of tertiary amines (Zheng et al., 2022). Sakwattanapong et al. compared the regeneration energy consumption of CO<sub>2</sub> capture with the blended amine and single amines (Sakwattanapong et al., 2005). The blended amine AMP-MEA has lower energy consumption for desorption than the single amines. Similarly, the regeneration energy of the blended amine

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## Nomenclature

1A2P	1-amino-2- propanol
1DMA2P	1-dimethylamino-2-propanol
2A1P	2-amino-1-propanol
AEPAZ	1-(2-aminoethyl)piperazine
AMP	2-amino-2-methyl-1-propanol
DEA	diethanolamine
DEEA	2-(diethylamino)ethanol
DETA	diethylenetriamine
DMAE	n,n-dimethylaminoethanol
DMCA	n,n-dimethylcyclohexylamine
DMEA	n,n-dimethylethanolamine
HMDA	1,6-hexamethyldiamine
MAE	2-methylaminoethanol
MCA	n-methylcyclohexylamine
MDEA	methyldiethanolamine
MEA	monoethanolamine
PZ	piperazine
TBAE	2-[(1,1-dimethylethyl)amino]ethanol
TEA	triethanolamine
TETA	triethylenetetramine

DMCA-MCA was estimated to be 2.20 GJ/t CO<sub>2</sub> (Sakwattanapong et al., 2005). These studies show that the blended approach can effectively increase the level of CO<sub>2</sub> absorption and compensate for the limitations of single amines (Wang et al., 2021b). Therefore, it is imperative to create the novel blended amine solvents for CO<sub>2</sub> capture that are very effective and need low energy consumption.

HMDA is a typical primary amine. It has two amino groups, so its aqueous solution is highly alkaline and can react quickly with CO<sub>2</sub> to separate it from flue gas, with about twice the CO<sub>2</sub> absorption capacity of MEA (Singh et al., 2011). Nevertheless, the carbamate produced by the reaction of HMDA with CO<sub>2</sub> is relatively stable, which is not conducive to desorption, resulting in increased energy consumption in desorption operation. Based on the above, adding the tertiary amine DEEA, which has low regeneration energy consumption and low reaction rate with CO<sub>2</sub>, to HMDA, a blended amine solvent DEEA-HMDA with both advantages is obtained (Sutar et al., 2013). In addition, based on earlier finds, the blend of DEEA and HMDA showed excellent absorption, desorption, and regeneration potential. Moreover, DEEA-HMDA has a moderate viscosity and does not adhere heavily to the packing surface when operating in the column. Therefore, the use of blended amine DEEA-HMDA has great potential for CO<sub>2</sub> capture in coal-fired power plants.

However, conducting a comprehensive technical analysis of the blended amine DEEA-HMDA is necessary before it can be considered for industrial use. Although many experiments have been conducted to examine the CO<sub>2</sub> capture effectiveness of newly developed blended amines, the technical evaluation of these novel solvents and systems is a key issue in proving the feasibility of new absorbents (Kim et al., 2019). When developing a novel solvent, a comprehensive evaluation of the overall performance of CO<sub>2</sub> capture from a technical viewpoint must be carried out. Therefore, this work aims to justify the advantages of the blended amine DEEA-HMDA compared to conventional absorbents through a comprehensive technical analysis.

This work provides the method to fully evaluate the possibility of industrial application from a comprehensive technical analysis. The blended amine DEEA-HMDA solution was used as an example to perform the whole procedure, including calculating its CO<sub>2</sub> equilibrium solubility, volumetric overall mass transfer coefficient ( $K_{G\alpha_v}$ ), and absorption heat experimentally and comparing them with conventional absorbents. Furthermore, based on the above three technical indicators, a screening

guide for promising amines was presented to quickly determine the level of new amine solutions for CO<sub>2</sub> capture. The technical indicators for different amine solutions were calculated regarding solvent consumption, packed column design, and regeneration energy consumption.

## 2. Reaction mechanism of DEEA-HMDA

When CO<sub>2</sub> is captured using a blended amine solvent, the underlying chemical mechanism is an acid-base neutralization reaction involving several intricate reversible reactions. The main equilibrium-controlled reaction equations of DEEA-HMDA used in this study are as follows (Sutar et al., 2013; Kumar and Mondal, 2018):

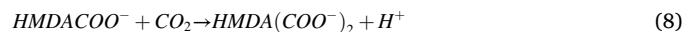
Typical ionization reactions:



The protonation of DEEA and HMDA:



The reaction of DEEA-HMDA with CO<sub>2</sub>:



Typical ionization reactions for the DEEA-HMDA are represented in Eq.(1)-(3). Eq.(4)-(5) show the protonation of DEEA and HMDA, respectively. Moreover, the solvent HMDA has two active amino groups, which have a two-step reaction with CO<sub>2</sub> (Eq.(6)-(8)). Moreover, DEEA also played a reaction role with CO<sub>2</sub> as Eq.(9). Furthermore, it is clear from the reaction mechanism that DEEA mainly deprotonates the amphoteric ion HMDACOO<sup>-</sup>H<sup>+</sup>, thus increasing the CO<sub>2</sub> capture capacity of the blended amine DEEA-HMDA. The blended amine DEEA-HMDA solution has good potential for capturing CO<sub>2</sub> because it has a high CO<sub>2</sub> absorption capacity with a value of 1.143 mol CO<sub>2</sub>/mol amine at 313 K, 100.3 kPa (Fig. 6).

## 3. Experimental section

### 3.1. Chemicals

MEA (98%), DEEA (99%) and HMDA (AR  $\geq$  98%) were purchased from Macklin Co., Ltd., China. CO<sub>2</sub> and N<sub>2</sub> gas (99.999%) were purchased from Beijing Wansheng Da Feng Gas Co., Ltd, China. All materials used in this work were received without further purification.

### 3.2. CO<sub>2</sub> analysis

#### 3.2.1. CO<sub>2</sub> loading in liquid phase

The measurement of CO<sub>2</sub> loading in the liquid phase is the basis of the subsequent CO<sub>2</sub> equilibrium solubility and  $K_{G\alpha_v}$  experiments. The CO<sub>2</sub> loading in the liquid phase should be titrated before and after each set of experiments with the apparatus shown in Fig. 1.

The titration process for CO<sub>2</sub> loading in the liquid phase ( $\alpha$ , mol CO<sub>2</sub>/mol amine) was described below. Firstly, a 1 mL liquid sample ( $V_{\text{amine}}$ , mL) was taken, added to a 50 mL conical flask and diluted with deionized water. Methyl orange was then added as an indicator. At the end of the above step, the plug was tightened to prevent the resulting gas from

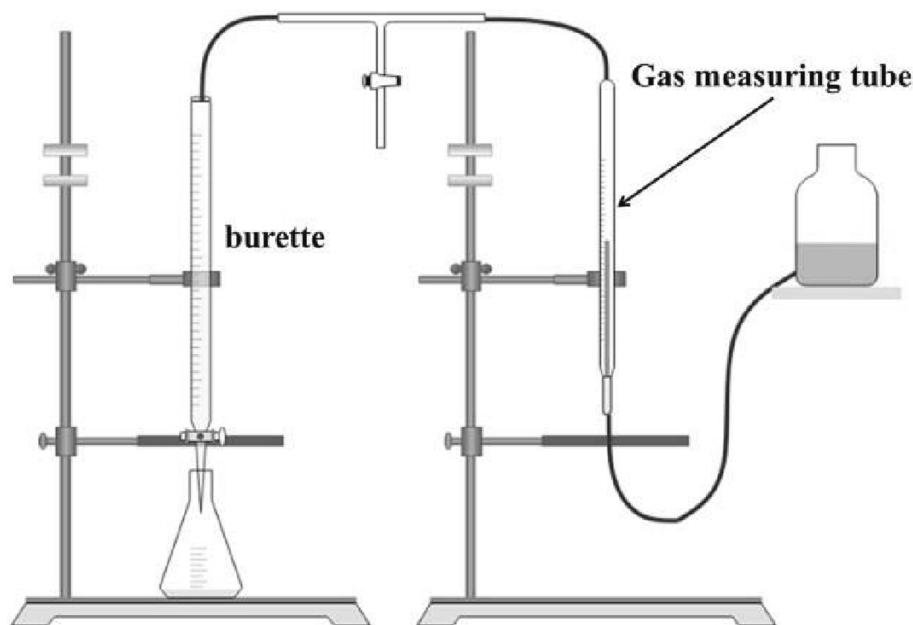


Fig. 1.  $\text{CO}_2$  loading titration device.

escaping. Furthermore, titrated with 1 mol/L hydrochloric acid ( $C_{\text{HCl}}$ , mol/L) after calibration. Record the initial volume of hydrochloric acid ( $V_0$ , mL) and measure the initial volume of the trachea ( $V_1$ , mL). The hydrochloric acid volume ( $V_2$ , mL) recorded when the indicator color turned to light red at the end of the titration. The excess hydrochloric acid was continued to be dripped to react fully, and the final volume of hydrochloric acid ( $V_3$ , mL) and the trachea ( $V_4$ , mL) was recorded. In addition, the experiments's room temperature ( $T$ , K) was recorded. After the above experiments, Eq.(10) and Eq.(11) were used to calculate the amine concentration and the  $\text{CO}_2$  loading in the liquid phase (Bai et al., 2022).

$$C_{\text{amine}} = nC_{\text{HCl}}(V_2 - V_0)/V_{\text{amine}} \quad (10)$$

$$\alpha = ((V_4 - V_1) - (V_3 - V_0)/22.4C_{\text{amine}}V_{\text{amine}}) \times 273.15/(273.15 + T) \quad (11)$$

### 3.2.2. $\text{CO}_2$ concentration in the gas phase

The gases from the column are introduced through a drying tube to remove the moisture. The dried gas is sent to  $\text{CO}_2$  analyzers (MOT-500, Shenzhen Korno Electronic Technology Co., LTD) to obtain  $\text{CO}_2$  concentration in the gas phase.

This experimental setup was validated by the whole packed column for material balance. To its error within 8.0%, the experimental data can be considered available. Material balance is calculated using Eq.(12).

$$L_{\text{out}} - L_{\text{in}} = G_{\text{in}} - G_{\text{out}} \quad (12)$$

where  $L_{\text{out}}$  and  $L_{\text{in}}$  are the liquid outlet and inlet  $\text{CO}_2$  flow rates, respectively.  $G_{\text{out}}$  and  $G_{\text{in}}$  are the gas outlet and inlet  $\text{CO}_2$  flow rates, respectively.

### 3.3. $\text{CO}_2$ equilibrium solubility

The  $\text{CO}_2$  equilibrium solubility measurement method adopted in this paper uses the same experimental device (Fig. 2.) and experimental method as our previous work (Liu et al., 2017). The average absolute deviation (AAD) of  $\text{CO}_2$  equilibrium solubility measured by this method is 1.06% compared with the results in the references, which verifies the effectiveness of this method. Moreover, the measurement process of  $\text{CO}_2$  solubility as follows: Firstly, the prepared amine solution was added to the sand core reactor for reaction, and the temperature was kept

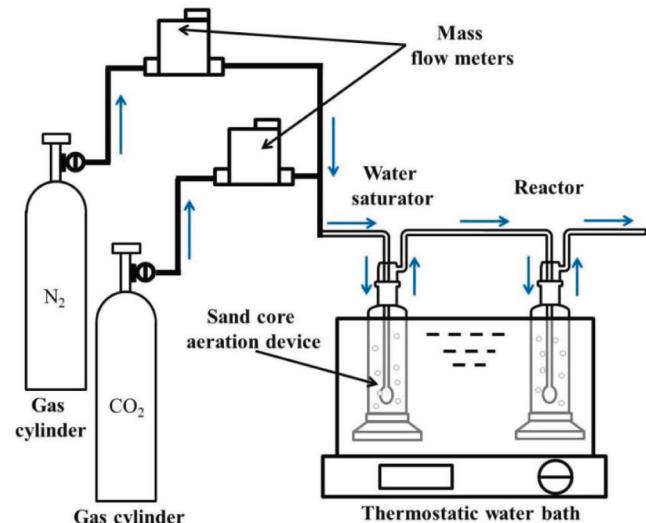


Fig. 2. Schematic diagram for equilibrium solubility measurement.

constant through water bath. Secondly, the gas mass flowmeters (Beijing Qixinhuachuang Gas Co., Ltd) were used to control the flow of  $\text{N}_2$  and  $\text{CO}_2$  to obtain 15%  $\text{CO}_2$ . Thirdly, the mixed gas was passed into the sand core tube containing amine solution at a constant gas rate. Finally, 1 mL of the sample was taken to determine  $\text{CO}_2$  loading. In the above process, a condensing device should be installed at the gas outlet to reduce the loss of amine and improve the accuracy of the experiment (Horwitz, 1975).

### 3.4. Mass transfer coefficient

The  $K_{\text{Gav}}$  was determined by the experimental device shown in Fig. 3. Among them, the height of the two-section double-layer vacuum glass column is 0.97 m, the diameter is 0.026 m, and the structural packing (DX-type with a specific surface area of  $1000 \text{ m}^2/\text{m}^3$ ) is adopted. The column was equipped with six  $\text{CO}_2$  concentration and temperature measurement points distributed on both sides of the column.

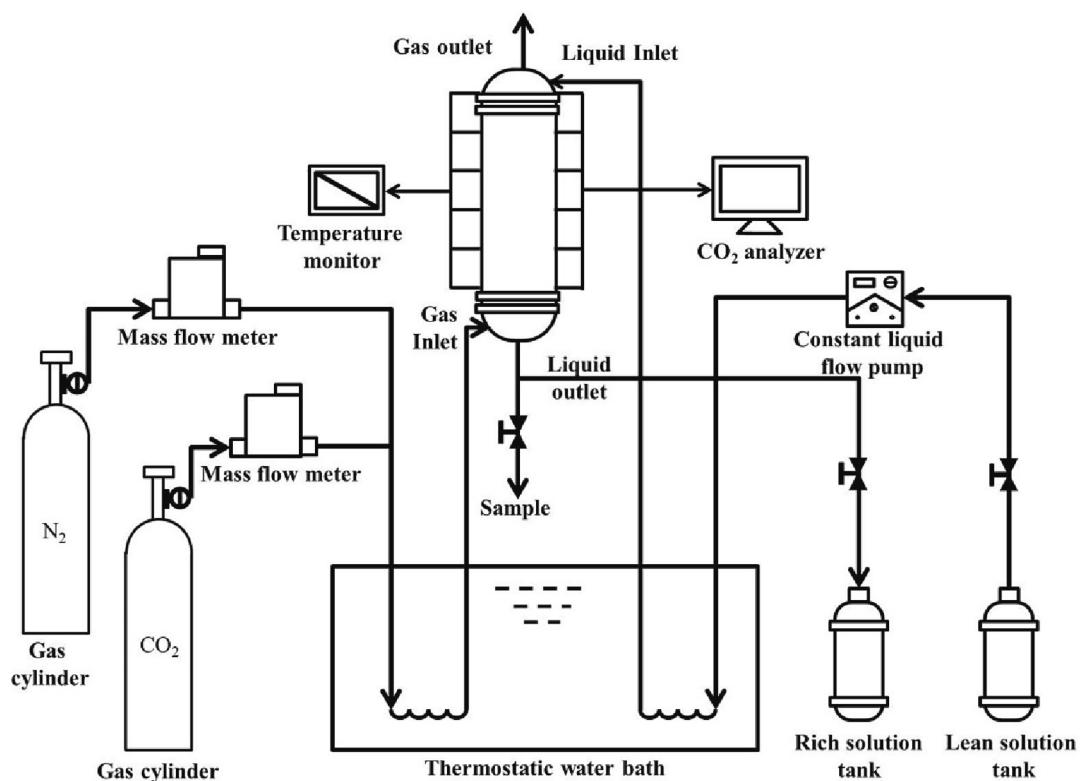


Fig. 3. Schematic diagram of mass transfer experimental device.

The experimental procedure was briefly presented as the following: Firstly,  $\text{N}_2$  and  $\text{CO}_2$  were mixed using the gas mass flowmeters to obtain a 15%  $\text{CO}_2$  gas mixture, which was made to enter from the bottom of the packed column. At the same time, the lean liquid was pumped through a constant temperature water bath to the top of the packed column. Secondly, the lean liquid was in counter-current contact with 15%  $\text{CO}_2$  in the packed column to obtain a full  $\text{CO}_2$  capture. A pump fed the absorbed rich liquid to the rich liquid storage tank. Furthermore, the captured exhaust gas was condensed and discharged directly into the atmosphere. The gas  $\text{CO}_2$  concentration was measured at six sampling points using a  $\text{CO}_2$  analysis detector (MOT-500, Shenzhen Korno Electronic Technology Co., LTD) during the reaction. The  $\text{CO}_2$  loadings of the lean and rich liquids before and after absorption were also titrated.

Eq.(13) was used to calculate the mass transfer flux, and according to the two-film theory, the mass transfer flux was the product of the mass transfer driving force and the mass transfer coefficient under the steady-state condition (Afkhamipour and Mofarahi, 2017; Fu et al., 2012; Green and Perry, 2007).

$$N_A = K_G P (y_A - y'_A) \quad (13)$$

where  $N_A$  ( $\text{kmol}/(\text{m}^2 \cdot \text{h})$ ) is the absorption mass transfer flux;  $K_G$  ( $\text{kmol}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$ ) is the total gas phase mass transfer coefficient;  $P$  (kPa) is the total gas pressure;  $y_A$  and  $y'_A$  are the gas phase volume concentrations, respectively, in equilibrium with the liquid phase volume concentrations.

For counterflow continuous contact packed columns, any height  $dZ$ , based on gas-liquid material balance, can be calculated using Eq.(14).

$$N_A a_V dZ = G_{N_2} dY_A \quad (14)$$

where  $a_V$  ( $\text{m}^2/\text{m}^3$ ) is the effective phase boundary area;  $G_{N_2}$  ( $\text{kmol}/(\text{m}^2 \cdot \text{h})$ ) is the  $\text{N}_2$  flow rate;  $Y_A$  (%) is the molar fraction of  $\text{CO}_2$  in the gas phase.

By combining Eq.(13) with Eq.(14) to obtain Eq.(15).

$$K_{Gav} = (G_{N_2}/P(y_A - y'_A)) (dY_A/dZ) \quad (15)$$

where  $dY_A/dZ$  is obtained by measuring the gas phase  $\text{CO}_2$  concentration at different column heights and fitting it to the corresponding column height to obtain the fitted curve  $Y-Z$ . The  $dY_A/dZ$  values at different heights can be obtained by deriving  $Z$ , as shown in Fig. 4.

#### 4. Results and discussion

##### 4.1. Calculation of technical properties

###### 4.1.1. Mass transfer coefficient of DEEA-HMDA

The mass transfer performance of the blended amine DEEA-HMDA was determined under the conditions of 0.6–2.4 mol/L amine

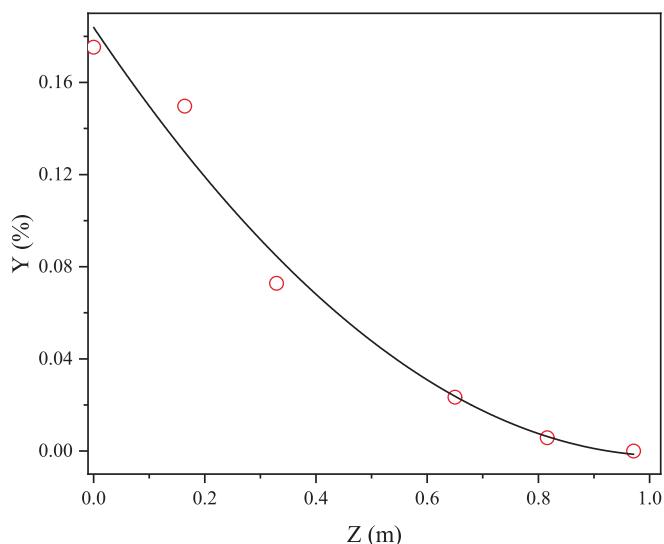


Fig. 4. Fitting curve of  $\text{CO}_2$  concentration as a function of packed column height.

concentration and 22.5 kmol/(m<sup>2</sup>·h) inert gas flow and 0.06 m<sup>3</sup>/(m<sup>2</sup>·h) liquid flow rate, respectively. Fig. 5 shows the  $K_{GA_v}$  results of the blended amine DEEA-HMDA solution. It was obviously found that  $K_{GA_v}$  increased significantly with the increase of HMDA concentration, and the highest  $K_{GA_v}$  was 0.9143 kmol/(m<sup>2</sup>·h·kPa). The reason for this phenomenon may be due to the small size of the packing column used in this paper, which makes the gas-liquid contact area smaller (Quan et al., 2023a). So, the DEEA as a tertiary amine does not have sufficient gas-liquid contact time to enhance the reaction of CO<sub>2</sub> in the flue-gas to the corresponding bicarbonate. It leads to the DEEA not being able to take advantage of its high CO<sub>2</sub> solubility as a tertiary amine during the mass transfer process. Therefore, the mass transfer performance of blended amine DEEA-HMDA is mainly dominated by HMDA (Quan et al., 2023b). And the higher the molar ratio of HMDA, the larger the  $K_{GA_v}$ . However, a greater proportion of HMDA is only sometimes better. Because HMDA is a secondary amine with two amino groups, and the reaction product with CO<sub>2</sub> is a stable carbamate, resulting in high energy consumption for regeneration (Mondal et al., 2017). So, reaching a trade-off between CO<sub>2</sub> absorption performance and regeneration consumption is essential. Based on the above discussion, 1.5 M DEEA:1.5 M HMDA could be the best ratio to reconcile a high mass transfer performance (0.7560 kmol/(m<sup>2</sup>·h·kPa)) with low energy consumption (67.1 kJ/mol). Therefore, this work selected 1.5 M DEEA:1.5 M HMDA for further study.

#### 4.1.2. CO<sub>2</sub> equilibrium solubility and absorption heat of DEEA-HMDA

Through the above experiments, 1.5 M DEEA:1.5 M HMDA was selected as the research object, and its CO<sub>2</sub> equilibrium solubility was measured under 313 K with a CO<sub>2</sub> partial pressure range of 8.1–101.3 kPa. The experimental results are shown in Fig. 6. It can be seen that with the increase of CO<sub>2</sub> partial pressure, the CO<sub>2</sub> equilibrium solubility in the blended amine DEEA-HMDA solution increases. The main reason for this phenomenon is that the increase of partial pressure of CO<sub>2</sub> enhances the driving force of gas mass transfer and thus improves the equilibrium solubility of CO<sub>2</sub>.

It can be seen from the above experimental results that pressure and temperature are the key factors affecting CO<sub>2</sub> equilibrium solubility. Therefore, the correlation between CO<sub>2</sub> equilibrium solubility and

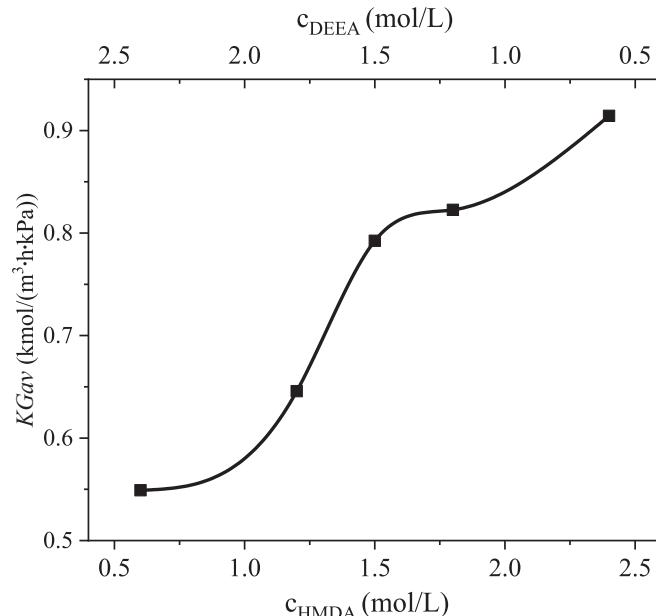


Fig. 5. Effect of different proportions of DEEA-HMDA solution in terms of  $K_{GA_v}$ . (Gas flow rate (G) = 22.5 kmol/m<sup>2</sup>·h, Liquid flow rate (L) = 0.06 L/min, feed temperature (T) = 313 K, CO<sub>2</sub> loading = 0.1 mol CO<sub>2</sub>/mol amine, CO<sub>2</sub> partial pressure = 15.0 kPa.).

temperature and pressure was listed by an empirical equation, and the equation could be defined as follows (Mondal et al., 2017):

$$P_{CO_2} = \exp[A \times \ln a + a/T + b + B/(1 + \exp(-c/T + d) \times \exp(-k_3 \ln a))] \quad (16)$$

where A, B, a, b, c, d and k<sub>3</sub> are undetermined coefficients of the equation. All coefficients can be obtained by fitting the equilibrium solubility with temperature and pressure through MATLAB, as shown in Table 1.

According to Fig. 6, the fitting effect under this experimental condition is good, and the AARD of CO<sub>2</sub> equilibrium solubility predicted by the empirical model is only 1.00%.

The absorption heat ( $\Delta H_{reac}$ , kJ·mol<sup>-1</sup>) is another important property reflecting the effect of CO<sub>2</sub> capture, which is closely related to the energy requirement of rich liquid regeneration process. As shown in Fig. 6, the CO<sub>2</sub> solubility data within the range of 8.1–101.3 kPa of CO<sub>2</sub> partial pressure were measured at 313 K, and Eq.(17) was used to calculate the absorption heat (Liu et al., 2019a). The VLE curves for the DEEA-HMDA solvent are shown in Fig. S1. The reaction heat of DEEA-HMDA was 67.1 kJ/mol and the authors put the following Figure into the SI.

$$d(\ln P_{CO_2})/d(1/T) = -\Delta H_{abs}/R \quad (17)$$

where  $P_{CO_2}$  is the partial pressure of CO<sub>2</sub>, R (J/(mol·K)) is the ideal gas constant, and  $\Delta H_{abs}$  (kJ/mol) is the absorption heat of CO<sub>2</sub>.

#### 4.2. Technical properties analysis of DEEA-HMDA

Currently, it is costly and time-consuming to compare the high-performance absorbent through comprehensive performance screening. Therefore, how to evaluate the CO<sub>2</sub> capture properties of amine solvents by using their technical properties, including CO<sub>2</sub> equilibrium solubility,  $K_{GA_v}$ , and absorption heat. A screening criterion for amine solvents was established to guide its industrial application in CO<sub>2</sub> capture. Comparing conventional amine solvents' technical properties has been the key to building rapid screening methods.

##### 4.2.1. Comparison the $K_{GA_v}$ of DEEA-HMDA with those of conventional amines

As shown in Table 2, the  $K_{GA_v}$  of DEEA-HMDA solution and conventional amine solutions were compared at almost identical conditions (including  $v_G$ ,  $v_L$ ,  $P_{CO_2}$ , CO<sub>2</sub> loading, T). The data were from references except those of DEEA-HMDA. The  $K_{GA_v}$  of DEEA-HMDA was the highest up to 0.7560 kmol/(m<sup>2</sup>·h·kPa), which was 26.3% higher than the most commonly used MEA, indicating the mass transfer performance of DEEA-HMDA had better CO<sub>2</sub> capturing potential than MEA.

##### 4.2.2. Comparison CO<sub>2</sub> equilibrium solubility of DEEA-HMDA with those of conventional amines

The performance of amines in the CO<sub>2</sub> capture process must be evaluated using the CO<sub>2</sub> equilibrium solubility as a crucial parameter. This work examined the blended amine DEEA-HMDA'CO<sub>2</sub> equilibrium solubility at 313 K, and under various partial CO<sub>2</sub> pressures, and it was compared to other conventional amine solutions stated in the references (Fig. 7). As shown in Fig. 7, the single amine PZ and AMP have higher CO<sub>2</sub> equilibrium solubility (>0.60 mol CO<sub>2</sub>/mol amine) than MEA, which is by far the most commonly used. The higher CO<sub>2</sub> equilibrium solubility of PZ is the presence of two NH-based (amine and amide) bonds, which significantly increase the CO<sub>2</sub> absorption capability. The various groups linked to the carbon adjacent to the amino group cause steric hindrance, which is why the CO<sub>2</sub> equilibrium solubility of AMP is 0.78 mol CO<sub>2</sub>/mol amine. Due to the unstable carbamate created by this arrangement, hydrolysis will take place, forming free amines in the solution that will react with CO<sub>2</sub> to enhance CO<sub>2</sub> loading. As a tertiary amine that cannot generate carbamate, MDEA is less reactive with CO<sub>2</sub>.

**Table 1**  
Empirical model fitting coefficients.

Notation	A	B	a	b	c	d	$k_3$
Coefficient	8.8847	6.4719	-11.6151	3.3803	2.5239	29.9375	189.8206

**Table 2**  
Comparison of  $K_{GA_v}$  of different amine solvents in literature under the similar conditions.

Category	Amine	$v_G$ kmol/m <sup>2</sup> ·h	$v_L$ L/min	$P_{CO_2}$ kPa	CO <sub>2</sub> loading mol/mol	T K	$K_{GA_v}$ kmol/(m <sup>2</sup> ·h·kPa)	Ref.
Primary amines	MEA	39.45	3.98	15.0	0.19	313	0.3563	(Xu et al., 2016)
	AMP	46.2	9.73	10.0	0.15			
Secondary amines	PZ	28.4	6.36	14.2	—	313	0.6280	(Ghaemi and Hemmati, 2020)
	MDEA	23.9	6.82	14.5	0.13			
Tertiary amines	DEEA	39.17	5.85	15.0	0.05	313	0.1671	(Xu et al., 2016)
	DMEA	39.17	5.85	15.0	0.2			
Blended amines	1DMA2P	23.9	6.82	14.5	0.04	313	0.5121	(Wen et al., 2015)
	DETA	23.9	6.82	14.5	0.04			
Blended amines	DETA-PZ	38.0	9.23	14.4	—	313	0.6593	(Sheng et al., 2016)
	MEA-DEEA	39.2	5.85	15.0	0.32			
Blended amines	MDEA-MEA	15.99	5.00	15.0	0.04	318	0.3984	(Naami et al., 2013)
	MEA-DMEA	44.21	3.7	15.0	0.28			
Blended amines	DEEA-HMDA	22.5	6.78	15.0	0.10	313	0.7560	This work
	DETA-AEPZ	38.0	9.23	14.3	—			
Blended amines	PZ-MDEA	—	—	—	—			

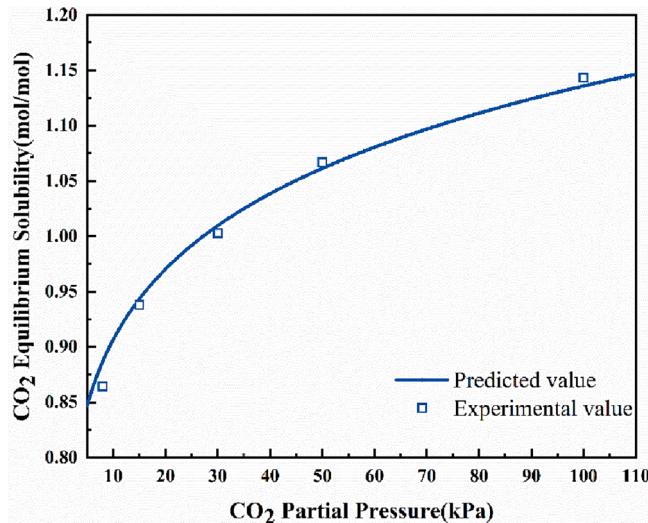


Fig. 6. The  $\alpha_{cal}$  calculated by empirical model is compared with the experimental data  $\alpha_{exp}$ .

As a result, the CO<sub>2</sub> capture procedure at low-pressure operations cannot be effectively carried out with a single MDEA solvent. However, MDEA has the advantages of low regeneration energy requirements and corrosiveness. Therefore, blending MDEA with other primary or secondary (such as DEA and PZ), which have high CO<sub>2</sub> solubility, to form a blended amine can increase CO<sub>2</sub> absorption while maintaining relatively low energy consumption. Similarly, MEA-DEEA is also composed of a mixture of the same causes. The CO<sub>2</sub> equilibrium solubility for MEA-DEEA, DEA-MDEA and PZ-MDEA at 313 K 101.3 kPa are 0.61 mol CO<sub>2</sub>/mol amine, 0.73 mol CO<sub>2</sub>/mol amine and 0.62 mol CO<sub>2</sub>/mol amine, respectively. Additionally, since DETA contains two primary and one secondary amino group, it is a blended amine with two amine functionalities. Compared to other amines, the blended amine DETA has the highest CO<sub>2</sub> equilibrium solubility of 1.20 mol CO<sub>2</sub>/mol amine at 313 K and 101.3 kPa. The blended amine DEEA-HMDA solution has the second-highest CO<sub>2</sub> equilibrium solubility, 0.94 mol CO<sub>2</sub>/mol amine at 313 K and 101.3 kPa, second only to DETA. Although DEEA-HMDA contains the tertiary amine DEEA, the presence of two amino groups in the primary amine HMDA gives it a significant kinetics advantage.

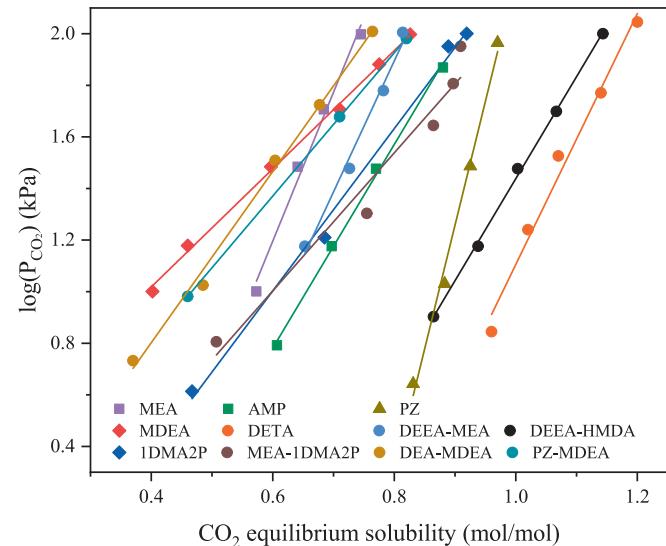
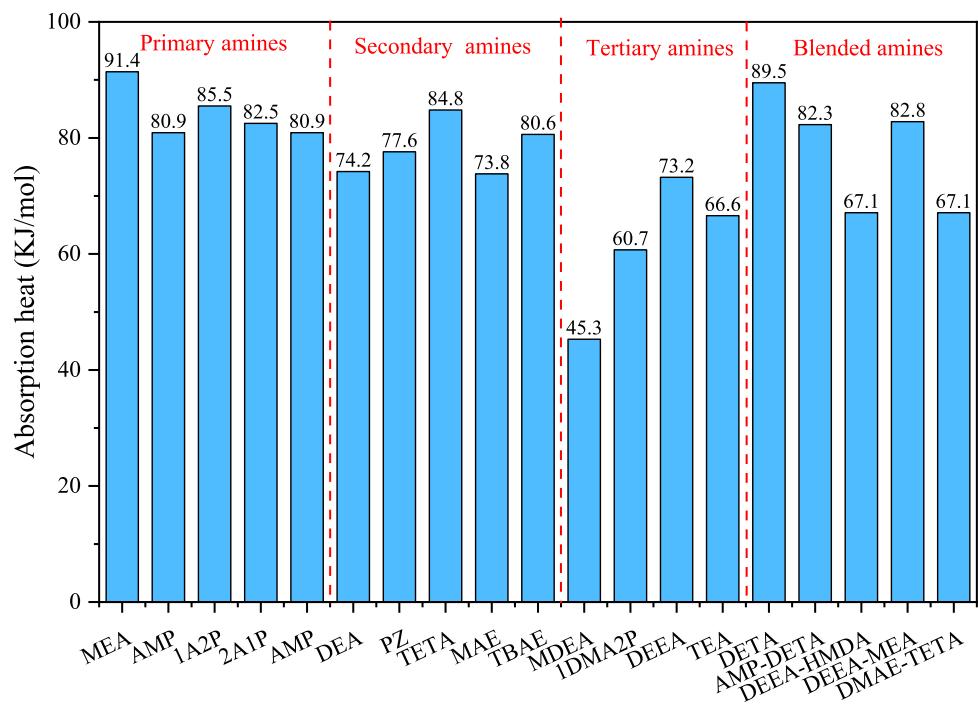


Fig. 7. Comparison of the CO<sub>2</sub> equilibrium solubility of different amine solvents in literature (where  $\square$ ,  $\triangle$ ,  $\diamond$ , and  $\circ$  represent primary, secondary, tertiary and blended amines, respectively) (Afkhampour and Mofarahi, 2018a; Afkhampour et al., 2019; Ali and Aroua, 2004; Benamor and Aroua, 2005; Chang et al., 2013; Dash et al., 2011; Gabrielsen et al., 2006; Gao et al., 2017a; Maneeintr et al., 2009; Xiao et al., 2021).

Therefore, the DEEA-HMDA solution with a large absorption capacity and reaction rate could be an ideal solvent for industrial CO<sub>2</sub> capture.

#### 4.2.3. Comparison reaction heat of DEEA-HMDA with those of conventional solvents

The absorption heat of CO<sub>2</sub> captured by amine solutions is similar to that required for the desorption of CO<sub>2</sub> molecules (Kim et al., 2013). In this paper, the absorption heat of the blended amine DEEA-HMDA solution was measured and compared under different pressure conditions at 313 K (El Hadri et al., 2017; Inna and Svendsen, 2007; Kim and Svendsen, 2008; Liu et al., 2019b; Wai et al., 2018; Xiao et al., 2016). As seen from Fig. 8, the absorption heat of tertiary amine solvent was significantly lower than that of primary/secondary amines and blended amine solutions with an absorption heat range of 45.3 KJ/mol-73.2 KJ/mol. This phenomenon is because there is no active hydrogen on the



**Fig. 8.** Comparison of the absorption heat of different amine solvents in literature (Inna and Svendsen, 2007; Kim and Svendsen, 2008; Liu et al., 2019b; Wai et al., 2018; Xiao et al., 2016).

nitrogen atom of tertiary amine solvent, which can not react directly with  $\text{CO}_2$  to form stable carbamate. Instead, it reacts with  $\text{CO}_2$  under the action of hydrogen bonding in an aqueous solvent to form an unstable  $\text{HCO}_3^-$ , as shown in Eq.(18). Among them,  $\text{HCO}_3^-$  desorption requires lower energy, resulting in lower regeneration energy of tertiary amine. Therefore, tertiary amines such as TEA (66.6 kJ/mol), MDEA (45.3 kJ/mol), and 1DMA2P (kJ/mol) have relatively low absorption heat. On the contrary, due to the reaction of primary/secondary amines with  $\text{CO}_2$  to form stable amine carbamate, the renewable energy consumption was relatively high, ranging from 73.8 kJ/mol-91.4 kJ/mol. Moreover, the maximum renewable energy consumption of MEA was 91.4 kJ/mol.



The absorption heat of blended amine solutions is between the primary/secondary amines and the tertiary amines. The blended amine solutions containing tertiary amines (such as DEEA and DMAE) have relatively low reaction heat, with MEA-DEEA, DEEA-HMDA, DMAE-TETA of 82.8 kJ/mol, 67.1 kJ/mol, and 67.1 kJ/mol, respectively. It has been observed that the present blended amine solution DEEA-HMDA has a lower absorption heat than the previously studied amine mixtures. DETA (89.5 kJ/mol) and AMP-DETA (82.3 kJ/mol) are blended amine solutions consisting of primary and secondary amines with relatively

**Table 3**  
Summarized of  $\text{CO}_2$  solubility, heat of absorption,  $K_{\text{G}}a_v$ , and price of different amine solutions.

Amine	Structure	$\text{CO}_2$ solubility (mol $\text{CO}_2$ /mol amine)	Absorption heat (kJ/mol)	$K_{\text{G}}a_v$ kmol/(m <sup>2</sup> ·h·kPa )
MEA		0.56	85.1	0.3563
AMP		0.78	80.9	0.5988
PZ		0.91	80.6	0.6695
MDEA		0.52	52.5	0.3101
1DMA2P		0.72	60.7	0.5121
DETA		1.02	89.5	0.6280
MEA-DEEA		0.61	82.8	0.3984
DEEA-HMDA		0.94	67.1	0.7560

high regeneration energy. In a word, the blended amine solution DEEA-HMDA has superior kinetic properties while maintaining the tertiary amine DEEA's good characteristics while having a high  $\text{CO}_2$  solubility. Thus, DEEA-HMDA is a promising amine solution for removing  $\text{CO}_2$  from the gas stream of coal-fired power plants.

Based on the technical analysis of DEEA-HMDA, eight amines were selected for further investigation. The selected solvents represent various categories, structures, and the chemical group of amines, including primary amines (MEA, AMP), secondary amines (PZ), tertiary amines (MDEA, 1DMA2P), and blended amines (DETA, MEA-DEEA, DEEA-HMDA). It is beneficial to investigate the impact of the amine structure on the technical assessment of  $\text{CO}_2$  capture. The  $\text{CO}_2$  solubility, absorption heat,  $K_{GA_v}$  and price of these amines are summarised in Table 3.

According to the analysis of technical indicators, the higher values of  $\text{CO}_2$  equilibrium solubility mean the same amount of amine solution obtains a higher  $\text{CO}_2$  capture capacity and more  $\text{CO}_2$ . The larger values of  $K_{GA_v}$  mean a faster reaction rate with  $\text{CO}_2$  and a correspondingly smaller packed column size. The lower absorption heat values mean less energy is required to regenerate the  $\text{CO}_2$  reaction products. Therefore, the existing experimental data were sorted out and summarized. The T-K and B-D-T diagram for screening amines for  $\text{CO}_2$  capture was established from the perspectives of kinetics and thermodynamics to establish a fast and accurate judgment method. As shown in Fig. 9, the effective area of B-D-T and T-K can be divided into three different regions after B-D-T and T-K are put together. When in the overlap region, the amine solvent has outstanding kinetic and thermodynamic properties. For example, the blended amine DEEA-HMDA is in the overlap region, indicating that it has low regeneration energy consumption (67.1 KJ/mol), high  $K_{GA_v}$  (0.7560 kmol/(m<sup>2</sup>·h·kPa)) and high  $\text{CO}_2$  solubility (0.94 mol  $\text{CO}_2$ /mol amine), and have  $\text{CO}_2$  capture potential. Conversely, when one or more of the two points are not in the overlap region, the  $\text{CO}_2$  capture potential of this amine solvent is less prominent, such as MEA, MDEA, AMP, and MEA-DEEA. Meanwhile, these amines can be shifted towards the overlap region by adjusting operating conditions or ratios. Importantly, before a novel solvent is used in industry, its relevant parameters can be brought into Fig. 9 to quickly assess the  $\text{CO}_2$  capture potential by regions.

#### 4.3. Calculation of technical indicators

The technical indicators of amine solvent depend on outstanding solvent properties. A reasonable, meaningful, and comprehensive technical analysis based on its solvent properties will benefit the industrial application of new amines. Therefore, this paper uses blended amine DEEA-HMDA solution as an example to calculate conventional amines' technical indicators (including solvent consumption, design of packed column, and regeneration energy requirement) with different structures. Meanwhile, other processes and equipment are not considered, including pre-treatment steps (such as inlet gas purification or cooling), post-compression treatment steps, equipment (such as flue gas fan, pump, heat change, reboiler, etc.), and more (Ali et al., 2019).

##### 4.3.1. Design of packed columns

The packed column is a central component of the  $\text{CO}_2$  capture process due to its high mass transfer efficiency, large handling capacity and operational stability. Therefore, the sizing of the packed column is very essential. In this work, the column height ( $H$ , m) and diameter ( $R$ , m) for different amine solutions were calculated at current parameters of industrial flue gas with a gas flow rate of 4500 kg/h, partial pressure of  $\text{CO}_2$  of 15 kPa, a total gas pressure of 101.325 kPa with an operating requirement of 90%  $\text{CO}_2$  removal. This calculation method still applies when changing to other  $\text{CO}_2$  flow rates, partial pressures of  $\text{CO}_2$ , removal efficiencies, and other conditions. As another important part of a packed column, the primary function of the packing is to provide a contact area for heat and mass transfer between the gas and liquid phases. This article used regular corrugated packing DX-100. The calculation process is expressed in Eq.(19) and Eq.(20).

$$X = (L/G) \times (\rho_G/\rho_L)^{0.5} \quad (19)$$

where  $X$  is flow parameter.  $G$  (kg/h) and  $L$  (kg/h) are the gas flow rate and liquid flow rate, respectively;  $\rho_G$  (kg/m<sup>3</sup>) and  $\rho_L$  (kg/m<sup>3</sup>) are the gas and liquid densities, respectively.

$$S = 5.0314 \times 10^{-4} F_P^{0.5} \times \nu^{0.05} \times \left( G/Y(\rho_G(\rho_L - \rho_G))^{0.5} \right) \quad (20)$$

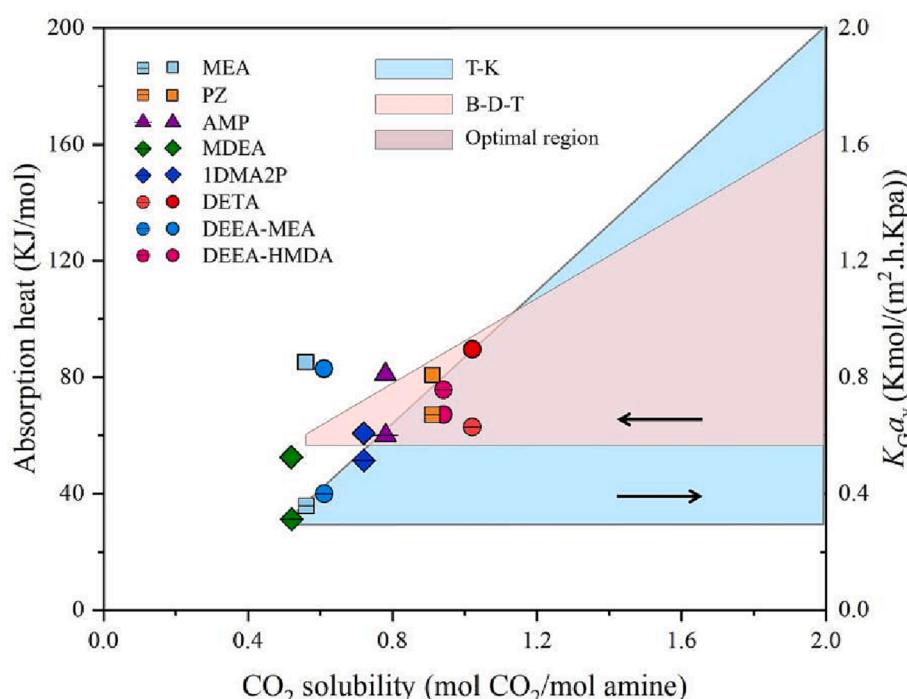


Fig. 9. Screening guideline for promising amines. Where B-D-T is the abbreviation of absorption-desorption-thermodynamics and K-T is the abbreviation of kinetics-thermodynamics.

$$R = (S/(\pi/4))^{0.5} \quad (21)$$

where  $S$  ( $\text{m}^2$ ) is the cross-sectional area of the column. The packing factor of the regular packing  $F_p$  is  $60 \text{ m}^{-1}$ .  $\nu$  ( $\text{m}^2/\text{s}$ ) is the kinematic viscosity of the liquid. Flow parameter ( $X$ ) corresponds to the loading factor  $Y$  in the Kister pressure drop diagram.

$$H = H_{OG} \times N_{OG} \quad (22)$$

where  $H_{OG}$  (m) and  $N_{OG}$  are the height and the number of mass transfer units, respectively. They are defined as Eq.(23) and Eq.(24).

$$H_{OG} = G/(K_{GA_v} \times P \times S) \quad (23)$$

$$N_{OG} = \ln(y_1/y_2) \quad (24)$$

The heights and diameters of the packed columns for different amine solutions were calculated according to Eqs. (18)-(23). Moreover, the results are shown in Fig. 10. The size of the packed column is influenced by several factors, including gas flow rate, liquid flow rate, liquid viscosity,  $K_{GA_v}$ , packing type, etc. The column diameter of the MDEA solution (5.1 m) was significantly larger than that of the other amine solutions. This result may be due to the lower  $\text{CO}_2$  equilibrium solubility of MDEA, which requires a higher solvent flow rate to meet the process constraint of a 90%  $\text{CO}_2$  removal rate. Therefore, the column's inner diameter is increased to maintain sufficient  $\text{CO}_2$ -solvent contact time. Meanwhile, Eq.(22)-(24) shows that the column height is closely related to the  $K_{GA_v}$  of the amine solution. The smaller the  $K_{GA_v}$  is, the higher the column height becomes. As shown in Fig. 10, the volume ranking of the packed column is DEEA-HMDA < DETA < PZ < MEA < AMP < 1DMA2P < MEA-DEEA < MDEA. Increasing the column height will increase the stay time of the flue gas in the column and the contact area between the solvent and the flue gas, thus increasing the  $\text{CO}_2$  capture efficiency. However, increasing the column height will undoubtedly increase the packed column construction cost, especially the column construction and packing costs. DEEA-HMDA has the smallest packed column volume compared to other amine solutions at  $44.5 \text{ m}^3$ , with a 23.3% reduction compared to MEA ( $58.0 \text{ m}^3$ ). In contrast, MDEA and MEA-DEEA have volumes of  $108.4 \text{ m}^3$  and  $96.1 \text{ m}^3$ , respectively, with  $86.9 \text{ m}^3$ , and  $65.7 \text{ m}^3$  increases compared to MEA.

#### 4.3.2. Solvent consumption

Solvent consumption is the amount of solvent required to capture two years of flue gas ( $4500 \text{ kg/h}$ , 15%  $\text{CO}_2$ ) with considering 5% amine losses. The solvent consumption was calculated from the  $\text{CO}_2$  equilibrium solubility, using the MEA as the basis for the calculation. The difference between the outlet loading of the MEA and the  $\text{CO}_2$  equilibrium solubility is  $0.16 \text{ mol CO}_2/\text{mol amine}$ . The  $\text{CO}_2$  equilibrium solubility used for calculating solvent consumption was obtained at  $313 \text{ K}$ . Therefore, the outlet loading for other amines was set to the  $\text{CO}_2$  equilibrium solubility subtracted by  $0.16 \text{ mol CO}_2/\text{mol amine}$ . At the same time, the inlet loading was set to  $0.20 \text{ mol CO}_2/\text{mol amine}$  in comparison to different amine solutions. The higher the outlet loading is, the

higher the  $\text{CO}_2$  absorption capacity could be expected and thus the lower solvent consumption. As shown in the Fig. 11(a), the ranking of the solvent consumption is DETA < DEEA-HMDA < PZ < AMP < 1DMA2P < MEA-DEEA < MEA < MDEA. Capturing the same amount of  $\text{CO}_2$  for a given condition, DETA (2.02 kg/t $\text{CO}_2$ ) and DEEA-HMDA (2.28 kg/t $\text{CO}_2$ ) require less solvent consumption, which means lower technical costs.

#### 4.3.3. Regeneration energy consumption

In the evaluation of the technical indicators, the regenerative energy requirements were calculated on the basis of absorption heat with a calculation period of two years. Besides, the energy requirements of pumps, blowers and reboilers were not taken into account in the calculations. As shown in Fig. 11(c), the regeneration energy requirements of the different amine solutions are ranked: MDEA < 1DMA2P < DEEA-HMDA < PZ < AMP < MEA-DEEA < DETA < MEA. The regeneration energy requirements of MDEA and 1DMA2P as tertiary amines are significantly lower than other amines, at  $14.6 \text{ KW}\cdot\text{h/tCO}_2$  and  $16.9 \text{ KW}\cdot\text{h/tCO}_2$ , respectively. The reaction products of tertiary amines are unstable and easier to desorb than primary/secondary amines, which brings about the lowest energy consumption for desorption. The addition of the tertiary amine DEEA results in a lower absorption heat for the blended amine solution DEEA-HMDA and an regeneration energy requirements ( $18.6 \text{ KW}\cdot\text{h/tCO}_2$ ) second only to that of the tertiary amine.

## 5. Conclusion

In this work, compared with the conventional amine solutions, the blended amine solution DEEA-HMDA has higher  $\text{CO}_2$  solubility ( $0.94 \text{ mol/mol}$ ) and  $K_{GA_v}$  ( $0.7560 \text{ kmol}/(\text{m}^2\cdot\text{h}\cdot\text{kPa})$ ), and lower heat of absorption ( $67.1 \text{ KJ/mol}$ ). On the basis of these three technical properties, technical indicators were calculated for eight representative amine solutions (MEA, AMP, PZ, MDEA, 1DMA2P, DETA, MEA-DEEA, DEEA-HMDA), including solvent consumption, energy consumption and packed column design. The column height and diameter are lower with DEEA-HMDA as adsorbent,  $4.1 \text{ m}$  and  $3.7 \text{ m}$  respectively, and the column volume is reduced by 43.5% compared to MEA as adsorbent. Meanwhile, this study establishes a technical evaluation method for amine-based  $\text{CO}_2$  capture, highlighting the impact of different technical parameters on  $\text{CO}_2$  capture and identifying the key technical factors. The method provides an overview of the main technological drivers and allows for a simple and rapid analysis of the technical evaluation of potential amine solvents, providing guidance for their industrial applications.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

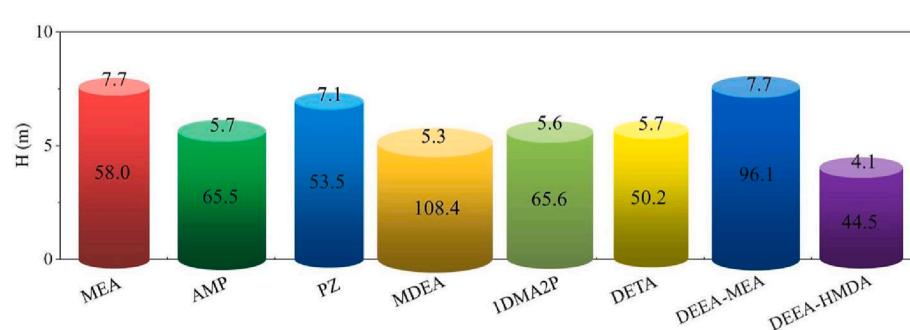
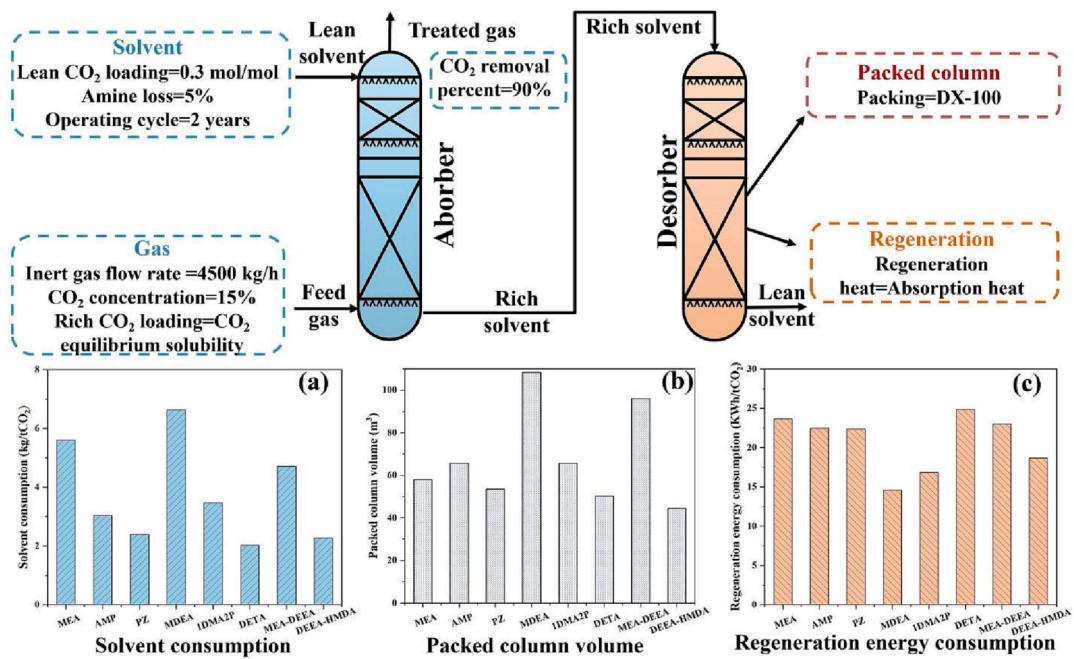


Fig. 10. Column height and column diameter of packed column with different amine solution (The number in the middle is the volume of the packed column).



**Fig. 11.** (a) The solvent consumption of different amine solutions; (b) The volume of packed columns; (c) Regeneration energy requirements of different amine solvents for CO<sub>2</sub> capture.

## Data availability

The authors do not have permission to share data.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2023.119025>.

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