



GHGT-12

Experimental Studies of Regeneration Heat Duty for CO₂ Desorption from Aqueous DETA Solution in a Randomly Packed Column

Xu Zhang, Kaiyun Fu, Zhiwu Liang*, Zhen Yang, Wichitpan Rongwong, Yanqing Na
Joint International Center for CO₂ Capture and Storage (iCCS), College of Chemistry and Chemical Engineering,
Hunan University, Changsha, 410082, P.R. China

Abstract

The regeneration heat duty (Q_{reg} , kJ/kg CO₂) is a critical parameter in post-combustion CO₂ capture using a chemical solvent. In this study, the Q_{reg} of CO₂ desorption from CO₂ rich diethylenetriamine (DETA) solutions were experimentally evaluated in a bench-scale stripper column as a function of CO₂ lean loading, solvent flow rate and CO₂ rich loading. It was found that the Q_{reg} was greatly influenced by all the three operating parameters. In addition, a comparison of the regeneration performance between DETA and monoethanolamine (MEA) was performed to evaluate the potential for DETA's application in the CO₂ capture process. The results obtained in this work showed that for the regeneration at the same CO₂ cyclic capacity, the regeneration heat duty of DETA was lower than that of MEA.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: Desorption; carbon dioxide; regeneration heat duty; Diethylenetriamine; Dixon ring.

1. Introduction

Chemical absorption of carbon dioxide (CO₂) from a post-combustion process using conventional alkanolamines such as monoethanolamine (MEA) has been employed industrially for decades. However, high energy consumption for the regeneration of the chemical solvent is one of the main shortcomings of this technology. Regeneration energy accounts for about 70% of the overall operating cost [1]. Thus, the study of regeneration heat duty (Q_{reg} , kJ/kg CO₂) for chemical solvent regeneration is very important.

In the industrial CO₂ capture process, the Q_{reg} , which is provided by heat transfer from an external higher-

* Corresponding author. Tel.: +86-13618481627; fax: +86-731-88573033;
E-mail address: zwliang@hnu.edu.cn (Z. Liang).

temperature energy source such as low-pressure steam or hot oil in the reboiler, consists of three parts: (1) absorption heat (q_{abs}) for breaking the chemical bonds between CO_2 and the amine-type solvent, (2) sensible heat (q_{sen}) for raising the temperature of solution, and (3) vaporization heat (q_{vap}) for evaporating liquid water to water vapor for CO_2 stripping. Given this, the Q_{reg} can be significantly affected by both solvent types and operating conditions. Therefore, a comprehensive study of the Q_{reg} requirement for amine regeneration is crucial to provide accurate and reliable experimental data for the design of units and for economic evaluation of the amine-based CO_2 capture process.

Diethylenetriamine (DETA) is a promising amine for CO_2 capture given its high performance in terms of absorption capacity, kinetics and mass transfer characteristics compared with that of MEA, which is considered as the benchmark solvent for CO_2 absorption [2-5]. Despite these advantages, energy consumption for solvent regeneration for DETA, which is one of the important evaluation factors, has not yet been studied, rendering the evaluation of its potential application in CO_2 capture to be incomplete.

In this work, the regeneration heat duty of CO_2 desorption from aqueous DETA and MEA solution were evaluated experimentally in a bench-scale stripper packed with Dixon ring. The packed column was made of glass with 28.0 mm internal diameter and 0.50 packed height. The glass column was wrapped with vacuum cylinder to minimize heat loss. The regeneration heat duty for solvent regeneration is presented in terms of reboiler heat duty per unit CO_2 . The experiments were conducted at various operating conditions of solvent flow rate (2.92, 3.9 and 4.87 $\text{m}^3/\text{m}^2\text{-h}$), amine concentration (5.0 M for MEA and 2.0 & 3.0 M for DETA), and CO_2 rich loading (0.5 mol/mol for MEA and 1.2 & 1.4 mol/mol for DETA).

2. Experimental Section

2.1 Chemicals and Experimental apparatus

Reagent grade DETA and MEA were purchased from Tianjin Kermel Chemical Reagent Co. Ltd., China, each with purity of $\geq 98.0\%$. Commercial grade CO_2 was supplied by Changsha Rizhen Gas Co. LTD., China, with a purity of $\geq 99.9\%$.

Two constant liquid-flow pumps for amine solution with ± 0.1 rpm accuracy (model BT100-02, Baoding Qili Precision Pump Co., Ltd, China), two thermostatic water baths with ± 1 K accuracy (model DZKW-4, Beijing Zhongxingweiye Instrument Co., Ltd, China), a circulator for pumping heating oil (model GX-2005, Zhengzhou Boke Instrument Equipment Co., Ltd, China), a metal tube rotameter for measuring the flow rate of heating oil with $\pm 1.5\%$ accuracy (model STZ-15M2H, Shaanxi Shangtai Automation Instrumentation Co., Ltd, China), an intelligent multi point temperature data logger with $\pm 0.5\%$ FS accuracy (model XMX-2008-11, Beijing Gilise Instrumentation Science & Technology Co., Ltd, China), a gas flow meter with $\pm (1.5+0.2\text{FS})\%$ accuracy (model MF4003-3-08-CV-C, Siargo (Chengdu), Ltd, China).

2.2 Typical Degradation Experimental Run

The rich solution used in this work was prepared by initially diluting concentrated amine with deionized water until the desired concentration was reached as confirmed by titration against 1.0 N HCl using methyl orange as indicator. Confirmation for both the DETA concentration and CO_2 loading was obtained by titration against 1.0 N HCl in a Chittick apparatus using methyl orange as indicator.

Each experimental run began by introducing about 2L of rich solution into the reboiler, then the heating oil was circulated and the cooling water was flowed through the condenser. Once the solution in the reboiler reached the desired temperature, the rich solution was fed from the top of the stripper at a given flow rate after the preheating in the heat exchanger. The solvent flow rate of the rich DETA solution was calibrated by measuring the volume of the rich liquid over a specified length of time into a graduated cylinder. The flow rate was calculated as volume/time. In the stripper, the rich-solution flowed down from the top of the stripper and counter-currently contacted the steam vaporized from the reboiler. In the overhead condenser, the vapor was condensed and returned to the stripper while only the stripped CO_2 was allowed to leave the system. The hot lean solution exiting from the reboiler was fed through a heat exchanger and then fed to a stainless steel liquid reservoir.

The desorption process was operated for a long time to achieve steady state when the temperature and CO₂ loading in the liquid phase at all locations were stable (usually took 3 hours). When the operational conditions reached steady state, several parameters were measured to calculate the energy consumptions: (i) CO₂ loading and amine concentration from the inlet and outlet of the stripper, (ii) solvent flow rate, (iii) temperatures from the inlet and outlet of the reboiler, (iv) heat transferred by the oil based on the oil flow rate. After collecting all the steady state data, the supply of the rich solution to the stripper was stopped, while the circulations of heating oil through the reboiler and cooling water through the overhead condenser continued until there was no more CO₂ generated from the amine solution in the reboiler, i.e. no CO₂ flowed through the gas flow meter. This was done in order to estimate the heat loss consumed by the reboiler and the overhead condenser under non-stripping conditions. The schematic diagram of the desorption process is shown in Figure 1.

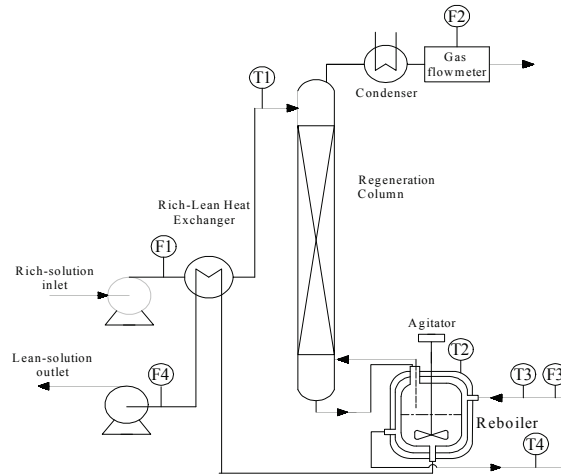


Figure 1. Schematic diagram of desorption process.

2.3 Analyses

In this work, the reboiler heat duty (H_{reb} , kJ/h), which was supplied by a heat transfer oil, was calculated by the following equation:

$$H_{reb} = m_{oil} C_{oil,f} (T_{in} - T_{out}) \quad (1)$$

Where m_{oil} represent the mass flow rate (kg/h), and $C_{oil,f}$ is the specific heat of the heat transfer oil (2.3 kJ/kg·°C, as provided by the vendor). T_{in} and T_{out} are the inlet and outlet temperatures of the heat transfer oil from the reboiler (°C), respectively.

The Q_{reg} (kJ/kg) for solvent regeneration can be calculated from the ratio of effective reboiler heat duty and the CO₂ mass flow rate as follows:

$$Q_{reg} = \frac{H_{reb} - H_{loss}}{m_{CO_2}} \quad (2)$$

$$m_{CO_2} = n_{amine} (a_{rich} - a_{lean}) M_{CO_2} \quad (3)$$

Where H_{loss} is the system energy loss (kJ/h), m_{CO_2} is the CO₂ mass flow rate (kg/h), n_{amine} is the molar flow rate of amine solution (kmol/h), M_{CO_2} is the molecular weight of CO₂ (g/mol). a_{rich} and a_{lean} are the CO₂ loadings of the rich and lean solutions (mol/mol), respectively.

As mentioned above, the regeneration heat duty Q_{reg} provided for the solvent regeneration generally includes three parts, namely q_{abs} , q_{sen} and q_{vap} (kJ/kg), as follows.

$$Q_{reg} = q_{abs} + q_{sen} + q_{vap} \quad (4)$$

Where q_{abs} , q_{sen} , and q_{vap} can be calculated by the following equations:

$$q_{\text{abs}} = R \frac{d(\ln P_{\text{CO}_2})}{d(1/T)} \quad (5)$$

$$q_{\text{sen}} = m_s C_s (T_{\text{reb}} - T_{\text{feed}}) / m_{\text{CO}_2} \quad (6)$$

$$q_{\text{vap}} = Q_{\text{reg}} - q_{\text{abs}} - q_{\text{sen}} \quad (7)$$

Where R is the universal gas constant ($\text{J}/(\text{mol}\cdot^\circ\text{C})$), P_{CO_2} is the CO_2 partial pressure (kPa), T is the temperature ($^\circ\text{C}$), m_s and C_s denote the molar flow rate (kmol/h) and the specific heat of the solution ($\text{J}/(\text{mol}\cdot^\circ\text{C})$), respectively. T_{reb} and T_{feed} are the temperatures of the solution in the reboiler and the stripper inlet ($^\circ\text{C}$), respectively. The reaction heat and the specific heat of solution for DETA and MEA were obtained from the literature [6-8].

3. Results and discussion

3.1 Effect of CO_2 lean loading on the regeneration heat duty

In the CO_2 capture process, the CO_2 lean loading has a significant effect on the Q_{reg} since it directly influences the equilibrium partial pressure of CO_2 and the driving force for mass transfer in the system. In this work, the effect of CO_2 lean loading on the regeneration heat duty consumption for CO_2 stripped from aqueous solution of DETA was experimentally investigated using the fixed CO_2 rich loading at 1.40 mol/mol, solvent flow rate of 4.87 $\text{m}^3/\text{m}^2\text{-h}$, and DETA concentration ranging from 2.0-3.0 kmol/m^3 . It should be noted that the investigated CO_2 lean loading of aqueous DETA solution in this work was in the range of 0.66~1.03 mol/mol, which was much higher than those of MEA solution (normally in the range of 0.20~0.35 mol/mol). This ratio was selected because (i) the equilibrium solubility of aqueous DETA (>1.40 mol/mol) and the mass transfer performance of DETA were much higher than those of MEA [3, 4], and (ii) preventing excessive regeneration energy consumption in the low CO_2 loading region [9, 10].

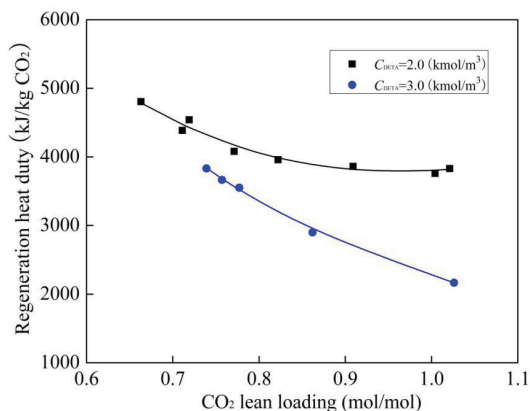


Figure 2. Effect of CO_2 lean loading on the regeneration heat duty.

It can be found from Fig.2 that the Q_{reg} decreased as the CO_2 lean loading and DETA concentration increased. The Q_{reg} of 2.0 and 3.0 kmol/m^3 DETA reduced from 4806 to 3831 kJ/kgCO_2 and 3832 to 2167 kJ/kgCO_2 , respectively as the CO_2 lean loading increased from 0.66 to 1.02 mol/mol and 0.74 to 1.03 mol/mol. This is because the increases of CO_2 lean loading and DETA concentration result in the increase of equilibrium partial pressure of CO_2 , and leading to less amount of water vapor requirement to achieve the equilibrium CO_2 partial pressure, thereby lowering Q_{reg} consumption.

3.2 Effect of solvent flow rate on the regeneration heat duty

In the absorption/desorption process for CO_2 capture, solvent flow rate is a key operational parameter. It greatly influences the mass transfer performance in both the absorber and desorber columns. In these experiments, the CO_2

lean loadings were 1.0 mol/mol and 0.84 mol/mol to provide the cyclic capacity at 0.40 mol/mol and 0.56 mol/mol, respectively. The concentrations were all 2.0 kmol/m³.

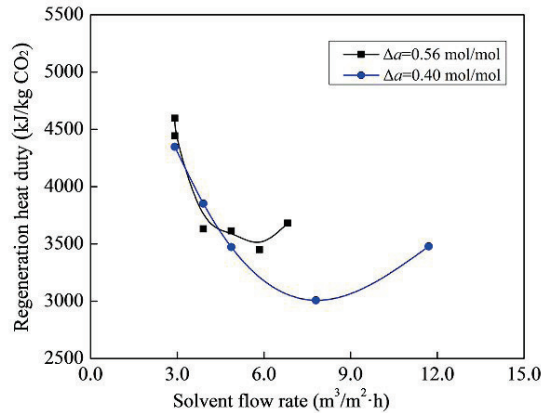


Figure 3. Effect of solvent flow rate of the CO₂ rich solution on the regeneration heat duty.

The effect of the solvent flow rate on the regeneration heat duty was not straight forward, as shown in Fig.3. The Q_{reg} reduced with the solvent flow rate at the low solvent flow rate because the effective interfacial area in the stripper was increased [11], resulting in the enhancements of both mass and heat transfer performances. At the higher solvent flow rate, the Q_{reg} was increased due to the shorter residence time of the solvent in the stripper column and more heat being required in the reboiler to achieve the same Δa .

3.3 Effect of CO₂ rich loading on the regeneration heat duty

As mentioned above, the CO₂ loading has significant effect on the Q_{reg} since it directly relates to the equilibrium CO₂ partial pressure. In this work, the effect of CO₂ rich loadings (1.20 and 1.40 mol/mol) on the Q_{reg} were investigated. These are presented in the plot between Q_{reg} and CO₂ loading difference ($\Delta a = a_{rich} - a_{lean}$) as shown in Fig. 4 which represents the ability of the solvent to circulate CO₂. In each case, the concentration of DETA was 2.0 kmol/m³.

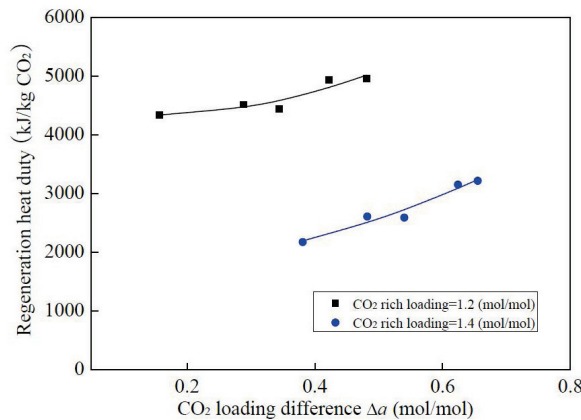


Figure 4. Effect of CO₂ rich loading on the regeneration heat duty.

The results show that the Q_{reg} increased significantly as the CO₂ rich loading decreased. The solution with CO₂ rich loading of 1.40 mol/mol required a Q_{reg} of 2609 kJ/kg to get the Δa at 0.5, while the solution with CO₂ rich loading of 1.20 mol/mol consumed a Q_{reg} of 4962 kJ/kg to get the same Δa . This observation corresponds well with the works of Sakwattanapong et al. [9] and Galindo et al. [10]. This is because of the significant differences of equilibrium CO₂ partial pressure at different CO₂ rich loadings, the equilibrium CO₂ partial pressure of solution with

high CO₂ rich loading was higher, thus requiring less energy consumption to generate water vapor to get the given driving force for mass transfer, thereby decreasing the heat duty significantly.

In addition, it can be found that with higher CO₂ loading difference, lower CO₂ lean loading was obtained, leading to a higher regeneration heat duty consumption. Since regeneration heat duty is very sensitive to the change of rich CO₂ loading, it is highly suggested to maximize the CO₂ rich loading in the absorption column. However, when the CO₂ loading is close to equilibrium solubility, it leads to the requirement of extremely tall packed height for reaching the high CO₂ loading.

3.4 Comparative regeneration performances of DETA and MEA

In order to compare the regeneration performances of DETA with those of MEA, the relationship of regeneration heat duty Q_{reg} vs. CO₂ cyclic capacity ($L \times C \times \Delta a$) for both solvents were comprehensively investigated. In this work, a comparison of all 38 runs of desorption experiments for DETA and MEA was conducted under various regeneration conditions of solvent flow rates, amine concentrations, and CO₂ rich loadings. In this comparison, the concentrations of DETA (2.0 & 3.0 M) were relatively lower than that of MEA with concentration of 5.0 kmol/m³. This was based on the consideration that the viscosity of DETA solutions are higher than those of MEA, for example, the viscosity of DETA and MEA at 4.0 kmol/m³ are 8.928 and 1.832 mPa/s, respectively [12, 13]. The high viscosity of solution can cause poor mass and heat transfer performances and high transport cost of the equipment since the solution is difficult to pass through the absorber, the stripper and the pipeline. In addition, the increase of amine concentration could also lead to some potential problems, such as solvent degradation, and equipment corrosion [14, 15].

It can be seen from Fig.5 that for all the cases, the heat duty required for regeneration of a certain amount of CO₂ varied greatly with changes of operational conditions. These experimental data indicated that the Q_{reg} increased nonlinearly as the $L \times C \times \Delta a$ increased, indicating that the Q_{reg} was highly sensitive to any change of the CO₂ cyclic capacity ($L \times C \times \Delta a$). With the same CO₂ cyclic capacity, the regeneration heat duty of DETA was lower than that of MEA under certain conditions.

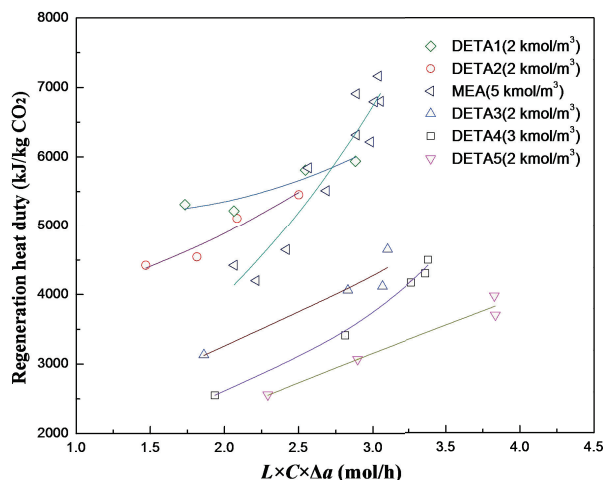


Figure 5. Regeneration heat duty at various operating conditions.

4. Conclusions

In this work, the desorption performances in terms of regeneration heat duty Q_{reg} (kJ/kg) of aqueous DETA were evaluated and compared with those of MEA solution in a laboratory scale stripper column. Three parameters were researched, including CO₂ lean loading, solvent flow rate and CO₂ rich loading. The effects of the three operating

parameters on Q_{reg} were comprehensively investigated. It is concluded that the Q_{reg} is very sensitive to the operating parameters within the range presented in this work. The Q_{reg} decreased as the CO₂ lean loading and DETA concentration increased, but increased when the CO₂ cyclic capacity increased. The solvent flow rate also had a great impact on Q_{reg} . In addition, with the same CO₂ cyclic capacity, the regeneration heat duty of DETA was lower than that of MEA under certain conditions.

Acknowledgements

The financial supports from the National Natural Science Foundation of China (Nos. 21276068, 21376067 and U1362112), Doctoral Program Foundation (20130161110025), National Key Technology R&D Program (Nos. 2012BAC26B01 and 2014BAC18B04), Technology Development contract of Shaanxi Yanchang Petroleum (Group) Co., LTD (No. Shanyan 12-34), Innovative Research Team Development Plan-Ministry of Education of China (No. IRT1238), and China's State "Project 985" in Hunan University Novel Technology Research & Development for CO₂ Capture are gratefully acknowledged.

References

- [1] Kohl AL, Nielsen R. Gas purification. Gulf Professional Publishing. 1997.
- [2] Fu K, Chen G, Sema T, Zhang X, Liang Z, Idem R, Tontiwachwuthikul P. Experimental study on mass transfer and prediction using artificial neural network for CO₂ absorption into aqueous DETA. *Chem Eng Sci* 2013; 100: 195-202.
- [3] Fu K, Sema T, Liang Z, Liu H, Na Y, Shi H, Idem R, Tontiwachwuthikul P. Investigation of Mass-Transfer Performance for CO₂ Absorption into Diethylenetriamine (DETA) in a Randomly Packed Column. *Ind Eng Chem Res* 2012; 51: 12058-12064.
- [4] Hartono A, Hoff KA, Mejdell T, Svendsen HF. Solubility of carbon dioxide in aqueous 2.5 M of diethylenetriamine (DETA) solution. *Energy Procedia* 2011; 4: 179-186.
- [5] Hartono A, da Silva EF, Svendsen HF. Kinetics of carbon dioxide absorption in aqueous solution of diethylenetriamine (DETA). *Chem Eng Sci* 2009; 64: 3205-3213.
- [6] Kim I, Svendsen HF. Comparative study of the heats of absorption of post-combustion CO₂ absorbents. *Int J Greenhouse Gas Control* 2011; 5: 390-395.
- [7] Kolska Z, Kukul J, ZAbransk M, Ruzicka V. Estimation of the heat capacity of organic liquids as a function of temperature by a three-level group contribution method. *Ind Eng Chem Res* 2008; 47: 2075-2085.
- [8] Marrero J, Gani R. Group-contribution based estimation of pure component properties. *Fluid Phase Equilib* 2001; 183: 183-208.
- [9] Sakwattanapong R, Aroonwilas A, Veawab A. Behavior of reboiler heat duty for CO₂ capture plants using regenerable single and blended alkanolamines. *Ind Eng Chem Res* 2005; 44: 4465-4473.
- [10] Galindo P, Schaffer A, Brechtel K, Unterberger S, Scheffknecht G. Experimental research on the performance of CO₂-loaded solutions of MEA and DEA at regeneration conditions. *Fuel* 2012; 101: 2-8.
- [11] Perry RH, Green D, Maloney J. *Perry's Handbook of Chemical Engineering* 7th ed. McGraw-Hill Book Company: New York 1997.
- [12] Hartono A, Svendsen HF. Density, viscosity, and excess properties of aqueous solution of diethylenetriamine (DETA). *J Chem Thermodyn* 2009; 41: 973-979.
- [13] Maham Y, Liew CN, Mather AE. Viscosities and excess properties of aqueous solutions of ethanolamines from 25 to 80 °C. *J Solution Chem*. 2002; 31: 743-756.
- [14] Gouedard C, Picq D, Launay F, Carrette PL. Amine degradation in CO₂ capture. I. A review. *Int J Greenhouse Gas Control* 2012; 10: 244-270.
- [15] Veawab A, Tontiwachwuthikul P, Chakma A. Corrosion behavior of carbon steel in the CO₂ absorption process using aqueous amine solutions. *Ind Eng Chem Res* 1999; 38: 3917-3924.